

JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION



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Further papers from the Eastbourne Conference

Curing reactions in isocyanate-based surface coatings

C. Barker and A. Lowe

Electron and ultra-violet curing of coatings

W. Deninger and M. Patheiger

Process characteristics of electron beam curing

W. H. T. Davison

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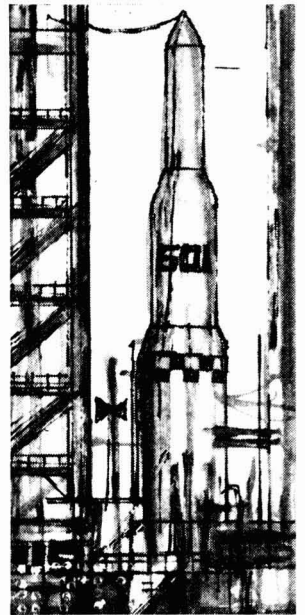
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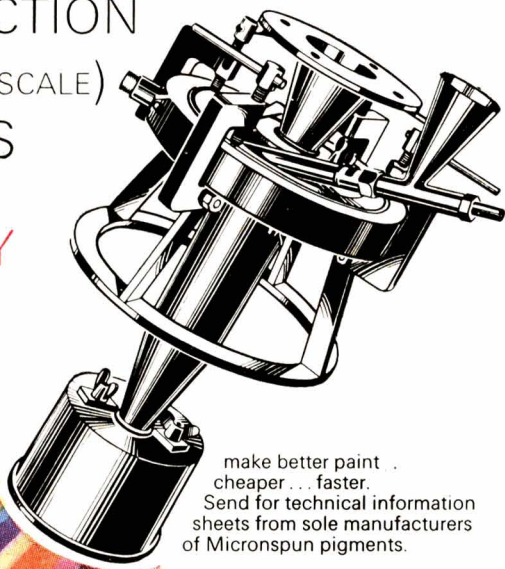


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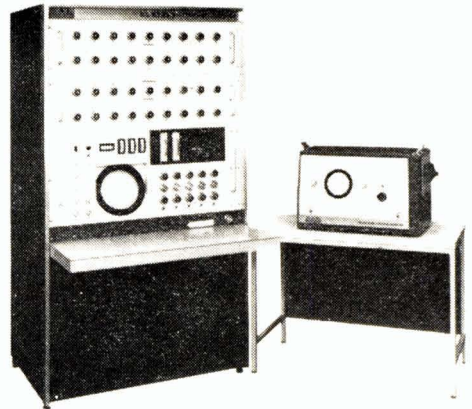


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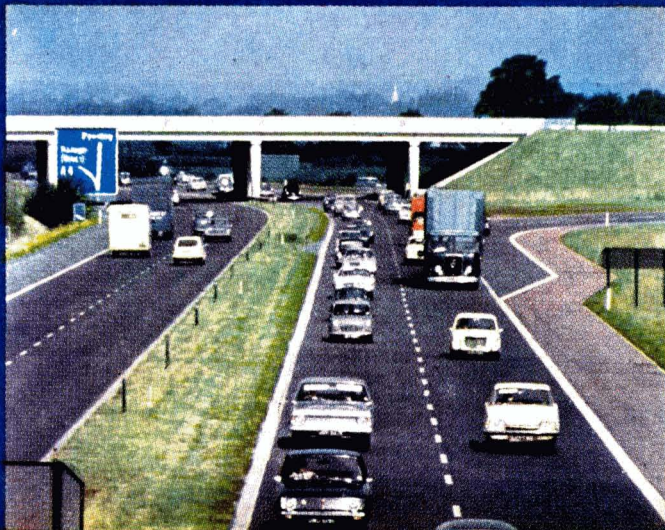
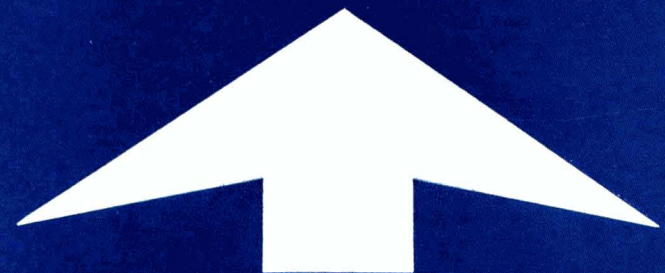


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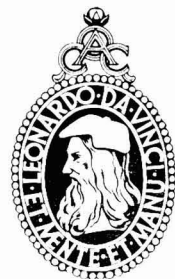
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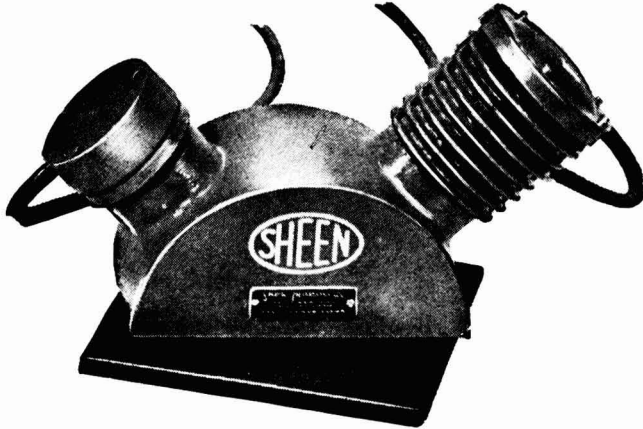


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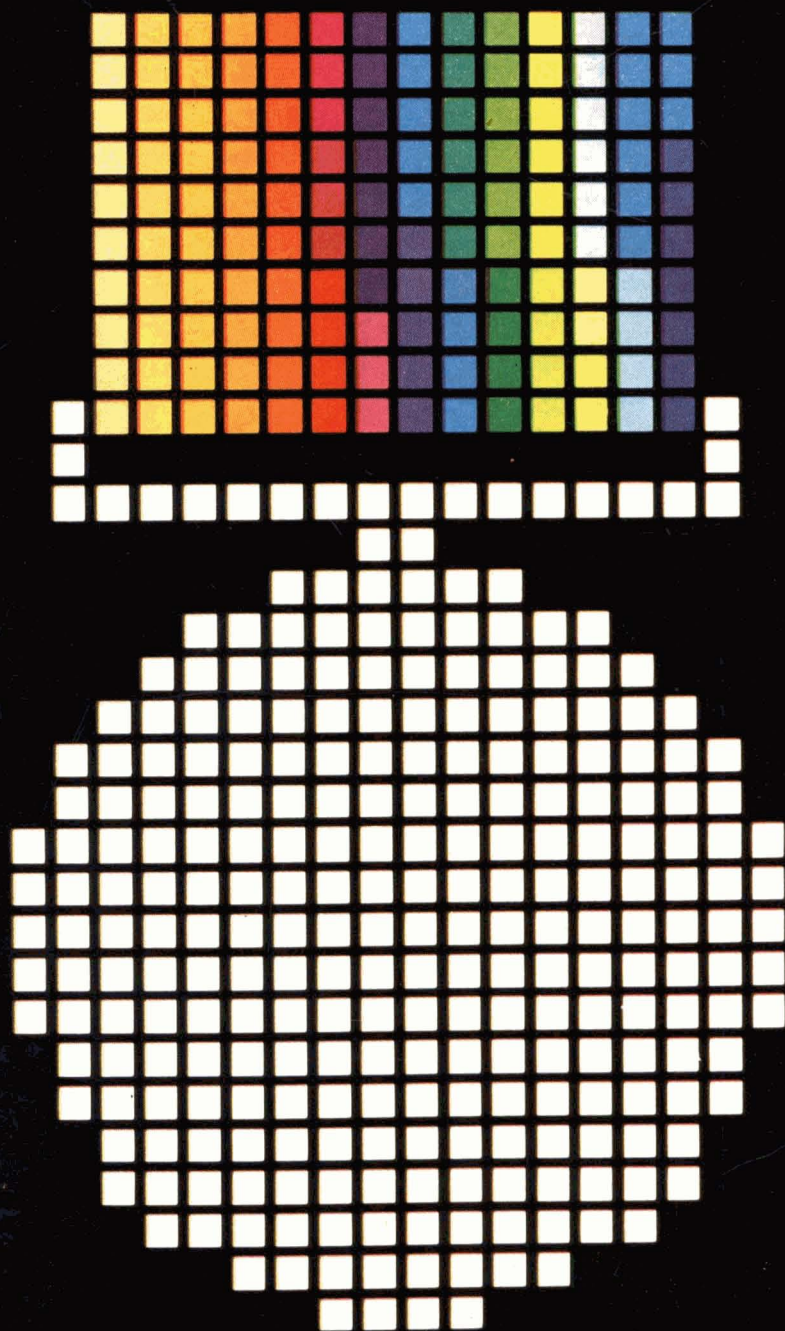
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Transactions and Communications

Curing reactions in isocyanate-based surface coatings*

By C. Barker and A. Lowe

Imperial Chemical Industries Ltd., Dyestuffs Division, Blackley, Manchester 9

Summary

The chemical mechanism of cure of "polyurethane" surface coatings of the isocyanate reactive type is now recognised to be complex. The formation of urea and biuret structures, by interaction of isocyanate with water, equals in importance urethane formation from the isocyanate-hydroxyl reaction. Polyureas, in which no urethane linkages are present, can now be designed. The colour stability of coatings based on various types of polyisocyanate is discussed and a hypothesis is advanced relating to the reduced yellowing of aromatic polyisocyanurates compared with isocyanate/polyol adducts.

Major practical developments in urethane-urea coatings can be foreseen in the combination of polyisocyanates and prepolymers with epoxy and vinyl resins, particularly hydroxyl-containing acrylic copolymers and methacrylated alkyd resins.

The toxicological hazards of handling isocyanates are considered.

Key words

Types and classes of coating

one compartment urethane coating

two compartment urethane coating

Binders

urethane resin

Manufacture and synthesis

Raw materials

isocyanate adduct

Processes and methods

polymerisation

Réactions de durcissement en revêtements à base d'isocyanate

Résumé

Actuellement on reconnaît la complexité du mécanisme de durcissement de revêtements "Polyuréthane" du type isocyanate-réactif. La formation des structures urée et biuret, par l'interaction d'isocyanate et d'eau, est de même importance que la formation des uréthanes à partir de la réaction isocyanate-hydroxyl. On peut préparer maintenant des polyuréées ou il n'existe par de liaisons uréthanes.

On discute la permanence de couleur des revêtements basés sur de divers types de polyisocyanate et l'on propose une hypothèse à l'égard du jaunissement réduit des polyisocyanurates aromatiques en comparaison des adducts isocyanate/polyol.

On peut prévoir d'importants développements pratiques dans le domaine de revêtements uréthane-urée provenant de la combinaison des polyisocyanates et prépolymères avec des résines époxyde ou vinylique, surtout des copolymères acryliques contenant des groupements hydroxyliques, et des résines alkydes méthacrylées. On considère les hasards toxicologiques au cours de la manipulation des isocyanates.

Vernetzungsreaktionen in auf Isozyanat Basierenden Lacken

Zusammenfassung

Der chemische Mechanismus bei der Härtung von "Polyurethan"-Beschichtungsmassen von der Art reaktiver Isozyanate ist nach neueren Anschauungen kompliziert. Die durch Zwischenreaktion von Isozyanat mit Wasser zustandekommende Bildung von Harnstoff und Biuretstrukturen kommt der Bedeutung der Bildung von Urethan mittels der Isozyanat-

*Presented at the Eastbourne Conference, 19 June 1969

Hydroxylreaktion gleich. Polyharnstoffe können nunmehr ausgedacht werden, in welchen keine Urethanbindungen zugegen sind.

Die Farbbeständigkeit von auf Polyisocyanaten verschiedener Art beruhenden Lacken wird besprochen, und eine Hypothese vorgetragen, die mit der verringerten Vergilbung aromatischer Polyisocyanursäureverbindungen, verglichen mit Isozyanat-Polyoladdukten in Beziehung steht.

Für die praktische Verwendung wichtige Entwicklungen auf dem Gebiete der Urethan-Harnstofflacke können in der Kombination von Polyisocyanaten und Präpolymeren mit Epoxid- und Vinylharzen vorausgesehen werden, besonders mit hydroxylhaltigen Akrylmischpolymeren und mit Methakrylsäure modifizierten Alkydharzen.

Die toxikologischen Gefahren bei der Handhabung von Isozyanaten werden in Betracht gezogen.

Реакции при сушке поверхностных покрытий на основе изоцианата

Резюме

В настоящее время признано, что химический механизм сушки «полиуретановых» поверхностных покрытий изоцианато-реактивного типа, весьма сложен. Образование карбамидовых и биуретовых структур, путем взаимодействия изоцианата с водой, равноважно образованию уретана в изоцианато-гидроксильной реакции. Поликарбамиды, с отсутствием наличия уретановых связей, могут быть проектированы в настоящее время.

Обсуждается цветная устойчивость покрытий основанных на различных типах полиизоцианата и предлагается гипотеза об уменьшении пожелтения ароматических полиизоциануратов, по сравнению с изоцианато/полиоловыми аддитивными соединениями. Существенное практическое развитие уретано-карбамидных покрытий может предвидеться в связи с соединениями полиизоцианатов и полуполимеров с эпоксидными и виниловыми смолами, в частности с акриловыми сополимерами содержащими гидроксилы и с метакриловыми алкидными смолами.

Рассматриваются токсикологические опасности манипулирования изоцианатов.

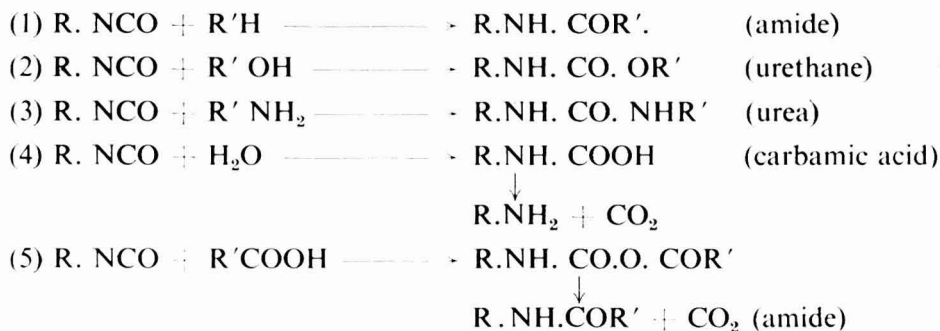
Introduction

The potential utility of isocyanates as highly reactive raw materials has been appreciated for many years, both as novel materials for the development of superior products in established fields and in the formation of new industries. One of the major factors in this appreciation is the reactivity of the isocyanate group itself, which enables chemical combination with compounds having suitably reactive hydrogen atoms to be achieved at ambient temperatures.

Clearly, with such reactive materials, normal resin synthesis can be operated under factory conditions, and a feature of the industrial utilisation of polyisocyanates in the last decade has been the growth of urethane oils and urethane alkyds in which tolylene diisocyanate has replaced phthalic anhydride. This development, however, does not do justice to the full possibilities inherent in isocyanate technology. Reactions which take place at temperatures as low as 0°C must offer considerable scope in many on-site applications and the surface coatings industry is undoubtedly in this category.

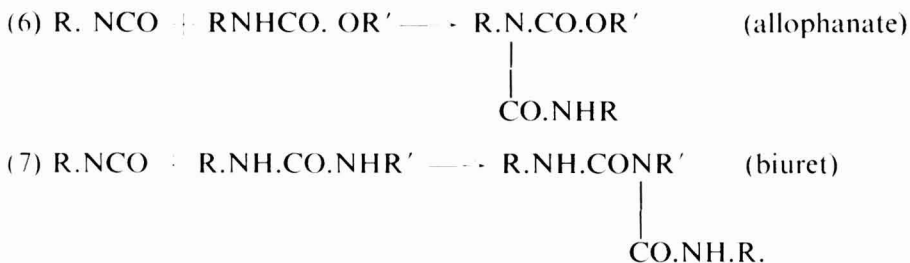
In any fundamental study of polymer production, the chemical factors involved are the primary considerations. Physical characteristics certainly affect the ease with which materials are handled and mixed, but fulfil a secondary role in the appreciation of the possibilities. Reference has been made in many previous papers to the chemistry of polyisocyanates and their utilisation in many industries¹, but the reactions likely to be involved in the mechanisms of cure and actual film formation are few.

Virtually all fall in the general class of reaction with reactive hydrogen atoms and can be summed up in the first equation below.



In more specific terms, isocyanates react with hydroxyl compounds to give urethanes and with amines to give ureas. Similar reactions occur with water, with the formation of a carbamic acid, and with carboxylic acids, with the formation of mixed acid anhydrides. However, in both of these cases the intermediates thus formed then break down; in the case of water with the formation of an amine which reacts with more isocyanate to give a urea; in the case of the carboxylic acids the mixed anhydrides break down to form amine groups.

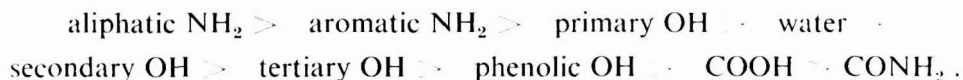
It will be seen from the above formal representation that the urethane and urea still contain reactive hydrogen atoms and these compounds are, therefore, capable of addition reactions with more isocyanate to form allophanates and biurets respectively



A full understanding of the value of isocyanate utilisation, however, must take into account not only the formation of the addition products, but also their stability. The primary and secondary addition reactions of isocyanates with active hydrogen compounds are reversible, apart from the reactions with water and with carboxylic acids which are condensations rather than additions, involving the elimination of carbon dioxide. Since the reaction of water and carboxylic acid groups is immediately followed by elimination of carbon dioxide, the reaction cannot simply be reversed, although the urea group derived from the water reaction may split on heating. These considerations may, therefore, have a bearing on the stability of the films produced by reaction of isocyanates with hydroxyl-containing materials or with water.

The types of active-hydrogen-containing compounds differ very considerably in their reactivity. Thus, amines on the whole react more readily with isocyanates

than do alcohols, and different amines with different basicities can give a wide spectrum of reactivities even in that class. An indication of the different rates of reaction with different types of groups² is as follows:

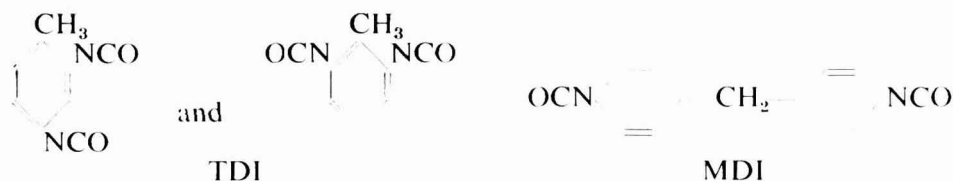


These relative rates of reaction indicate that, in a system of hydroxyl-containing materials and water, the participation of the latter in reactions with isocyanates must effectively reduce true urethane formation, since the primary amine produced will be markedly more reactive than the hydroxyl group. Attention has already been drawn to this competitive situation existing where isocyanates are used as *in-situ* curing agents³ and it is clear that further clarification of the role of water in such coating systems is necessary.

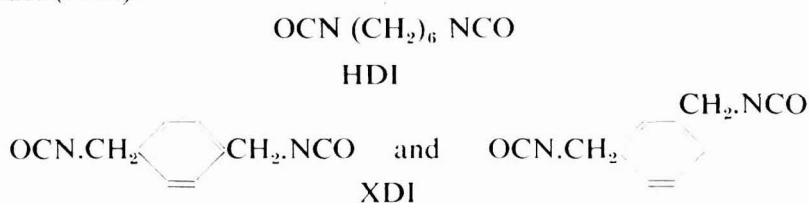
Isocyanate structures

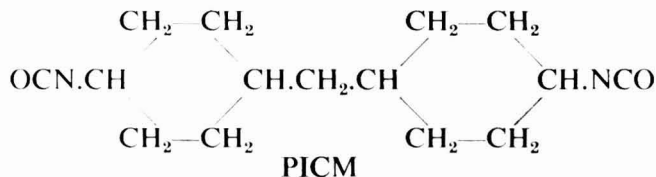
The surface coatings industry can rarely support the economic large scale production of synthetic, as opposed to natural, raw materials, and in the normal course of development progress is confined initially to the utilisation of products manufactured primarily for other purposes. The isocyanate field is no exception to this general thesis and the coatings industry has had to base its urethane technology on those isocyanates whose scale of production for foams and elastomers offers the right economic possibilities.

The isocyanates most readily available, therefore, are the mixed 2, 4- and 2, 6- isomers of tolylene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI), represented below as a single isomer although other isomers may be present in a complex mixture used primarily for rigid foams.



Greater appreciation of the practical possibilities of isocyanate utilisation, however, has stimulated manufacture of other isocyanates which confer particularly attractive properties on coatings for outlets where economic considerations are not so stringent. Such primary isocyanates are hexamethylene diisocyanate (HDI), dicyclohexylmethane diisocyanate (PICM) and xylylene diisocyanate (XDI).





The foregoing abbreviations for these diisocyanates are used where appropriate throughout the paper.

Formulation considerations

In the formulation of a reactive mixture of isocyanate- and hydroxyl- containing material, control of the properties of the final film is effected by selection of the appropriate degree of cross-linking in the two components. The hydroxylated resins may be polyethers or polyesters³, and branching can readily be built into their structures. For many purposes, however, some branching in the isocyanate is desirable, and the majority of isocyanates used in the coatings industry are derivatives of simple or primary diisocyanates. Thus, TDI is modified by reaction with trihydric alcohols to give a triisocyanate (Fig. 1) or by polymerisation to give a polyisocyanate through isocyanurate formation (Fig. 2).

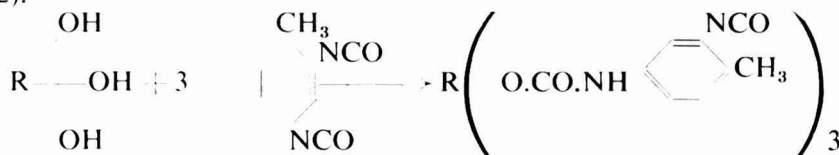


Fig. 1. Modification of TDI

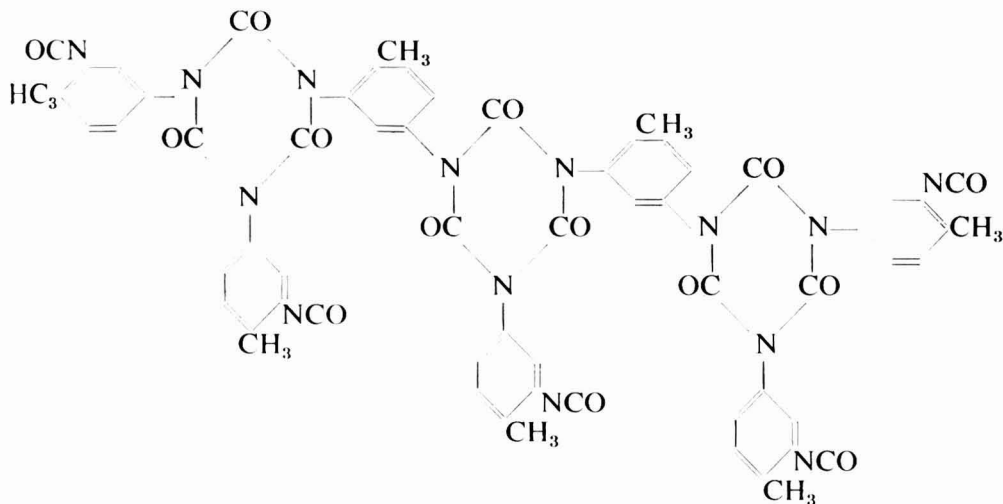


Fig. 2. Polymerisation of TDI

In practice, products of both types contain other reaction products, and these may confer still greater branching than those illustrated figuratively above. This additional branching, especially in the case of the isocyanurate polymers,

confers greater reactivity and speed of dry, and may require less branching in the resin component. It must also be borne in mind that the isocyanurate ring is extremely stable, the polymerisation reaction being irreversible. Films based on this type of isocyanate, therefore, have an inherent resistance to heat degradation not found so readily in the simpler urethanes.

Similar variations can be applied to HDI but, in this case, the low reactivity of the isocyanate groups enables branching to be introduced by means of water leading to the formation of a biuret triisocyanate. (Fig. 3).

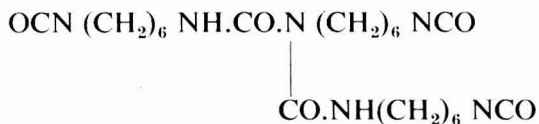


Fig. 3. Biuret triisocyanate

General reactions influencing cure

Previous papers^{1,3} have laid considerable stress on the importance of the role of water in the curing mechanism of formulations containing free isocyanate groups. If the isocyanate contains a high proportion of poly-reactive isocyanurates the problem of excessive brittleness in the final film must be accentuated by the additional cross-linking promoted by the urea formation. The polymerisation products themselves do not yield films on reaction with water alone and careful formulation work is needed to devise the best compromise between pot life, speed of cure and a robust practical performance under a range of conditions. Polyol adducts, on the other hand, are less highly branched and, even with simple polyhydric alcohols can give hard, tough films by reaction with water alone.

It would seem desirable, therefore, on all counts, to devote attention to the development of isocyanates which will give films with really valuable properties by reaction with water alone. Sufficient experience has been accumulated to show that a large polyisocyanate molecule, formed perhaps in the same way as a polyol adduct of the type illustrated by Fig. 1 but using a polymeric polyol, need be no less stable than the simple adduct. Certainly this type of polyisocyanate, or moisture-curing prepolymer as it is commonly termed, will contain urethane linkages capable of reaction with the isocyanate groups to form allophanates, but such reactions are slow at normal ambient temperatures and can in any case be inhibited by the addition of small quantities of reactive halogens. There is, therefore, no obstacle to the manufacture and sale of such materials, and their use in the production of clear lacquers on a variety of substrates by reaction with atmospheric moisture is well established.

It will be appreciated that the end product will, if made from an isocyanate and a hydroxyl-ended polyether or polyester, contain a multiplicity of urethane groups. The final cure, however, will be achieved solely by the formation of ureas and the coating should properly be designated a "urethane-urea." The prepolymer development, however, does entail some careful selection of polyol/isocyanate ratios, not least on account of the viscosities of the reacted materials^{4,5}.

In the general study of prepolymers, another important facet of their usefulness has emerged. Since the moisture-curing prepolymer is itself a polyiso-

cyanate, the possibility of using it in the normal two-pack systems should not be overlooked. It may be a more complex isocyanate and have a higher molecular weight, but there can be no theoretical objection to its use in this way. Since the normal curing process by water yields films, two-pack systems containing prepolymers cannot be subject to the same critical conditions surrounding the use of an excess quantity as are encountered with the isocyanates of lower molecular weight normally used in such systems. Thus, the flexibility of the final film need not be impaired by the use of such a prepolymer in stoichiometric excess, and, by the correct choice of polyhydroxylic resin as the second component, even more attractive films might be obtained.

This theory has been fully borne out in practice and, by the use of reactive resins in less than stoichiometric quantities, very attractive coatings have been produced. This technique is applicable to the production of extremely flexible or hard coatings. The pot-lives of such systems are very good indeed, and highly abrasion resistant flexible lacquers suitable for rubber or leather can be obtained. If hard resins are used, the films will be more cross-linked, and the products can be used as sanding sealers or as the final coating itself.

Advantage can also be taken of the use of hydroxylic resins in this way to introduce pigments under circumstances which will minimise the effect of the water contained therein. Less difficulty with flocculation is encountered when a pigment dispersed in a reactive resin is added to a prepolymer than occurs when the isocyanate is a highly cross-linked type of lower molecular weight.

It has also been observed that the deliberate addition of relatively massive quantities of water to the resin component of a two-pot diisocyanate system^{2,3,6} confers many advantageous properties. The water added may be as much as 2-6 per cent of the weight of polyol used, and extra isocyanate must be added to react with the additional water. This technique is especially suited to diisocyanates, since additional branching is introduced by these means and, if the isocyanate were already highly cross-linking, the film might become too brittle. Moreover, excess diisocyanate can be used, even up to 25 per cent, to confer greater chemical resistance.

Practical effect has been given to this type of coating by examination of a wide variety of polyols and diisocyanates with water. Polyols containing either primary or secondary hydroxy groups have been used successfully but, in order to obtain the most reliable balance between the water/isocyanate and hydroxyl/isocyanate reactions, polyols containing secondary hydroxyl groups have been examined most extensively.

The precise ratios used must depend on the practical considerations of viscosity and pot-life, but a good compromise is readily reached. The preparation of the coatings can be carried out by conventional techniques, water and the polyol being dissolved in solvent and the two solutions mixed just before application. The mixed materials can then be sprayed, dip-coated or brushed onto the desired substrate in the normal manner. The principal advantage obtained by the introduction of water in this way is an enhanced resistance to chemical attack and this is attributed to the preponderance of urea linkages in the final film.

Hazards

From the chemistry of formulation it will be seen that modification of the primary diisocyanate has enabled further branching to be incorporated. It was necessary, however, to modify some diisocyanates to reduce the hazard which is encountered when these moderately volatile, low molecular weight materials are used. This hazard arises particularly with TDI and is most severe when the coatings are applied by spray techniques.

The medical hazards associated with isocyanates have been given wide publicity and, since TDI is the isocyanate most widely used and can cause sensitisation at very low levels of atmospheric concentration, the greatest attention has been focussed on the difficulties and hazards arising from its use⁷. In the earliest development of urethane surface coatings it was soon realised that it would be impossible to use TDI alone, and modification by adduct formation or polymerisation offered sound methods whereby atmospheric contamination might be minimised. It is now abundantly clear that, whilst there are real hazards involved, they are predictable, and suitable precautions can be taken which will eliminate the dangers.

The production of isocyanates of higher molecular weight by the methods previously described, and moisture-curing prepolymers fall into this category, gives materials whose only serious hazard lies in the amount of volatile monomer contained therein. Much attention has been paid to the assessment of this hazard and to relating analytical methods to practical conditions. Obviously, the hazard is directly related to the concentration of the primary diisocyanate in the lacquer or paint to be sprayed, but it is also evident that the nature of the higher molecular weight isocyanate affects the liberation of primary diisocyanate.

Unfortunately, this means that analytical determination of the free primary diisocyanate in the polyisocyanate or prepolymer does not tell the whole story. Determinations of the atmospheric contaminations with TDI vapour from a number of urethane coating formulations under proper conditions of application, showed that the amount of TDI liberated does not rise above 0.01 ppm by volume. This is half the maximum allowable concentration which has been accepted by most countries in which the polyurethane industry has become established. The results confirmed earlier tentative conclusions³ but emphasised the need for a test corresponding more closely to industrial practice.

Trials carried out with a test method of this type⁸ confirmed that isocyanurates, which in general have higher reactivity than simple polyol/TDI adducts, can tolerate greater amounts of free TDI for a given degree of atmospheric contamination. In both types, however, the residual TDI can be reduced to a low level by processes readily operated by chemical manufacturers. With the advent of moisture-curing prepolymers and widespread encouragement of all and sundry to make such materials by the dissemination of literature suggesting that it is simplicity itself, a more dangerous situation has arisen.

Where the prepolymer is made by reaction of a polyol with an adduct in which the free TDI has already been reduced to an acceptable low level, obviously no hazard will arise. On the other hand, many suggestions have been made that prepolymers can be made simply by reaction of a polyol with TDI itself and the residual TDI be very low indeed. Such suggestions assume that all the

methods for the determination of free TDI in isocyanates and prepolymers give accurate results and that an assessment of hazard in use can be assumed from a figure for free TDI determined by any method. This is not yet wholly possible; the ultimate risk is run by the operator who applies the coating and the only fully satisfactory assessment must be made by a method which determines the amount of primary isocyanate liberated in the vicinity of the operator under normal conditions of use. Correlation of a test of this type with a specific method for accurate determination of free TDI in isocyanates and prepolymers is needed and the first results of work to this end have been described⁹. More detailed study has been undertaken and a proper procedure can be foreseen.

Colour stability of isocyanate-based systems

It is widely known that aromatic isocyanates and derivatives have inferior colour stability to aliphatic isocyanates. However, between the two extremes of MDI at one end and HDI biuret and polyol adducts at the other, lie all those products based on TDI as primary diisocyanate which at present constitute the bulk of the commercially used "urethane" coatings, and which, for economic reasons, are likely to remain so for many years ahead. At the same time, it is less clearly understood that within this group there are significant differences in observable colour stability which are broadly explicable in terms of the chemical structure of the isocyanate.

The colour retention of the main classes of coatings curing by means of isocyanate reactions may be expressed in terms of the type of isocyanate used. Such an assessment is made in Table 1.

Table 1
Colour retention of white pigmented coatings exposed to natural daylight

Serial no.	System and type of isocyanate	Type: 1- or 2-pack	Observed resistance to discoloration	Rating
1	MDI (undistilled)/polyester	2	Very poor	1
2	TDI-polyol adduct/polyester	2	Fair	3
3	TDI/polyol/polyether prepolymer	1	Moderate	4
4	Polyisocyanurate-polyester prepolymer	1	Good	5-6
5	Polyisocyanurate/polyester	2	Good	6
6	HDI prepolymer/polyisocyanurate (ex. TDI)	1	Very good	7-8
7	Aromatic-aliphatic polyisocyanurate/polyester	2	Very good	8
8	PICM polyol adduct/polyester	2	VG-Excellent	8-9
9	HDI polyol adduct/phthalic polyester	2	Excellent	10
10	HDI biuret/phthalic polyester	2	Excellent	10

Before considering these differences it is advantageous to examine the possible primary causes of lack of colour stability in urethane/urea coatings. It has been demonstrated that water enters into both one-pack and two-pack systems and that the preliminary reaction of this water with isocyanate gives amine which reacts with further isocyanate to form urea linkages. However, as film cure proceeds, the degree of cross-linking increases and the mobility of the remaining

reactive groups must decrease. Eventually a point will be reached at which spatial considerations no longer allow reaction of amine groups, continually being formed by diffusion of the small water molecule into the "green" film, with another isocyanate group, and residual amine groups will remain in the film.

The presence of unreacted amine in an aromatic isocyanate cured film has been confirmed by diazotisation and coupling with β -naphthol. The vulnerability of these residual amine groups to degradation accounts for the change in colour ("yellowing") which occurs in the early stages of the film's life. As is well known, aromatic amines are less stable to oxidation than aliphatic amines.

If this were the only cause of colour formation, it would be expected that yellowing would be rapid in the early life of an exposed film (one-two weeks), but would then slow down. This is not so, and a full aromatic urethane coating system (serial nos. 1-3 above) yellows progressively. The longer term discoloration (where this occurs) must be attributed to degradation of some of the urethane and/or urea linkages to a coloured derivative of the original amine, perhaps preceded by a hydrolytic step. It has been shown¹⁰ that a model aromatic urethane hydrolyses 100 times more rapidly than a corresponding model aliphatic urethane. However, it must be admitted that many urethane coatings discolour rapidly under very dry, high-light conditions, e.g. six months in South Africa, and so the hydrolytic step is not certain.

Though conclusive proof is lacking, it is widely believed that the degradation is an oxidative process, that occurring in the long term being initiated by free radicals generated by UV radiation. This is supported by observations such as:

- (i) TDI discolours in presence of air but not under inert gas,
- (ii) this process is accelerated by light and oxidation catalysts, e.g. lead naphthenate drier,
- (iii) fully saturated polyesters give best results in two-pack coatings: an oil modified alkyd containing even a mono-unsaturated acid (oleic acid) gives inferior initial colour and colour retention,
- (iv) the presence of hydroperoxides in a polyether leads to a yellow product when it is combined with pure TDI in prepolymer preparation,
- (v) anti-oxidants are effective, in a limited way, in stabilising isocyanates and derived coatings.

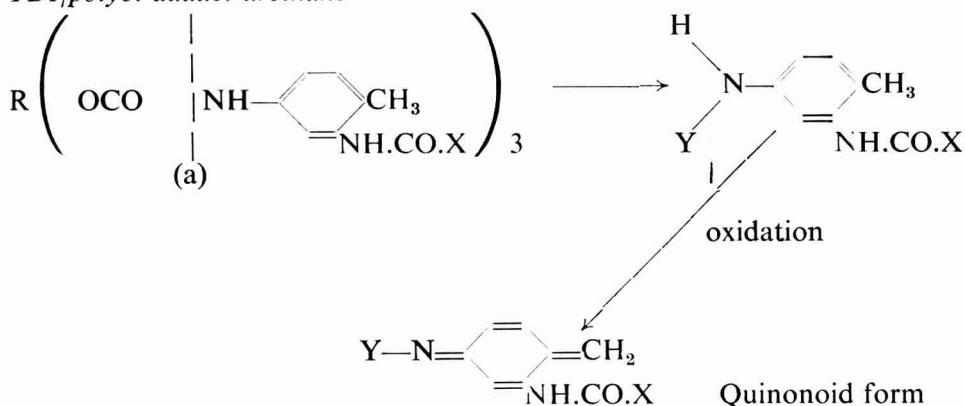
Moreover, it has been shown¹¹ that hydrogen peroxide can be used to detect the contamination of an aliphatic polyisocyanate with an aromatic isocyanate. The same technique can also be used to demonstrate the different susceptibility to colour change of white pigmented films derived from (i) a TDI/polyol adduct, (ii) an aromatic polyisocyanurate, and (iii) HDI biuret compound. The last type is unaffected in colour by hydrogen peroxide.

The differences in colour stability of coatings based on the various type of polyisocyanate can now be seen in better perspective. Aromatic amines, such as aniline and tolylene diamine, oxidise rapidly at normal temperatures, soon becoming yellow or brown, the latter being affected to a much greater extent. Quinonoid structures, produced by rearrangement of the aromatic ring, undoubtedly contribute significantly to the colour. On the other hand, aliphatic amines such as hexamethylene diamine, from which HDI is derived, are far more resistant to oxidation and the products are not highly coloured. The

absence of an aromatic nucleus ensures that no enhancement of colour arises from conjugation with an unsaturated ring structure, either benzenoid or quinonoid.

It is therefore possible to offer a *hypothesis* to explain the colour retention properties of TDI polyisocyanurate based coatings which are superior to TDI/polyol adducts in this respect. Firstly, the isocyanurate ring is more thermally and hydrolytically stable than an aromatic urethane group, Ar NH.CO.O . Secondly, its presence alters the possible degradation sequence as is expressed diagrammatically below:

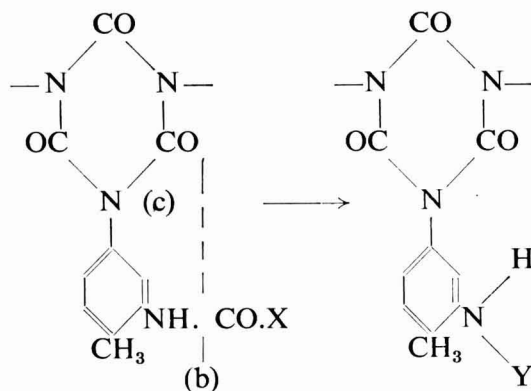
TDI/polyol adduct urethane



X = OR' urethane link
or NH.R'' urea link

(a) and (b) = hydrolytic/oxidative scission of urethane
Y = H or unknown

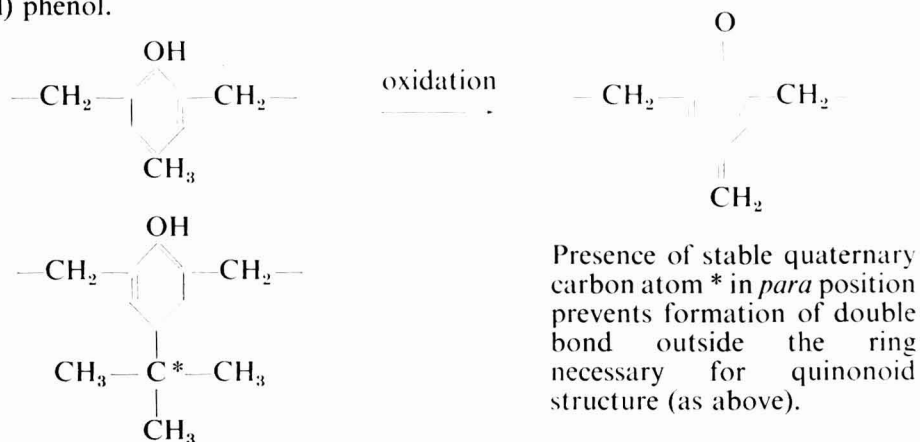
Polyisocyanurate urethane



- Note (1) Nitrogen (c) carries no hydrogen and is stabilised by the isocyanurate ring.
- (2) Tertiary nitrogen (c) prevents formation of quinonoid structure even when scission occurs at (b).

The isocyanurate ring acts as a chromophore block, thereby preventing the formation of more strongly auxochromic quinonoid structure. Under these circumstances it is to be expected that the discoloration due to the action of light would be more akin to that produced with a monoamine than with a diamine, and this does correspond well with the behaviour observed under practical conditions.

A parallel can be drawn here with the comparative colour stability of oil soluble phenol/formaldehyde resins having different *para* alkyl substituents. *Para*-cresol resins have inferior colour stability to resins from *p*-*tertiary* butyl (or octyl) phenol.

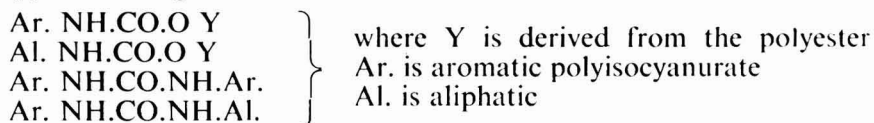


Naturally, the greater resistance of the aliphatic isocyanate derivative to discoloration by light has stimulated considerable interest and many attempts have been made to improve the methods whereby such isocyanates can be used more readily. Their reactivity towards hydroxylated resins is very markedly lower than that of many aromatic isocyanates, such as TDI, and they are inherently more expensive at present. The first point can be largely overcome by the use of catalysts but the second is unaffected. Another, more practical, approach has been to combine the aliphatic and aromatic isocyanate groups in one molecule so that, from the standpoint of cure, the total system is more effective, whilst the economics benefit from the incorporation of the cheaper aromatic isocyanate.

The polymerisation techniques developed for isocyanurates lend themselves well to this approach and a combined tolylene/hexamethylene isocyanurate polyisocyanate is now available¹². Systems based on this isocyanate have a desirable combination of cure with a resistance to degradation by light which is adequate for many purposes.

Similarly, prepolymers derived from polyols and HDI, which alone might be too slow-curing to be of practical use, can be combined with aromatic isocyanurate isocyanates in a single-pack coating and good colour retention conferred on the final coating¹³. The presence of both aliphatic and aromatic isocyanate groups is appropriate and logical, for it is clear from the foregoing that, during actual film formation, the relatively slow-reacting aliphatic isocyanate is integrated with the other components by reaction with the aromatic amine

groups arising from the water/isocyanate reaction. In a two-pack system a proportion of the aliphatic isocyanate is able to react directly with hydroxyl groups. Either way, the resulting composite product, which will contain all the following types of linkage,



must have superior colour retention over analogues in which all the :NH is attached to an aromatic ring.

Further commercial exploitation of the principle of employing aliphatic and aromatic isocyanate systems in combination or admixture can be expected to follow, in order to combine the advantages of low cost and fast cure characteristics of TDI based polyisocyanates with the proven colour retention of aliphatic isocyanates.

Coatings (one- and two-pack) based on cycloaliphatic and aralkyl diisocyanates have been given less detailed study. Firm theories to explain their improved colour stability have not been developed. However, it is probable that the explanation lies in the reduced ease of oxidation of the amines, and absence of auxochromic effect of an unsaturated ring, rather than in any inherent greater resistance to hydrolysis of the urethane and urea links formed.

Polyureas

The urea grouping is never the sole polymer building unit in cured films from conventional two-pack and one-pack (moisture-cured) media because, even in the latter case, the prepolymer is invariably a urethane linked polymer. Brief mention must be made here, therefore, of film forming systems in which the urethane is absent: the so-called polyurea coatings. These are formed by reaction of an isocyanate (usually di-) with a polyamine derivative. Aromatic isocyanate reacts very rapidly with primary amines in reactivity order exemplified as follows.

n-octylamine > tertiary octyl primary amine >> *o*-toluidine >> primary alcohol.

The rate of reaction is, in all cases, too fast with free amine to form the basis of practical two-pack polyureas. To achieve more than transient pot-life, it is necessary to protect the amine, generally by condensation with an aldehyde to form a stable aldimine, $\text{R.N:CH.R}'$, or a ketone, to form a ketimine, $\text{R.N:C R}' \text{R}''$.

The resulting protected amine may be sufficiently unreactive towards isocyanates to allow the formation of one-pack polyureas, stable in the can. On application as a thin film, the aldimine or ketimine is hydrolysed by atmospheric moisture back to the parent diamine which reacts immediately with the isocyanate present to give the cured polyurea film. Aldimines are more stable than comparable ketimines, but the ketones released from the latter are more acceptable in practice than the aldehydes formed when an aldimine is hydrolysed *in situ*.

The pot-life (sealed container) of such coatings is still dependent upon the reactivity of the isocyanate; aromatic polyisocyanates, for example, TDI/

polyol adducts and prepolymers, and particularly polyisocyanurates, give pot-lives measured only in hours or a few days. Aliphatic polyisocyanate aliphatic diamine (as aldimine) combinations can have pot-lives measured in weeks. However, commercial development of polyureas from protected amines has concentrated on the use of a long chain aliphatic diisocyanate which has low intrinsic reactivity with water and hydroxyl groups, but reacts conveniently with aliphatic ketimines in the presence of atmospheric moisture. This diisocyanate¹⁴ confers on the final polyurea coating a high level of flexibility and extensibility, as well as good colour retention in line with the aliphatic structure.

Table 2
Stability of polyisocyanate/protected polyamine combinations

Polyisocyanate	Polyamine	Protected as	Pot-life (sealed container)
HMDI/polyester prepolymer	Hexamethylene diamine	Free amine unprotected	Less than 1 minute
	Hexamethylene diamine	Ketimine	48 hours
	Hexamethylene diamine	Aldimine	32 days
	1:8- <i>p</i> -menthane diamine	Aldimine	12 weeks
TDI/polyol/polyester prepolymer	Hexamethylene diamine	Aldimine	18 hours
	1:8- <i>p</i> -menthane diamine	Aldimine	7 days
DDI diisocyanate	Long chain aliphatic diamine	Ketimine	72 hours minimum

Note: Pot-life depends on solids content as in isocyanate polyol combinations. As far as possible, the above pot-lives are quoted for comparable concentrations.

The greater reactivity of the aromatic isocyanates, even with the more stable aldimines, is evident. Additionally, the sterically hindered 1, 8 -*p*-menthane diamine gives more stable compositions than hexamethylene diamine when both are protected as aldimines by reaction with isobutyraldehyde¹⁵.

The negligible pot-life resulting from combination of free hexamethylene diamine with even the HDI prepolymer, which would react slowly with water or hydroxyl, underlines the impracticability as yet of designing polyurea coatings by direct reaction with free amines. Nevertheless, interest in polyureas seems likely to increase.

Isocyanates (and derivatives) in conjunction with other polymers

It will be appreciated that all the work described in the first part of the paper relates to, or is based on, the accumulated experience of the usage of isocyanates with polyols, both polyether and polyester type, in two-pack and one-pack moisture-curing systems. The main characteristics of the formulation requirements of such systems are well understood, and it seems probable that further developments will arise from the discovery of new, cheaper and more colour-stable isocyanates.

There is, however, considerable scope for the use of isocyanates in conjunction with other film-forming resins. Two types of resins are particularly attractive:

- (i) the large and diverse vinyl copolymers, formed by free-radical initiated copolymerisation of monomers, and
- (ii) epoxide resins and their derivative.

Just as the bulk availability of TDI and MDI for urethane foams promoted their application in surface coatings, so the availability for plastics applications of, amongst other vinyl monomers, cheap vinyl chloride, styrene and methyl methacrylate, has extended the use of these materials into surface coatings during the last 20 years. Primary monomers such as methyl methacrylate and acrylic acid have been used to develop higher alkyl esters which, when appropriately copolymerised, yield film-forming polymers having the desirable properties of solvent solubility, flexibility and adhesion to substrates. In addition, by the inclusion of minor proportions of a polar acrylic monomer, e.g. acrylic acid, acrylamide (or derivative) or hydroxyalkyl methacrylate, reactive copolymers are obtained which can be cured by a variety of cross-linking agents, including polyisocyanates.

Solvent-borne acrylic coatings may be classified as follows:

1. thermoplastic polymers, e.g. poly *n*-butyl methacrylate and copolymers of methyl methacrylate with higher methacrylates,
2. cross-linkable copolymers—often referred to as thermosetting acrylics.
3. methacrylic ester modified drying oil alkyd resins.

The polymers in category 1 dry by solvent evaporation alone, and, while some reinforcement of properties is possible by blending with isocyanate prepolymers, the compatibility is generally low and the effect marginal. In particular, the solvent sensitivity of the basic linear acrylic polymer remains. This topic will not be considered further here.

The cross-linkable acrylic copolymers in category 2 have probably the greatest scope for continued technical development of any known coating system and it is natural that interest should be shown in the use of isocyanates as curing agents. Their reactivity at normal temperatures offers the prospect of designing "cold-cure acrylic coatings" having comparable properties to those of coatings stoved at up to 80°C from less reactive combinations of polar monomer and cross-linking agent.

It is useful to sub-classify the types of cross-linkable acrylic coatings, as is shown in Table 3.

Consideration of the relative rates of reaction of the isocyanate group with the reactive groups in column 3, as displayed in the Introduction, indicates that only copolymers of type D having hydroxyl groups are of real interest for use in conjunction with isocyanates. This indication is borne out in practice, and the behaviour of these hydroxyacrylic copolymer/isocyanate combinations is briefly illustrated below.

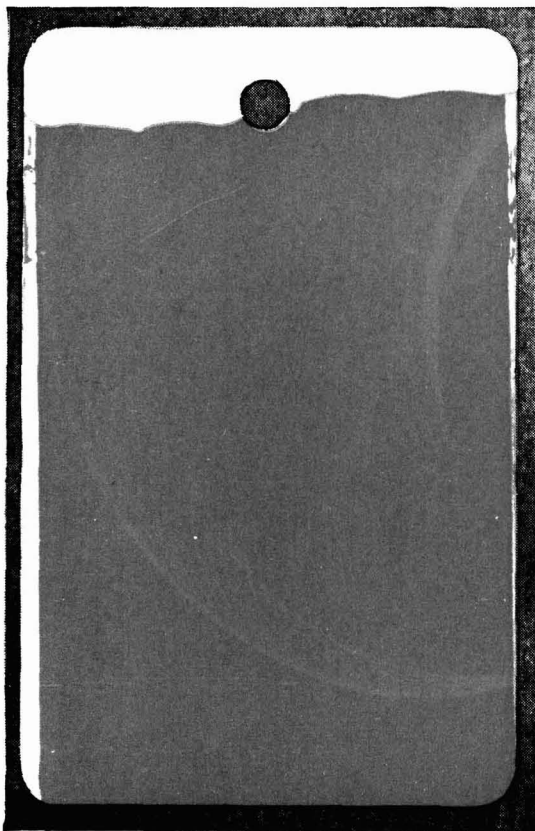
Table 3

Type	Polar co-monomer	Substituent grouping	Curing agent	Conditions
A	Acrylic acid	COOH	Liquid epoxy resin (optionally with M/F)	120-180 C
B	Acrylamide	CONH ₂	Melamine/formaldehyde	120-150 C
C	Alkoxymethyl acrylamide	CO.NH.CH ₂ .O.R.	Self-cure	120-180 C
D	Hydroxypropyl methacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CO.OCH}_2\text{-CH.OH} \\ \\ \text{O} \end{array}$	(melamine epoxy) (polyisocyanate)	120-150 C > 100°C 0- 60 C
E	Glycidyl methacrylate	CO.O.CH ₂ .CH-CH ₂	Self-cure (catalysed) or polyamine	25-150 C

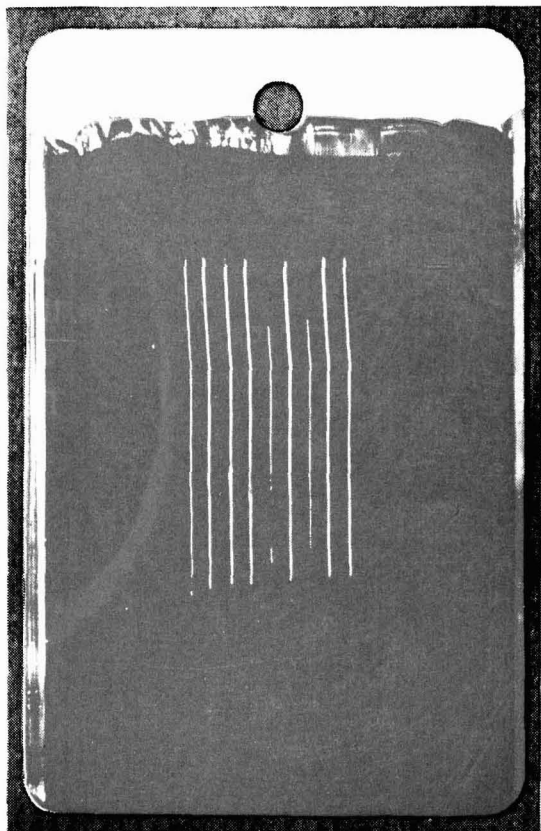
As a starting point, a standard carboxy acrylic copolymer of type A (comprising 65/25/10 = MMA/2-ethyl hexyl acrylate/acrylic acid) was taken as a basis for both calculation and practical comparison. Experience had shown that this, when cured with *bis*-epoxide at 150°C, had the right order of cross-linking density. To introduce the same molar proportion of hydroxyl required twice the amount of hydroxypropyl methacrylate. A series of three copolymers containing 20 per cent HPMA and increasing amounts of 2-ethyl hexyl methacrylate as plasticisers were made and cured with various polyisocyanates, with the results summarised in Table 4.

From these preliminary results and general observation of these systems, the following points have emerged.

1. Isocyanate/polyol adducts from TDI and HDI, and some TDI prepolymers, are compatible with hydroxy-acrylic copolymers. However, the speed of cure is slow by the standard of conventional "polyurethane" coatings, though the long pot-lives achieved have significantly practical value.
Films cross-linked with aliphatic HDI/polyol adduct (C) are probably incompletely cured even after 7 days at 20°C.
2. As far as comparison is possible, polyisocyanate cure of hydroxy-acrylic copolymers at 20°C and 60°C gives much less flexible films than are obtained by epoxide cure at 150°C of a carboxyl containing copolymer of similar reactive hydrogen content and methyl methacrylate/plasticising monomer ratio. This would be expected from the chemical structure of the isocyanate and its partial reaction with atmospheric moisture leading to additional polymer branching.
3. Isocyanate prepolymers of the TDI/polyol/polyether type are compatible, and on preliminary tests offer a good prospect of achieving a satisfactory balance of speed of cure to film flexibility and solvent resistance. However, a high plasticising monomer content (>35 per cent of 2-ethylhexyl



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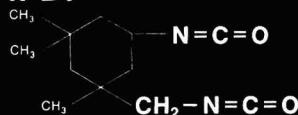


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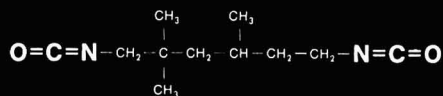
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Table 4

Film properties of hydroxy acrylic copolymer/polyisocyanate combinations

Copolymer	Curing agent	Effective pot-life	Film air-dried or stoved	Flexibility, mandrel	Pencil hardness	Solvent sensitivity, toluene (10 min/20°C)	
65/25/10 MMA/EtHxA/ A.Acid	Liquid bis-epoxide	3 months	150°C/30 min	pass $\frac{3}{16}$ in	H	unaffected	
52.5/27.5/20 MMA/EtHxA/ HPMA	Poly-isocyanate	A	7 days	20°C/7 days	fail 1 in	3H	unaffected
		B	2-3 days	20°C/7 days 60°C/1hr	pass $\frac{3}{16}$ in pass 1 in	H 2H	slight softening
		C	> 1 week	20°C/7 days 60°C/1hr	pass $\frac{3}{16}$ in pass $\frac{1}{8}$ in	B HB	badly softened
45/35/20 MMA/EtHxA/ HPMA	Poly-isocyanate	A	7 days	20°C/7 days	fail $\frac{3}{16}$ in	H	very slight softening
		B	3 days	20°C/7 days 60°C/1hr	pass $\frac{5}{16}$ in pass $\frac{3}{16}$ in	H HB	slight softened
		C	> 1 week	20°C/7 days 60°C/1hr	pass $\frac{1}{8}$ in pass $\frac{1}{8}$ in	3B B	stripped wrinkled
37.5/42.5/20 MMA/EtHxA/ HPMA	Poly-isocyanate	A	7-10 days	20°C/7 days	pass $\frac{3}{16}$ in	HB	softened
		B	4 days	20°C/7 days 60°C/1hr	pass $\frac{1}{8}$ in pass $\frac{1}{8}$ in	HB HB	moderate

Notes

Polyisocyanates A=TDI/polyol adduct (18% NCO on solids)
 B=TDI/polyether prepolymer (11% NCO on solids)
 C=HDI/polyol adduct (17% NCO on solids)
 (catalysed by 0.25% zinc naphthenate)

Monomers

MMA =methyl methacrylate
 Et HxA=2-ethylhexylacrylate
 A.Acid =acrylic acid
 HPMA =2-hydroxypropyl methacrylate

Liquid bis-epoxide — Epikote 828 ex. Shell Chemicals, catalysed by 0.2% Armeen DMCD.

Curing conditions --- films stoved 60°C for 1 hour, after 1 hour flash off, were air-dried at 20°C for a further 2 days before test.

acrylate) seems to be essential and must clearly detract at present from the economics of these coatings.

4. Polyisocyanurates and PICM polyol adducts are incompatible with hydroxy acrylic copolymers of the above type, though no attempt has been made to prepare alternative copolymers compatible with these isocyanates, for example, by use of different monomer combinations.

All the above films display good resistance to water and aqueous chemicals, as would be expected. Further development of isocyanate-cured acrylic resins should lead to early realisation of a fully satisfactory "cold-cure," or at least moderate temperature ($\leq 75^{\circ}\text{C}$) force-dry systems which will eliminate the high stoving temperatures ($120\text{--}180^{\circ}\text{C}$) needed to cure present thermosetting acrylics resin coatings.

The versatile modern alkyds of category 3 are one group of the class of vinylated alkyds which find wide use in rapid air-drying and low temperature stoving industrial paints. They are formed by polymerising methyl methacrylate monomer in presence of a drying oil modified alkyd resin containing a proportion of conjugated unsaturated oil, such as dehydrated castor oil. It is now generally recognised that these resins are not true alkyd/vinyl copolymers, as they are sometimes described, but that the main function of the oil-modified alkyd is that of a chain transfer agent, or perhaps just a retarder, which restricts the molecular weight of the vinyl polymer formed to a level at which it is compatible with the alkyd. It should be remembered that moulding grade poly (methyl methacrylate) is almost completely incompatible with alkyds. The final methacrylated alkyd is a mixture of

- (a) normal alkyd molecules which contain hydroxyl end groups,
- (b) polymethacrylic ester of low molecular weight,
- (c) a small proportion of true alkyd/methacrylate copolymer.

It will be readily seen that the cure of a methacrylated alkyd with a polyisocyanate is a complex process varying between mere reinforcement of the thermoplastic poly (methyl methacrylate) and true cross-linking; the drying oil alkyd molecules are tied into the polyurethane as in a normal two-pack polyester/polyisocyanate combination. In addition, oxidative cure of the drying oil also occurs, as in an unmodified alkyd.

It has been found that fast-drying coatings of considerable practical utility can be made by combining standard methyl methacrylate modified DCO alkyds with isocyanate prepolymers. Polyether/polyol/TDI prepolymers are especially attractive on account of their compatibility, whereas those containing isocyanurates, being more highly branched, are less useful in this context.

The principle can be extended to the introduction of isocyanate reactive groups into the vinyl portion (b) of the modified alkyd. Typical practical compositions are exemplified in Table 5. In type III, the introduction of hydroxypropyl methacrylate into the copolymer improves the drying speed slightly and the early-life solvent resistance. However, it does significantly reduce the long pot-life, which is one of the important attractions of these prepolymer/vinylated alkyd combinations arising from the use of stoichiometric excess of isocyanate groups over the alkyd hydroxyls.

Table 5
TDI prepolymer/methacrylated alkylid combinations

TDI/polyol/polyether prepolymer (10.5% NCO)	45% DCO/MMA alkylid		Pot-life of lacquer (33% solids)	Drying speed (20 C) 9g/sq ft sprayed		Solvent sensitivity Butyl acetate on 7 day old film		
	Parts by wt (solids)	Alkyd/ vinyl ratio		Type	Dust free (min)		Print free (hr)	Sands in (hr)
40	55	100/50	I	3 days	45	3-3½	5	slight swelling
48	50	100/125	II	2-3 days	20	2	3	slight softening
48	50	100/115 +10	III	24hr	15	1½-2	3	v. slight softening

*Resin III: 10 parts MMA in resin II replaced by hydroxypropyl methacrylate.

Lacquers of the above type, since they contain aromatic isocyanate prepolymer, have only fair colour retention properties, similar to those characteristic of prepolymer alone, but still superior to two-pack TDI/polyol adduct systems. In examples 2 and 3, however, significant dilution with the colour-stable methacrylate contributes to a decrease in yellowing to a level which is acceptable for many of the currently important applications.

This result is unexpected, since the presence of both free aromatic isocyanate groups and autoxidising fatty oil components should logically promote severe discoloration. No analogy should be drawn here with the oxidising urethane oils and "Uralkyds" since in these products all the isocyanate is converted to urethane before autoxidation (air-drying) enters into consideration.

The rapid rate of drying to the touch-dry state and to a condition in which they can be handled without damage makes the above system ideally suited to the formulation of economical furniture sealers and finishes, and also coatings for application to porous substrates such as chipboard. Undoubtedly, the good solvent release properties of the methacrylic polymer component contribute significantly to the hardening of the surface. The full cure of the isocyanate and drying oil components probably takes some days. Nevertheless, the films develop good abrasion resistance in less than one week, which is probably an acceptable storage period before use, for example, of a chipboard floor.

Epoxide resin/isocyanate combinations

The inclusion of *minor* amounts of epoxy resin of the diphenylolpropane epichlorhydrin type into various types of two-pack urethane coatings is an established practice which leads to improved adhesion of the film, amongst other desirable properties. The isocyanate reacts primarily with the "chain" hydroxyls of the epoxide resin, but the terminal epoxide groups enter into reaction when amine groups formed by reaction 4 (Fig. 1) become available. The epoxy resin is integrated with the urethane-urea film as in cure by a low molecular weight reactive polyamide having amine end groups. Coatings having excellent resistance to water and chemicals based on this principle have already been described^{1,3,6}.

Though epoxide resins alone, that is, as the sole hydroxylic component, can be cured by a polyisocyanate or compatible polyether prepolymer, the full potential reactivity of the terminal epoxide group may not be utilised. For this reason, attention has been focused on systems in which the resin has first been reacted with an amine or diethanolamine to convert the terminal epoxide groups into isocyanate-reactive hydroxyl and substituted amine groups (see opposite page).

Product *A*¹⁶ retains the chain hydroxyls of the original epoxy resin, but three new ones are added at each end plus a tertiary amine group which catalyses the isocyanate/hydroxyl reaction. In product *B*, reaction with sterically hindered *tertiary* octyl primary amine forms at each end one new hydroxyl and a hindered secondary amine which reacts with NCO to form a stable urea.

Both adducts of type *A* and *B* cure rapidly with polyisocyanates. Best results are obtained with isocyanate/polyol adducts and polyether prepolymers. Such compositions already form the basis of established fast drying anti-corrosive

A full consideration of the processes involved in curing isocyanate composition now shows that water is involved to some extent in the great majority of *in situ* coatings. Appreciation of the part played by this ubiquitous material is one of the most significant contributions of the last few years, and it will certainly enable even more desirable coatings to be devised. The colour retention properties of the coatings are primarily a function of the isocyanate used and means of harnessing the chemical structure to impart specific characteristics can now be forecast.

It is also clear that the moisture-curing prepolymers will play an increasing part in the coatings technology of the future. They are valuable not only in their own right as single-pack stable lacquers but also as polyisocyanates to be used as components in two-pack systems. Special properties, such as compatibility with other film-forming polymers, vinyl and acrylic resins being particularly attractive, can be built into their structure and much more will be heard of their use in this way.

There is no doubt that isocyanates, with their fundamental reactivity and versatility, will find increasing application in the coating technologies of the future. They have come of age and will be a growth feature for many years to come.

[Received 18 December 1968]

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Discussion at Eastbourne Conference

MR C. E. HOEY referred to the statement made in the paper that water had a reaction rate approximately the same as that of the hydroxyl containing polyesters. This was of particular importance when one had to consider the curing of urethanes in various parts of the world, where the humidity could vary considerably.

Considering the reactions in the paper, the reaction with water produced carbamic acid and then an amine. This amine could react again with any free isocyanate left, to produce a homopolymer of the original isocyanate. This presumably produced an extremely complicated polymer mixture at the end of the reaction.

Had the authors examined the chemical resistance of the various polyurethanes under various conditions of humidity and which was more important, relative humidity or total humidity?

One further point was that since the water for the curing reaction was obtained from the air, would there be a disproportionation between the surface of the reacting film and its bulk?

MR C. BARKER said that very little quantitative data was available about the effect of humidity on the absolute chemical resistance of the coatings. The humidity undoubtedly affected the speed of cure, and it was the absolute humidity which was critical, not the relative humidity, so that, for instance, urethane coatings would cure quite satisfactorily in the fringes of the Sahara, whereas there would be difficulty in Finland in the winter, where the absolute humidity had gone down to a very low level because all the water had been frozen out of the air.

Quite a lot of data was available on the question of whether the chemical resistance was effected. A paper had been given, which showed that if liquid water was deliberately added to urethane systems of particular types, the chemical resistance increased progressively, and this led to the conclusion that the substituted urea linkage, and possibly the biuret since little was known about the balance of these two in the particular context, imparted more chemical resistance than the urethane link, which was regarded as being the primary building unit. So improved chemical resistance would be expected when water intervened.

In the case of the disproportionation between the surface and the bulk of the film, he didn't have any details. It had been expected to take place. The film curing did take time in the thick film, but no analysis had been recorded of the layers next to the substrate as distinct from those at the top. He would expect there to be differences in the short run of the life of the film, but ultimately the isocyanate must be consumed up to the point where the terminal isocyanate could cease to be mobile within the film structures as a whole. These groups hydrolysed as a final step, and any further small molecules of water which diffused in through the more closely cured top layers would lead to an early yellowing process.

DR A. LOWE commented that in Dr O'Neill's paper reference was made to the speed of cure, both on the surface and on the substrate, and the centre part, if it was a thick film, certainly took longer. It was simply a question of diffusion of the water molecules through the film as a whole.

DR L. A. O'NEILL remarked that Mr Barker had said that the hydroxyl groups of the two-pack polyurethanes might be responsible for good adhesion. Could he comment as to why intercoat adhesion failures were sometimes obtained with two-pack polyurethanes and why the same hydroxyl group didn't serve to bond chemically on to the second coat? Also, did some of the newer polyurethane types vary in intercoat adhesion properties?

MR BARKER replied that he couldn't answer in detail. The question of intercoat adhesion in polyurethane was an enigma. There was the case of the urethane pre-polymers which, apparently, completely reacted. The curing mechanism was a fairly simple one, and yet properly designed these coatings could give quite good intercoat adhesion. He felt that intercoat adhesion did not depend simply on presence of residual hydroxyls, though there was the evidence that if one used an undercured primer system, that was, a system with lower than 1:1 molar ratio of isocyanate to hydroxyl, the second coat, which might be formulated at 1:1, had better adhesion.

MR W. W. GILLISON said that MDI was useful in preparing tear resistant rubbery films, and asked if HMDI (dimethyl methane diisocyanate hydrogenated, or PICM as in the paper) would give equally good tear resistance with better light fastness.

DR LOWE answered that when MDI was used in this connection, the properties of the final rubbery film were very good. HMDI, on the other hand, tended to impart less rigidity to the structure of the final film, and as far as he was aware the tear

resistance and the tensile strength had always been lower, although most of the work on HMDI had been done many years ago.

The best material for this purpose was methylene diisocyanate.

MR F. ARMITAGE commented on the statement in the paper, referring to the copolymers, vinyl monomers, and alkyds, which read: "It is now generally recognised that these resins are not true alkyd/vinyl copolymers." He did not agree that this was the case. This controversy had been started 20 years ago, and he had supposed that the paper by Kut in January 1952 had settled this controversy in favour of true copolymers being formed if the alkyd contained either conjugated fatty acids or maleic anhydride.

A second point was that no mention had been made in the paper of a relatively new coating system, which comprised unsaturated polyester, vinyl monomer with peroxide catalyst, and polyurethane prepolymer. Did Mr Barker know anything about the system?

MR BARKER took Mr Armitage's point, but did not accept that this applied in the context of methacrylic polymers. The evidence produced by fractionation studies, albeit carried out some time before by now old fashioned solution-graded non-solvent precipitation techniques, had suggested that in the type of methacrylated alkyd being dealt with, there was a significant content of non-polar or very low polarity polymer, which could only be described as low molecular weight homopolymer. Quite recently, gel permeation chromatography had become available, and the evidence from this suggested that there were significant proportions of non-polar materials present, which were not true copolymers.

It was true that different catalysts used in the formation of vinylated alkyds led to different degrees of hydrogen abstraction from the base alkyd, and he suspected that many commercial products were designed to the point where the overall system was compatible.

The paper had merely tried to point out that the system was complex, in which one could see direct chemical links. Considering the true copolymer which was present, one had a dehydrated castor oil alkyd in the presence of which one had copolymerised a vinyl monomer, in this case methyl methacrylate. A significant proportion of the material present would be methacrylic copolymer chains of low molecular weight attached to the conjugated fatty acids which, through the alkyd, would have hydroxyl-amine groups. It was these that imparted the compatibility of the system.

On the second point, he had no knowledge of the use of unsaturated polyesters.

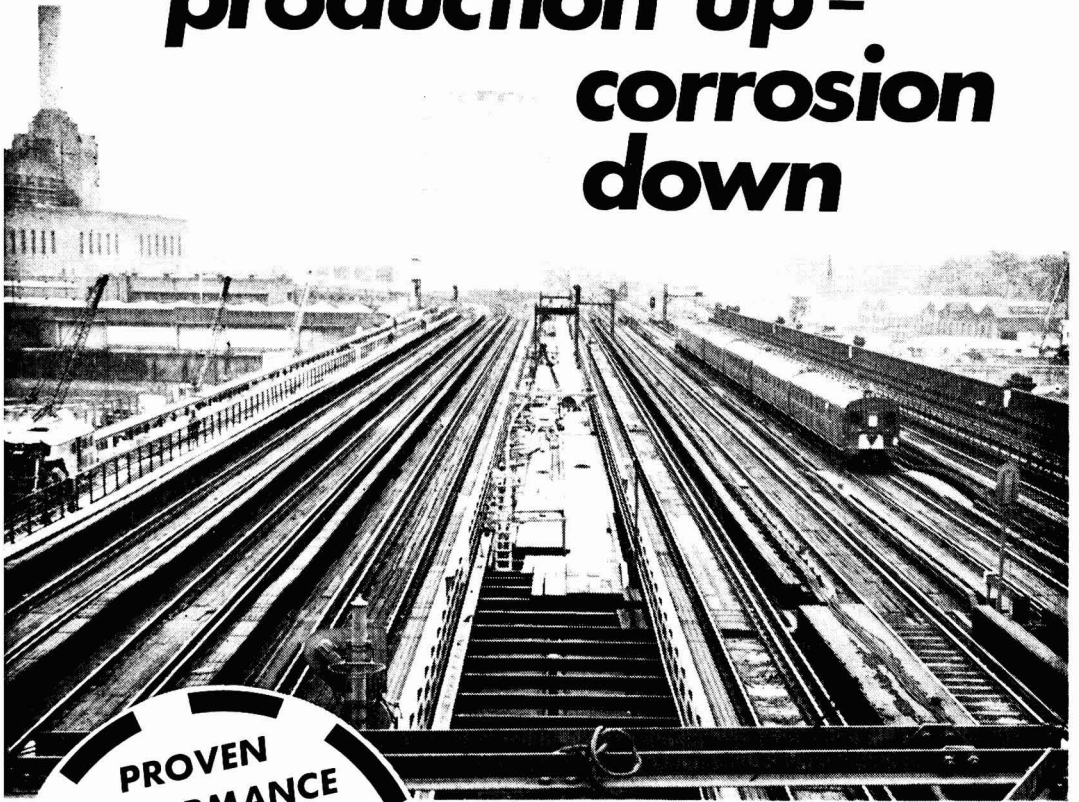
The only comment he might make was that there seemed to be an increasing tendency to use the low molecular weight polyisocyanates as reinforcing agents in a very wide variety of systems. Nitrocellulose was the classic case. All one could say was that in the context of mixing a highly cross-linkable system with thermoplastic materials, it was not surprising that improvements in solvent resistance, whether by simple mixing or true reaction, were obtained.

MR N. MACLEOD had noticed that when hydroxy-acrylics had been reacted with isocyanate copolymers, hydroxypropyl methacrylate, which contained a secondary hydroxyl, had been used. Had the author had any experience with primary hydroxyls, such as hydroxyethyl acrylate, where there wasn't a water branching interference, thus giving better film properties?

MR BARKER replied that there was no reason why one shouldn't use hydroxyethyl acrylate or methacrylate as the polar component in this context. He thought that the use of hydroxy-acrylic polymers for subsequent cross-linking was a most interesting system. Faster reaction would be expected with hydroxyethyl acrylate. It was possible that when some of the results in Table 4 were analysed, it might be found that they

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had been working with an adverse reactivity balance. A hydroxyl on a fairly large chain was reacting with an isocyanate in competition with water, and the competition was barely equal when dealing with small molecules. He suspected that some of the results, which were a little disappointing, were due to this competition.

A high level of reaction of the polyisocyanate was not being obtained, whether it was the polyol adduct, the prepolymer, or the aliphatic type. It was unlikely to be significantly different with a hydroxyethyl compared to a hydroxypropyl. Specific catalysts might have to be obtained to increase the degree of reaction.

To bring up another line of thought, he pointed out that, as with the thermosetting acrylics when curing with melamines, it was no longer a two component system, at least not two components in the sense of a polar monomer and a non-polar monomer. These systems had other components which produced self-catalysis, and it was from these systems that changes might stem. Bases and similar groups might be incorporated into the copolymer initially, which would help to promote reactivity.

THE CHAIRMAN, DR J. GAUNT, remarked that he would not have thought that with acrylics it would matter whether there was an ethoxy or methoxy end group. One of the major contributors to the slowness of the reaction was the steric hindrance effect due to the large size of the molecules. Presumably by the addition of base catalysts, this reaction could be improved, but even water would speed up the reaction.

MR BARKER agreed, and said that this would lead to work like that carried out on urethane foams, where catalysts which would promote the urethane reaction in preference to the water reaction were sought.

MR M. F. RING asked if the authors could comment on the toxic properties of the polymers as distinct from the monomer. He had gathered that there was a possibility of unreacted isocyanate groups in some cases, and, in the case of cold curing materials, he would expect this to reach quite reasonable proportions. Had any work been carried out to determine unchanged isocyanate content, and what sort of effect would this have on the uses to which coatings based on this type of material could be put?

DR LOWE replied that this was an important question. Toxicity of isocyanates in general had been a problem for many years. Obviously, if one was dealing with factory production of foams or rubbers one could take precautions quite easily. In the surface coatings field, where isocyanates were used *in situ*, in domestic circumstances, then the major hazard had been the presence of small quantities of a primary diisocyanate, such as tolylene diisocyanate or diphenylmethane diisocyanate. Many factories had taken this responsibility very seriously, and had endeavoured to produce larger isocyanate molecules, containing only small proportions of the primary material. It seemed from the work which had been carried out over the last few years, that once the molecular weight was somewhere in the region of 500 or more, very little hazard existed. Hence the moisture curing prepolymer, for example, which could be regarded as a film forming isocyanate by reaction with water only, so far as could be seen from medical tests which had been carried out, had very little effect on animals, and he knew of no case where humans had been affected by material of this kind.

The hazard with tolylene diisocyanate and hexamethylene diisocyanate was a vapour hazard, producing irritation in the bronchial passages. MDI on the other hand did not, at ordinary temperature, have a significant vapour pressure. Nevertheless its molecular weight of 250 did put it into the class of a primary irritant, so that droplets which were produced by spraying and aerosols could be a hazard. However for products which Mr Barker had mentioned, such as polyol adducts, where the molecular weight was over 500, or polymerised isocyanurates, no symptoms had been observed.

Electron and ultra-violet curing of coatings*

By W. Deninger and M. Patheiger

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Summary

The electron beam curing of coatings has for some time attracted a great deal of attention, especially since it is claimed that coatings can be fully cured in a fraction of a second. However, as far as the authors are aware, no paint processor in Europe is yet using electron beam curing equipment commercially. Various commercially available electron accelerators are described and statements in the literature regarding the output and profitability of the process are considered critically and compared with the authors' findings.

Experiments with unsaturated polyesters, which are the usual binding media mentioned in this connection in the literature, are reported and compared with the authors' results. For the most part, it has been found that the reported information is not given in sufficient detail.

A second, and very fast, curing method for polyester resin systems is polymerisation by means of ultra-violet light irradiation. Suitable techniques and binding media have reached the stage where they can be used industrially and they are discussed. Finally, the two curing processes have been compared and an attempt has been made—as far as is possible at the present time—to identify their relative importances.

Key words

Binders—resins, etc.
polyester resin

Drying or curing of coatings
Apparatus *Methods and processes*
linear accelerator electron curing
radiation source ultra-violet curing

Durcissement de peintures par faisceaux d'électrons et rayons ultraviolets

Résumé

Le durcissement de peinture par faisceaux d'électrons a été activement discuté depuis quelque temps, notamment à l'égard de la tendance actuelle vers rationalisation; on affirme que la peinture peut être durcie dans une fraction de seconde. A cet égard on doit souligner qu'à présent il n'y a pas d'utilisateur de peinture s'en servant d'un appareil de durcissement à faisceau d'électrons. Cependant, de diverses entreprises, telles que High Voltage Engineering, Radiation Dynamics, BBC, et d'autres offrent des appareils à irradiation, ou elles sont en train de les affecter. Pour la plupart, ce sont de classiques accélérateurs d'électrons, ayant des caractéristiques opératoires convenables au durcissement de peinture. C'est-à-dire il s'agit des voltages accélérateurs de 300,000 à 500,000 volts. Etant donné que la densité des feuillets de peinture soit l'unité, ces voltages accélérateurs correspondent aux profondeurs de pénétration de $\frac{1}{2}$ mm environs dans le feuillet de peinture.

On décrit les appareils disponibles et l'on considère critiquement les données sur leurs débit et rendement et l'on les compare auprès des résultats obtenus par les auteurs. La dose de radiation exerce une influence sur tous les calculs de coût. Ainsi ces calculs sont inexacts à cause des inexactitudes à l'égard du dosage de radiation.

Parmi les produits mentionnés dans la littérature en tant que liants convenables au durcissement par faisceau d'électrons il y a; mélanges de monomère avec des polymères acryliques, polyesters non-saturés, polyesters acryliques, polymères fluorés, plastisols de CPV, systèmes vulcanisables d'hydrocarbure.

Les auteurs rendent compte de leurs expériences sur des résines polyesters non-saturées et d'autres liants. Ils font une comparaison des résultats de leurs études avec des faisceaux d'électrons, auprès des données déjà publiées, et ils considèrent les différences mises en évidence.

*Presented at the Eastbourne Conference, 19 June, 1969

Les auteurs concluent que, sauf pour les polyesters non-saturés, il n'existe pas d'autres liants sur le marché actuel qui sont convenables au durcissement par faisceau d'électrons.

Un alternatif processus de durcissement très rapide des systèmes de résines polyesters est fourni par la polymérisation aux rayons ultraviolets. Le liant et le processus sont à la fois déjà à la disposition des utilisateurs de commerce. Les auteurs donnent des détails sur le durcissement de polyesters, et enfin ils font une comparaison des deux processus, et ils apprécient leur importance à l'avenir.

Lackhärtung mit Elektronenbündeln und Ultravioletten Strahlen

Zusammenfassung

Besonders im Hinblick auf den heutigen Trend zu rationalisieren, hat man schon seit einiger Zeit das Vernetzen von Lack mit Hilfe von Elektronenbündeln diskutiert; es wird behauptet, dass Lacke in dem Bruchteil einer Sekunde gehärtet werden könnten. In diesem Zusammenhang muss darauf hingewiesen werden, dass bis jetzt noch keine Anlage zur Lackhärtung mittels Elektronenbündeln von einem Lackverbraucher verwandt wird. Verschiedene Firmen, wie z.B. High Voltage Engineering, Radiation Dynamics, BBC und andere bieten bereits Bestrahlungsapparate an oder entwerfen dieselben. Diese bestehen meistens aus Elektronenbeschleunigern, deren Arbeitskonstanten auf die Erfordernisse der Lackhärtung eingestellt wurden. Dies bedeutet, dass sie mit Beschleuniger-Spannungen von 300,000 bis 500,000 Volt arbeiten. Diese Beschleunigungsspannungen entsprechen, wenn die Dichte der Lackfilme gleich 1 ist, Eindringtiefen für die Elektronen in den Lackfilm von etwa $\frac{1}{2}$ mm.

Die zur Verfügung stehenden Apparaturen werden beschrieben, und Zahlenwerte für Durchsatz und Wirtschaftlichkeit werden kritisch geprüft, sowie mit den eigenen Resultaten der Autoren verglichen. In allen Berechnungen der Wirtschaftlichkeit spielt Strahlendosis eine Rolle. Solche Berechnungen sind daher ungenau, ebenso wie das Messen der Dosis heute noch unsicher ist.

Zu den in der Literatur als für die Vernetzung mit Hilfe von Elektronenbündeln geeigneten Bindemitteln erwähnten Produkten gehören:

Akrylmonomer/Polymer-Mischungen, ungesättigte Polyester, Acrylpolyester, fluoridierte Polymere, pvc Plastisole und vulkanisierbare Kohlenwasserstoffsysteme.

Die Autoren berichten über Versuche, in welchen sie mit ungesättigten Polyesterharzen und anderen Bindemitteln experimentiert haben. Die eigenen Resultate werden mit veröffentlichten Werten verglichen, und die Unterschiede geprüft. Sie kommen zu dem Ergebnis, dass sich ausser ungesättigten Polyestern keine anderen heute zur Verfügung stehenden Bindemittel für die Härtung mittels Elektronenbündeln eignen.

Ein zweites sehr schnell Polyesterharzsysteme vernetzendes Verfahren besteht in der Polymerisation durch ultraviolette Bestrahlung. Sowohl geeignete Bindemittel, als auch das Verfahren selbst stehen bereits zur praktischen Anwendung zur Verfügung.

Die Autoren machen detaillierte Angaben über die Ultravioletthärtung von Polyestern und vergleichen zum Schluss die beiden Verfahren und beurteilen die Bedeutung, welche sie möglicherweise gewinnen könnten.

Упрочнение красок при помощи электронных пучков и ультрафиолетовых лучей

Резюме

Упрочнение красок электронными лучами активно обосуждалось уже некоторое время, особенно в виду тенденции в настоящее время к рационализации; претендуется что краски могут быть затверждены в течение доли секунды. В связи с этим следует заметить, что до настоящего времени нет еще установок применяемых потребителями для упрочнения красок электронными лучами. Различные фирмы как например Хай Волтедж Енджиниринг, Радиэшен Дайнамикс, ББЦ и другие уже однако предлагают клиентам оборудования облучения или уже проектируют их. Последние в большинстве случаев являются классическими электронными ускорителями, оперативные данные которых основаны на требованиях для упрочнения красок т. е. они функционируют с напряжениями ускорителя в 300000 до 500000 вольт. Эти ускоряющие напряжения соответствуют глубине проникания электронов в пленку краски примерно в $\frac{1}{2}$ мм, если плотность красочных пленок равна 1.

Дается описание имеющихся в распоряжении оборудований и данные пропускной способности и экономической производительности подвергаются критическому обсуждению и сравниваются с результатами полученными самими авторами. Доза излучения играет роль во всех расчетах экономии. Эти расчеты поэтому не точны, точно так же как и измерения дозирования в настоящее время еще не ясны.

Среди продуктов упоминаемых в литературе в качестве подходящих крепителей для упрочнения при помощи электронного пучка, цитируются следующие:

акриловые мономерно/полимерные смеси, ненасыщенные полиэфирные, акриловые полиэфирные, фторированные полимеры, поливиниловые хлоридные пластисолы и углеводородные системы.

Авторы докладывают об опытах проведенных ими с ненасыщенными полиэфирными смолами и другими крепителями. Результаты их работы с электронными лучами сравниваются с опубликованными данными и различия в результатах анализируются. Авторы приходят к заключению что кроме ненасыщенных полиэфиров нет в настоящее время других закрепителей красок, которые являются пригодными для упрочнения электронными лучами.

Вторым весьма быстрым затвердевающим процессом для полиэфирных смольных систем является полимеризация ультрафиолетовым облучением. Связующее вещество и процесс готовы для коммерческого применения. Авторы дают подробности ультрафиолетного упрочнения полиэфиров и в заключение сравнивают оба процесса и оценивают их роль и значение.

Introduction

Although various descriptions of curing polyester coatings by electron beams have appeared in the literature, no experimental results have so far been published. Experimental plant for this work is said to be in use on an industrial scale in the USA¹ but, as far as is known, no similar equipment is being used in Europe at the present time.

It has been claimed that coatings can be cured by electron beams in seconds, or even fractions of a second, so the process should have great economic advantages, particularly for such applications as coil-coating. Coil-coating is being carried out in Europe at strip speeds of 20 to 30m per min, but in the USA speeds of 50m per min are common and it is hoped to reach speeds of 100m per min in the future. The process is also of interest to the furniture industry where, although the cycle of operations does not permit the high speeds used in coil-coating, speeds of 10 to 20m per min can be attained.

The manufacturers of electron accelerators already have practical experience of the use of electron beams for other purposes, such as post-curing plastics (e.g. in the production of shrunk films and tubes), vulcanising rubber, the polymerisation of monomers in plastics production, and the sterilisation of medical instruments and foodstuffs, but their application to coatings is at the moment still largely theoretical. Nevertheless, they calculate that the process will have economic advantages because of the low radiation doses required, the high throughput speeds, the small amount of space required for the accelerator, the low operating costs, and the low labour content required.

Different types of radiation of comparable energy differ from one another in their linear ionisation density. This is the number of ions formed by the radiation in the target material per unit of distance. As ionisation proceeds, the radiation loses energy, and it follows that the depth to which the rays penetrate the material is inversely proportional to the intensity of ionisation.

Gamma rays ionise very weakly and are therefore capable of penetrating materials for large distances. Tests using a Caesium 137 source in an "Irma" mobile irradiation plant developed by Euratom of Brussels have shown that polyester systems can be copolymerised with gamma rays, although the complete cure of a filler composition tested by the authors required an irradiation time of six hours.

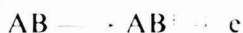
The strongest ionising effect is that exercised by α -radiation, i.e. helium nuclei, but even in a material with a density of 0.001, such as air, they have a range of only a few centimetres. As the distance between the source of the beam and the surface of the coating is unlikely to be less than 5cm in practice, almost no radiation would reach the coating.

To cure coatings effectively, radiation which ionises intensively, yet penetrates materials for large distances—that is to say a compromise between the two extremes described above—is required. Electron or β -radiation ionises intensively, although its ionisation density is not equal to that of α -radiation, and its ability to penetrate depends on the accelerating voltage to which it has been subjected. For curing coatings, this voltage is 300 to 500kV which gives a useful depth of penetration of 300 to 400 microns in a material with a density of one.

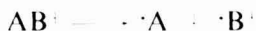
Three primary processes are capable of occurring when high energy electrons interact with materials.

1. Ionisation

An electron is eliminated,



and the ionised molecule immediately dissociates to form a free radical and a radical ion,



2. Excitation

Where the irradiation energy is not sufficient for ionisation, only for excitation,



The most important reaction of excited molecules is dissociation into free radicals,

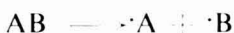


3. Electron capture

A similar process to ionisation,



which splits into a radical and a radical ion,



Further details regarding the above reactions have been given by Tawn².

The ability to form free radicals is essential for the electron beam curing process, and the following substances are stated in the literature to be suitable: mixtures of acrylic monomers and polymers, unsaturated mixtures of polyester monomers, mixtures of acrylic polyester monomers, acrylic modified epoxy resins and special polyurethanes. There is not much published information

available but it is known that only polymerisable, i.e. unsaturated, systems are suitable. It is also stated in the literature that several resin manufacturers are offering resins suitable for curing by radiation.

Sources of electron radiation

The β -ray isotopes obtained as waste products from nuclear reactors cannot be used because their β -radiation is always accompanied by strong γ -radiation, and the screens which must be used as a protection against the penetrating γ -radiation also hold back the electrons. Generators must therefore be used and, of these, only linear accelerators and not cyclotrons are suitable. Linear accelerators, usually of the types known as van de Graaff accelerators, cascade generators, or ICT accelerators, have been used in research and in industry for many years, but they have only recently been adapted for use in the curing of coatings. Because the voltage controls the depth of penetration, coatings (depending on their composition) require accelerating voltages of only 200 to 500kV—less than is required for other applications. On the other hand, whereas low current strengths are sufficient for classical applications, relatively high current strengths are necessary for curing coatings because it is desirable to produce as many reactive centres as possible in a given time.

Fig. 1 shows the working principle of an accelerator which uses a thermionic cathode as the electron source. The electrons are accelerated in the acceleration tube and the narrow electron beam is deflected backwards and forwards over

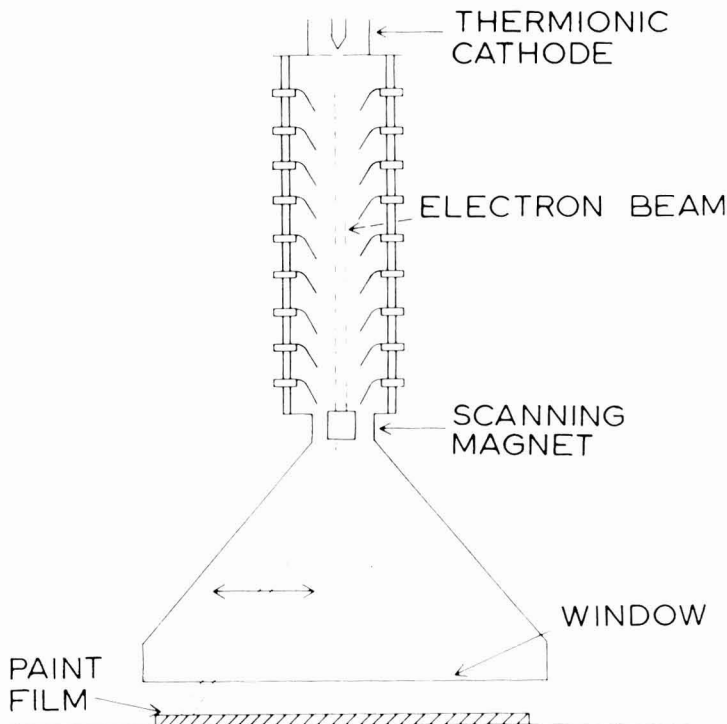


Fig. 1. Cascade accelerator

the area of the scanner at 50 cycles per second by a deflection magnet. The scanner is a shallow funnel from which the electrons emerge through a window made from metallic titanium or aluminium. A high vacuum is maintained inside the apparatus. Scanners capable of irradiating objects up to 1.8m wide are now in production. As the window is constantly bombarded by electrons, it becomes very hot, depending on the voltage and current strength. Excessive electron flux can cause the window to melt, whereupon the high vacuum is lost and the apparatus ceases to function. Replacement of the window takes at least 30 minutes, which is a very long time in relation to the high strip speeds envisaged. Although titanium and aluminium windows are usual, the use of beryllium is also being considered.

The linear deflection of the electron beam is not necessarily restricted to the direction at right angles to the conveyor belt but can also include the direction parallel to the belt. In this way a larger area of the window can be covered and the window can withstand a heavier load. The beam has to be deflected inharmonically to prevent it covering the same path every time, the aim being to "smear" the beam. It is also necessary to cool the window. At the present time a powerful current of air is used for this purpose and this causes problems because the surface of the coating has to be protected from it.

A titanium window, which usually has a thickness of 25 microns, absorbs about 7 per cent of the energy at 300kV, and as much as 10 per cent when the voltage is reduced to 150kV. This has an important effect as far as the irradiation of thin films is concerned. As the accelerating voltage is reduced, the loss of energy in the window becomes larger and larger until finally a voltage is reached at which all the electrons are absorbed in the window. This voltage is about 80 to 100kV. Therefore, although low accelerating voltages would permit penetration of thin films of organic matter, higher accelerating voltages must be used to force the beam through the metallic window.

The design described above is simply a conventional electron accelerator modified to permit the curing of thin films. However, an accelerator has now been developed in Britain, by physicists working in co-operation with paint specialists, which looks completely different from the conventional designs³ (Fig. 2). The accelerator uses an accelerating voltage of 125kV. Its thermionic cathode, instead of being a small tungsten helix giving a more or less concentrated beam which would have to be scanned as in a conventional unit, is a tungsten wire with a diameter of 1mm and a length of 1 to 2m, the length of the wire being equal to the width of the object to be irradiated. The electrons, therefore, no longer have to be deflected; instead they pass through the window and reach the object directly. The window, indeed the whole unit, is the result of development work that has covered several years and differs fundamentally from the window of a conventional accelerator. This unit is more flexible in operation than the conventional ones, and also makes it possible to use considerably higher doses without a great increase in technical difficulties. The window raises fewer problems and finally the unit enables experimental conditions to be varied to a greater extent.

Conventional accelerators give an electron current of 0.3mA per cm of scanner width but, according to its sponsors, the British unit gives a current of 8mA per cm—about 25 times greater. This corresponds to a radiation dose of

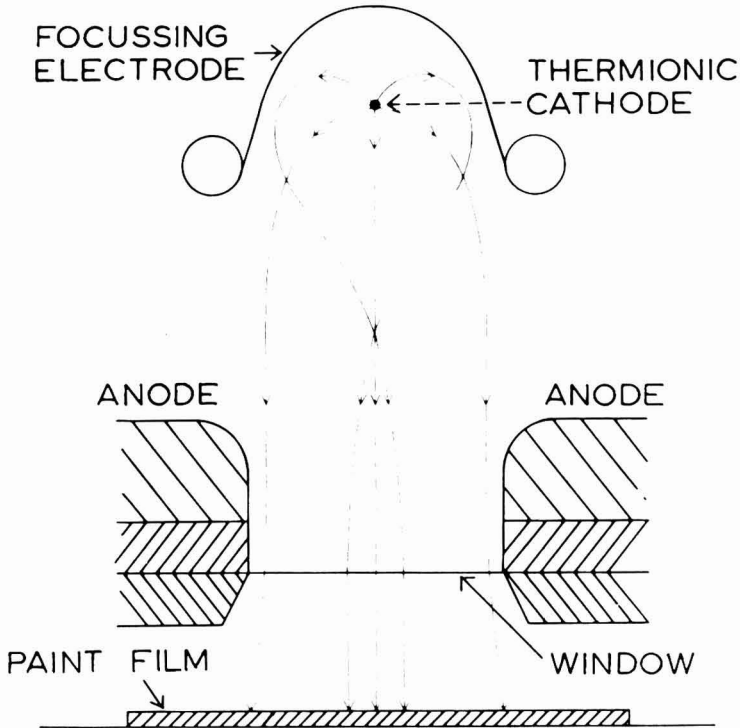


Fig. 2. Electron gun

50 megarad per pass at a substrate speed of 70m per min. A dose of 1rad corresponds to the absorption of 100ergs per gm of the irradiated material, which corresponds to 6.25×10^{13} eV per gm. 1 megarad = 10^6 rad, and a radiation current of 1mA corresponds to about 10^{16} electrons per second.

Although this high dose rate is of great value to the experimenter it should not be assumed that the speed of the substrate can be increased indefinitely.

The dose rate can be calculated from the specification of the equipment, but such a calculation is open to error because the current and voltage may fluctuate, and losses undoubtedly occur in the window and in the air. At first sight, it appears infinitely preferable to measure every radiation dose directly, and this can be done by placing a small piece of foil beside the object and determining the different light transmittances with a photometer after electron irradiation. However, closer inspection shows that this method can also be unreliable. It has been found that even when the foil has indicated the same dose there have been remarkable differences between the states of cure and between different throughput rates for identical coating systems. On one occasion, after measuring a radiation dose of 16 megarad at a given conveyor speed the authors measured 13 megarad at half that speed instead of the expected 32 megarad. It is possible that the explanation lies in the measurement foil which, apart from undergoing the intended discoloration, also undergoes unintentional decomposition. Attempts are being made to overcome this difficulty but no results are available at the present time.

What is the cost of an electron accelerator for the curing of coatings? Manufacturers quote the following prices: a plant operating at 300kV and 25mA (scanner width 1.2m) costs about 250,000 DM, and a plant with a cathode current of 50mA and a scanner width of 1.8m costs about 280,000 DM. However, after taking losses in the window and air into account, unsaturated polyester coatings of normal thickness, i.e. 300 to 500 microns, require a penetration depth corresponding to at least $400 \times 10^3 \text{eV}$. After all, it is not sufficient for only a few electrons to reach the lowest part of the film; they should be evenly distributed. Also, some reserve is required because the coating is bound to be thicker in some places owing to unevenness in the substrate.

A 400kV accelerator with a scanner 1.2m wide costs about 330,000 DM. A second single radiation head with a width of 1.2m costs about 150,000 DM. The latter is useful when two 1.2m scanners are to be operated from a 50mA unit at a current of 25mA each. It is not possible to operate more than two scanners from one power supply and another complete unit is required if more than two scanners are to be operated in succession.

To the best of the authors' knowledge, the above prices are the lowest quoted. Another manufacturer has quoted a price of 1,000,000 DM for a 500kV accelerator, but this included radiation protection. A 300kV accelerator requires either 12mm thick lead or 50cm thick concrete for radiation protection. A suitable lead screen would cost about 150,000 DM per scanner.

Electron beam curing of unsaturated polyester systems

Solutions of unsaturated polyester resins in styrene can be hardened by electron radiation and the writers' studies were concentrated on them for two reasons. First, because their company's range of products includes unsaturated polyester resins and secondly, because no other class of commercially available resins seems to behave as well under irradiation. The results which are now described have been obtained with a 500kV cascade accelerator.

Unsaturated polyester resins containing styrene could be polymerised without cobalt and peroxide under an electron beam, and no improvement in cure was observed when cobalt and peroxide were included. The polyester resin without styrene underwent no macroscopically visible changes when irradiated with the dose which had proved to cure the styrene/polyester mixture entirely satisfactorily. The same applied to styrene without polyester. This does not mean that these substances cannot be polymerised under an electron beam when a higher dose is used. It is, therefore, not surprising that, as the proportion of styrene in the coating material is raised, the dose required for a full cure increases rapidly.

The familiar inhibiting effect of air at the surface of the film also occurs during electron irradiation. Even when heavy radiation doses and high conveyor speeds are used, such that oxygen has very little time to act on the surface, the top of the film does not become cross-linked. The resulting films are easily scratched and their surface is not resistant to solvents; they also do not meet one of the most important practical requirements, which is that they should be capable of being sanded in the dry state.

To overcome this problem, paraffin wax has commonly been included, but it is found that, when polyester coatings containing paraffin wax are irradiated,

the surface does not lose its tack. In other words, the coatings gel so fast that there is not sufficient time for a continuous protective film of paraffin wax to form on the surface. Thus, when paraffin wax is included, the coatings must not be exposed to the electron beam until they have gelled sufficiently to enable a film of paraffin wax to form. In practice, the extremely fast cure under the electron beam would have to be preceded by a disproportionately long gelling time. In addition, conventional polyester finishes would then again require a cobalt accelerator and peroxide to bring about the gelling process. The formation of the film of paraffin wax would take at least five to ten minutes. All these factors considerably reduce the advantages of the electron beam cure, particularly the very fast hardening and the absence of peroxide, and the system once again has the disadvantage of a limited pot-life. It is possible that the initial gelling could also be accomplished with an electron beam but the coating would have to be polymerised slowly at a low dose rate before being subjected to the full radiation for the quick cure. In practice, it would be necessary to have a series of scanners situated one after the other, which would greatly increase the cost of the equipment.

The only reasonable way of pre-gelling coatings is to irradiate them with UV light. UV-curing polyesters became commercially available a short while ago and they are the only ones which can be polymerised sufficiently within an irradiation time of 30 to 60 seconds—a time which is comparable with that taken by the electron curing process—and which ensure that a continuous film of paraffin wax is formed.

This problem does not arise with air-drying polyesters because they are processed without paraffin wax. The surface-drying of air-drying polyesters, unlike that of polyesters containing paraffin wax, depends on the presence of a cobalt drier. However, they cannot be used in all cases because they are considerably more expensive and require roughly twice as much electron radiation.

With regard to radiation doses, widely differing figures are given by different authors, although generally they are between 2 and 5 megarad. The published figures from work on the Tube Investments plant are an order of magnitude higher, 50 megarad being given as a "typical radiation dose." The present authors have not been successful in obtaining fully cured coatings with doses of less than 15 to 20 megarad, even after preliminary gelling. Under the most favourable circumstances, 2 to 5 megarad only just succeeded in gelling some films. It would seem that the dose of 2 megarad quoted by equipment manufacturers is a mere assumption and has not been obtained by experiment. This point is emphasised because other authors appear to have accepted this figure and many profitability calculations for the process have been based on a dose of 2 megarad.

A dose of 15 to 20 megarad is required for polyester coatings containing paraffin wax on which perfect films of paraffin wax have formed. It will undoubtedly be possible to develop media which require smaller doses, and promoters for this purpose have been mentioned in the literature. Polyamines, polyfunctional monomers, chlorine compounds, reactive fillers, and other selected chemicals are claimed to be efficient sensitisers which, in relatively small quantities, reduce the irradiation dose needed for cure.

At the present time, figures of 15 to 20 megarad may be considered to be optimistic because such doses are only sufficient when the coating has been pre-gelled. If the coating is irradiated whilst still wet, the required dose is approximately doubled. This applies equally to air-drying polyester resins and to ones containing paraffin wax.

The time taken to subject the coating to a given dose, and hence the speed at which the conveyor belt is run, is also important. For example, consider the case where two coatings, moving at speeds of 6 and 3m per min respectively, are irradiated with 20 megarad. The coating which moves at the lower speed will be found to be harder because, although it requires only half the electron current, it is subjected to it for twice as long. The higher electron current needed for the higher belt speed produces, within a given time, more reactive centres which recombine or cause chain termination. The hardening of the coating requires a certain time, during the whole of which the coating must be irradiated with electrons, and this time cannot be reduced by intensifying the irradiation. It follows that it will not be possible to increase the speed of the belt indefinitely, even if more powerful equipment should become available in the future.

On the other hand, if scanners extending in the direction of the conveyor belt for 50 to 100cm, instead of 10cm as at present, are built, or if a number of scanners of the existing types are placed in succession, higher belt speeds will be possible because the coatings will be subjected to the electrons for a longer distance and hence the period of exposure will be increased. This example indicates that it will be better in the future to develop special equipment for curing coatings, rather than try to adapt the characteristics of existing accelerators.

The depth of penetration depends on the density of the coating, and the curing of pigmented and heavily loaded coatings requires higher accelerating voltages than do other equally thick films. It is very noticeable that thin films of heavily loaded coating materials, under a given dose and at a given belt speed, cure better than thick films. Although the thick films cure equally well at the surface, their lower layers do not receive enough radiation because of the energy absorbed in reaching them. This appears to offer an explanation for the view that electron cured polyester finishes adhere to metals better than those cured in the conventional way. They may be under-cured and still "sticky" at the interface, and one could argue that this apparent increase in adhesion would be lost on full cure. It is also of interest to note that coatings applied to metal require lower radiation doses than those applied to wood, possibly because the scattered radiation is reflected into the film by the surface of the metal.

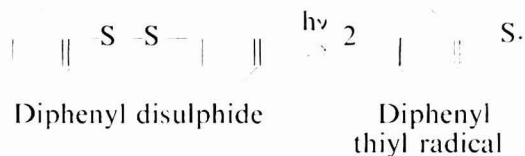
Although the coatings no longer radiate after leaving the curing plant, they continue to cure. This is of fundamental importance: if a coated material is to be packed, or given some after-treatment immediately, the coating material must be given a higher dose than it would require if it were to be given a chance to post-cure. The authors were unable to measure the post-cure quantitatively, first, because they could not measure the properties of the film and, secondly, because no method was available by which the sandability of a coating to be cured on a conveyor belt could be simulated. However, the film could clearly be seen to post-cure within the first ten minutes although this was not long

enough for it to reach its final hardness. The above considerations apply when the smallest radiation dose is used. The final hardness can, of course, be obtained more quickly by further irradiation of the fully cured coating but this may lead to embrittlement, which in turn can be counteracted to some extent by conventional plasticisation with suitable resins.

Unsaturated polyester coatings yellow noticeably when irradiated, the amount of yellowing depending on the type of resin, but much of the yellowing later disappears. It is stated in the literature that electron beams do not subject the coatings to severe conditions, especially thermally, and that the substrate is also not affected. This would seem to be only partly true. Light coloured and bleached woods undergo irreversible greying; stained woods discolour conspicuously and irreversibly, and even natural woods change their colour and appearance. In addition, the treatment does make the substrate and coating warm and, at the higher dose rates, a wet film may even begin to boil.

UV curing of unsaturated polyester systems

It is now well known that coatings can be cured by ultra-violet light. Many types of medium have been suggested as suitable for curing by electrons but, so far, only unsaturated polyesters have been cured by UV light. Electron radiation has such a high quantum energy that the radicals required for polymerisation are formed directly from the bombarded material, but UV radiation has considerably lower quantum energy and requires the use of photo-initiators. These have been proved by electron spin resonance measurements to decompose in resonance with the UV light and thus form radicals¹.



Only lamps which primarily emit UV light of wavelengths longer than 300nm are suitable because shorter wavelengths do not penetrate the coatings and are absorbed in their topmost layers. Low or high pressure mercury vapour lamps can be used depending on the application or coating system.

Low pressure mercury vapour lamps are coated on the inside with a fluorescent material which, at 256nm, converts the monochromatic radiation into long wave UV light. They emit a continuum with a maximum at 360nm and only develop an operating temperature of 45°C so are, therefore, particularly suitable for the preliminary gelling of polyester finishes containing paraffin wax which are sensitive to high temperatures.

High pressure mercury vapour lamps, unlike low pressure lamps, emit a line spectrum at 366nm and a much more intense light. They also reach an operating temperature of 700°C. The infra-red portion may be useful or troublesome, depending on the application.

A liquid polyester coating containing paraffin wax behaves in the same way under a high pressure lamp as when bombarded with electrons, i.e. it reacts so quickly that there is not enough time for a film of paraffin wax to form. It is,

therefore, necessary for the coating to be pre-gelled. This can be accomplished most quickly by using a low pressure lamp.

Systems which do not require preliminary gelling because they contain no paraffin wax, e.g. roll-applied fillers, can be cured directly and extremely quickly under the intensive light of a high pressure lamp. Paraffin wax can be dispensed with because such systems contain up to 200 per cent of filler, which reduces the amount of binding medium at the surface and enables the coating to be sanded in the dry state after the cure. They are, in fact, similar to the familiar vehicle repair fillers.

One of the great advantages of UV sensitive formulations is that peroxide and cobalt are not necessary for the curing process and the system is "one-component." Another great advantage is their high reaction speed. Conventional polyester coatings containing paraffin wax have to be left for at least 20 minutes before they can be stacked, and then they have to be left for a further 20 hours for additional hardening. On the other hand, the exposure time for a UV sensitive polyester coating can be less than 3 minutes; exposure of a primer to irradiation for 30 seconds; exposure of the preliminary gelling of the top finish under a low pressure lamp for 60 to 90 seconds, and a final cure under a high-pressure lamp for 30 seconds. UV polymerisation of a roll-applied filler can take only 30 seconds, which closely approaches the speeds obtained using electron beams.

Conclusions

The use of electron beams and UV radiation for curing unsaturated polyesters can be compared as follows. Electron beam curing has a wider range of applications than UV curing. It is suitable for both clear and pigmented systems, whereas UV curing is only suitable for clear or, at most, semi-transparent systems. On the other hand, electron accelerators are considerably more expensive and have not yet been developed to the stage where they can be generally used industrially. Further modification appears to be needed to meet the requirements of the curing of coatings.

Both processes, at least in the foreseeable future, can only be used to cure flat surfaces. There have been reports of attempts to cure car body finishes with electron beams but many problems remain unsolved and, in any case, the equipment would be expected to be very expensive.

Both processes are restricted to polymerisable systems, and the choice of media, and the properties attainable, are therefore limited.

Solvents cannot be used because, at the high conveyor speeds used, there is not sufficient time for them to evaporate. Monomers such as styrene and methyl methacrylate, which take part in the polymerisation, are not solvents in this sense.

Both processes cure very quickly and thus give high outputs.

Both processes dispense with catalysts and it is possible to have one-component systems with long pot-lives, instead of the more usual two-component systems which have limited pot-lives.

UV-curing finishes will continue to be used mainly for wood and similar substrates, but the extent of the applications for electron beam curing is still uncertain.

UV-curing can be introduced into existing plants and has been developed to industrial utility. It also permits uninterrupted movement and automatic control of the conveyor belt.

UV-curing resins are already available, but binding media and formulations equal to or better than the present standards still have to be developed for electron beam curing.

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Discussion at Eastbourne Conference

THE CHAIRMAN, DR J. GAUNT, suggested that, in view of the fact that the next paper, that by Mr Davison, also covered electron-beam curing, any questions on this aspect could be answered in the final discussion session, and, therefore, that questions at this stage be confined to the part of the paper concerned with ultra-violet curing.

DR V. G. W. HARRISON asked if the authors could give information about the intensity of the ultra-violet sources used in the work in terms of kilowatt power consumed and the distances between the tube and the surface being dried.

Ultra-violet drying was being used for printing inks with a certain amount of success. With printing inks one had a much thinner film, but the drying had to be complete in about two seconds to be of any use, so the problem was not quite the same. His information was that the manufacturers of ultra-violet sources were developing very high power tubes with the light concentrated in the desired wave bands specially for use in drying. Were the tubes used in this work developed specially for ultra-violet drying or were they ordinary tubes?

DR W. DENINGER replied that the tubes had been more or less just ordinary tubes. They had been developed for photostatic copiers or similar machinery.

In any case, choice of lamp was not merely a question of strength because polymerisation needed a certain time for reaction. There was no point in having too much energy at hand as speed of polymerisation was the limiting factor.

Several types of special lamps had been tried, and his recommendation for a strong lamp was a Philips HTQ, which was about 20 times as strong as the other one used, the Philips TLO5. The HTQ was a quartz burner which operated at about 600-700°C, while the TLO5 operated no higher than 40-45°C. The weaker lamp was certainly not of interest for printing. The HTQ type might be of use, but it was a question of the dispersion of the initiator, but it was unlikely that complete cure, even of thin films, could be achieved in two seconds.

MR A. G. NORTH referred to the use of an inert gas. It would seem economically sensible to cure in the presence of an inert gas, as was the case with the commercial operation of electron beam curing in the States. It would seem particularly economically sensible for UV-curing because it eliminated not only the use of wax and the rather slow curing time necessary to allow it to rise to the surface, but also the subsequent polishing and sanding operations. Also, the hazard of having a lamp at 700°C with styrene just below it might be obviated.

Had the authors examined the economics of this procedure?

DR M. PATHEIGER replied that if inert gas was used to prevent the oxidation reaction, trouble was caused by dust falling on to the films, and it was still necessary to sand and polish the surface to get a really good finish. As one always had to sand and polish the films, there was no extra effort in using the wax.

DR DENINGER answered the question of hazard. Official experiments had been carried out to find out whether there was any hazard for the people working with these systems. It was found that there was no hazard of inflammation or explosion of the styrene, even with lamps of 600-700°C, because it didn't have time to evaporate. Immediately under curing polymerisation started.

MR NORTH asked about the question of pigmentation of the coating. It had been stated that one could not cure pigmented finishing coats, but that one could cure fairly heavily pigmented filler coats. Could the speaker explain, and give quantitative information about film thicknesses, pigment volumes and types of pigment?

DR DENINGER said that for 100 parts of resin 200 parts of asbestos, talc, barium sulphate etc., had been used, and a maximum layer thickness of about 200 microns was found. A 200 micron film still cured under an HTQ lamp within 30 seconds. However, the reaction itself had not been measured, the criterion used was whether the coating was sandable or not. Coating thicknesses of 200 microns were still sandable, but there was, at the present time, no method of curing, say, titanium dioxide pigmented systems with more than 5 per cent PVC with UV radiation, owing to UV absorption by the filler, and reflection by the pigment.

THE CHAIRMAN, DR J. GAUNT, commented that he would like to return to the question of inert gas curing after Mr Davison's paper, because he thought that this was a very controversial point.

DR R. BULT asked if anything was known about differences in properties of films cured in a classical way and cured by UV radiation.

DR DENINGER said that the behaviour of the varnishes had been compared with those applied by curtain coating for surface deficiencies, curing speed, sandability, ease of sandability, their performances after the films were polished and finally whether kitchen furniture or sleeping room furniture in practical use showed film cracking or not. All these investigations showed that UV-curing systems performed as well as classical ones.

DR BULT commented that the UV cured coatings did not, therefore, have improved chemical resistance.

DR DENINGER said that this was the case. They were usually classical polyesters.

DR BULT asked if there was any danger of ozone formation with UV curing and could this lead to health hazards?

DR PATHEIGER replied that ozone was a strong inhibitor for the curing reaction, and, therefore, one should use lamps which did not produce ozone. The special lamps used for UV curing of coatings didn't produce ozone, and therefore it was no problem.

MR W. H. T. DAVISON referred to the question of scatter by the pigments. He would have thought that scatter, in the case of UV, was as important in terms of effective penetration as was absorption in the case of clays. The particular question

was whether, in the case of a 200 micron thickness coating, the degree of cure through to the substrate had been tested. He would have suspected that the underpart of the coating would have been completely undercured. Had any experiments been carried out to verify this?

DR DENINGER said that this had been suspected because the same thing occurred with electron beam curing as did with UV curing; curing started from the surface, and undercuring could easily occur. 200 microns had been shown by experiments to be the maximum thickness for a particular composition to form films that cured perfectly even in the lower layers in 30 seconds.

DR PATHEIGER pointed out that the thickness of films which could be cured with ultra-violet light was limited, and they had been merely interested in resins used for lacquer application. If it was intended to cure a thickness of approximately 1cm, very long exposure times were needed. Even using a high pressure lamp to cure 1cm thick coatings at least half an hour exposure from both sides was needed to cure the film. Therefore, the application was limited to thin layers, of about 500 microns or less.

MR D. J. MURRAY enquired about lamps which gave light of wavelength less than 300nm. To quote from the paper, "only lamps which primarily emit UV light of wavelengths longer than 300nm are suitable because shorter wavelengths do not penetrate the coatings . . ." Many lamps emitted quite a strong band at 254nm. What depth would these penetrate to, and what would be the limiting film thickness at 254nm.

DR DENINGER said that no attempt had been made to find out to what depth these lamps cured in, say, a film of 300 microns thickness, but, after an exposure of 60 seconds, a sandable surface had not been obtained.

MR MURRAY asked about the effect of temperature. High pressure lamps had a very high heat output, and very often a strong air current was used to carry this away. Had any attempt been made to cut down the heat by using a quartz jacket on the lamp?

DR DENINGER confirmed that this had been done. One could use either a jacket around the lamp or crude glass plates, but it was better to use two, because one would heat up and radiate in the infra-red. When two layers were used, air could be blown in between for cooling. The lamp could not be cooled, because the output was at the optimum between 600 and 700°C. Lower than 600°C and higher than 700°C the yield of the lamp was much less than within the range, so cooling was a difficult business. However, two glass plates could be used and air blown in between them so that the lower one was cooled.

DR PATHEIGER added that high pressure lamps had recently become available with water cooled tubes around the lamp to get cool irradiation to the substrate, but there was no difference between using this or using two glass plates between the lamp and the substrate. In such case UV light was lost, and therefore, if heat did not cause difficulty, the quartz lamp should be used directly. This was the case in curing wax-free components, putties applied to chipboard for instance. When using wax containing materials, such as lacquers, it was important to cool the lamps, or to use a low pressure lamp before irradiating with the high pressure lamp, so that the wax could form a homogeneous layer on the film.

MR J. WEAVER asked what a typical temperature of the workpiece was as it emerged after exposure to both lamps.

DR DENINGER said that this depended upon the system and its thickness, because the polymerisation energy was set free immediately under the strong lamps. Films were at a distance of 15cm from the lamp. Filled systems showed temperatures

of 45-50°C after irradiation. The thick, clear varnishes showed about 60-65°C. The polymerisation energy added to the energy of infra-red radiation.

MR J. SIMMONDS wondered if the authors could give some idea of the chemical resistance of the polyester resins referred to in the paper, and state whether it was possible to cure chemically resistant polyesters based on Bisphenol for instance, by use of the UV activated initiators described.

DR DENINGER replied that this had not been investigated yet. They had not been interested in the chemical resistance except that implicit in the normal demands in a household.

Process characteristics of electron beam curing*

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Summary

A brief historical review of electron-beam curing ("radiation curing") of coatings is given, together with a bibliography.

The characteristics and parameters of the process are presented as a basis for technological and economic evaluation and development, in terms of:

- (1) output characteristics of electron beam sources (voltage, current and beam dimensions),
- (2) Absorption of electrons in matter and the calculation of dose and dose-rate,
- (3) degree of cure as a function of dose, dose-rate and other parameters,
- (4) special problems in paint technology and application techniques.

From (1) to (3), overall relationships are suggested between the various parameters, the most important of which is "dose-to-cure."

Published doses to cure range from 2 to 15 Mrads; the lower values are regarded as optimistic. The need for development work based on facilities which simulate realistic speeds, application techniques and source characteristics is stressed and illustrated by TIGER, the Tube Investments prototype equipment.

Economic trends are discussed and compared with those for thermal cure in order to indicate the areas in which electron beam curing will compete with or replace thermal curing.

Key words

*Types and classes
of coating*
solventless paint

<i>Drying or curing of coatings</i>	
<i>Apparatus primarily associated</i>	<i>Processes primarily associated</i>
radiation source	electron curing polymerisation

Caractéristiques du processus de durcissement par faisceau d'électrons

Résumé

L'auteur donne une brève revue chronologique du durcissement de revêtements par faisceau d'électrons ("durcissement à radiation"), ainsi qu'une bibliographie.

Les caractéristiques et paramètres du processus se présentent en tant qu'une base d'évaluation technologique ou économique et également du développement en termes de:

- (1) Caractéristiques opératoires des sources de faisceaux d'électrons. (cotes de voltages, de courant et faisceaux).
- (2) Absorption d'électrons par matière, et le calcul de la dose et du taux de dose.
- (3) Degré de durcissement en fonction de la dose, du taux de dose, et d'autres paramètres.
- (4) Problèmes particuliers de la technologie des peintures et des techniques d'application.

A partir de (1) à (3) on suggère des associations globales entre les divers paramètres, dont "la dose à durcir complètement" est le plus important.

Les doses mentionnées dans la littérature varient de 2 à 15 Mrads; on considère que les cotes inférieures soient optimistes. On souligne le besoin des études de développement basées sur les appareils qui simulent à la fois des allures raisonnables, des techniques d'application, des caractéristiques de la source, et l'on le démontre à l'aide de TIGER.

On discute des tendances économiques, et l'on les compare auprès de celles de durcissement thermique, afin de faire indiquer les domaines où durcissement par faisceaux d'électrons peut faire concurrence au durcissement thermique ou peut le remplacer.

*Presented at the Eastbourne Conference, 19 June 1969

Prozesscharakteristika der Härtung mit Elektronenbündeln

Zusammenfassung

Es wird ein kurzer historischer Überblick über das mit Hilfe von Elektronenbündeln mögliche Vernetzen von Beschichtungsmitteln ("radiation curing") gegeben, ebenfalls eine Bibliographie.

Als Grundlage für die technologische und wirtschaftliche Bewertung und Weiterentwicklung werden die charakteristischen Merkmale und Parameter des Prozesses vorgetragen unter Hinweis auf:

- (1) Leistungscharakteristika der Elektronenbündelquellen (Spannung, Strom- und Bündeldimensionen).
- (2) Absorption von Elektronen in der Materie und Berechnung von Dosis und Dosiszuteilung.
- (3) Vernetzungsgrad als Funktion von Dosis, Dosiszuteilung und anderer Parameter.
- (4) Spezielle Probleme in der Anstrichtechnologie und den Anwendungstechniken.

Es wird vorgeschlagen, anzunehmen dass von (1) bis (3) zwischen den verschiedenen Parametern gegenseitige Beziehungen bestehen, deren wichtigste "dose to cure" (Dosis zur Härtung) ist.

Mengen von 2 bis 15 Mrads wurden veröffentlicht; die niedrigen Werte werden als optimistisch angesehen. Die Notwendigkeit Entwicklungsarbeiten mit Hilfe von Einrichtungen, welche realistische Geschwindigkeiten, Anwendungstechniken und Quellen-Charakteristika simulieren, durchzuführen wird betont und durch TIGER illustriert.

Wirtschaftliche Trends werden besprochen und mit denen für Wärmehärtung verglichen, um die Gebiete aufzuzeigen, in welchen Elektronenbündelvernetzung mit ihnen konkurrieren, oder sie ersetzen wird.

Характеристики процесса сушки электронными лучами

Резюме

Дается краткий исторический обзор сушки покрытий электронными лучами («радиационная сушка»), с приложением библиографии.

Характеристики и параметры процесса излагаются в виде основы для технологической и экономической оценки и развития, с точки зрения:

1. Характеристик мощности источников электронных лучей. (Напряжение, ток и размеры лучка.)
2. Поглощения электронов в веществах и вычисления дозы и мощности дозы.
3. Степени сушки как функции дозы, мощности дозы и других параметров.
4. Особых проблем в технологии красок и в технике применения.

От 1. до 3. предлагаются общие зависимости между различными параметрами, причем самой важной зависимостью является отношение «дозы к сушке».

Опубликованные дозы колеблются между 2 и 15 мг рад; более низкие величины считаются оптимистичными. Подчеркивается необходимость развития исследований основанных на способности симулирования реалистичных мощностей, техники применения и характеристики источников, которые иллюстрируются процессом фирмы ТИГЕР.

Обсуждаются экономические тенденции и сравниваются с термической сушкой, для указания областей в которых электронная сушка может конкурировать с тепловой сушкой или ее заместить.

Introduction

Historical

Earlier work in these Laboratories, 1958-60, with a 0.5kW, 2 MeV Van de Graaff electron accelerator, had shown that electron irradiation would cure special lacquers and paint films and that such a process would be commercially attractive if high power electron generators of between about 100 and 250kV were available; a British patent for the process was applied for in 1960, and granted in 1964¹.

Since liquid paints or lacquers almost inevitably contain volatiles, it was decided that irradiation should take place at approximately atmospheric pressure. The electrons, which are produced and accelerated in a vacuum, must, therefore, be transmitted through a vacuum-tight window into approximately atmospheric pressure.

No equipment existed in 1960 which could deliver a powerful and wide beam of electrons into the atmosphere at energies of less than about 500kV, and the window problem was considered sufficiently intractable that no electron generators were known to be under development below about 300kV.

Preliminary² work led to a design of window which could transmit significant currents of electrons at 100kV by using a thin aluminium foil on a cooled supporting grid³.

A development contract was placed with Mullard Equipment Ltd. to supply a source of electrons of voltage 100 to 150kV over a 6in by 1in window, using a linear filament and simple rectified three-phase oil transformer as power supply. This was delivered in 1962, and used for development work with Drynamels Ltd. in an overall experimental coating line from about 1963. During this period the window output was increased to the maximum current available from the power supply, i.e. 120mA at 125kV, over 6in width.

In the USA, several organisations started work in this field in the early 'sixties. The Ford Motor Company had filed a basic process patent⁴, but did not publicise their interest until 1966⁵. High Voltage Engineering Corporation had published a general account of their preliminary work in 1964, in a journal of limited circulation⁶. Radiation Dynamics Inc. also indicated their activities in 1966 and 1967⁷.

In the UK, the AERE began a programme in 1964-65 which included the development of an electron beam source⁸, and Porter Paints Ltd., on the basis of preliminary work at Wantage, approached Tube Investments, leading to an agreement in 1967 for joint exploitation of the process. The Tube Investments facility was transferred to Hull⁹ under this agreement.

Properties of electron beam sources

Few paint technologists will be familiar with the properties of electron beam sources, but a basic knowledge of these is essential in so far as it affects the overall process and interacts with the compositions and overall process. All electron beam machines consist basically of:

- (a) a source of electrons, usually a heated cathode or filament,
- (b) an accelerating field, usually achieved by operating the cathode at a high negative voltage with respect to earth,
- (c) some form of beam defining or focusing, which may include time-scanning,
- (d) since (a) to (c) occur in a vacuum, for electron beams to operate in air, a "window" is required which prevents the flow of air into the vacuum but transmits the electrons.

Absorption characteristics of monoenergetic electrons

The maximum range (r_o) of electrons in matter is primarily dependent upon voltage and the mass-thickness of the absorbing material¹⁰ (Fig. 1). Mass thicknesses are in g.m^{-2} ; $1 \text{ g.m}^{-2} = 0.1 \text{ mg.cm}^{-2} = 0.0929 \text{ g.ft}^{-2}$.

The range (r_o) is, also, to a lesser extent, dependent upon the atomic (not the molecular) composition of the absorbing medium¹¹.

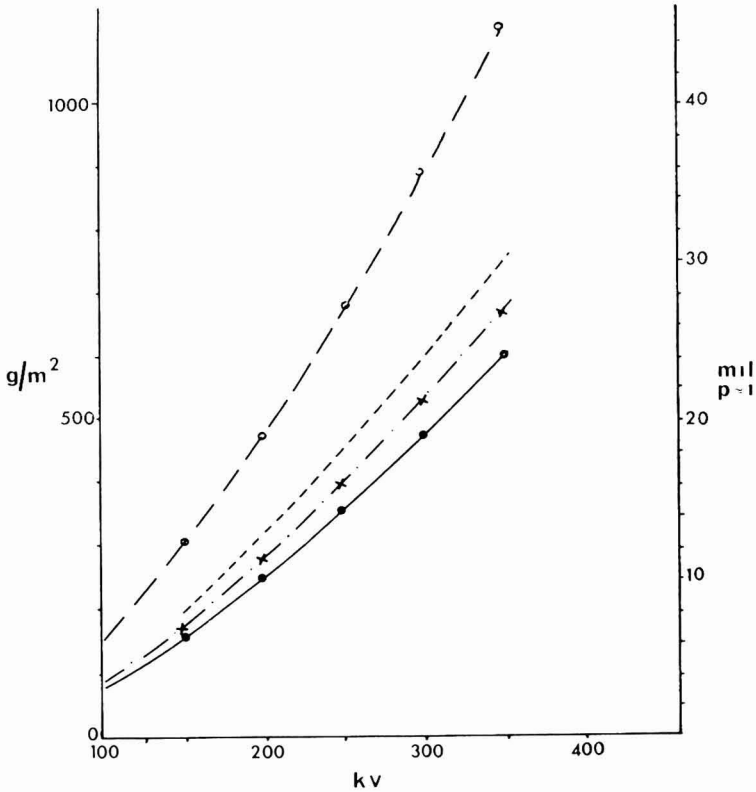


Fig. 1. Ranges of electrons v voltage

			Notes
r_o	—	Al	— — — — — (i) Polyester "lacquer" $C_{17}H_{16}O$
r_{70}	—	Al	• — — — — • (ii) Polyester paint—lacquer
r_{70}	—	"Lacquer"	o — — — — o with 20% TiO_2 .
r_{70}	—	"Paint"	x — . — . — . x (iii) $10.76 \text{ g.m}^{-2} = 1 \text{ g.ft}^{-2}$

In Fig. 2, the relative doses (at 300kV) are plotted against depth of penetration into 1mil blue cellophane film of specific gravity *ca.*1.38, manufactured by DuPont and used for dosimetry¹². The author's experimental data (using a 300kV Dynacote¹³) are compared with other published data^{4,14}, and with theoretical curves¹⁵. The values of points at which the dose falls to 70 per cent of maximum are superimposed to correct for varying windows and air gaps.

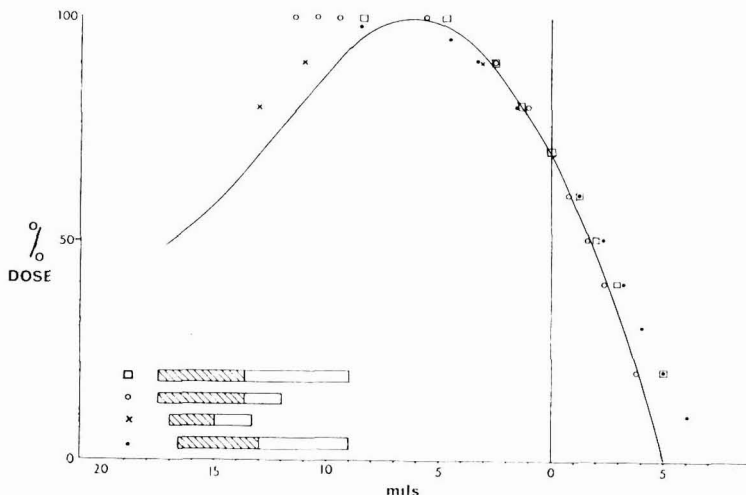


Fig. 2. Relative dose v depth absorption in cellophane

Notes

- Ford, 6in air¹
- Ford, 2in air¹
- × Boise, 2in air¹⁴
- Dynacote, 5in air¹³
- Theoretical¹⁵

- (i) Cellophane film¹² nominally 1 mil and s.g. 1.38, i.e. 1 mil \approx 35 g.m⁻²
- (ii) 25 μ Ti Window on Dynacote and other window thicknesses tentative.

-  Air Gap
-  Window

An arbitrary “useful range” is defined here as the range at which the dose falls to 70 per cent, r_{70} , and values are plotted in Fig. 1 for a range of atomic compositions¹⁵. It should be noted that the composition has a significant effect on r_{70}/r_0 , that is, the shape of the “Trump curve” is very dependent upon composition (Fig. 1). For higher atomic numbers the peak of the Trump curve moves to lower proportions of the range.

In all cases, it is assumed that the beam is of monoenergetic electrons and is substantially parallel. In spite of scatter, which spreads the beam, this is a basically valid assumption in terms of the *total* dose (rather than dose-rate) a material receives in passing through a wide beam, and the curves relate to such cases.

Effective penetration for curing coatings

The variation in properties of the paint through its film thickness depends primarily upon the dose, but there are secondary dose-rate effects and surface and interface factors which are considered later. In general, all parts of the coating must receive some minimum dose (e.g. at the interface) to give full conversion and properties, but the top surface normally requires a greater degree of cure than this minimum to give extra surface hardness, mar resistance, etc.

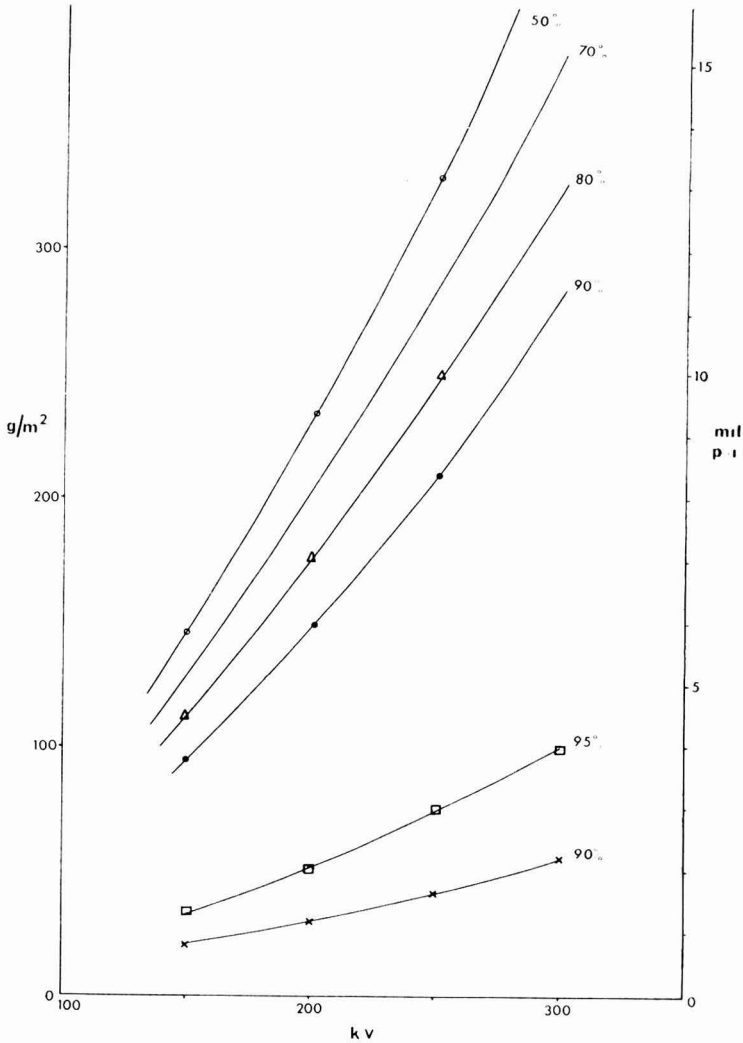


Fig. 3. Useable penetration v voltage

- (i) Upper curves are penetration from relative dose of 80% at surface to 90, 80, 70 and 50% at substrate.
- (ii) Lower curves are the thickness to be deducted from above penetrations for relative doses at surface of 90 and 95%.
- (iii) Relative doses are in percentage of maximum of Trump curve (Fig. 2).

The useful penetration, therefore, depends upon relative doses acceptable at various points within the coating; Fig. 4 gives values of useable penetration for assumed relative doses at the interface with the substrate, and at the surface of the coating. While the paint technologist is not expected to specify his requirements in these terms, they illustrate the dependence of useful coating thickness upon the acceptable dose variation. The latter also depends upon the "tolerance" of the paint or lacquer to dose variations.

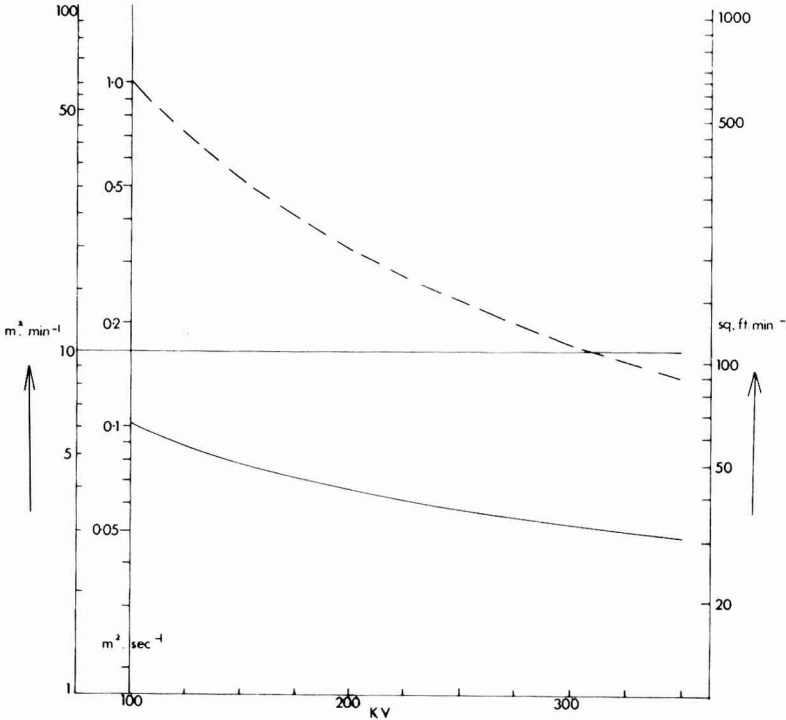


Fig. 4. Theoretical maximum area outputs v voltage

- Area output for 1 Mrad (at maximum dose), per mA
- Area output for 1 Mrad (at maximum dose), per kW

(NOTE: Outputs are mean of those for "standard lacquer" and "standard paint" (Fig. 1).)

Output calculations

A Mrad is defined as $10^6 \cdot 10^2 \text{ erg.g}^{-1}$ or $10 \text{ watt.sec.g}^{-1}$ so that, ignoring losses, 1 watt will irradiate 0.1 g.sec^{-1} to 1 Mrad, i.e. $0.1 \text{ Mrad g.sec}^{-1}$. An electron beam accelerator of voltage E (kV) and current I (mA) will therefore irradiate $0.1 EI \text{ Mrad g.sec}^{-1}$, ignoring losses.

For organic coatings, including pigmented ones, the average dose over the range r_o (in g.m^{-2}) is $0.69 \pm .01$ of the maximum dose R_{max} , at the top of the Trump curve.

The output for a linear speed of u (m.sec^{-1}) and width w (m) is therefore:—

$$(0.69R_{\text{max}}) \cdot (r_o \cdot u \cdot w) \text{ Mrad g.sec}^{-1}$$

which = $0.1 EI$

$$\text{or: } R_{\text{max}}u \simeq 0.145 \left(\frac{E}{r_o} \right) \left(\frac{I}{w} \right) \qquad \text{Equation 1}$$

Values of E/r_o vary from $0.34 \pm .005$ at 300kV to 0.57 ± 0.01 at 125kV, so that where lower voltages can be used, the output increases significantly

for a given current and even more so for a given power (in kW). In Fig. 4, calculated values¹⁵ are given for K against E in the equation.

$$R_{\max}u = K \cdot \frac{I}{w} \quad \text{Equation 2}$$

The units of K are Mrad.m².s⁻¹(mA)⁻¹ in terms of *maximum* dose (at the top of the Trump curve).

These theoretical outputs must be corrected for losses arising from the following.

- (a) Electrons not reaching the thin, transmitting foil. (This is particularly important if the window has thick cooling supports which absorb all electrons incident upon them—in one TI window this loss is 20 per cent.)
- (b) Back-scattering of electrons from the foil; this loss increases with thickness and atomic number and can be up to 10 per cent for a 1mil titanium foil at 300kV.
- (c) Anomalous energy absorption of foil compared with air and/or coating for an equivalent mass-thickness.
- (d) Scatter losses in the air.
- (e) Back-scatter from the coating. This is increased when high atomic number pigments are used.

The overall losses arising from (a) to (d) are basic characteristics of a specific design of electron beam equipment for which measured output constants K' should be determined and used in the output equation:

$$R_{\max}u = K' \cdot I/w \quad \text{Equation 3}$$

These losses also lead to a dose-depth curve which differs from that for homogeneous absorption and from theory. In general, this results in measured useful penetrations which are somewhat less than those calculated.

These calculations only apply for relatively thin windows and air gaps such that the maximum of the Trump curve occurs within the coating; for thicker windows and air gaps significantly lower maximum doses will occur.

Dose-rates

Since most radiation-sensitive compositions are dose-rate dependent, i.e. the total dose required is less when lower dose-rates are used, it is advantageous to operate at lower dose-rates. This can be achieved by increasing the total area irradiated for a given current and voltage, by spreading the electron beam along the direction of movement of the coating,

- (a) by normal scatter from large air gaps
- (b) by scatter in a Ford window¹⁶
- (c) by two-dimensional spread of beam before the window.

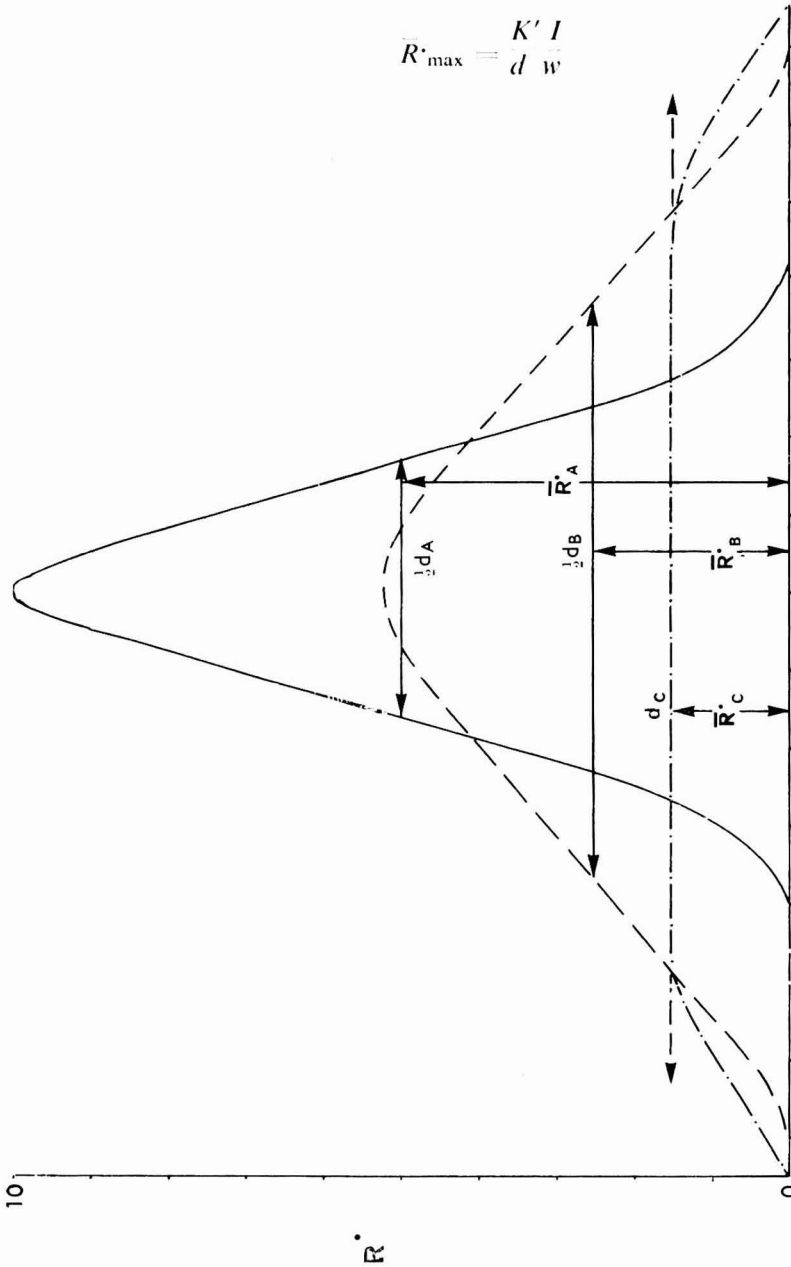
Fig. 5 illustrates the beam profiles for (a) and (b) (based on ref. 16) and a calculated beam profile for case (c), together with approximate dose-rates (R in Mrad.sec.⁻¹), average dose-rates (\bar{R}) and effective beam spreads d (metres). In each case ($\bar{R} \cdot d$) is made equal to the integrated area under the curve, so that

the total dose R received by an element of coating passing through the beam at u m.sec⁻¹ is given by

$$R = \frac{\bar{R} \cdot d}{u} \tag{Equation 4}$$

From first principles, or from Equation 3

$$\bar{R}_{\max} = \frac{K' I}{d w} \tag{Equation 5}$$



DISTANCE ACROSS BEAM

Fig. 5. Dose-rates for various beam profiles

- (a) — Normal scatter in 2in air¹⁶
- (b) - - - Scatter in Ford window¹⁶ and 2in air.
- (c) - . - . - Theoretical for 2-dimensional beam and 2in air.
- \bar{R} dose-rate (Mrad.sec⁻¹)
- \bar{R} average dose-rate
- d effective beam spread

Notes: (i) Beam profiles are normal to direction of movement of coating
 (ii) $\bar{R} \cdot d$ is constant, i.e. same R for all cases.

In principle, methods (a) and (b) suffer from the disadvantage that there is a reduction in penetration and output (in Mrads, not necessarily in coating outputs), but avoid the problems associated with large area windows, and two-dimensional beam spreading or scanning. For narrow beams (i.e. small values of w) excessive scatter at the beam ends lowers the overall efficiency of the process.

Secondary heat and temperature

Since 1 Mrad is 2.39 cal, the adiabatic temperature rise (ignoring heats of reaction) is given by:

$$\Delta T = \frac{2.39}{s} R^{\circ}\text{C where } s \text{ is the specific heat.}$$

For most organic materials $s \sim 0.5$, so that the adiabatic temperature rise is about $5^{\circ}\text{C}/\text{Mrad}$. For high speed lines on thermally insulating substrates, temperature rises may be near to (or with severe exotherms greater than) this.

For thin coatings on metal substrates, however, the heat is rapidly dissipated and the temperature rise "diluted" by the total heat capacity of substrate and coating.

Since the air above the coating also absorbs energy and has in general a specific heat of about 0.25, the air temperature will rise some $10^{\circ}\text{C}/\text{Mrad}$. At a linear gas flow equal to that of the coating, therefore, the air temperature will rise by $10^{\circ}\text{C}/\text{Mrad}$ of dose given to the coating.

Radiation hazards

Electron ranges are low and electrons can be readily stopped so that no danger arises from these.

When electrons are stopped they emit X-rays, the energy of which increases with voltage and atomic number of the absorbing medium.

Properly designed and engineered screening is essential and must be suitable for operation by normal production staff, without necessitating the use of film badges, etc. (i.e. $<0.5 \text{ mrad}\cdot\text{hr}^{-1}$).

No radioactivity is induced at these voltages, in either the products or the equipment.

Electron beam sources

Prior to about 1961, the main emphasis was on high voltage machines (800kV to several MeV) for nuclear work and bulk irradiation. Resulting from demands for radiation processing of polymers (e.g. thin polyethylene film), H.V.E.C. developed an I.C.T. 500kV model⁶ and later a 300kV adaptation¹⁷. These used circularly symmetrical beams of electrons scanned across the desired processing width; at high scan rates, the beam is equivalent to a constant but spread beam. Since about 1965, several other manufacturers have developed similar scanned beam equipment operating in the 200 to 400kV region and normally limited to between 25 and 50mA over a 4 or 6ft width of window. The power supplies for such scanned beams require a DC source with little ripple, and tend to be specially developed for these machines.

The windows used normally consist of unsupported foils of titanium, stainless steel or aluminium alloys of thicknesses 15 to 40μ (0.6 to 1.7mil). The foils are

cooled by a flow of gas and/or by conduction of heat through the foil to a water-cooled surround.

Tube Investments electron beam equipment (TIGER)

The developments in these laboratories were based on different approaches in three respects:

- (a) the emphasis on special lower voltage equipment between about 100 and 150kV,
- (b) the use of special windows for high current loadings and low voltages,
- (c) the use of simple linear filaments rather than focused and scanned beams.

Arising from (a) and (c), it was possible to utilise power supplies based on full-wave rectification of outputs from conventional three-phase oil-filled transformers.

The Tube Investments prototype electron beam source (TIGER) utilises a simple linear filament of tungsten wire as a cathode (Fig. 6). This is at the same negative HT potential as the focusing electrode, and gives a dispersed beam of electrons about 6in by 1in at the window aperture in the anode. The whole is mounted within a glass dome and insulated (up to 160kV) by submerging in a tank of transformer oil.

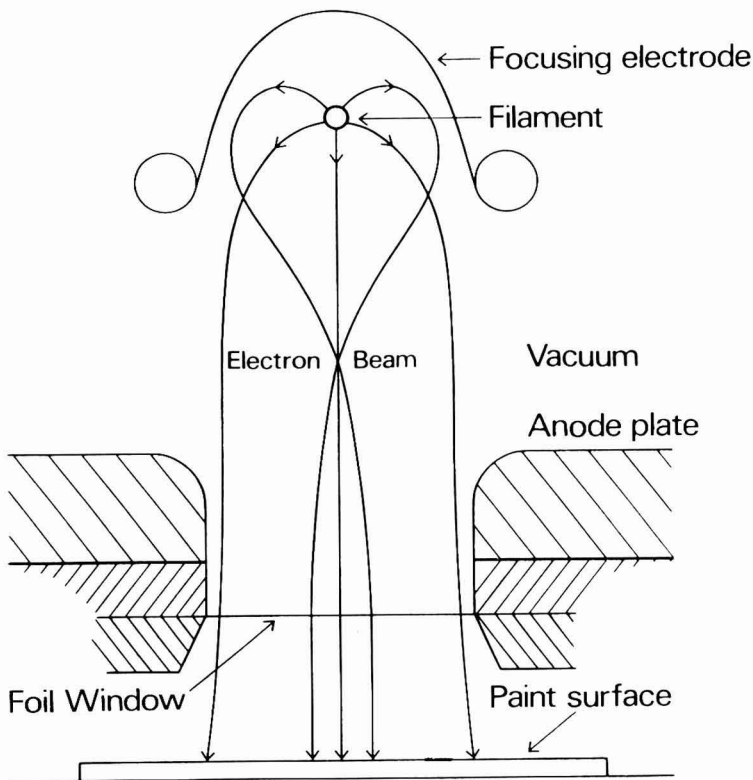


Fig. 6. Schematic of electron gun—TIGER

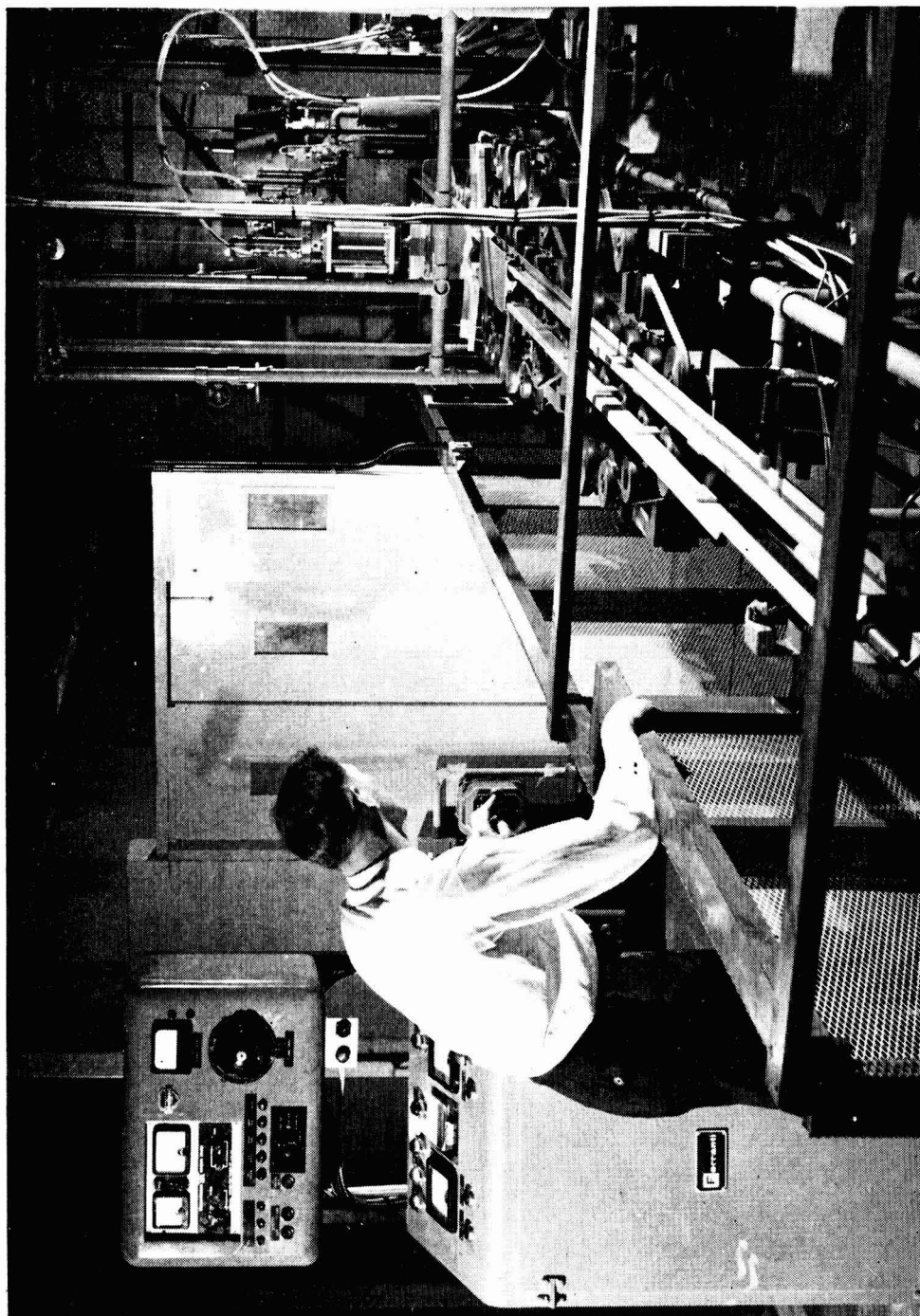


Fig. 7. TIGER—installation at Hull

The DC power supply (Ferranti) is 150kV, 30kVA with full-wave rectification of the secondary output of an oil-filled three-phase transformer. The HT power, together with the filament supply from an isolation transformer, is connected to the accelerator head by simple air-insulated busbars. These would obviously be replaced by insulated HT cables for a production model.

The whole equipment (Fig. 7) is operated from a remote control console which includes provision for setting the accelerating voltage and current. A range of meters and signal lights show the state of all aspects of the equipment: they are connected to various cut-outs and interlocks which prevent damage to the equipment in the event of mains surges, discharges or window failures.

Samples of up to 2ft \times 6in can be mounted on trolleys, which are automatically passed through the various stages of the complete line (i.e. curtain coating application, retarder or flow-out zone, and irradiation) at speeds which can also be controlled from the operating console. Automatic gates shield against any X-rays and, although the operating staff wear film badges, these have not recorded a measurable radiation dose in some five years of operation.

The window operates at a beam current up to the maximum available from the power supply (without a drop in voltage), i.e. 120mA at 125kV. This is equivalent to about 800mA m^{-1} at 125kV, and well over 1.2A m^{-1} at 300kV; such currents are not normally required, except for very high speed trials.

Normally the equipment runs at between 10 and 50mA. Even with intermittent and experimental operation, 0.7mil aluminium window foils normally last between about 40 and 100 hours or more; they can be readily replaced by low cost commercial aluminium foils on a regular maintenance schedule. Failures are normally due to accidents, rather than thermal or creep failures, and the use of voltages of not less than 150kV is recommended to enable more robust foils to be used.

Summary of known electron beam sources

The linear filament approach is considered potentially cheaper and more reliable, particularly for voltages below about 200kV. It must be emphasised, however, that the output and processing characteristics of linear filament and scanned beam machines are similar, as long as the scan-rates are fast compared with the reaction rates and linear processing speeds.

The linear filament approach is also used by the UKAERE, and possibly by Ford (see Fig. 1 in ref. 16).

From the previous sections, it can be seen that an electron beam source can be fully characterised in terms of:

- (a) its dose-depth characteristics for various voltages and air gaps,
- (b) its maximum output (in Mrad.m².s⁻¹) for its range of operating voltage,
- (c) its average dose-rate, or the spread of beam in the direction of movement,
- (d) capital cost,
- (e) operating and maintenance costs,

although the technical information (a) to (c) is not usually available in explicit form.

Radiation curable coatings

Basic radiation chemistry

The interaction of ionising radiations (i.e. electrons and other particles, X-rays and γ -rays) with matter and the chemical changes produced are a highly specialised subject^{18,19}.

In simple terms, radiation produces active species such as excited molecules and atoms, free-radicals and ions, and the yield depends upon the dose and G (the G -value or number of molecules reacted per 100eV of absorbed energy).

$$\text{Yield } (\mu\text{mol.g}^{-1}) = 1.04 G.R \quad \text{Equation 6}$$

Values of G depend upon the specific product being considered and on the chemical composition, state and temperature of the material irradiated. G -values for major products are usually between about 1 and 10, unless the products are produced by chain reactions which can give much higher overall values of G .

In the case of polymers (or polymerisation of monomers) even low yields in terms of $\mu\text{mol.g}^{-1}$ can yield important changes in properties, as a result of molecular weight changes and the formation of cross-linked networks¹⁹.

The mechanical properties of cross-linked networks are largely dependent upon the value of M_c , the average molecular weight between cross-links, and the solvent resistance (e.g. sol fraction) upon the ratio of M_c/M_w (where M_w is the wt. average molecular wt.). The dose required, R_c , to crosslink to a value of M_c is given by:—

$$R_c = \frac{0.48 \times 10^6}{G.M_c} \quad \text{Equation 7}$$

and, for highly cross-linked networks when M_c/M_w is 0.2 or less, values of the initial molecular weight are of only secondary importance.

In order to achieve reasonable viscosities and flow properties of coatings for radiation curing, values of M_w must be relatively low, and to avoid excessive doses, chain reactions must be utilised to give high G -values.

Radiation polymerisation

Such chain reactions normally involve either the direct polymerisation of monomer or, more normally, the polymerisation of monomer with a polymer to give various forms of graft polymer or polymerisation cross-linking network.

Although the radiation-induced ionic polymerisation of isobutene was demonstrated in 1957²⁰, the author considers that only free-radical initiated polymerisation reactions are appropriate to the curing of surface coatings.

However, free-radical polymerisations tend to terminate by bimolecular reactions, so that the chain length is reduced as the radical concentration increases. The rate of primary production of free radicals is proportional to the dose-rate R (Mrads. sec⁻¹) so that the conversion decreases as the dose-rate increases. This "dose-rate effect" for a classical bimolecular termination mechanism, means that the rate of conversion is proportional to $(R)^{-0.5}$, and the dose required (R_c) to achieve a given degree of conversion or cure is proportional to $(R)^{0.5}$.

In general, it appears that combinations of reactive polymers and monomers (which if liquid also act as solvents and/or thinners) are necessary for high-speed (and therefore high dose-rate) curing. Unsaturated polyesters blended with liquid monomers such as styrene, acrylates or methacrylates have shown most promise to date.

Owing to commercial security, little has been published on actual coating compositions. Relevant published work on the reactions of polymers with monomers, covers studies of conversion, sol/gel ratio and properties as a function of dose and dose-rate^{21,22,23,24}.

Some dose-rate dependence is normally observed, although it rarely corresponds to a simple $(R\cdot)^{0.5}$ relationship, and care must be taken in extrapolating the doses required to higher linear speeds and dose-rates. Since one effect of higher dose-rates and doses is to change the chain length, the properties of the coatings may also change.

(Note: A similar dose-rate dependence should also apply to other sources of free-radical initiation, i.e. UV sensitisers and peroxides, as attempts are made to increase their operating speeds.)

Dose to cure

A basic parameter of the process is the dose-to-cure. The definition of cure is itself very vague; it is often taken to be the dose required to achieve an arbitrary property such as hardness, irrespective of the degree of conversion or polymerisation achieved.

Incomplete conversion may result in a post-irradiation cure (over a period of hours or days) to a more fully cured product. Alternatively, monomer loss with or without oxidative degradation can also occur and cause a reduction in the properties over a period of time.

Even if a technologically acceptable cure is defined, it is advisable to determine the ultimate properties of coatings under development (i.e. at their plateau) and to measure their reactivity by the dose required to achieve a given proportion (say 70 per cent) of these ultimate properties.

Apart from the conditions of irradiation such as dose-rate, the dose-to-cure (however defined) depends upon:

- (a) the monomer used, its reactivity and functionality,
- (b) the polymer and its reactivity and functionality,
- (c) the ratio of monomer to polymer.

The latter, the feed ratio, is particularly important (Fig. 3 of ref. 23).

It is also desirable to have compositions which are tolerant to variations in dose and composition (e.g. feed ratio).

Surface inhibition

Undercured surfaces may arise for several reasons:

- (a) oxygen inhibition,
- (b) "corrosion" attack by ozone and oxides of nitrogen,
- (c) surface variations in composition, such as loss of monomer.

All of these factors are reduced by operating at higher speeds and dose-rates,

and may also be obviated by chemical modifications. However, (a) and (b) can also be simply eliminated by use of a flow of an inert gas such as nitrogen.

Paint technology and application techniques

In thermal curing, solvents can be added to improve the flow characteristics (for application and subsequent flow-out) and they are readily removed by heat before or during the oven cure. Flow-out is further assisted by the reduction in viscosity with increased temperatures.

In order to take full advantage of the characteristics of electron beam cure (i.e. lack of heat and short curing times) the only solvents which can be used are convertible monomers.

Viscosity of the coating can be reduced in four main ways:

- (a) by lowering the molecular weight, and increasing the molecular flexibility of the polymeric component,
- (b) by choice of liquid monomers with good solvent and thinning power,
- (c) by increasing the liquid monomer/polymer ratio,
- (d) by raising the temperature of application.

Experimental high-speed curtain-coating in these laboratories in 1960-61 (based on a BISRA project²⁵) showed:

- (a) that stable curtains could be produced with total mass flows of down to about $35\text{g.m.}^{-1}\text{sec}^{-1}$,
- (b) that viscosities up to 6 or more poise could be used,
- (c) that such curtains could deposit even coatings of 2μ thickness at linear speeds of up to $1,000\text{m.min}^{-1}$.

It is suggested that more effort is required to develop or adapt techniques which are compatible with the particular requirements of coatings for electron-beam curing.

Overall process parameters

The energy absorbed by the substrate is usually wasted, and may be harmful to it. If possible, therefore, the voltage should be adjusted to give an acceptable level of dose variation, which can also be modified by the air gap (the window is normally of fixed, minimum, thickness). In doing this, the output or efficiency of the overall process is affected and a compromise is made between quality of cure and output.

In order to estimate the plant required for a given output and application, it is necessary to know R_c , the dose required to give the required properties in the coating. If the system is dose-rate dependent, and a facility does not exist which enables a direct measurement to be made, extrapolation is required.

Assuming that, over a reasonable range of dose-rates, the dose-rate dependence can be expressed by :

$$R_c \propto (R \cdot)^x \text{ (where } x \text{ is usually between } 0 \text{ and } 0.5)$$

Equation 8

From Equation 4 and 8,

$$R_c \propto \left(\frac{u}{d}\right)^x / (1-x) \quad \text{Equation 9}$$

And with Equation 3

$$u \propto d^x \left(\frac{K \cdot I}{w}\right)^{1-x} \quad \text{Equation 10}$$

With spread beams, it is difficult to measure or define R_c and d , and a direct measurement of the dependence of R_c on u , (Equation 9) is a better basis of extrapolation, since d is substantially constant for a given beam geometry.

Irradiation by a series of n equispaced beams, each of dimension d , with an overall irradiation length D is formally equivalent to a single irradiation over a new distance $n \cdot d$, so

$$R_c \propto \left(\frac{u}{n \cdot d}\right)^{x/(1-x)} \quad \text{Equation 11}$$

For all the above equations, steady-state kinetics have been assumed. These, however, only apply when the time of irradiation $d/u \gg t_{1/2}$, where $t_{1/2}$ is the radical or reaction half-life. For second order reactions, $t_{1/2}$ depends upon the radical concentration and dose-rate; it is of the order of 0.1 sec for polyester/styrene compositions and dose-rates of 10-100 Mrad sec⁻¹.

Fig. 8 (based on ref. 26) illustrates four special cases of non-steady-state kinetics.

- A — pseudo-steady-state (d/u of the order of $3t_{1/2}$)
- B — an isolated non-steady-state irradiation (which may be one of a series)

$$(d/u \leq t_{1/2}; \frac{D}{(n-1)u} > 3t_{1/2})$$
- B' — an "instantaneous" irradiation, an extreme case of B, where $d/u \ll t_{1/2}$
- C — a series of interacting non-steady-state irradiations

$$(d/u < t_{1/2}; \frac{D}{(n-1)u} < 3t_{1/2})$$

Case A approaches steady-state conditions as d/u becomes greater than about $3t_{1/2}$, when Equations 8-11 become applicable.

Case C becomes equivalent to uniform irradiation over a distance D , as n increases, and

$$(R_c)_{n \rightarrow \infty} \propto \left(\frac{u}{D}\right)^{x/(1-x)} \quad \text{Equation 12}$$

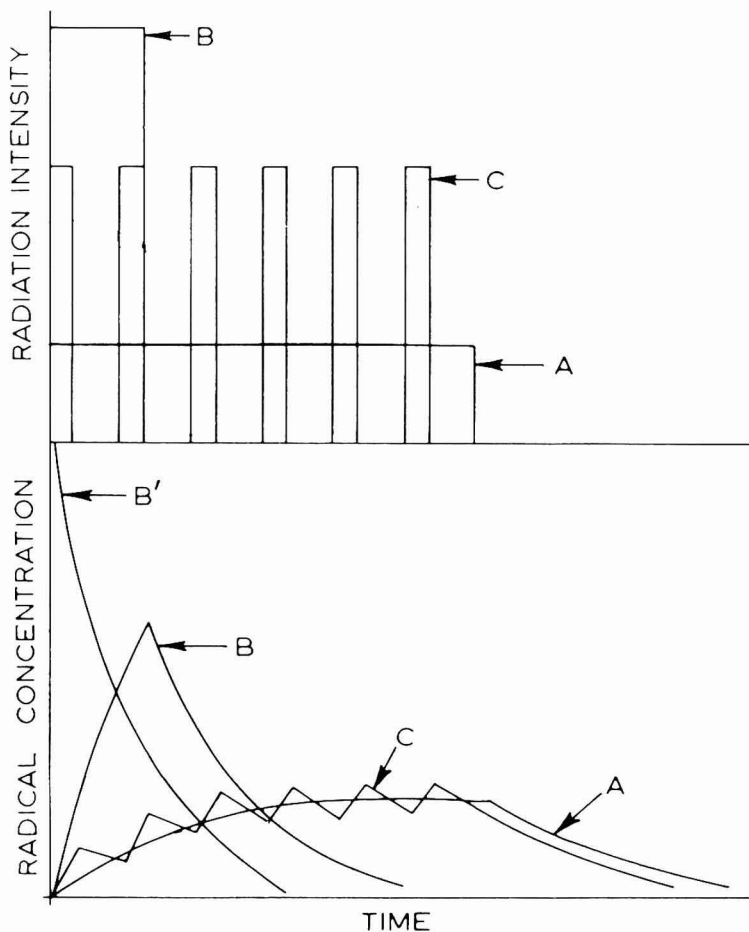


Fig. 8. Four cases of non-steady-state kinetics

Case B requires a more detailed analysis²⁷ than can be given here, but two factors emerge:

- (a) R_c is relatively insensitive to $R\cdot$ and d
- (b) $R_c \propto \frac{1}{n^y}$ (where y varies between 0 and about 1.5) Equation 13

All of the above relationships assume bimolecular kinetics such that $R_c \propto (R\cdot)^x$, where x is normally between 0 and 0.5.

The author has studied the doses to cure over a wide range of irradiation conditions (u from 0.1 to 3m sec⁻¹, n from 1 to 30 and over, $R\cdot$ from 10 to 500 Mrad sec⁻¹ and d at about 0.2 or 0.15m). At very low dose-rates and/or long overall irradiation times (say over 30sec) it has been found that secondary oxygen inhibition and/or monomer losses occur, and at high doses and dose-rates secondary heat and monomer losses occur; both these regions give anomalous results.

With these two provisos, however, it has been found that a very wide range of results fit the general relationship

$$R_c \propto \frac{1}{n^y}$$

in agreement with Equations 11 and 13.

The dependence on u , d and R^* is however, less consistent; this is interpreted as evidence that many of the irradiations are under non-steady-state conditions.

Costs

No attempt will be made to cost the overall process, nor to compare it numerically with thermal cure; instead attention will be drawn to the factors and trends which operate.

Capital cost

Gantt¹⁷ has indicated the reduction in capital cost for higher power equipment, and we have made similar estimates for 150kV equipment. These are shown in Fig. 9 (together with other capital cost figures) against current, since output is more directly related to current than to power.

No allowance is made for import duties, shielding or auxiliary equipment;

Figure 9, therefore, mainly illustrates the relative dependence of cost on current and voltage, and the cost advantage of using lower voltage and larger current plant.

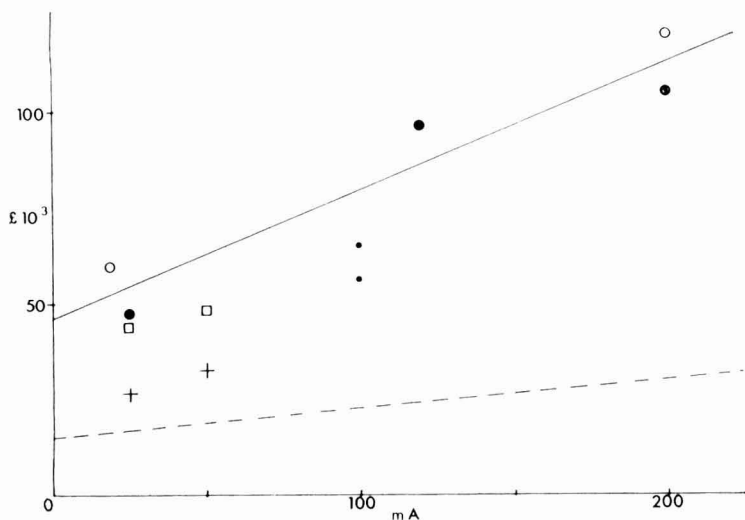


Fig. 9. Capital cost of electron beam sources v mA

	500kV	300kV
High voltage (Gantt)	●	•
Radiation dynamics	○	+
Average line for 500kV	—————	
Estimated line for 125kV	- - - - -	

Operating costs

Electricity costs are substantially those of the power supply, and are very low compared with thermal curing. Maintenance costs depend upon reliability and design of a specific piece of equipment but are variously estimated as 8s. to £1 per hour for 300kV machines operating at about 50mA.

Comparison with thermal curing

In spite of the relative flatness of the cost/current lines in Fig. 9, an important factor is the dose required. This has been quoted⁷ as between 2 and 20 Mrads, depending on speed, dose-rate and composition. Realistic cost comparisons can only be made on the basis of definite applications for which coatings have been developed, and for which the dose required has been determined for the particular plant and line speed.

Assuming comparable costs for coating materials, electron beam curing becomes more economical than thermal cure at an annual output level which depends upon:

- (a) the dose required,
- (b) the thickness of coating (which determines the voltage),
- (c) whether single or two-sided coating is required,
- (d) the number of hours operation per annum,
- (e) the temperature and time required for thermal cure,
- (f) whether thermal cure uses electricity, oil or gas heating.

The author's estimates are that annual outputs of less than 10⁶sq ft are probably not economically attractive for electron beam curing. These estimates assume doses of 10 to 20 Mrads and current 300kV plant operating at 25 to 50mA on single shift working.

Equipment under development may make electron beam curing more economical for lower output requirements, but is in general being designed for appreciably higher outputs at significantly lower costs.

Conclusions

The early research and development of the process for curing coatings by electron beam irradiation has reached a stage where it can be technically evaluated, in terms of overall process characteristics.

While no theoretical limit can be set for maximum speeds, there are problems in quantitatively extrapolating present results to very high speeds when materials are dose-rate dependent.

Electron beam equipment is available for smaller output plant, but only limited operating experience on pilot-plant curing is available¹⁴. Sufficient information is available for costing, when the doses required are known, and cost trends for higher output plant are also available.

The present range of coating materials is rather restricted (mainly unsaturated polyesters with liquid monomers such as styrene), and more work is necessary to develop other classes of coating amenable to electron beam cure. Ideally, such materials should cure at relatively low doses, (<10 Mrad), have a low dose-rate effect, and be relatively "tolerant" to dose variations.

Since solventless coatings are desirable, and flow-out is less than with thermal cure, application can be more difficult, and novel or modified application techniques may be needed for higher speeds.

Acknowledgments

The author thanks all those who have assisted in the TIGER project, in particular Mr D. R. Bailey, Mr G. E. Bucknell, Mr R. Norman and Mr T. T. Greenwood, who also assisted in the preparation of the paper.

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Discussion at Eastbourne Conference

THE CHAIRMAN, DR J. GAUNT, asked for questions on both Mr Davison's paper and on the part of Dr Deninger's paper which referred to electron-beam curing.

MR J. GOUGH asked if Mr Davison would elaborate on the use of very high intensity beams. Figures had been mentioned in the paper which were about ten times the intensity that had been quoted for the commercially available American accelerators. A patented window design had been mentioned which permitted these high intensities. Was it envisaged that this window would be available in commercial equipment?

MR W. H. T. DAVISON said that it might be made available if the need was clear. There were other methods whereby intensity could be increased, but a more important aspect was that a lot of the latest development work was in the area of speed, or throughput range, where it was arguable whether the best thing was to increase the width of the beam, cut the dose rate and thus increase the overall efficiency, or to narrow it. This was a very complicated matter. If an instantaneous irradiation condition was obtained then dose rate and intensity, as such, didn't matter.

On the whole, he thought that the window design had overshot present needs in that it made possible loadings which were not yet required. Discussions were taking place with organisations both in this country and in the USA on the supply of windows, and a range of modular windows was being designed to cover a wider range of current throughput, because the windows used on TIGER, as described briefly in the paper, were overshooting in terms of the electron beam density required. But this type of window would be available as and when the need was there. Roughly speaking, for a 4ft window, with air cooling alone, currents of about 50 or even 100mA at 300kV could be achieved by fairly simple techniques. The techniques shown in the paper enabled increases of a factor of ten, but there was some cross-over area.

DR V. G. W. HARRISON said that some thought had been given to the possibility of very rapid drying of printing inks by electron beam techniques. The film thicknesses to be dried were much less than with paint, from a few microns up to perhaps 50 microns, but unfortunately the paper substrate was to a large measure exposed to the electron beam, and was adversely affected. It had been established that with a dosage of 20 Mrad good quality banknote paper was not seriously discoloured, but it was rendered so fragile as to be useless. The folding endurance, for example, dropped from about 4,000 folds to breakage down to 3. Therefore, it was felt that the maximum dose would be about 1 Mrad, and the curing would have to take place in about 2 seconds maximum to be of any use.

Judging by the information in the two papers, it did not seem that the possibilities of using this technique successfully were very good. Had Mr Davison any comments?

MR DAVISON said that these were indeed the problems, and a further one was that in vacuo working was more appropriate with very low thicknesses, in order to use very low electron beam voltages, and this was unlikely to be applicable to paper. He was not actively working on this, but thought that there were possibilities of work of a fundamental nature on radiation chemical degradation of cellulose; there might, for example, be inhibitors that could be used. So, although it would be difficult to develop this application, he didn't feel that it was impossible.

DR L. VALENTINE remarked that he was very pleased, but slightly surprised, to find estimates of the economic potential for this system to be as low as 10⁶sq ft per annum production figure. This was much lower than other people had estimated. It did seem a rather low figure in relation to the willingness that people in this country had to install expensive production facilities. Would Mr Davison care to elaborate further?

MR DAVISON agreed, saying that he had intended to indicate that he didn't expect anything below a million sq ft to be practical. The potential was more likely to be

between 1-10 million sq ft per annum depending on the thickness of the coating to be cured.

THE CHAIRMAN, DR GAUNT, commented that he didn't disagree with Mr Davison but felt that a lot depended upon whether one was considering present situations or future situations.

The development of this technique would have to be extremely good in order to replace existing processes, and he didn't believe it was at the present time. But looking ahead ten years, which was the area of most interest, new substrate materials would be used (for instance he expected car bodies would be made of carbon fibre reinforced plastics and not of metal), and this technique was likely to be of more value than one could visualise today. There were certainly definite indications that this was the trend.

MR DAVISON pointed out that the consideration of dimensions was based on the assumption that it was a straight comparison with present applications. If, for example, there was increased interest in painting or coating of polymers, particularly thermo-plastic polymers, this could distort the picture, as thermal curing was not applicable.

Another point was that the cost of equipment at the moment very much reflected a very high development/low sale position. The price of a piece of commercial electron beam equipment was, therefore, much higher than the ultimate potential cost. This was inevitable, as for one design only three to five installations were sold.

DR W. FUNKE referred to the cross-linking reaction which took place during curing on metal surfaces. It had been mentioned that flat surfaces were preferred for electron beam curing, but it might be necessary to deform these surfaces afterwards, perhaps by deep drawing, and if there was a high cross-link density, it would be difficult to deform the surfaces without damaging the film. Had Mr Davison any idea of the solution to this problem? Did one stop at an intermediate stage and then deform, and then apply normal methods for completion of the curing reaction after deformation?

MR DAVISON replied that there was a very broad contradiction in coating technology, in that high flexibilities and high cross-linking densities were difficult to achieve together. A two-stage system was a possibility, and this technique had been applied to polymer irradiation. Irradiation was used before deformation, catalysts were incorporated in the formulation, and heat applied to complete the reaction.

This technique might be applicable to coatings. However a more profitable line was probably to see whether, in fact, the correct flexibility and properties could be obtained so that the coated material could be deep drawn. However, as he was not a paint technologist he couldn't comment on this.

DR DENINGER said that application of any radiation curing systems on surfaces which were intended to be deep drawn had not yet been tried, and he doubted whether it could ever be possible to do this and equal the performance of present day coatings applied by more conventional means.

It should, however, be possible to irradiate curved surfaces, although obviously not if the curvature was great, as in, for example, car bodies.

MR DAVISON added that 180° bend test adhesion had been obtained on aluminium, and he had seen materials which had been cup drawn after irradiation curing, so this was possible.

In many cases what was lost in the way of gloss, hardness, and scratch resistance, had to be balanced with the saving in time; this applied to any process. However, the problem was not insoluble, particularly if one considered tailor-making polymer systems for the job. In the USA 300kV radiation had been used successfully to cure coatings on curved objects with smooth contours. The electron scatter in air, and the tolerance of the paint to varying doses, had made it quite practical. In his own laboratories, at a voltage of 135kV, which gave less freedom for air scatter, coatings on quite sharply curved objects had been cured. The scatter of electrons was quite

appreciable, and it was possible, for example with a 300kV machine, to cure paint on the underside of a piece of metal at 45° to the source, although it was not an efficient process.

Again, negative prediction was difficult. Technically, car bodies could be cured, but the economics of such a process would not be competitive at this stage.

MR F. ARMITAGE remarked that Mr Davison, in answer to the question on printing ink on bank notes, referred to a vacuum process, and he wondered whether this was, in fact, the BISRA Videlac process. In this connection, BISRA were claiming to cure epoxy resins and phenol/formaldehyde resins, which had not been mentioned by Mr Davison in connection with his particular instrument.

MR DAVISON said that there was some difficulty in commenting on this as some of the data was confidential. However, he could answer in general terms. The point was that if very low thicknesses were used, the voltage *in vacuo* could be dropped to a point at which the cost of the irradiation was trivial. One could then think in terms of using not 10 Mrad or 100 Mrad, but 1,000 Mrad; this was still economically viable. If this thin coating was then put on a metal which would act as a heat-sink, secondary heat wasn't important. Therefore, a straight cross-linking reaction could be carried out. A low molecular weight polymer which had no special reactivity built into it, such as polythene or an epoxy resin, could be cross-linked. But this was not paint in the normal sense. It was applying a material and then cross-linking it in the solid form, so one was free of the need for a chain reaction because one was free from the need to have the coating in liquid form.

MR ARMITAGE asked if the mechanism of cross-linking was due to the epoxy or the phenolic, and if it was the same as that induced by heat treatment. Also, would there be any danger of decomposition with the very high dosages with these very different materials?

MR DAVISON replied that, at these very high doses, there might be a flash-heating effect. But the mechanism should be a straight cross-linking arising from the elimination of a hydrogen atom to form a bridge. Pyrolytic decomposition might occur, but the heat-sink, and the very small thickness of the film, potentially obviated this.

THE CHAIRMAN, DR GAUNT, added that the UKAERA at Harwell had, in fact, cured for BISRA a wide variety of substances, including things like tung oil, deposited on metal using the vacuum technique that BISRA had patented.

MR DAVISON commented that Tube Investments, in conjunction with the Paint Research Station, had carried out a programme on electron beam curing of conventional paint, and found that a large number of conventional paint systems would give a good cure at about 700 Mrad. But with the type of process and equipment described in the paper it was thoroughly uneconomical. If very low voltages, say 15kV, could be used, shielding was no problem, costs of power and irradiation equipment were very low, and economic considerations were very different.

This was the main aspect of the BISRA process.

DR J. C. WEAVER asked both authors whether they had encountered any post embrittlement or other undesirable features from either curing process, as distinguished from conventional ones. In this respect, it had been found, in public libraries in the USA, that UV exposure of valuable books in photo-copying equipment was causing serious degradation. Also, personal experience had shown that not only was Southern Yellow Pine difficult to paint, but the longer it was exposed before painting the poorer the performance of the paint was. There was also the classic test by General Motors, in which a typical old-fashioned nitrocellulose lacquer, exposed on a mountain in the Andes for years, in absence of water, did not chalk until exposed to water in the laboratory. Were similar effects likely to occur with these systems in the years to come?

MR DAVISON replied that he couldn't answer for UV curing. For irradiation techniques, a convincing argument was that the Boise Cascade Company had sold

more than 200,000sq ft of electron beam irradiated materials. This company had gone into the question of ageing, for outdoor wood application, including long term ageing, and although there were problems, these were soluble.

THE CHAIRMAN, DR GAUNT, thought that the question had not been fully answered as there was another point.

It was well known that both UV and electrons, when they fell upon certain inorganic materials, caused dislocations to occur in the lattice, resulting in F-centre coloration.

Some of the paints, or rather surface coatings, that had been economical did not discolour in this way; but some of them did. The authors' views and experiences on this would be welcome, both on the UV and the electron beam coating processes.

MR DAVISON said that it was the pigment which was the cause of this phenomenon, not the substrate. Some pigments did change colour. Selection of pigments was obviously one method of avoiding the effect, but some of the colour changes were transient, and as long as one could accept, from a control point of view, that there might be a colour change immediately on irradiation, in 24 hours' time it was back to normal. Therefore, from the customer's point of view, there was no problem.

DR DENINGER pointed out that UV curing, having much less energy than electron beam curing, was only applicable to clear systems. These systems discolored to some extent, and different initiators showed different degrees of discoloration, but it was not yet known whether it was the initiator alone, the resin, or the two together which caused the discoloration.

DR W. SCHOO said that he would like to return to the question of air inhibition. He felt that if air inhibition couldn't be avoided by means of applying an inert gas, electron beam curing was a rather worthless technique. When a tacky surface could only be avoided by adding paraffin wax, he felt the point of the process was lost. Could the authors comment on work done using inert gases such as nitrogen or argon?

MR DAVISON agreed that it would be uneconomical to use pure nitrogen, but there was an ordinary combustion gas product which could be used, without any very sophisticated shielding to prevent gas leakage from the system, which prevented significant oxygen uptake at a cost of the order of 5s to 10s an hour. This was on an output of, say, 4ft wide by 30ft a minute. This was not prohibitive, and the technique was simple and had the advantage of clearing potential ozone or nitrogen oxide.

In fact, the surface softening, or surface damage, in electron beam curing was quite a complex effect; it depended, for example, on dose rate and speeds. It could be caused by oxygen uptake, by what was referred to in the paper as "corrosion," that was attack of ozone or nitrogen oxides, or by disturbance of the monomer, affecting the feed ratio at the surface. All three factors contributed. However, the Boise system, using an inert atmosphere, was quite a simple method of dealing with the problem.

Next month's issue

The Honorary Editor has accepted the following papers for publication and these are expected to appear in the November issue:

- "An approach to paint formulation for optimising performance by statistical design and interpretation of experimental work,"** by *D. W. Brooker, G. R. Edwards and A. McIntosh*
- "An electron microscope study of titanium dioxide dispersion in paint films,"** by *M. R. Hornby and R. D. Murley*
- "Chemical reactions in paint films,"** by *L. A. O'Neill and R. A. Brett*
- "Efficient film forming from thermosetting acrylic resins,"** by *R. J. King*

Editorial

FATIPEC Congress

It has not been easy in the past to obtain the printed volume of the papers presented to the Congress. Recent correspondence in this *Journal* has indicated that there is an interest amongst our members in these volumes.

It has now been possible to come to an arrangement with the publishers, *Chimie des Peintures*, by which the printed volume of the papers from the IXth Congress may be obtained through OCCA. Details of the arrangement, together with a letter giving publishers of earlier volumes from Dr H. W. Talen, the Honorary Director of the Verfinstituut TNO, and a member of the FATIPEC Technical Committee, appear on page 973 of this issue.

A copy of the collected papers given at the IXth Congress, held in Brussels in May 1968, has been received by the Association. The theme at this meeting was "Fundamental aspects of the test and control methods peculiar to the industry of paints, varnishes, printing inks and related materials."

It would be impossible to mention all the 84 papers given in any detail within the space available in this issue of the *Journal*.

The eight "Plenary lectures" are reported in full; these cover a fairly wide range of topics and include the "Hardness behaviour of thin coatings of paints and plastics (Infinitesimal hardness behaviour)" by Oesterle, Brugger and Landolt, a paper by Asbeck on the "Measurement of adhesion in absolute units by knife cutting methods—the Hesiometer," Tysall and Snowden's paper on evaporation rates in relation to the effect of retained solvent on film properties, and a paper by Geuskens on the "Mechanism of degradation and stabilisation of polymers," which is one of the very few papers on a chemical topic.

Section I is entitled "Tests for specific raw materials"; it contains 25 papers and covers 169 pages. Most of the papers in this section refer in some way to optical properties and a few to adsorption.

Papers which are of particular interest are: the "Evaluation of colour differences in colour matching under various illuminants using a metamerism index" by Brockes; "An investigation of pigment surfaces by phenol adsorption"; "The colorimetric determination of tinctorial strength of coloured pigments"; "The determination of the dispersibility of pigments by means of reflectance measurements"; "Theoretical considerations of the Kubelka-Munk and Ryde theories", and the "Determination of CPVC by means of a gonio-photometer."

Section II is entitled "Tests for specific paints and related products." It again contains 25 papers, in 141 pages. A rather wider range of subjects is covered and includes interesting papers on the "Gloss determination of transparent colours," "The permissibility of forecasts on the practical service properties, as obtained from laboratory testing," "Dirt pick-up evaluation of vinyl dispersion paints," the "Permeation of liquid water through swollen pigmented paint films," the "Relationship of certain analytical characteristics of alkyd resins and their properties," and several papers on mould resistance.

Section III is entitled "General test methods" (mechanical properties, rheology, microscopy, colorimetry, methodology, etc.), contains 26 contributions and covers 165 pages. The range of subjects, as indicated by the title, is fairly wide, and includes papers on: "Electrochemical control problems in the application of paints by electrophoresis"; "Measurements and test methods in electrocoating techniques"; and several papers on mechanical properties, for example dynamic indentation tests, torsional modulus, mechanical pulse techniques and the extensibility of films. There is a very

interesting "Cinematographic recording of electrostatic paint spraying mechanism"; a paper on the measurement of gel strengths of thixotropic resins and paints and another on the viscoelastic behaviour of films made from plastic dispersion. There are also a few papers on corrosion and, again, on gloss measurement.

The volume is well produced and appears reasonably free from errors. Most, but by no means all, papers give references to earlier work, although in some cases these are rather restricted. No discussions are reported. Naturally, much of the work described has been reported elsewhere, but it is believed that the volume brings together a wide range of test methods, and, in spite of its high cost, should justify its purchase.

The volume contains, in all, 84 papers of which 35 are in German, 28 in English and 21 in French.

Erratum

We regret that, in the August issue of the *Journal*, an error occurred in the Student Review by G. H. Hutchinson. In Fig. 2, page 746, the illustrations for captions (a) unit triglyceride molecule, and (d) saponification—6 moles monomeric acid; 1 mole trimeric acid; 3 moles glycerol, were transposed.

Correspondence

SIR,—Referring to the Letter to the Editor of Dr H. Warson in JOCCA July 1969, p. 637, it may be useful to give a list of the FATIPEC Congress Books published so far, with the names and addresses of their publishers. I am sure the publishers will be glad to sell the Congress Books, unless out of print, through the intermediary of OCCA or of the normal book-trade.

Yours sincerely,
H. W. Talen

Survey of FATIPEC Congress Books

Congress Number	Year	Place & Country	Congress Book published by	Address of publishers
1	1951	Paris, France	Librairie Dunod	92 rue Bonaparte, Paris 6e, France
2	1953	Noordwijk, the Netherlands	Vereniging van Vernis- en Verf-fabrikanten in Nederland	Wassenaar, Netherlands Berkenrode, 1 Groot Haesebroekse weg
3	1955	Spa, Belgium	ATIPIIC	49 Square Marie-Louise, Bruxelles 4, Belgium
4	1957	Luzern, Switzerland	Verlag P. Keller	Winterthur, Switzerland
5	1959	Milano, Italy	AITIVA	c/o Prof. Dr Dante Pagani, Istituto Politecnico, Piazza Leonardo da Vinci 32, Milano 1, Italy
6	1962	Wiesbaden, W. Germany	Verlag Chemie GmbH	Weinheim/Bergstrasse W. Germany
7	1964	Vichy, France	Verlag Chemie GmbH	idem
8	1966	The Hague, Scheveningen, the Netherlands	Verlag Chemie GmbH	idem
9	1968	Brussels, Belgium	Chimie des Peintures	49, Square Marie-Louise, Bruxelles 4, Belgium

124 Roelofsstraat,
den Haag, the Netherlands

Editor's Note: We have also been informed independently by La Chimie des Peintures that they have stocks of the book of the 1968 Congress, and will be pleased to supply them to the Association. Any Member who requires a copy should apply to the Association's offices; the books will be supplied at a cost of £18, post free in the UK.

SIR,—As an ex-member of the South African Section, I congratulate you and the South African Section on your South African issue. It is good to see the South African Bureau of Standards still going strong. They have done a great deal, by co-operation with industry, to raise quality levels in the Republic. They are a great example to government testing authorities in other countries who, unhappily, are not always so willing to listen to industry.

It is also good to see the increasing level of international co-operation in the field of surface coatings. Your summaries in French, German and Russian were a great step forward. Perhaps international co-operation could be further advanced by OCCA offering a Conference Paper to the U.S. Journal of Paint Technology and by publishing a Federation Paper in JOCCA. It is by our efforts in such things as these, that we build in OCCA the things that are greater than OCCA.

With best wishes for your continued success,

Yours sincerely,

L. A. Hill

*13 Melby Avenue,
Balaclava,
Victoria 3183,
Australia.*

Editor's Note: We greatly appreciate the comments and good wishes expressed by Mr Hill. Any opportunity that may arise for international co-operation on the lines suggested in his letter will be very welcome to OCCA.

Reviews

THE PRODUCTION OF TITANIUM TETRACHLORIDE

By D. J. JONES. London: R. N. Chandler, Ltd., 1969. Pp. 39. Price £3.

This book comprises a review of patents and journal literature published in the period January 1962 to December 1968 on $TiCl_4$, arranged under the principal headings of thermodynamics of chlorination of Ti compounds, pretreatment of raw materials prior to chlorination, raw materials used, chlorinating agents, reducing agents, plant, procedure, recovery and purification and analysis. There are 59 patent and 67 literature references. The treatment is concise and adequate.

J. L. PROSSER

INFRARED SPECTROSCOPY: ITS USE IN THE COATINGS INDUSTRY

Infrared Spectroscopy Committee of the Chicago Society for Paint Technology: Federation of Societies for Paint Technology, 1969. Pp. x + 456. Price \$30.00.

The successful application of infrared spectroscopic techniques necessitates the compilation of a library of reference spectra of materials relevant to the field in which the spectroscopist is employed.

With this aim in view, the Chicago Society for Paint Technology published in 1961 a collection of spectra of coating materials together with a treatise on the theory and application of infrared techniques in the coatings industry. The original publication was somewhat limited in scope, since it was produced as a supplement to the "Official Digest" of the FSPT. However, it proved to be extremely useful and its popularity was such that the Society has produced an enlarged and updated second edition, this time in book form.

Like its predecessor, the book contains two main sections, the first being concerned with the theory, instrumentation, experimental techniques, analytical methods and applications of infrared spectroscopy. There is also a bibliography containing some 500 references to works relevant to the coatings industry.

The second section consists of a collection of spectra which are classified but not indexed individually. Within each class the materials are listed "either by homologous series, similarity of spectra, alphabetically by supplier, or by chemical class."

The first section has been written concisely, is reasonably comprehensive and should provide the paint or polymer chemist with sufficient understanding to enable him to make full and proper use of infrared techniques. This may not be entirely true for chemists whose main concern is with raw materials, since the written section of the book is concerned largely with polymers. The inclusion of some information on non-polymeric substances would have been worth-while, e.g. the progression bands in the $1,250\text{cm}^{-1}$ region which, together with the 720cm^{-1} band, can provide information about the chain lengths of aliphatic materials.

A table of correlations to aid the classification of polymers is included, together with the well-known Colthup charts for the $4,000\text{-}600\text{cm}^{-1}$ region, and a similar chart for the $700\text{-}300\text{cm}^{-1}$ region.

The interpretation of spectra is dealt with in a logical manner using both the negative and the positive approach. Several examples of these methods of interpreting the spectra of a variety of materials are worked through.

Applications of the absorption laws to quantitative analyses by both baseline and integrated intensity techniques are described. The selection of the analytical band and deviations from the absorption laws are discussed. Quantitative methods which are described include the direct calculation, working curve, standard addition, absorbance ratio, internal standard and coincident band methods.

The somewhat brief coverage of reflection techniques may tend to give newcomers to infrared spectroscopic analysis an impression that reflection methods are of little value in the analysis of coating materials. This impression may be enhanced by a complete lack of reflection spectra in the reference section.

Selected examples of the application of infrared spectroscopy are given in the form of a review, and include chain orientation and crystallinity studies, quantitative analysis, pyrolysis methods and chemical reaction techniques for the verification of functional groups.

The collection of 740 reference spectra (nearly four times the original number) is certainly the most valuable section of the book, whose publication would have been warranted for this alone. Printed two to a page, they cover a wide range of materials commonly used in the coatings industry and include some used in the plastics and fibres industries as well. Predictably, the majority (319) are of binders, with pigments and extenders (118) and solvents (105) well represented. The remaining miscellaneous materials include monomers, plasticisers, wetting agents, etc.

All of the reference spectra are presented in a standard linear frequency *versus* percentage absorbance format and, for those using the older wavelength presentation, wavelengths are indexed at the top of the spectrum. A close inspection of the spectra reveals considerable variation in contrast together with a number of blemishes introduced at the printing stage. Some lack of clarity in the legends printed on the spectra and the omission, in some cases, of the source and purity of the material used as reference, were noted.

Most of the spectra show a little more "noise" than is normally considered acceptable as an indication that the spectrometer is "live." However, it does not detract significantly from their spectral quality. A little stray light is evident in some of the spectra and a few of the inorganic materials show relatively strong $-\text{CH}_2-$ absorption bands suggesting the presence of some mineral oil. There is no reference to this either on the spectra or in the text, although much weaker bands are labelled as being "impurity." Some of the spectra of liquids show scatter, indicating that the windows of the cells used to obtain the spectra required some attention. An obvious error is the labelling of Thixatrol ST as DCO, despite the spectral evidence of amide groups.

In general, the quality of the printing is high but a number of faults in proof-reading have tended to spoil the result. On page 5 for example, the legends on a potential energy diagram are incomplete and mis-spelled. The term "on the order" was noted on p. 11 and in paragraph 1 section 2 on p. 16 the lines of the text are out of sequence. The indiscriminate use of initial letters and molecular

formulae as abbreviations proves a source of some irritation. Terms such as "a AgCl cell" do not roll off the mental tongue very readily. The reference to VPC (p. 18) is surprising in view of the abandonment some ten years ago of the term vapour phase chromatography in favour of gas liquid, or gas, chromatography.

Despite these apparent inattentions to detail, the diminution in value of this book to the coatings chemist is negligible. Alongside such books as Haslam & Willis's "Identification and Analysis of Plastics" (Ilfle, 1965) and Hummel's "IR Spectra of Polymers" (Interscience, 1966) it should provide a very useful addition to the analyst's armoury. At \$30 a copy (\$20 to members) the Chicago Society has provided not only an introduction to infrared spectroscopy but a comprehensive library of reference spectra costing less than fourpence each; a very economical purchase indeed.

D. GRIME

PRINTING INK MANUAL, 2ND EDITION 1969

Commissioned by The Technical Training Board of the Society of British Printing Ink Manufacturers. Editor in Chief DR F. A. ASKEW. London: W. Heffer & Sons Ltd. Pp. ix + 848. Price £8 8s.

This work, in its 1st edition, was guided by the late Dr Bowles as Editor-in-Chief, and quickly came to be accepted widely by all branches of industry contributing to printing and printing ink technology. The 2nd edition has undergone considerable revision, and, in following the advances in the industry, a considerable amount of new matter has been introduced. Additional contributors have been called on, thus maintaining the authority on each subject indispensable to the student. The extent to which the presentation succeeds in maintaining clarity, and the interdependence of various sections from so many contributors, without abrupt changes of technical level and style, is a credit to the editors.

The first six chapters deal with early history and printing processes and include printing rollers, blankets, and substrates, ranging from paper to plastics and metals. Additional matter and re-arrangement in these sections make for improvement; in particular, the tabulation of rollers and blanket uses in relation to ink and process, and the more clearly drawn definition of paper qualities affecting print quality. Deferment of print recognition and printing faults to Chapter 23 may seem irksome to ink students wishing to look at a process as a whole, and the inevitable repetition is more noticeable when turning back 700 pages.

Chapters 7 to 10 cover the chemistry and physics underlying the technology, and emphasise the importance of recognising the unique nature of a printed film as well as essential studies for a sound approach to ink formulation. Chapter 7, Dispersion, is a new chapter and a timely one, since coating industries, to the confusion of students, have indulged for many years in loose thinking on pigment-vehicle relationships, despite the increased discussion and publications by research workers in recent years. This particular chapter, although short, is concise and well illustrated. By defining influence on rheology and implying effects on film properties, it should profoundly influence the ink maker's approach to the subject.

Chapter 8, Rheology and ink distribution, follows the dispersion chapter logically, dealing not only with classical rheology but interpretations of behaviour in films breaking at printing speeds. Chapter 9 deals with drying—chemical and physical. Theories of polymerisation, gelation and functionality are clearly discussed and link easily with the later chapter on varnishes. Physical film formation is considered in relation to familiar types of ink. The already excellent chapter on colour and colour vision has been enhanced by improved clarity when dealing with the Kubelka-Munk analysis and its application to colour match predictions, with mention of the complications which are involved in treatment of printed colours and have still to be resolved.

These four chapters, amply illustrated and documented with references, can be said to be the most stimulating part of the manual.

The chapter on raw materials is enlarged and much improved over the 1st Edition, but the depth of treatment for some pigments is not always proportional to their importance in everyday ink use.

The chapters on inks have all been subjected to revision, extension and considerable re-writing. The news inks section now has more logical presentation and each of the other chapters brought up to date.

The chapter on ink manufacture has been enlarged, giving discussion on the merits of modern examples of dispersing machines and additional illustrations. Safety regulations and factory legislation is dealt with, but modern management techniques, such as operational research, with its approach to stock control and production planning, have not found a place, even though younger students of ink manufacture are destined to be involved in the changing patterns of management.

Under testing and control, many routine tests are described, including the BS.4321 originally conceived by the European Committee of Paint and Printing Ink Manufacturers Association (CEI Standards). There is good description and discussion of the individual tests. Since the shortcomings and pitfalls inherent in testing are mentioned, it may be suggested that the manual will need to embrace, in a future edition, further discussion on the significance of observations in these tests, interpretation by correlation with printing practice and, perhaps, the use of statistical methods for research studies involving so many subjective evaluations.

The manual, although increased by some thirty per cent in contents, is about the same size and weight as the 1st Edition. Nevertheless, its weight and volume does make it difficult to handle, and to this extent the title is inept. From the original conception as an aid to students, it has become a major reference book for all interests contributing to the evolution of print, and this fact justifies the price.

The rapid growth of the technology makes inevitable the more frequent revisions and additions for the future and the wide range of subject matter will justify separation into several volumes. The division of the 1st Edition into two parts has been dropped in the new edition, presumably because the editors have already visualised a more logical separation into four or five parts.

Information Received

(In case of difficulty regarding addresses, members and subscribers to the JOURNAL should apply for details to the Director & Secretary of the Association at the address shown on the front cover.)

It has recently been announced that the Dublin firm of **Preston & Hadfields Ltd.** has been acquired by the **Donald Macpherson Group Ltd.** It is said that this acquisition, as well as consolidating Macpherson's position in the paint market, will establish it in the retail field, with Preston & Hadfields well-known *Heolin* and *Mulsomatt* brands.

A new company, **Aerosol Equipment Ltd.**, has recently been formed to act as selling agents in the British Isles for the range of electronically controlled aerosol filling machinery manufactured by **Aerosol Corporation** of Switzerland (previously K. Mader & Co.).

The **Mickle Laboratory Engineering Company** has announced the availability of the new *BK Drying Recorder*. This instrument is a modification of the original instrument designed by Dr H. W. Keenan, a Past President and Hon. Member of the Association.

The new model has been designed to operate at a speed of 24 hours only, with a view to economy, this speed being judged the most useful. However, motors and scales can be obtained and fitted easily to provide other speeds. Improved features in the new design include a more convenient method of holding the test strips, a redesigned needle-carrier, a starting switch with red neon light in circuit, and a louvred endplate for ventilation of the motor unit. As previously, six strips can be accommodated.

Also available is the *Mickle Casterguide*, for preparing castings quickly and easily for use on the *BK Drying Recorder*.

Paraloid B-48-N, a thermoplastic acrylic polymer supplied as 45 per cent solids in toluene, is now commercially available in the UK, announce **Lennig Chemicals Limited**. *B-48-N*, which is a replacement product for *Paraloid B-48*, is claimed to have a unique combination of adhesion and flexibility on many metal substrates and primed surfaces, as well as good solvent release characteristics and excellent durability.

The Carborundum Company Ltd. has recently issued a new leaflet giving details of its range of *Crestalkyd* resins.

A new fine particle sized polyolefin, *Polymist A-12*, has been introduced by **Allied Chemical Corporation**. The product, which is claimed to have an average particle size of 12 microns and exceptional hardness, is said to have potential for use as a stir-in additive for improving the rub resistance of printing inks. Details are available from **Kingsley & Keith (Chemicals) Ltd.**

"Sales Information Bulletin 44," issued by **The Pyrene Company Limited**, gives details of *Pyroclean 211*, a dry powder chemical for use in cleaning and descaling spray phosphating plants.

Blythe Colours Limited has recently introduced a new range of concentrated cadmium pigments. The new *K-range* is available in the colour range light orange to maroon,

and the pigments are claimed to be brighter, stronger, and more economical in use than previous types, for applications in surface coatings and thermoplastics.

A complete bibliography of its publications on corrosion during the period 1963-68 has recently been published by **BISRA**. This booklet, which implements the previously-published bibliography from 1931-63, also contains details of the Corrosion Advice Bureau, and is available free of charge from **BISRA**.

Two new grades of titanium dioxide pigments are now available from **NV Titaandioxydefabriek Tiofine**. The new grades are *Tiofine R65*, for use in high-grade interior and exterior enamels, and in particular industrial finishes, and *Tiofine R70A*, for use in high-grade enamels requiring maximum weather resistance.

A new range of horizontal, electrically fired, forced convection conveyor ovens for stoving, drying, annealing, and similar operations has been developed by **Mechanical Coatings Limited**.

Ovens are available in the temperature ranges 40°-100°C, 100°-250°C and higher temperatures up to 500°C, all units being thermostatically controlled.

International Colloids Limited has recently announced the availability of a new range of pigmented dispersed chips, known as *Microperse SE* and *SA*, which are said to have excellent compatibility with materials such as nitrocellulose, acrylics and chlorinated rubber, as well as systems containing trichlorethylene, and stoving and styrenated alkyds.

Microperse SA is alcohol soluble, and *Microperse SE* ester soluble, and both are claimed to be easily dispersible in solvent by stirring-in. There are 135 standard colours available, and special colours will be made to order.

A. Gilby & Sons Ltd. has recently announced a new black ink for the printing industry, which is to be named *Hyjon* as a tribute to Mr Johnnie High, who recently retired from the position of London and Leicester area representative of the company after 20 years' service.

A 12 page brochure entitled "Colour and research" has recently been published by **Carl Zeiss**. The brochure, which covers the use of colour as an aid to research and as its object, is available in this country from **Degenhardt & Co. Ltd.**

It has recently been announced that **A. P. V. Holdings Ltd.** has made an offer for the whole of the issued share capital of **L. A. Mitchell (Holdings) Ltd.** **S. Pearson & Son Ltd.** and its subsidiary, who own over 92 per cent of the capital, have accepted the offer and the Directors of Mitchell's recommend other shareholders to accept. It is said that the acquisition of Mitchell's by APV will broaden the manufacturing and engineering activities of the APV group in the supply of plant and equipment to the chemical and process industries, and will enable it to offer a more efficient service to customers and to compete more effectively overseas.

In the September issue of the *Journal*, reference was made to additions to the *Paliotol* and *Heliogen* ranges of pigments. These ranges are manufactured by **Badische Anilin- and Soda-Fabrik AG**, and not by **Farbwerke Hoechst AG**, as was stated.

Section Proceedings

Scottish

Eastern Branch

The use and development of pva emulsions in the field of paper, coatings, paint and adhesives

The final meeting of the session, with Mr P. A. Gower in the chair, was held in the Carlton Hotel, Edinburgh, on Wednesday 23 April, when Mr R. A. C. Kuenzli, of Resinous Chemicals Ltd., spoke on "The use and development of pva emulsions in the field of paper, coating, paint and adhesives." This was a joint meeting with the Scottish Division of the British Paper and Board Makers Association (Technical Section).

An outline of the emulsion polymerisation process was given, attention being drawn to the high molecular weight polymer which resulted. The importance of the surfactant system, and its relation to the particle size, chemical and mechanical stability, and other properties of the emulsion, were stressed. Coalescence, minimum film forming temperature, binding power, and water and chemical resistance, were related to the means available to control them by choice of comonomers and polymerisation conditions. The speaker illustrated how the principles involved were applied to produce emulsions suitable for the widely differing properties required for paints, adhesives and paper coating.

A lively discussion followed, and the vote of thanks was given by Mr Farquhar, Scottish Chairman BPBMA, who congratulated the speaker on his presentation before expressing his pleasure that the two associations had been able to meet together in Edinburgh; an encouraging sign for the future.

J.H.S.



Technical Exhibition

Strong support for move to Olympia

Although the closing date for applications to exhibit at next year's 22nd Technical Exhibition is 3 October, it is already clear that the move to the Empire Hall, Olympia, has the support not only of most of the United Kingdom exhibitors but also of those from overseas.

The Exhibition will take place from 27-30 April, 1970, and the hours of opening each day have been slightly extended, since it is felt that so many visitors from overseas will be staying in London hotels that they will welcome an earlier start and a later finish each day. The Exhibition will, therefore, be open at the following times:

Monday 27 April	..	15.00 to 18.30
Tuesday 28 April	..	09.30 to 18.30
Wednesday 29 April	..	09.30 to 18.30
Thursday 30 April	..	09.30 to 18.30

The Association has prepared information leaflets in six languages (English, French, German, Italian, Russian, and Spanish) and these will be distributed widely to paint manufacturing companies abroad. Copies of the *Official Guide* to the Exhibition will be distributed in the New Year to all members of the Association wherever resident, to paint and ink

manufacturing companies in the United Kingdom, and individually to scientists and technologists in Western Europe. Intending visitors can obtain copies of the *Official Guide* and the information leaflet in six languages by making application to the Association's offices.

21 OCCA was visited by representatives from more than 30 overseas countries, and it is confidently expected that next year's Exhibition, being held nearer the West End of London, will attract even more visitors.

As before, invitations will be extended to schools where science is taken at "A" level, to send parties of students to the Exhibition on the three mornings, where they will be given introductory talks on careers before being conducted round the stands.

Details of the Exhibition Luncheon to be held at the Savoy Hotel, London WC2, on 27 April will be included in forthcoming issues of this *Journal*; an application form will be included in each copy of the *Official Guide*.

The April issue of this *Journal* will contain a preview of the Exhibition and the June issue will contain an illustrated technical review compiled by members of the Association.

South African Section

Transvaal Branch



A view of the joint OCCA/SAPMA stand at the exhibition

OCCA Stand at Chemical Industries Exhibition

The Transvaal Branch of the South African Section, in collaboration with the South African Paint Manufacturers Association, occupied and manned a stand at the 1st South African Chemical Industries Exhibition, held at Milner Park, Johannesburg, from 14-19 July.

The object of this, the first OCCA participation in an exhibition in the Republic, was to encourage technical training and to attract technically trained personnel to the paint industry. The timing of the step was also considered to be particularly appropriate, as 1969 was the 21st Anniversary of the formation of the Section.

The exhibition attracted an estimated 3,500 people, of whom the bulk were thought to be connected with the chemical industry.

The opportunity was taken to demonstrate modern paint application methods, up-to-the-minute surface coatings and modern methods of analysis and quality control. These special exhibits drew the attention of the chemists and chemical engineers present, and perhaps through this the primary object may have been achieved. To most of the non-technical people who attended the exhibition, the OCCA/SAPMA stand became a source of advice on both household and industrial painting problems. All questions were answered on a strictly non-partisan basis by volunteers who manned the stand. Through this gesture on the part of members of OCCA and staff of members of the SAPMA, the standing of both associations has been enhanced in the eyes of the general public, and the joint venture can be considered, on both counts, most successful.

New extension at the Borough Polytechnic

On 9 July, an extension to the Borough Polytechnic was opened by H.R.H. The Duke of Edinburgh. The new building, which is eight storeys high, provides about 105,000sq ft of administration, communal, and specialised teaching accommodation, and will allow the student population eventually to be doubled.

The land was made available by the closure of Thomas Doyle Street, Lancaster Street, and the north end of Ontario Street, and design features in the extension include facades at 45° to the nearby thoroughfares and double windows with sound-attenuated air conditioning, to reduce noise, and walkways at first floor level to connect with the three existing buildings on the site.

The Borough Polytechnic occupies a virtually unique position in the field of education for the surface coatings industries, and the new extension, which includes laboratory space for the Department of Chemical Technology, will ensure the development of facilities in this field.

Courses at Washington University

Two short courses are to be held at Washington University in November, organised jointly by the University and the American Chemical Society. These are entitled "Combined gas chromatography/mass spectrometry," 10-13 November 1969, and "Biomedical and clinical applications of gas chromatography," 5-8 November 1969. Full details are available from Dr R. L. Levy,

Division of Continuing Professional Education, Box 1048, Washington University, St. Louis, Missouri 63130.

FSPT Publications

The Federation of Societies for Paint Technology have recently announced the publication of Unit 11 "Paint driers and additives" by W. J. Stewart, and Unit 12 "Principles of formulation and paint calculation" by W. R. Fuller, in the "Federation series on coating technology." The booklets are available from the FSPT at a cost of \$1 per copy.

Second international conference on plastic powder coatings

Powder Coating 1970, the second international conference on plastic powder coatings to be organised by *Surface Coatings* journal, is to be held at the Criterion-in-Piccadilly, London, from 10 to 12 February 1970.

The organisers state that, owing to the success of the first conference in February this year, and the considerable advances in the field since this time, the 1970 conference will be increased in size.

Additives for R and P conference

A conference entitled "Additives and auxiliaries for the rubber and plastics industries in 1970-1980" will be held in Brussels on 18-19 March 1970.

Although arrangements are only at a preliminary stage, the organisers, the International Business Contact Club, expect an attendance of about 250 people from eighteen different countries. Further details are available from ib/cc, 99 Avenue Nouvelle, Brussels 4.

Register of Members

The following elections to membership have been approved by Council. The Sections to which the new members are attached are given in *Italics*.

Ordinary Members

CUNNINGHAM, ANGUS MACINTOSH, BSc, 59 Oak Drive, Higham, Rochester, Kent. (*London*)

FAGG, DAVID ARCHER, LRIC, API, 89 Parkway, Coxheath, Maidstone, Kent. (*London*)

- FERGUSON, JOHN JARDINE, BSc, ARCST, 17 Bath Crescent, Cheadle Hulme, Cheshire SK8 7QU. (*Manchester*)
- GREEN, BRIAN JAMES, BSc, ARIC, 19 The Grove, West Wickham, Kent. (*London*)
- KERR, JOHN ROBERT, MA, Overseas Dept., ICI Paints Division, Wexham Road, Slough, Bucks. (*General Overseas*)
- KIRK, GEORGE, 17 Birch Green, Hertford. (*London*)
- LANCASTER, IAN PETER, LRIC, Overseas Dept., ICI Paints Division, Wexham Road, Slough, Bucks. (*General Overseas*)
- NOWLAN, RONALD JOHN, 3 Lincoln Road, Forest Gate, London E7. (*London*)
- O'BRIEN, DENIS, G.I.P. (Ireland) Ltd., John F. Kennedy Drive, Bluebell, Dublin 12. (*Irish*)
- POPE, GODFREY ROBIN EGERTON, BA, 32 Parkside, Wimbledon Common, London SW19. (*London*)
- PORCARO, ANTONIO, Tradex Colori S.A.S., Via Carlo Goldoni 1, Milan, Italy. (*General Overseas*)
- VERSTER, GERRIT PIERRE, MSc, MSACI, S.A. Bureau of Standards, Private Bag 191, Pretoria, South Africa. (*South African*)
- VIDELI, OSCAR JORGE, Pampa 2654, Piso 10, Dto. "8," Buenos Aires, Argentina. (*General Overseas*)
- WADDINGTON, KEITH JOHN, BSc, 48 The Bramblings, Chingford, London E4. (*London*)
- WRIGHT, EDWARD PHILIP, c/o Shell Chemical South Africa (PTY) Ltd., PO Box 494, Johannesburg, South Africa. (*South African*)
- ZONE, ANITA, 18 Winton Close, Edmonton, London N9. (*London*)

Associate Members

- AGBEJA, OLAGOKE, British Paints (W.A.) Ltd., PMB 1052, Ikeja, Lagos State, Nigeria. (*General Overseas*)
- BAVERSTOCK, TERENCE GORDON, Box No. 74, Pietermaritzburg, Natal, South Africa. (*South African*)
- BLANCO, CARLOS GUIDO, Mitre 1152, San Martin, Pcia. de Buenos Aires, Argentina. (*General Overseas*)
- GROVE, ROBERT MICHAEL, 3 Fullbrooks Avenue, Worcester Park, Surrey. (*London*)
- HAROON, SHEKH MOHAMMED, U/1206, Bazar Bansanwaca, Rawalpindi, W. Pakistan. (*General Overseas*)
- LACEY, JOHN CHARLES, 78 Vegal Crescent, Englefield Green, Egham, Surrey. (*London*)
- LARKIN, BERNARD M., "Marianna," 59 All Saints Road, Raheny, Dublin 5. (*Irish*)

Student Members

- FOLEY, JOHN, 27 Botanic Road, Glasnevin, Dublin 9. (*Irish*)
- PHILLIPS, MARTYN ANTHONY, 270 Kingsway, Doonside, South Coast, Natal, South Africa. (*South African*)
- RAMSDALE, GEOFFREY STUART, Blundell-Permoglaze Limited, Sculcoates Lane, Hull. (*Hull*)
- WILSON, ERIC DANIEL, 28 Chester Street, Swinton, Lancs. (*Manchester*)

Forthcoming Events

Details are given of meetings in the United Kingdom up to the end of the month following publication, and in South Africa and the Commonwealth up to the end of the second month.

Thursday 2 October

Bristol Section. Joint meeting with Birmingham Paint Varnish and Lacquer Club, to be held at the Imperial Hotel, Birmingham, at 7.15 p.m. "A Paint Manufacturer's view of Industrialised Building" by Mr T. Jones of John Hall & Sons (Bristol and London) Limited.

Newcastle Section. "Statistical Techniques in the optimisation of Paint Formulation—by Computer" by D. W. Brooker of Shell Research Ltd., to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Monday 6 October

Hull Section. "Reactivity of Titanium Dioxide in Pigmented Vinyl Chloride/Vinyl Acetate Copolymer Surface Coatings" by Mr F. D. Robinson of Laporte Industries Limited, to be held at the Bullock Lecture Theatre, Hull College of Technology, at 7.00 p.m.

Wednesday 8 October

Newcastle Section—Student Group. "The use of Acrylic Materials in the Paint Industry" by Mr A. J. Becalick of Lennig Chemicals Ltd., to be held in Lecture Theatre A406, Rutherford College of Technology, Newcastle upon Tyne, at 3.00 p.m.

Thursday 9 October

Scottish Section. "Problems of Pigmentation of Thermosetting Acrylic Finishes" by Mr G. Willison of British Titan Products Co. Ltd., to be held at the St. Enoch Hotel, Glasgow, at 6.00 p.m.

Friday 10 October

Hull Section. Annual Dinner Dance at the Hotel Eden, Willerby.

Manchester Section. "Dispersymers"

by Mr C. D. Cook of ICI Limited, to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester 1, at 6.30 p.m.

Saturday 11 October

Scottish Section—Student Group. Student Paint Project, by Mr J. Devine of Craig Hubbock Ltd., to be held at the "Wee Windaes" Restaurant, 142 High Street, Edinburgh, at 10.30 a.m., followed by lunch and a skittles match.

Monday 13 October

London Section. Joint Meeting with Society of Chemical Industry (Colloid & Surface Chemical Group). "A Theory of Polymeric Dispersant Action" by E. J. Clayfield, to be held at 14 Belgrave Square, London SW1, at 6 p.m.

Tuesday 14 October

West Riding Section. "Future Developments in Paint," by Dr L. A. O'Neill of the Paint Research Station, to be held at the Griffin Hotel, Boar Lane, Leeds 1, at 7.30 p.m.

Saturday 18 October

Scottish Section—Student Group. "Colour Systems," to be held at the St. Enoch Hotel, Glasgow, at 10.00 a.m.

Tuesday 21 October

London Section—Southern Branch. "Chemical Solvents for Paints" by Mr D. P. Sephon of Shell Research Limited, to be held at the Pendragon Hotel, Clarence Parade, Southsea, at 7.00 p.m.

Wednesday 22 October

Scottish Section—Eastern Branch. "Colour Measurements and Specifications" by Dr Latowski of Edinburgh University, to be held at the Carlton Hotel, North Bridge, Edinburgh, at 7.30 p.m.

Thursday 23 October

London Section. European Liaison Lecture: "Some Aspects of the Protection of Exterior Joinery" by R. Dooper of Verfinstituut TNO, to be held at the New Engineering Block, University College, London WC1, at 6.30 p.m.

Midlands Section. One day Symposium, "Management and Training in the Surface Coating Industry," to be held at the Regency Club, Stratford Road, Shirley, Solihull, Warks., at 10.00 a.m.

Friday 24 October

Irish Section. "Driers" by Mr J. H. W. Turner of Hardman & Holden Ltd., to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

Manchester Section. Annual Dinner Dance at the Piccadilly Hotel, Piccadilly Plaza, Manchester 1.

Wednesday 29 October

Thames Valley Section. "Glossy Emulsion Paints" by Mr J. Bax of Scott Bader & Co. Ltd., to be held at the Manor Hotel, Datchet, Bucks, at 7.00 p.m.

Thursday 30 October

Midlands Section—Trent Valley Branch. "The Influence of British Rail Modernisation on Paints and Painting" by F. D. Timmins, to be held at the British Rail School of Transport, London Road, Derby, at 6.30 p.m.

Friday 31 October

Bristol Section. "Packaging" by Mr F. P. Bull of E. S. & A. Robinson Limited, to be held at the Royal Hotel, Bristol, at 7.15 p.m.

Monday 3 November

Hull Section. "Operational Research" by Mr S. J. Morrison of Hull University, to be held at the Bullock Lecture Theatre, Hull College of Technology, at 7.00 p.m.

Thursday 6 November

Newcastle Section. "Paint and Protective Coatings for High Speed Aircraft" by C. E. Hoey of the Ministry of Technology, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Scottish Section. "Historical Development of the Scottish Paint Industry" by Mr G. Scott of Federated Paints Ltd., to be held at the St. Enoch Hotel, Glasgow, at 6.00 p.m.

Tuesday 11 November

London Section—Southern Branch. "Emulsions for Paper and Paint" by a speaker from Vinyl Products Limited, to be held at the Pendragon Hotel, Clarence Parade, Southsea, at 7.00 p.m.

West Riding Section. "Rheology and Measurement in Printing Inks," by Dr Cartwright of Metal Box Ltd., to be held at the Griffin Hotel, Boar Lane, Leeds 1, at 7.30 p.m.

Wednesday 12 November

Newcastle Section Student Group. "Easily Dispersible Pigments" by Mr G. R. Robson of ICI Ltd., to be held in Lecture Theatre A406, Rutherford College of Technology, Newcastle-upon-Tyne, at 3.00 p.m.

Friday 14 November

Manchester Section. "Particle Size Reduction in Ball Milling and Sand Grinding" by Dr W. Carr of Geigy (UK) Limited, to be held at the Swan Hotel, Churchgate, Bolton, at 6.30 p.m.

Saturday 15 November

Scottish Section—Student Group "Epoxy Coatings," to be held at the St. Enoch Hotel, Glasgow, at 10.00 a.m.

Wednesday 19 November

London Section. "Rheology in Gloss Paints" by T. R. Bullett of the Paint Research Station, to be held at East Ham Technical College, High Street South, London E6, at 6.30 p.m.

Scottish Section—Eastern Branch. “Applications of Science to Paintings and Antiques” by Dr H. McKerrel of the Royal Scottish Museum, to be held at the Carlton Hotel, North Bridge, Edinburgh 1, at 7.30 p.m.

Friday 21 November

Irish Section. “Resins for Printing Inks” by Mr L. J. Lees of Hercules Boehm, to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

Thursday 27 November

Midlands Section—Trent Valley Branch. “Selected Aspects of Recent Developments in Coated Titanium Pigments” by a member of the staff of British Titan Products Company Limited, to be held at the British Rail School of Transport, London Road, Derby, at 6.30 p.m.

Thames Valley Section. A Forum on the subject of “Toxicity, Hazards and Factory Regulations.” On the Panel: Mr Ward—Chief Fire Officer for Buckinghamshire. Mr R. L. Such—H. M. District Inspector of Factories. To be held at the Manor Hotel, Datchet, Bucks, at 7.00 p.m.

Friday 28 November

Bristol Section. “Management by Objectives in Research and Development” by Mr N. R. Felstead and Mr R. J. Woodbridge of John Hall & Sons (Bristol & London) Limited, to be held at the Royal Hotel, Bristol, at 7.15 p.m.

Midland Section. “Tinplate Coating” by A. K. Unsworth of Ault & Wiborg, to be held at the Chamber of Commerce House, 75 Harbourne Road, Birmingham 15, at 6.30 p.m.

West Riding Section. Dinner and Dance at the Granby Hotel, Harrogate.

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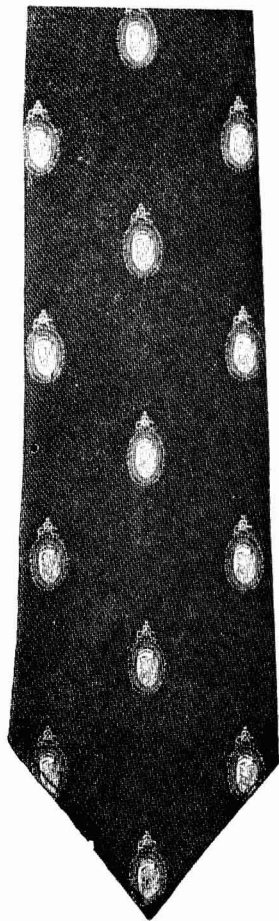
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