

Papers presented at the Eastbourne Conference



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**JOURNAL OF THE
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Polymers: Developments for the future

C. E. H. Bawn

The influence of supermolecular structure on the properties of polymer films

W. Funke and U. Zörl

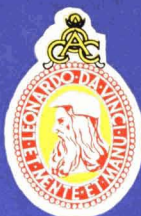
Hardening of organic coatings with infra-red lasers

E. Ladstädter and H. D. Hanus

The American paint industry: Present trends and future possibilities

F. Armitage

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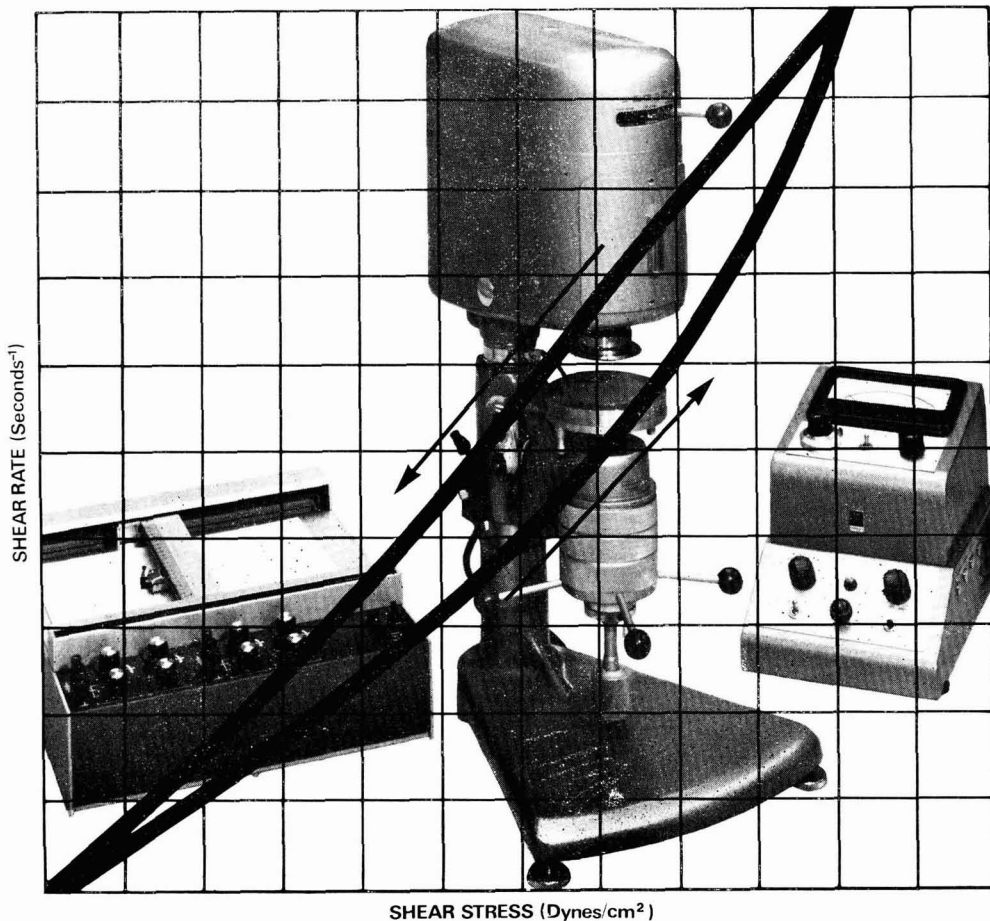
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Polymers: Developments for the future*

By C. E. H. Bawn

Donnan Laboratories, University of Liverpool, Grove Street, P.O. Box 147, Liverpool L69 3BX

Summary

The manner in which the mechanical properties of polymeric substances are governed by their molecular structures and orientations are discussed. The provision for strong and stiff materials, and for heat resistant polymers is described, and the lines upon which future developments might be made are outlined.

It is suggested that (a) no completely new mass plastic will be developed in the next ten years, (b) there will be a series of develop-

ments from copolymers, or of modifications of existing plastics, (c) within the next twenty years, a new range of plastics will be developed and, (d) other sophisticated plastic materials will be discovered within the same period of time.

Broadly speaking, the advances in polymers have followed the introduction of new catalysts, and it is suggested that the synthesis of enzymes will open up a new field of polymer chemistry.

Keywords

Properties, characteristics and conditions primarily associated with materials in general

mechanical property

melting point

Miscellaneous

polymers

Polymères—développements pour l'avenir

Résumé

On discute la façon par laquelle leurs structures moléculaires et leurs orientations exercent une influence décisive sur les caractéristiques mécaniques des substances polymères. On décrit la mise au point des matières robustes et rigides, et également des polymères résistants à la chaleur. D'ailleurs on trace les grandes lignes des développements éventuels de l'avenir.

On suggère que:

(a) Pendant la prochaine décennie on ne perfectionnera pas de matière plastique de base entièrement nouvelle.

(b) Il y'aura une série de développements à partir de copolymères, ou des modifications de matières plastiques actuelles.

(c) Au cours de la prochaine vingtaine d'années, une nouvelle gamme de matières plastiques seront mises au point.

(d) D'autres matières plastiques évoluées seront découvertes pendant la même époque.

En général, les avances dans le domaine de polymères ont suivies l'introduction de nouveaux catalyseurs, et l'on suggère que la synthèse des enzymes donnera accès à un nouveau domaine de la chimie polymère.

Polymerentwicklungen der Zukunft

Zusammenfassung

Eine Erörterung der Art und Weise, in welcher die mechanischen Eigenschaften polymerer Substanzen durch ihre molekularen Strukturen und Orientierungen dirigiert werden. Die zur Erzeugung von kräftigen und steifen Materialien und von hitzebeständigen Polymeren nötigen Massnahmen werden geschildert, sowie die Pfade umrissen, entlang denen sich künftige Entwicklungen bewegen mögen.

Es wird als wahrscheinlich vorausgesagt, dass

(a) innerhalb der nächsten zehn Jahre keine völlig neue plastische Masse entwickelt werden wird,

(b) eine Reihe von Weiterentwicklungen aus Mischpolymeren

oder Modifizierungen bestehender Kunststoffe stattfinden werden,

(c) innerhalb der nächsten zwanzig Jahre eine neue Gruppe von Kunststoffen entwickelt werden wird, und

(d) während der gleichen Zeit andere spitzfindige, synthetische Kunststoffe entdeckt werden.

Die Fortschritte auf dem Gebiete der Polymere folgten im grossen und ganzen der Einführung neuer Katalysatoren, und es wird als naheliegend angenommen, dass die Enzymsynthese ein neues Gebiet der Polymerchemie erschliessen wird.

Полимеры и их будущее развитие

Резюме

Обсуждается процесс которым механические свойства полимерных веществ определяются их молекулярными структурами и ориентациями. Описывается обеспечение прочными и жесткими материалами и жаропрочными полимерами и намечаются направления возможного будущего развития.

Сделаны следующие предположения:

(а) что в течение следующих десяти лет не будет развито никаких исключительно новых пластмасс,

(б) будет ряд развитий из сополимеров или модификаций существующих пластиков,

(в) в течение следующих двадцати лет будет развит ряд новых пластмасс и

(г) будут обнаружены другие более сложные пластические материалы в течение того же периода времени.

Вообще говоря, прогресс в полимерах последовал после введения новых катализаторов и предполагается что синтез ферментов раскроет новую область в химии полимеров.

* Presented at the 1973 Eastbourne Conference. Plenary lecture.

Introduction

The polymer industry is not only the youngest but also the fastest growing section of the chemical industry. Recent forecasts indicate a three-times growth in manufacture and processing by 1980. It is not the author's intention to discuss this volume of growth or the motives which determine it, however, but to consider the trends in the future developments of polymeric materials and the likely future achievements.

Man-made polymers are not only applied as substitutes for metals, glass, paper, natural fibres and other materials, but have found novel uses in their own right. In general, applications are associated either with specific properties, such as toughness, flexibility, elasticity, transparency, heat and environment resistance, or with specific fabrication techniques such as moulding, extrusion, calendaring, foaming, film casting, fibre spinning or surface coating. This breakdown indicates broadly the two main divisions of the industry that is synthesis oblique production and properties/processing. This paper is mainly concerned with the former, but the important interaction between production and application should always be borne in mind.

In spite of their widespread nature, certain future trends are already discernable:

1. Improvement of the physical and mechanical properties, especially permeability to gases and liquids, rigidity, toughness and surface hardness
2. Widening of the temperature range in which the material can be used
3. Increase in the endurance of materials, namely in their ability to withstand ageing both under load (fatigue, stress cracking) and without load against attack from the environment (chemicals, weather).

Although significant progress is being made in these and other areas, one of the widely accepted reasons for the continuing significant growth of the industry is the belief that it still has great potential, as yet only dimly perceived, for producing many new and useful effects, not only in the improvement of present day materials, but also in the synthesis of polymers either using controlled structures or by combining polymers in composite structures.

At the present time, low cost and large-scale production polymers (using the term in its widest sense to include plastics, synthetic fibres and elastomers) are made from a small group of inexpensive monomers produced by the petrochemical industries, namely ethylene, propylene, isobutylene, butadiene, styrene, vinyl chloride, vinyl acetate and the acrylics. It is likely that in the next decade at least 80 per cent of polymeric materials will be made from the above monomers, or a combination of them, and it is fairly certain that other industrially produced monomers will be added to this list. Nevertheless, there still remains considerable opportunity for the production of new materials from existing, cheap monomers by copolymerisation (graft and block copolymers), polyblending and cross-linking. Another approach is the use of physical (and manufacturing) processes for making structured materials. Progress in already defined areas (such as orientated films, paper like materials based on fibres or film, multicomponent structures such as synthetic leathers, the reinforced materials based on glass, carbon, and polymer fibres) will continue, and new applications for multicomponent materials is expected.

Structured materials

Molecular properties

In general terms, the properties of a polymer and its usefulness are determined firstly by the chemical structure and properties of the assembly of polymer molecules, such as molecular size and shape, and secondly by the supermolecular structure which defines the structural features characterising the arrangement of the polymer molecules in three dimensional space. In the solid state, polymers exist in an amorphous or semi-crystalline condition. The ability to crystallise is probably the most important property when determining the thermal and mechanical properties of polymers, and the principal factors which determine crystallinity are the structural regularity of the chains, the intra-molecular bonding between chains, and chain conformation.

At sufficiently high temperatures, a linear or branched polymer is an amorphous rubbery melt in which the chains are entangled with one another. On cooling, the melt forms a hard rigid solid which may be (a) crystalline, and thus characterised by a melting point T_m , or (b) a glassy amorphous solid with a well-defined glass transition temperature T_g . Nearly all the useful mechanical properties are determined by these transitions and by the temperatures at which they occur. As with the melting point, the glass transition temperature depends strikingly on the molecular structure of the polymer, and the most important factor determining T_g is the flexibility of the polymer chain. In fact those factors which determine high melting points, namely rigid chains and strong intra-molecular forces, also favour high glass transition temperatures in semi-crystalline polymers.

Within the general family of linear polymeric structure, an approximate and significant correspondence exists between T_g and T_m , namely $T_g = 2/3 T_m$. It is evident that, in order to synthesize a polymer with both a high melting point and high T_g , rigid chains and high inter-molecular forces are necessary, and thus there is no great likelihood of T_m and T_g being controlled independently. In order to do this it is necessary to modify the main structural characteristics of the polymer. By using a combination of monomers it is possible to build irregularities into the supermolecular organisation, and accommodation into the crystal lattice may be controlled. The melting points and transition temperatures of copolymers as a function of composition show the general behaviour represented in Fig. 1. It is clear that copolymerisation allows the polymer chemist to attain an independent control over T_g and T_m .

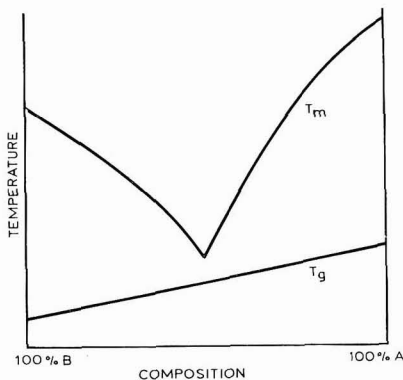


Fig. 1. Melting point and glass-transition temperature as functions of copolymer composition

A further structural irregularity arises if the units *A* and *B* forming the copolymers are arranged in long alternating sequences (that is, as block copolymers of the form $A_x B_y$). The poly-crystallinities of *A* might melt at a high temperature and those of *B* at a low temperature, and thus it is possible to combine a high crystalline melting point of the *A* component with a low transition or melting temperature of the *B* component (that is, a property combination achieved by neither linear polymers nor random copolymers). The second component may be totally amorphous, for example an elastomer, and the combination of a crystalline block *A* combined alternately with an elastomer block *B* constitutes the recently developed group of polymers known as thermoplastic elastomers $A_x B_y A_x$. The crystalline regions act in the same manner as do chemical cross-links which prevent chain molecules slipping over one another.

Another method for forming "labile" cross-linking is by ionic association or bonding. Thus, hydrogen bonding between carboxyl groups in polymeric acids, or in α -olefin carboxylic acid copolymers, constitutes a form of labile cross-link. The glass transition and elastic modulus of styrene/methacrylic acid copolymers has been increased considerably by the replacement of the acid by a metal salt. In these materials, strong inter-chain forces are developed between the ionised carboxyl pendant groups in the α -olefin and free metallic cations, mainly from groups I and II of the Periodic Table. Ionic association produces a profound effect on crystalline morphology leading to diminished haze and thus greater transparency.

The "ionomers" made by Du Pont are alkali salts of copolymers of ethylene with acrylic acid or methacrylic acid (approximately 10 per cent). The monovalent metal ion in the alkali acts only through an association of polar ion pairs and not, as with the bivalent zinc ion, through ionic bonding. The cross links are able to dissociate and re-associate freely, and permit easy injection moulding and extrusion.

These methods of physical cross-linking are in striking contrast to the more familiar method of cross-linking by covalent bonds which leads to hard, infusible and insoluble resins, such as melamine or urea-formaldehyde resins, and which is irreversible.

Heterophase polymer systems

Polymers, whether crystalline or amorphous, are not mutually soluble on the molecular scale. Consequently, polymer blends are heterophase systems, with few exceptions, and as a result the properties of these materials are significantly different from those of random copolymers of the same chemical composition which are homogeneous. Furthermore, whether the two polymers are formed end to end to the form of simple *AB* blocks or multiply to form block *ABAB* . . . copolymers does not alter significantly the degree of compatibility. These so-called "poly-alloys" have new and interesting properties.

When two polymers are blended mechanically the dispersed regions are irregular in size and shape. With block copolymers, however, as a result of the chemical bonds joining the blocks, phase separation occurs on a microscopic rather than on a macroscopic scale, and thus gives more uniform and more regular disperse regions. For example, consider copolymers formed from long alternating sequences of two monomers *A* and *B* (that is, block copolymers *AB*, *ABA* and *ABABA* and so on) where the *A* sections are rigid and can crystallise, and the *B* sections consist of flexible chains

which have typical elastomeric properties. These copolymers have the properties of a thermoplastic polymer above a certain temperature and behave as a typical rubber at lower temperatures. The strength and high elasticity of this new class of material is due to the high degree of contact between the rubbery and plastic phases. The plastic phase *A* is highly dispersed in the rubbery matrix, and, by virtue of its semi-crystalline nature, forms domains which function in a similar manner to cross links by incorporating the elastomeric chains into a three dimensional network structure as shown in Fig. 2. The concept is an extremely valuable one and much progress has already been made in the synthesis and manufacture of such block copolymers.

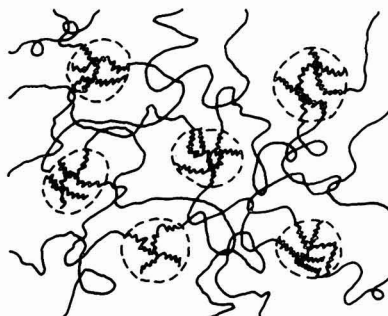


Fig. 2. Schematic representation of the polystyrene domain structure in S/B/S triblock copolymers

Mechanical properties

It is very revealing to consider the properties of polymers from the mechanical point of view. Stress-strain measurements (for example, of load versus extension) made over a range of temperature and speed of elongation indicate the conditions under which the material will break, whether or not it is brittle or ductile, and provide, in addition, much information about the stiffness of the material. The stress-strain behaviour of polymers depends upon a number of factors. Increase in crystallinity raises the modulus (stiffness), decreases the elongation at break, and generally tends to make the polymers more brittle. The amorphous form of a polymer can be expected to be more resistant to fracture at a given temperature than the semi-crystalline material.

From the mechanical point of view, a very desirable feature of any polymer is the ability to combine a high level of rigidity and low creep with a high impact strength. With impact, the specimen is put through a stress-strain cycle at high rates of strain. It is desirable to have a high energy requirement for fracture, and the energy absorption can be represented by the area under the stress-strain curve (Fig. 3). In order to combine toughness with rigidity, it appears necessary that the plastic yield should set in suddenly at high stresses, and should have a stress-strain curve which is linear at low stresses. Thus, the requirements for a tough rigid polymer are a high modulus and a high yield strength (although the latter must be less than the fracture strength).

In order to transform a brittle polymer into a tough material therefore, it is necessary either to increase the fracture stress until it exceeds the yield stress, or to reduce the yield stress until it is below the fracture stress. Considerable success has been achieved in this field by using

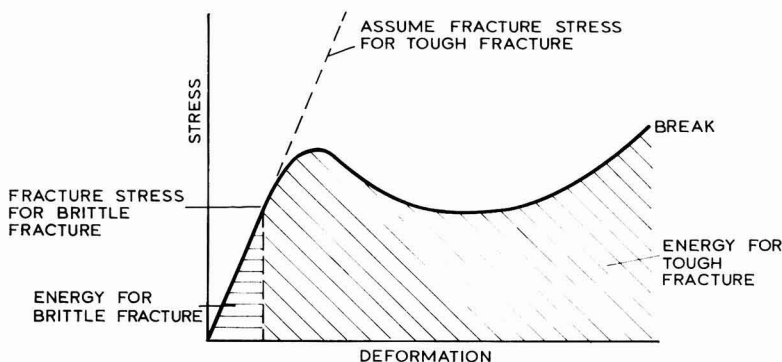


Fig. 3. Deformation and fracture of a typical thermoplastic

rubbery material in conjunction with an organic glass. High impact polystyrene, ABS resins, and similar products have been developed in this manner. The introduction of rubbery material has a softening action and causes reduction in overall rigidity and strength. However, this disadvantage is more than offset by the increased capacity of the polymer to deform and take up energy under impact conditions.

It has long been recognised that the strength of glass-like plastics is limited by flaws and cracks at the surface and within the structure. The presence of the rubber component confers on the polymer the additional property of interfering with crack propagation in the matrix. In practice, it is found that the rubber is more effective when used as a copolymer than as a blend, and it is found that the shape and dispersion of the rubber particles is more regular when copolymerisation is used.

In these materials, toughness is achieved by sacrificing rigidity or tensile strength. Naturally, it is desirable to minimise the loss of yield strength, and this is achieved by using a third monomer (one which gives a strong polymer such as acrylonitrile) and styrene together with the rubber. The acrylonitrile-styrene-butadiene terpolymers have superior rigidity and impact strength compared to high impact polystyrene. The tensile strength is provided by the ordered crystalline regions; the soft rubbery regions can undergo appreciable extension and are thus able to accept large deformations.

Strong and stiff materials

The tensile strength of most commercial thermoplastic materials is about 100 to 200 times less than the theoretical breaking stress of the covalent carbon-carbon bond. The strength can be raised considerably by careful orientation of highly crystalline polymers, for example polyethylene, but even under the most carefully controlled conditions of preparation and measurement, the strength is still an order of magnitude less than the ideal value, mainly because of flaws and surface cracks in the glassy amorphous regions.

It has been shown how the possibility of fracture might be reduced by dispersion of an elastomeric phase uniformly throughout the material. A method of much wider applicability is the reinforcement of plastics by fibres. The extensive use of glass fibres as reinforcement with unsaturated polyesters, epoxies, phenol-formaldehyde, or melamine-formaldehyde resins is well known. The technique is used for the production of glass-fibre mats and other fabric by laminat-

ing or moulding operations. Fig. 4 illustrates that the tensile modulus of a thermoplastic can be increased so as to approach that of die cast metal by the addition of 20 to 50 per cent of glass fibres as reinforcement. Modern technology, however, needs stronger and stiffer materials, and in recent years attention has been focused on the synthesis and production of stronger fibres. It is well established that the maximum strengths of fibres range from 0.03 to 0.10 E , where E is Young's modulus. The strength of "everyday" materials ranges from 0.001 to 0.01 E , mainly due to the fact that the strength is limited by structural faults in the material. Under certain conditions, it is possible to make flawless materials and not only to realise in practice the strength of the ideal fibre, but also to make fibres very much stronger than those commonly used. The materials which meet these requirements are beryllium, boron, graphite, silicon carbide and silicon nitride fibres.

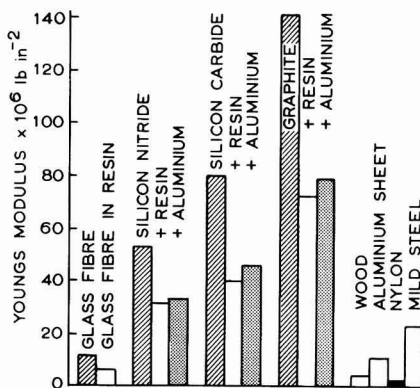


Fig. 4. Estimated Young's modulus of materials

Diagonal shading = fibre

Open area = fibre + resin (50 per cent by volume)

Cross-hatching = fibre + metal (50 per cent by volume)

Initially developed for aero-space application, graphite fibres made by the carbonisation of polyacrylonitrile are now being widely used, and it can be safely predicted that this and similar fibres will have an important place among materials which will be developed in the next decade. Graphite fibres, with an average tensile strength of 250 to 300 $\times 10^3$ lb in^{-2} and Young's modulus of about 60 $\times 10^6$ lb in^{-2} can be readily incorporated into conventional polyesters or

epoxy resins to give a product with a modulus (resistance to elongation) of about three times that of glass fibre of the same fibre content.

In recent years, considerable attention has been paid to the synthesis of high modulus organic fibres, and independent discoveries have been made in several laboratories. Dupont have announced high-modulus fibres of poly-p-benzamide and the terephthalamide of p-phenylene diamine (I) (Fig. 5).

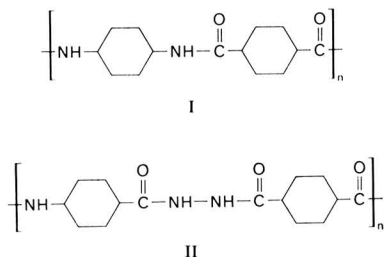


Fig. 5. Two examples of aromatic fibrous polymers

It is probable that the latter polymer is the one Dupont is now marketing as "Fibre B." Monsanto have a family of similar, wholly aromatic fibres known as X-500, produced from a variety of wholly para-oriented monomers, for example polyamide-hydrazides (II) (Fig. 5). These fibres are more than 25 per cent stronger than glass fibres, and have twice the modulus of elasticity, and are more than five times stronger than steel fibres and have twice the modulus of elasticity. Applications, initially, are expected to be in the field of tyre cords and specialised, rigid, reinforced plastics.

Heat resistant polymers

Much of the impetus behind the increased effort in polymer research during the past ten years arose from the need to synthesise new polymers with markedly higher temperature resistance than was available at the time. Most of the conventional thermoplastics cannot be used in air for long periods at temperatures above 100 to 120°C. Polymers possessing high strength, rigidity, solvent and chemical resistance and serviceability at temperatures from 200° up to 500°C would find a variety of new uses.

The general synthetic approach, to producing polymers with increased strength and thermal stability, has been directed towards regularity, high crystallinity and inflexible backbone chains. The bulk of the more recent effort has been based on synthesising inflexible polymer chains that would resist deformation and softening. The incorporation of ring structures into the chain has been extensively developed for the purpose of chain stiffening, especially by aromatic and heterocyclic rings because of their known thermal stability. Many new commercial polymers have resulted from these developments. The polyphenylene oxides, polycarbonates, aromatic polyethers, polysulfones and aromatic polyamides were the first members of the new breed of heat resistant polymers to become commercially available. All these polymers have aromatic rings in the backbone and members of this class of polymer are tough, have high impact strength and rigidity and good heat ageing properties above 150°C (Fig. 6). The building up of a polysulfone backbone without any aliphatic group results in a product of considerably improved resistance to oxidation which is usable above 200°C.

The polyimides, which are the best developed class of high-temperature polymers, are based on heterocyclic (and

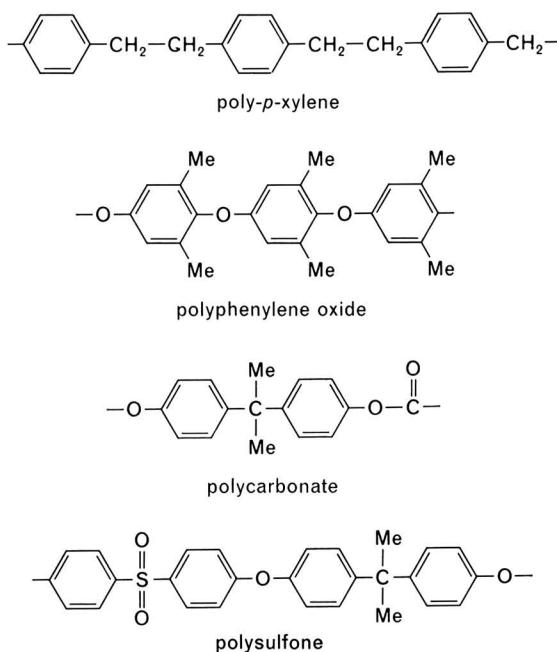


Fig. 6. The structure of several heat-resistant polymers containing aromatic rings in the main chain

aromatic) rings in the backbone. They are obtained by the condensation of aromatic diamines and aromatic dianhydrides, followed by intermolecular cyclodehydration (Fig. 7). The first step is usually carried out in dimethyl acetamide solution at room temperature. The intermediate polyamic acid, free from solvent, is cast into film and, above 150°C, dehydrates by cyclisation to form the insoluble polyimide. The polymer is stable for long periods at 300°C, and may be used for shorter periods at much higher temperatures.

nical properties in the range -253 to 650°C, at least for short periods.

The future

Looking into the future, the following four assumptions seem to be valid.

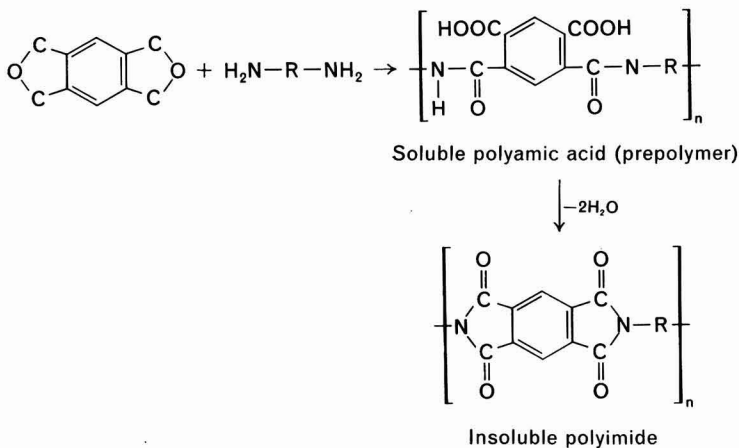


Fig. 7. Process involved in the formation of a high-temperature resistant polyimide

The polyimides are examples of polymers which have aliphatic and aromatic groups in the backbone, and this gives a compromise between chain stiffening and reduction of brittleness. Other heat resistant materials belonging to this class are the polyamide-polyimides and polyoxadiazoles.

A more advanced group of polymers, the so-called "semi-ladder" polymers, possess a backbone built entirely of aromatic and heterocyclic rings. The polymers are prepared by polycondensation and cyclodehydration from aromatic tetramines or diamphenols and aromatic dicarboxylic acids or dicarbonyl compounds. The polybenzimidazoles (Fig. 8) can be made in two steps (soluble prepolymers followed by ring closure) and, as with the polyimides, are stable in air at 300°C and are reported to have good mecha-

1. There will be no completely new mass plastic developed during the next ten years.
2. There will be a series of developments from copolymers, or modifications of existing plastics.

Generally, the output in Europe of "classical" plastic material will double every five years. In addition, the new and higher priced materials which have a low consumption at present (polyacetals, TPX, polysulfones and thermally stable polyamides, and fibre reinforced thermoplastics) will lead to the development of new materials.

3. Within the next twenty years a new range of plastics will be developed having a temperature resistance approximating to that of aluminium.

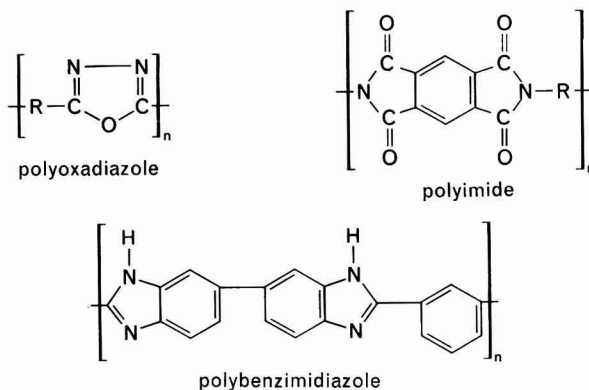


Fig. 8. "Semi-ladder" heat-resistant polymers

4. Other sophisticated plastic materials will be discovered within the same period of time.

A feature of the plastics industry is the speed at which developments can and do occur. A new material or processing technique can radically change the picture, both technically and economically (for example, polypropylene and thermo-plastic elastomers). Although much of the research today is "need oriented," products such as neoprene, nylon, polyethylene, silicones, and others, did not originate from a need for them. The need came after the materials had been discovered and developed. No-one can predict or forecast the future with any accuracy in the field of scientific discovery, but this does not mean that the future is unthinkable because it flows inextricably from the past. No forecasting can anticipate the flashes of innovative genius that leads to a major scientific or technical breakthrough. Nevertheless, it is possible to be imaginative about the future, and some of the trends of future progress are becoming evident.

The major breakthrough in the discovery of new polymeric materials in the recent past has been the direct outcome of new catalyst systems, which would not only polymerise monomers not previously polymerised, but would also lead to a greater stereochemical control of the addition polymerisation process. Even now it is clear that workers in this field are only at the beginning of the stereo-specification processes; they are still a long way from being able to imitate nature in her synthesis of the simplest of proteins.

Enzymes are more efficient catalysts, and of greater stereo-specificity than any man-made catalysts. They have two particular properties which set them apart from man-made catalysts. First, enzymes are highly specific; each catalyses one and only one type of reaction. The second property is their unusual catalytic power; enzyme catalysed reactions are usually 10^8 to 10^9 times more rapid than their man-made analogues. The chemist is only beginning to understand how enzymes work, but when he is able to prepare and synthesise enzymes he will be able to use them in new highly efficient processes for the preparation of new polymeric materials.

Progress will certainly be made in closing this gap, and it appears that this progress could occur initially in the development of surface catalysed polymerisation.

The use of copolymerisation as a powerful means of controlling the properties of polymers to meet particular technological requirements has already been discussed. The interest in this subject will continue in view of the infinite variety of products which can be obtained. Many copolymers obtained by combination of cheap monomers and, which might be expected to have valuable properties, have not yet been synthesised. For example, copolymerisation of ethylene with low-cost monomers such as formaldehyde, acetylene, carbon monoxide and so forth, could easily become more than possibilities with the discovery of new catalytic systems.

Present-day progress in plastics is largely in the field of technology and, in particular, in the use of forms of plastics which give high performance (in the sense of appropriate properties at the lowest cost). The combination of materials which incorporate structured materials, such as foams, impact resins, composites, are well known examples.

Plastics are uniquely suited to the automotive and building industries, where it is necessary to form complex shapes in a single operation. It is very likely that the car body will be made of plastic within the next decade. It can be envisaged that the present day tyre will be replaced by a cast plastic one, and the wheel assembly pressed from reinforced plastic.

During the last thirty years a number of synthetic fibres were developed with a range of properties and applicability much wider than that of natural fibres. With the decrease in fibre production costs, the synthetic materials have begun to invade the other large industries based on the production of goods from fibrous raw materials, namely paper and leather industries. These developments have been made possible by the use of new technologies for the formation of flat systems based on fibrous elements. The three great industries, textiles, paper and leather, are rapidly merging because the ultimate objective in all of these developments is a process which starts from a bulk polymer as a powder or granule, converts this into filaments, and then directly, and without interruption, converts the filaments into a flat system. Thus, there has been the emergence of the so-called non-woven materials for disposable clothing, microporous substitutes for leather, and synthetic papers. In these spun-bonded materials the fibrous structures are formed by laying down filaments on a moving belt as they emerge from a spinneret. The filaments are arranged in an irregular fashion, but are well separated and bonded permanently at cross-overs by heat treatment or thermoplastic binders. The spectrum of the fibres now used in these processes include polyolefine, nylon and polyester fibres.

Another area in which striking developments could occur is the electrical application of polymers. Polymers are usually regarded as insulating materials, but recent work has shown that it is possible to synthesise polymers which show electrical conduction. In fact, it has been predicted, theoretically, that it should be possible to synthesise polymers which are superconducting at room temperature. Much speculation and research has been done in the field, but so far no real success has been achieved.

These examples illustrate the areas in which the author hopes to witness considerable innovation. Traditional materials for construction will be replaced to a large extent by organic products, especially in the non-load bearing field. At the same time, the emergence of high performance composites is expected.

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The influence of supermolecular structure on the properties of polymer films*

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Summary

Whilst, in general, a homogeneous film structure is considered to be the most favourable state, various advantages in film behaviour can be brought about by a particular morphological structure. This structure is based on some features in the supermolecular range, such as "soft-phase" inclusions or microvoids, that affect mechanical and optical film properties in a special way.

Keywords

Properties, characteristics and conditions primarily associated with dried or cured films
mechanical property

The effect of inclusions was studied in an acrylic graft copolymer system as well as that of microvoids in a vinylchloride-vinylacetate copolymer, using films cast from solutions with various solvent blends. Electron-microscopic studies, as well as viscoelastic and rheological measurements, can be used to characterise heterogeneous film structures. Adhesion between films may be improved if the lower layer has a specific heterogeneous surface structure.

Miscellaneous

formulation
polymers

L'influence de la structure supermoléculaire sur les caractéristiques des feuillets de polymères

Résumé

Bien que l'on considère, en général, le feuillet de structure homogène d'être la condition la plus favorable, on peut effectuer de divers avantages à l'égard du comportement du feuillet au moyen d'une spécifique structure morphologique. Cette structure se base sur certaines caractéristiques dans la gamme supermoléculaire, telles que les inclusions "soft-phase" (phase molle) ou des microvoides qui influencent les caractéristiques mécanique ou optique du feuillet dans une manière exceptionnelle.

On a étudié l'effet des inclusions dans un système copolymère acrylique greffé; et celui des microvoides dans un copolymère chlorure de vinyle-acétate de vinyle au moyen des feuillets fondus à partir des solutions dans de divers mélanges de solvants. Afin de caractériser les structures hétérogènes de feuillets, on peut se servir des études au microscope électronique, de même que les mesures viscoélastiques et rhéologiques. On peut améliorer l'adhérence entre feuillets, dans le cas où la surface de la couche inférieure possède une structure spécifiquement hétérogène.

Der Einfluss Supermolekularer Struktur auf die Eigenschaften Polymerer Filme

Zusammenfassung

Während im allgemeinen eine homogene Filmstruktur als der günstigste Zustand betrachtet wird, so können doch im Verhalten von Filmen durch eine eigenartige morphologische Struktur verschiedene Vorteile im Verhalten von Filmen hervorgerufen werden. Diese Struktur beruht auf einigen Besonderheiten im supermolekularen Bereich, wie z.B. "weichphasische" Einschlüsse oder Mikrovacua, welche die mechanischen und optischen Filmeigenschaften auf spezielle Weise beeinflussen.

Die Gegenwart von Einschlüssen wurde in einem Akrylatpfropf-

polymersystem untersucht ebenso wie die Wirkung von Mikrovacua in einem Vinylchlorid-Vinylacetat-Kopolymer, wobei auch gegessene Filme aus verschiedenerlei Lösungsmittel enthaltenden Lösungen inbegriffen waren. Um die heterogene Filmstruktur zu charakterisieren, können sowohl elektronmikroskopische Studien als auch viskoelastische und rheologische Messungen benutzt werden. Haftung zwischen Filmen kann, wenn die untere Schicht eine spezifisch heterogene Oberflächenstruktur besitzt, verbessert werden.

Влияние сверхмолекулярных структур на свойства полимерных пленок

Резюме

Хотя вообще говоря однородная структура пленки принимается как самое благоприятное состояние, ряд преимуществ в поведении пленок может быть вызван особой морфологической структурой. Эта структура основана на некоторых особенностях в сверхмолекулярной области, как например включения «мягкой фазы» или микропустот, которые проявляют особое влияние на механические и оптические свойства пленки. Эффект включений изучался на прививочной акриловой

сополимерной системе, а эффект микропустот — на винилхлорид-винилацетатной сополимере, содержащими пленки полученные из растворов с различными смесями растворителя.

Электронно-микроскопические исследования и также вязкоупругие и реологические измерения могут применяться для характеристики неоднородных структур пленок. Адгезия между пленками может быть улучшена если нижний слой имеет специфическую неоднородную поверхностную структуру.

Introduction

The opinion that the structure of vehicles in paint films are predominantly in a so-called amorphous state still prevails. In other words, there is not supposed to be any noticeable structural order. Depending on the type of film formation, the structure of the solid state of a film can be characterised in two ways. When a film dries physically, by evaporation of

solvent, the molecular structure will consist of randomly coiled macro-molecules. Their shape is entirely fortuitous, and they penetrate each other to form a felt-like network. For vehicles which react chemically during drying the situation is somewhat different. In this case, the polymer chains are finally cross-linked, but the chain segments between the cross-links are considered to have a completely random arrangement.

* Presented at the 1973 Eastbourne Conference.

Whilst this view has been widely adopted in the paint field, the situation is different for plastics and fibres. Here considerable interest has long been taken in particular structural features, such as crystallinity and para-crystallinity. Accordingly, pertinent research during the past ten to fifteen years has disclosed the most essential structural characteristics of such partly crystalline polymers.

The simple idea of a two-phase system with adjacent crystalline and pure amorphous regions had to be abandoned. Rather, the material exhibits a continuous range of different kinds of order, ranging from a perfectly crystalline to a completely amorphous structure. However, neither of these extreme cases can be realised, even under most precise conditions. A perfectly crystalline polymer always contains dislocations or similar faults; a completely amorphous solution, or melt, of polymer is not a possible state also, because in both of these liquid states, regions of a certain near- or far-reaching order will exist which fluctuates to a greater or lesser extent. Hence, in order to characterise the state of a polymer film adequately, it should be considered as a non-crystalline rather than as an amorphous structure.

During the last few years, the phenomenon of molecular order in non-crystalline polymers has rapidly gained prominence in the field of solid state polymer physics.¹ It seems appropriate to extend these investigations to the paint field, where the morphological structure of the binder in the dry film has not yet been studied very extensively.

A paint film may be formed from the originally liquid material, starting with either a melt or a solution. In this work, only the latter case will be considered. As to the choice of the solvents in paint formulation, several aspects are relevant. Firstly, the solvent should promote and accelerate the grinding and dispersion of the pigments. Moreover, the solvent should give the correct paint viscosity. The solvent mainly determines the rate of drying and markedly affects the levelling. Finally, some plasticising effect may occur if too much solvent is retained in the film after its formation. All these relations are well known factors of paint production and processing techniques.

Not so much attention, however, has been paid to the fact that the solvent may also affect the morphological structure and the short-range order in the polymer film, thus contributing indirectly to the mechanical properties finally obtained. The effects are caused by intra-molecular as well as inter-molecular interaction between solvent and polymer molecules. The extent of intermolecular interaction depends also on the polymer concentration. Under comparable conditions, the interaction in very diluted solutions takes place mainly between segments belonging to the same chain molecule. A different situation is encountered in concentrated solutions: interactions between segments of different molecules will occur to a significant extent. This change in the segmental interactions not only affects the rheological properties, but also results in some specific forms of short-range order, which can be considered to be the beginning of some kind of molecular order in the solid polymer film.

Generally, two kinds of structure forming effects may be operative in the process of film formation from polymer solutions, each of which depends, essentially, on the particular type of solvent used and the temperature involved. One of these effects consists of a phase separation at some time during film formation, if the system develops some incompatibility due to the composition of the residual solvent mixture changing. The other effect may be brought about

by the influence of solvents on the short-range order of the polymer chains.

Heterogeneous structure and related mechanical properties

First of all, it should be remembered that every normally pigmented paint film already possesses some of the distinctive features of a heterogeneous system. The pigment particles, which are dispersed in the film, provide some additional hardness to that of the unpigmented film. But, with the exception of fillers, which are sometimes deliberately added for this purpose, the mechanical effects of pigments are tolerated, being considered more or less unavoidable if the required optical film properties are to be produced. The general influence of pigments, in mechanical terms, has often been studied, at least as far as film hardness is concerned, and is fairly well-known. The elastic modulus increases with the pigment volume concentration, and this is virtually independent on particle size, as van der Waal et al.² would indicate.

According to these authors, the influence of the temperature on the mechanical properties, which is very characteristic of any polymer film, is scarcely affected by pigments unless these are able to react with the polymer molecules. In particular, the glass transition temperature T_g of an unpigmented film is virtually maintained even in films of relatively high pigment content.³ Since the specific effects of the pigment can be adequately assessed from the basis of normal experience with ordinary paint films, it is justifiable here to restrict the treatment to the unpigmented film, and to discuss how film properties can be influenced by the deliberate variation of the supermolecular structure of the binder.

The incorporation of a disperse phase into an otherwise homogeneous polymer has yielded very significant results in so-called polymer blends. The most prominent example of such material is certainly high impact strength polystyrene. Obviously, the disperse soft phase in the hard continuous matrix renders the latter sufficiently stable to mechanical impact. The resistance is not simply due to the presence of a certain percentage of the soft component, which may absorb and dissipate the energy. According to recent theory, a more sophisticated mechanism has to be assumed⁴ because the effect of the disperse phase is mainly due to a state of stress in soft inclusions in the region adjacent to the hard matrix material, which impedes the formation of cracks when the material is subjected to mechanical impact.

The beneficial function of the disperse phase can, however, only be utilised completely if sufficient adhesion exists at the inter-face between inclusion and matrix. For example, graft copolymerisation may provide sufficient linking at the interface.⁵ Such a reinforcement principle, which is well known in the plastics field, can be used, in addition, to improve the mechanical properties of polymer films. Materials similar in their behaviour to high impact strength polystyrene, or to the much used ABS-polymers, have not yet found any significant application in the paint field. This is probably due to the well-known fact that translucency, normally considered as a sign of film quality, is naturally seldom attainable in such films. It is not realised, however, that this minor disadvantage in optical terms could be compensated for by markedly improved mechanical properties for such films.

In order to study a typical example of such a material, an acrylic graft copolymer system has been investigated. The

matrix consisted of methyl methacrylate that, alone, would be much too brittle for paint films despite of its otherwise advantageous properties. The expected advantages of a composite can, however, be obtained when butyl acrylate, as soft disperse phase, is incorporated into the brittle matrix. Films produced from this heterogeneous material are still rather translucent. Apparently, the difference between the refractive index of the inclusion and that of the matrix does not affect optical film properties too much. Moreover, the films exhibit the anticipated mechanical properties. Their flexibility should be sufficient even for coatings on substrates which may change their shape, such as wood. The deformability of these composite films can also be regarded as appropriate for most practical cases, because, as mechanical tests have shown, such films can be elongated up to about 20 per cent without any detrimental effect on the adhesion between the two adjoining phases.

The morphological structure may be demonstrated by taking electron micrographs of the interior of the film using the fractographic method⁶. A typical cross-section micrograph (Fig. 1) shows some of the essential features. Appar-

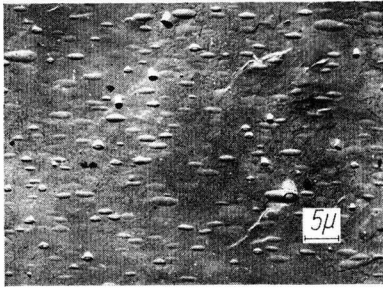


Fig. 1. Electron micrograph of an acrylic graft copolymer film

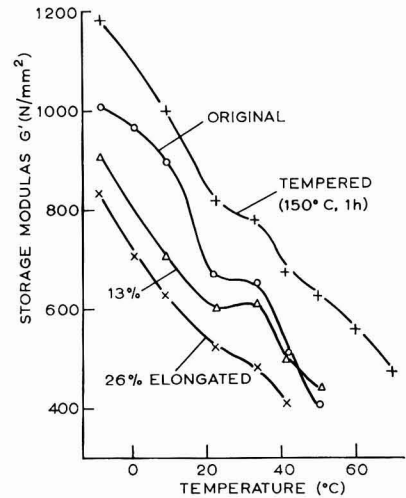
ently, the size of the inclusions is quite uniform. This should, in general, be appropriate to the use of the material as a vehicle, for then the disperse phase can be better adapted to the size of the pigment particles, if necessary. Any interaction of this component with the surrounding vehicle, which finally affects the mechanical behaviour, can be assessed more adequately when a definite relationship exists between the particle size of the pigments and that of the inclusions.

It is remarkable that the distribution of the disperse phase is fairly uniform. This is an additional requirement for the intended effect of the soft inclusions. Their shape is, however, not spherical as might be anticipated from the phenomena encountered in polymer blends in the plastics field. The inclusions in Fig. 1 appear in form of ellipsoids of which the greater extension is distinctly parallel to the plane of film. This feature clearly indicates that, to a certain extent, the process application may also affect the morphological structure. As a result of this, the film properties will exhibit some anisotropy.

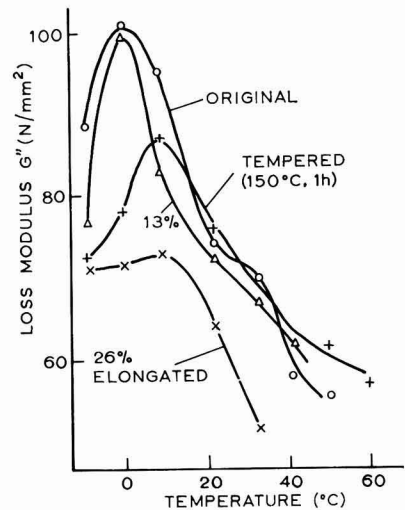
The mechanical properties of these acrylic copolymer films have been determined by a viscoelastic method, which yields information about hardness and on structural changes, both of which depend upon temperature. In this method, both components of the complex shear modulus, that is storage and loss modulus, are determined. The storage modulus can be considered as a direct measure of the deformability in the range sufficiently below the ultimate strength limits, and, if the temperature range studied coincides with the

softening region of the film material, the modulus discloses how the heterogeneous structure affects the mechanical properties. On the other hand, the loss modulus, which is characterised by a maximum in the softening region, is also influenced by structural factors.

A torsion pendulum was used for the measurement of these viscoelastic properties.⁷ The results are shown in Fig. 2. It is of particular interest to monitor the effects of additional film treatment. Alterations brought about in this way lead to some ideas of how the film's behaviour will change under similar conditions in practice.



(a)



(b)

Fig. 2. Viscoelastic properties as a function of temperature

Starting from the curve for modulus dependency on temperature of the film without any additional treatment, it can be observed that there is a distinct step in the centre

of the softening region, that is generally associated with the interface between soft and hard phase.⁸ When the film is stretched to about thirteen per cent the influence of the soft phase becomes somewhat more pronounced, but this occurs without any changes in the general mechanical behaviour. In particular, the connection between the phases must have remained intact despite the elongation of film, since otherwise the step in the curve would have vanished. Apparently, this is the case of a greater elongation, up to about twenty-six per cent, for which the resulting, nearly continuously descending curve is shown in Fig. 2. The coherence of the material must have suffered as a consequence of the stretching treatment, for the modulus has decreased markedly. Yet, still more important is the fact that the interfacial connection between the soft inclusions and their surrounding matrix has obviously now been ruptured.

This structural change can be observed macroscopically, for the originally clear film, stretched to such an extent, turns white and turbid. Strictly speaking, the film should then no longer be considered as composite, and the film should no longer be expected to possess the advantageous properties which would otherwise result from the combined action resulting from both phases being in intimate contact. Since this deterioration only appears at a rather large elongation of more than twenty per cent, however (which will seldom happen on rigid substrates), the risk of losing useful film properties is unlikely in practice.

The variation of mechanical properties of the material can also be seen from the curve for the loss modulus in Fig. 2. There is virtually no difference between the undeformed and the slightly stretched film. At an elongation of twenty-six per cent, however, the maximum has nearly disappeared, for the same reason given for the explanation of the missing step in the curve of storage modulus.

Another practical condition, which may influence the mechanical properties, is high temperature. Fig. 2 indicates what changes will occur in such a case if, for instance, the film is maintained at 150°C for one hour. Here the shift of the storage modulus to higher values, and particularly the fact that the step in the curve is no longer as pronounced as for the untreated material, may be explained by an additional cross-linking in the interfacial region. In other words, as a consequence of the heat treatment, the film becomes somewhat more homogeneous. The smoothly descending curve is considered to be characteristic of this state. The higher degree of cross-linking is also reflected by the shift of the maximum of loss modulus to correspond to a slightly higher temperature.

Both variations, large deformation and the use of elevated temperature, are beyond what would be anticipated for most practical situations. It can be concluded, therefore, that the morphological structure, as shown in Fig. 2, is sufficiently stable to maintain the mechanical properties for the purposes intended.

Effect of microvoids in the film

The heterogeneous structure of films which consist of a continuous and a discontinuous polymer phase are by no means the only unconventional way to modify mechanical film properties. An alternative procedure is the use of films containing air-filled voids of specified size and form. This method has already proved successful in conjunction with other developments; the so-called bubble-coatings,⁹ in which

the principle of "pittmentation" is realised,¹⁰ provide an example.

When considering the use of air-filled voids to determine the mechanical properties of a film, it must not be overlooked that any empty site in an otherwise continuous material is a potential volume of decreased strength. Thus some provision is necessary for avoiding this unwanted phenomenon without nullifying the effect of what is otherwise a useful modification. The most important point in this context is the size of the void. According to Griffith's ideas,¹¹ a void of sufficiently small dimensions would be stable under stress unless the elastic energy stored in its environment were high enough to increase the surface energy, when the size of void would increase. This simple model does not imply any plastic deformation of material adjacent to the void, and should not, therefore, be supposed to be entirely realistic—a certain stability is obtainable, in any case, in a material containing a percentage of empty sites.

The use of a solvent mixture rather than a pure solvent can be a proper means for producing a supermolecular structure, where the occurrence of voids is the pertinent feature. Generally, the composition of such a mixture is determined by various considerations. In practice, ease of production of the liquid paint and of its application are often essential factors in the economy of such a process. Thus the appropriate solution may often be found by using a solvent blend.

The employment of a certain amount of non-solvent in the mixture normally affects the conformation of macromolecules in the liquid medium.¹² The general rule that the more the chain of molecules is uncoiled the "better" the solvent in respect to the polymer remains valid in principle. Thus, in polymer solutions with some non-solvent content some changes in the behaviour of chains may be expected. The result should be a modification of the supermolecular structure after film formation. When such a condition is deliberately achieved, films with peculiar properties (due to the supermolecular structure) may be obtained.¹³⁻¹⁵

A very informative example of this idea is a vinyl-chloride-vinylacetate copolymer (VC-VA) with about 85 per cent by weight of the vinyl chloride monomer. The solvent mixture consists of methyl isobutyl ketone (MIBK) as solvent and of 2-methoxybutanol (MOB), as the non-solvent. Suitable films may be obtained with a non-solvent concentration of up to forty per cent.

At first, it is very instructive to study the behaviour of the solutions, especially when the dissolution temperature is varied. The sequence of adding the components of the mixture is another possible variation. Solutions of the VC-VA copolymer in various mixtures of the two components exhibited a pseudoplastic behaviour even for a polymer concentration as low as 90 gm l⁻¹. When solutions are heated to 90°C for a short time and then cooled, the rheology changes from pseudo-plastic to Newtonian, and the viscosity becomes distinctly lower than before. This phenomenon is in accordance with similar results obtained by Hengstenberg and Schuch,¹⁶ who found that in a solution polyvinyl chloride molecules tend to associate, but may dissociate again when the solution is heated.

For this reason, the viscosity of solutions in MIBK/MOB mixtures (of molar ratio 60:40) was measured at various rates of shear. Moreover, the sequence of adding the solvent components to the copolymer was varied, and portions of

the solutions were heated before measuring. The results are shown in Fig. 3.

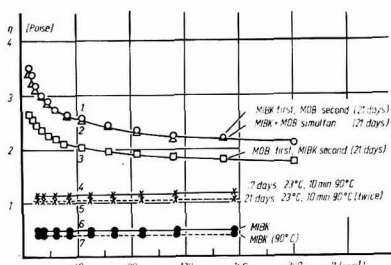


Fig. 3. Viscosity as a function of rate of shear for VCVA-copolymer solutions subject to different pre-treatments, as indicated; (solvent: mixture of MIBK and MOB)

It can be seen that the rheological behaviour depends on the sequence in which the solvent components are added to dissolve the polymer. When the polymer is first dispersed in the poor solvent and then the good solvent is added (curve 3), the rate of dissolution is high, and the viscosity of the resulting solution low. This is the usual procedure used for manufacturing paints. However, if the dissolution is begun by adding the good solvent, or a mixture of the good and bad components, then the dissolution proceeds more slowly, and the viscosity remains higher even after a long time (curves 1 and 2). The situation is changed completely after heating the solutions to 90°C. As indicated by the curves 4 and 5, the viscosity not only decreases distinctly and irreversibly, but the solutions now exhibit almost Newtonian flow. In contrast to this, the viscosity and the Newtonian behaviour of solutions of VC-VA copolymer in the pure solvent MIBK are not affected by heating (curves 6 and 7). Such behaviour could be observed up to a copolymer concentration of 20 per cent by weight.

It may be concluded from the decrease of viscosity, as well as from the approach to Newtonian behaviour, that in none of these three cases was the dissolution process complete, even after a long time. Obviously, the copolymer molecules are in a state of strong intermolecular association after the dissolution process, and this association can be destroyed only by using a sufficient excess of good solvent in a rather dilute solution. With higher polymer concentrations, a complete dissociation may be brought about only if the good solvent is used alone or at least in very high concentrations. In mixed solvent systems, the remaining associations are rather stable and only an increase in temperature can complete the dissociation. However, due to the deficiency of good solvent, a re-association takes place during cooling and, moreover, this is predominantly intramolecular association. As a consequence of this, not only does the viscosity remain at a lower level, but also the pseudo-plastic behaviour disappears. Viscometric studies thus yield additional evidence as to the shape of the macromolecules in solution which can be useful in assessing the supermolecular structure which finally exists in the polymer film.

The merits of structural modifications resulting from the use of specified solvent mixture can best be demonstrated by measuring mechanical properties, such as Young's modulus, tensile strength and elongation at break. For the stress-strain test, an Instron-Tester has been used in which the rate of deformation is well defined. Films of VC-VA copolymer were prepared using solvent mixtures of different compositions

varying from pure MIBK to 60 per cent MIBK : 40 per cent MOB.

The mechanical properties are shown in Fig. 4 as a function of the composition of the solvent mixture. Two distinct features appear in this diagram. The ultimate of strength does not attain an optimum when the good solvent alone is used for preparing the film. Instead, the highest values for both ultimate elongation ϵ_B and tensile strength σ_B are given by films which have been cast from solutions containing 10 per cent non-solvent. In addition to the possibility of

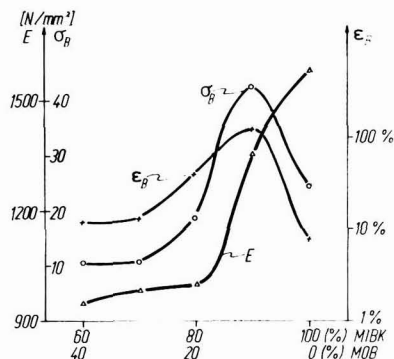


Fig. 4. Mechanical properties (Young's modulus E , elongation at break ϵ_B , tensile strength σ_B) as function of solvent composition in the liquid paint

improving film properties, a certain economic advantage also results, although only with respect to hardness, which may be characterised by Young's modulus E , this statement needs to be modified somewhat. Apparently, the hardest films are obtained using solutions with the good solvent alone. Yet the hardness of films which display maximum strength is only 15 per cent lower than those films which have the greatest hardness. Considering the increased strength, this decrease in hardness can certainly be tolerated. There may be some plasticising effect by retained traces of solvent, but this is supposed to affect the mechanical properties in a continuous way. It can hardly be expected that such an effect would bring about the maximisation of mechanical properties, or that it could be caused in such magnitude as observed here.

It is informative to compare these mechanical data with the supermolecular structure as revealed by electron microscopic studies. It can be seen macroscopically that the films become more heterogeneous as the content of non-solvent in the mixture is increased. Films are fairly translucent up to 10 per cent MOB. Higher concentrations of that component yield turbid films. A film from a solution with 40 per cent MOB appears perfectly white with excellent hiding power, even in pigment-free form; that is, this is nothing more than a bubble-coating. The reason for this peculiar optical behaviour can be seen from Fig. 5, which shows an electron micrograph of the film cross-section. Owing to the high non-solvent content, a phase separation takes place during film formation, and this causes the discontinuous structure. Since a rather large portion of the film does not contain a vehicle to provide strength and hardness, it is not surprising that such a film turns out to be inferior to the more compact ones in mechanical terms, for there is simply not sufficient mechanical support in the many thin interconnected lamellae of which the film is made up.



Fig. 5. Electron micrograph of a film made from a solution of forty per cent non-solvent in the solvent blend

The conspicuous strength of the films obtained with only 10 per cent non-solvent can be attributed, in addition, to a supermolecular feature. The translucent appearance of the film indicates that such structural details are of dimensions much smaller than the wavelength of light, that is about $0.5\mu\text{m}$. It is possible, however, to prove the existence of voids of that or a smaller size by fractographic electron microscopic studies. This is due to the occurrence of a parabolic pattern originating from the so-called secondary fractures, of which the void—situated in the focus of the parabola—is the cause. Fig. 6 demonstrates such a pattern and clearly shows that not only can the existence of micro-voids in the otherwise homogeneous film be easily perceived, but also that the concentration and distribution of these morphological details may be assessed.

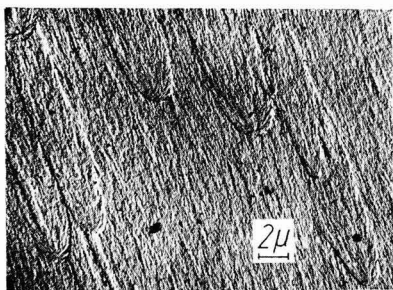


Fig. 6. Electron micrograph showing a fractured surface with secondary-fracture parabolas caused by micro-voids

It is now possible to give an explanation for the effect of these micro-voids on the mechanical film properties and, in particular, for how they can bring about the optimum deformability observed. Obviously, the micro-voids must be of a dimension small enough to be essentially stable in terms of the Griffith model¹¹. If, however, the film is loaded beyond the limit of stress which the micro-voids can bear, the fracture energy necessary to break the film will be markedly enhanced, for there will not only be one fracture surface, as would develop in the case of an homogeneous material, but a multiplicity of such surfaces, each essentially produced by and, therefore, to be allocated to a micro-void. Because a certain amount of energy is dissipated by this effect of the micro-voids, the required fracture energy is higher than for the homogeneous film. This increase of energy is, in turn, reflected in improved deformability. Such energy dissipation is not conceivable in films obtained with 100 per cent solvent in the solution. It is, therefore, quite in line with this

hypothesis that these films are again inferior to those in which micro-voids may become effective.

Consequently, the essential feature of the supermolecular structure is that a certain amount of voids, whose size is sufficiently small to avoid optical effects or to initiate fracture according to Griffith's theory, will even produce better mechanical film properties than can be obtained with a homogeneous film of the same material; which has previously been considered to have optimal properties.

A variation of the solvent mixture composition may be of advantage in other systems. Related studies have shown that a modification of mechanical properties can nearly always be observed. Attainment of optimal properties, however, requires testing a variety of combinations, but even for those systems which do not possess a maximum of properties, a variation in the solvent mixture may assist in the formulation of films which best meet specific requirements.

Improvement of adhesion by morphological surface structure

When modifications to the supermolecular structure extend over the whole film thickness, it is mostly the mechanical and optical properties of the film which are affected. However, for special purposes it is possible to restrict structural changes to certain portions of the film. The introduction of an open-porous structure in the surface layer of the film, that can be produced by various means, is of particular interest.

A film possessing such a surface structure will allow the adhesion of a subsequently applied paint layer to take place under more favourable conditions. Provided the liquid paint is able to penetrate sufficiently into the pores, this upper film layer will become mechanically linked to the undercoat. This is essential because good intrinsic adhesion between the two materials is not then necessary, as would be the case if the films formed a plane interface. Even if there are no adhesive forces at all, the top layer is still mechanically anchored to the substrate, so that the films cannot be separated easily.

In order to produce the effect, it is necessary, however, that the voids in the surface region of the lower coating are not only open in the direction of the surface but possess a particular shape that is denoted at best by an "ink-bottle" structure. The liquid paint is able to enter through the orifice and fill up the cavity, thus expelling completely the gaseous content from the voids. Some provision for a sufficiently low viscosity and proper wetting power of the paint would be indispensable.

This principle of predominantly mechanical anchoring has already been realised in practical cases. The surface voids can be obtained by a combined action of solvent and humidity in the case of VC-VA copolymer, as was recently shown by Funke and Zörrl¹². Another example, where a similar procedure was successful, is demonstrated in Fig. 7. The lower coating consists of nitro-cellulose, and the upper of a modified alkyd. It can readily be seen that the cavities in the nitro-cellulose film exactly meet the requirements for this concept of adhesion, and the same can be said of the capability of the alkyd paint to penetrate into the former. When employing this special kind of morphological structure, any difficulties in obtaining adequate adhesion can be avoided because coherence of each component in this stratified system determines the strength of the joint rather

than adhesion between components. Whereas this principle is already utilised in other technical areas, for instance in metallising surfaces of plastics, its application in the paint field is not yet usual. In the authors' opinion, it provides a very promising aspect for technical progress in the field of coatings.



Fig. 7. Electron micrograph of the interfacial region after the top layer of a modified alkyd paint (A) has penetrated into cavities in the nitro-cellulose (N) undercoat

Acknowledgment

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Discussion at Eastbourne Conference

MR J. PELGRIMS mentioned the influence of heating of MOB containing pva/pvc solutions to decrease pseudo-plasticity to obtain Newtonian flow, and asked whether this influence was larger than on pvc/pva solutions, not containing MOB. Pvc/pva copolymers made by emulsion or suspension polymerisation, when solubilised in MIBK inherently showed this "memory" effect and went from pseudoplastic solution behaviour into Newtonian behaviour after a similar heating process. What happened when pvc He/MIBK-MOB were cooled instead of heated?

DR U. ZORLL replied that Mr Pelgrims had probably noticed three curves; the lower, not exactly straight curve was obtained by first giving the methoxybutanol—that is, a non-solvent—to the material and then adding the MIBK, and there was not much difference in the opposite procedure. Adding the non-solvent to the material was more usual and allowed for quicker procedure for bringing this material to the liquid state; but the most striking difference was that only by heat could the rheological behaviour be changed in such a remarkable way as had been observed. This could be explained in terms of the interaction between the molecular segments. Temperature increase could be strong enough to bring about a dissociation of the molecular segments. Formerly they were connected by intermolecular association, that is some sort of network between various macromolecules was formed, but after heat treatment they became individuals. On cooling again, they tended to reassociate, but now there was a difference. The segments reassociated in an intramolecular way and the molecules, therefore, behaved more like little spheres so that the viscosity as a whole was lowered and the material became a Newtonian liquid.

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MR PELGRIMS said that this normal difference which Dr Zorll had shown was visible without addition of a non-solvent.

PROF. W. FUNKE commented on this second point. One had to consider also the concentration for, with solutions of relatively low concentration, there was such an excess of the good solvent that all molecules would be dissolved, and all associations would dissociate. For concentrated solutions, however, and this was what Dr Zorll was talking about, it was not possible to have enough good solvent to dissociate the associated parts of the molecules, which were probably the vinylchloride segments. These segments might have been intermolecularly associated from the production. As to the final viscosity, not much difference was shown by the way one added the solvent components, but if one increased the temperature, the associated sequences would dissociate and then reassociate on cooling, but now in a predominantly intramolecular way. It was to be expected, of course, that the different structuring had some effect on the mechanical properties of films obtained from heated solutions.

DR M. L. ELLINGER asked whether the effect of microvoids in the film promoting intercoat adhesion was also valid in cases where the primer coat has been cured at elevated temperature (for example, 150°C)?

DR ZORLL said that in most cases it would be expected because the treatment could be done after stoving, but this was a special treatment. One could combine the action of water vapour and solvent vapour, and this should be sufficient to dissolve the surface a little—this was a very simple explanation for the effect, in reality it was more

difficult. The little water droplets penetrated somewhat into the surface region and afterwards they evaporated again leaving beneath the surface spherical cavities with very small orifices. This could be done after any film drying procedure and, this was a most important point, one could apply this treatment, in principle, to a completely dried film.

MR J. S. BOROKY asked Dr Zorll to inform him about the practical manufacture of these heterogeneous polymer/solvent mixtures, what shelf-life the products had, and what was their colloidal stability.

PROF. FUNKE replied that, of course there was the question of the shelf-life for such mixtures and, for such concentrations as were usual in practice, it depended on whether enough solvent was available to dissolve associations, and it depended on time. It was well known that the time necessary for dissociation processes could be rather long; it might last from a few hours up to a few weeks. In the authors' experiments they usually waited until they had equilibrium conditions.

MR A. R. H. TAWN pointed out that the people who were going to try and apply this principle were obviously going to be very interested in the time scales involved. Professor Funke had said that he allowed the systems to reach equilibrium before making his studies. If this equilibrium was reached during the time it would take the paint to get from the manufacturer to the customer it was all right, but if it was going to be on a time scale of days or weeks, of course, it could conceivably lead to more serious problems. He asked Prof. Funke to indicate the order of the time scale he was talking about.

PROF. FUNKE replied that the question of colloidal stability of these solutions depended on whether one reached the equilibrium state during the dissolution process or not. In case of heated solutions, after cooling down the viscosity remained constant, at least during one week of observation. Non-heated solutions, however, took considerably longer until the viscosity did not change significantly any more. There was also a strong dependence on the way the solvent compounds were added to the copolymer. Obviously, the equilibrium state was reached much more quickly if the dissociation of associated segments were accelerated by the heating process.

MR BOROKY said that the preparation of these dispersed polymeric mixtures was a solvent dependent procedure, and he was mainly interested in the shelf life of such a mixture when one prepared it. Unless the two or more polymers had suitable built-in dipole moments they would not stay in a stable condition very long; but the speaker took this as a natural consequence of the system. He was really interested in the limitation of the system that one could not very well use it generally for pigmented laquers because there the solvent used surely competed with absorption of the polymer.

DR ZORLL agreed that one might expect this, but he had also used these films pigmented with titanium dioxide, and up to a pigment volume concentration of 10 to 15 per cent, fairly good films showing the same behaviour had been obtained; that is, a maximum of mechanical properties with a certain amount of non-solvent in the film. It was not possible, therefore, to say that as a rule pigmentation of such materials should cause a decrease in overall properties.

MR A. M. VAN LONDEN asked Dr Zorll to indicate the level of retained solvent, especially the non-solvent, in the films after drying and after the heat treatment, this in respect to the observed film properties.

PROF. FUNKE said that he had expected this question. Everybody thought about solvent retention and it was well known that polymer systems like polymers tended to retain solvents even after drying. Of course, they had made sure, by various methods of drying as well as by gas chromatography, that the effects observed, especially the mechanical effects of a certain mixture were not caused by the retained solvent. In this context, it had to be noted that there was no steady increase in the properties, but a decrease towards using the pure solvent system. This effect could only be allocated to a certain composition, to the structure, and not to retained solvent.

MR A. R. H. TAWN said that, presumably, from the thermodynamics of the system, Prof. Funke would expect the good solvent to be more tenaciously retained than the poor solvent, the non-solvent.

PROF. FUNKE replied that it was well known that the ketone used in this case might be strongly retained by this system, and he thought there were values published in literature which amount to 6 or 7 per cent retention, but this could not allow for the curves for mechanical properties going down again when 100 per cent solvent was used for preparing the film.

MR J. R. TAYLOR asked whether electron micrographs showed uniform pigment dispersion when pigmentation of these systems was undertaken. It might be expected that in such a heterogeneous resin systems, flocculation of the pigment would take place during the formation of the paint film.

DR ZORLL answered that they had observed from electro-micrographs of the pigmented systems that, as compared to ordinary paint films containing the same sort of pigment, there was somewhat more flocculation encountered than with such ordinary paints, but not so much that one should have to object to it. They did not feel it was necessary, therefore, to modify the procedure of pigment dispersion in order to obtain more homogeneous distribution of the pigment in the film.

DR L. VALENTINE, taking up a point raised by Mr Tawn on practicability and the time to get stable effects, asked whether the authors could comment on the reproducibility to be expected arising from the drying process. In industrial practice there were often considerable variations in drying processes and it would be interesting to know if reproducible effects could be obtained under these conditions.

PROF. FUNKE said that they had repeated the experiments with a wholly new series of test specimens, and could reproduce these to about 10 per cent. The characteristics could be reproduced and also the appearance in the electro-microscope. He added that they would like to show that the paint chemist must look at the solvents used from a viewpoint different from that of the past. The solvents also had an influence on the polymer structure of the film. It was not only the plasticising effect, which everyone had been well aware of in the past, but also the solvent which might effect the properties of the film. In this case, they had tried to show that there was a strong influence on the structure of the molecule in the film, and that this could be influenced by changing the solvent composition.

MR TAWN said he thought it was true to say that the influence of solvent had long been known, although it had not been particularly well understood, and that this work had shed a lot of light on some of the phenomena which have been known, or at least suspected, for a long time. By understanding what was happening, it was now becoming possible to exploit it, and this was the potential value of this work.

MR TUUKKANEN stated that, by varying the solvent/non-solvent composition, a maximum in mechanical properties was found. He asked what was the effect of test tempera-

ture. Was a maximum also found at temperatures below freezing point and at temperatures above room temperature?

DR ZORLL replied that this maximum was fairly independent of temperature as long as one remained below temperatures of approximately 40°C. If one went up to fairly high temperatures (120°C more or) one could bring this system into completely different state and, its favourable properties were more or less lost. All the systems showed a certain sensitivity to temperature and that could be easily explained because of the balance of the various forms of interactions between the segments of the macromolecules.

Hardening of organic coatings with infra-red lasers*

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Summary

The experiments carried out so far with a 100 W CO₂ laser emitting at a wavelength of 10.6 μm, although not complete, indicate that enamels used commercially only need very short irradiation times. The areas hardened in this way are of excellent quality. One of the most important advantages of this method is the exact control of the area irradiated and of the period of irradiation.

At present, the process is limited to curing of small areas. However, the intense development in the field of CO₂ lasers is expected to lead both to more efficient equipment and to the practice of irradiating objects with large surface areas.

Keywords

Process and methods primarily associated with drying or curing of coatings

infra-red drying
radiation curing

Miscellaneous

laser

Le durcissement des revêtements organiques au moyen des lasers à l'infra rouge

Résumé

Bien que les expériences effectuées jusqu'à présent à l'aide d'un laser-CO₂ de 100W émettant à une longueur d'onde de 10.6 μ ne soient pas déjà terminées, elles indiquent que les peintures-émaux de commerce n'exigent que les durées d'irradiation très courtes. Les feuillets durcis par cette technique sont d'une qualité excellente. Un des avantages les plus importants de cette méthode, c'est le contrôle précis que l'on saurait exercer sur la superficie à être

irradiée et aussi sur la durée d'irradiation.

A présent, le processus est limité au durcissement des superficies modestes. Cependant, on s'attend à ce que les développements acharnés dans le domaine des lasers-CO₂ aillent mettre en évidence du matériel plus efficace et la possibilité d'irradier les articles d'une superficie importante.

Härtung Organischer Beschichtungen mit Infrarot-Lasern

Zusammenfassung

Bisher mit einem 100W CO₂ Laser durchgeführte und noch keineswegs abgeschlossene Versuche zeigen, dass mit den handelsüblichen Einbrennsystemen sehr kurze Bestrahlungszeiten erzielt werden können.

Die so gehärteten Lackflächen sind von ausgezeichneter Qualität. Ein wesentlicher Vorteil dieser Methode ist die exakte räumliche

und zeitliche Kontrolle der eingestrahnten Energie.

Zur Zeit ist das Verfahren auf kleine Flächen beschränkt. Die stürmische Entwicklung gerade auf dem Gebiet der Kohlendioxid Laser lässt wesentlich leistungsfähigere Geräte und damit Anwendungsmöglichkeiten bei grossflächigen Objekten erwarten.

Отверждение органических покрытий инфракрасными лазерами

Резюме

Опыты проведенные до сих пор с 1000W CO₂ лазером излучающим с длиной волны в 10.6 мкм, хотя и не полностью окончены, все же указывают что промышленные эмали требуют лишь очень короткое время облучения. Площади отвержденные таким образом обладают отличными качествами. Одно из наиболее важных преимуществ этого метода является точный контроль облученной площади и периода облучения.

В настоящее время процесс ограничен сушкой небольших площадей, но быстрый темп развития в области CO₂ лазеров, надо ожидать, приведет к развитию более усовершенствованного оборудования и к возможности облучения больших поверхностей.

Introduction

Conventional thermal infra-red sources have been used to harden varnishes for more than 50 years. The recently discovered irasers (infra-red amplification by stimulated emission of radiation), open completely new possibilities for the curing of organic coatings by infra-red irradiation. The basic work to develop this method was mainly induced by the following considerations:

and 12 μm wave-length would be the optimum to harden varnishes, since the conditions of absorption and reflexion in the medium infra-red enable the paint film to warm up uniformly, independent of pigments and binding media.

- A. White paint on alkyd/MF resin; dry film thickness 28 μm
- B. Red paint on alkyd/MF resin; dry film thickness 26 μm
- C. Clear varnish on alkyd/MF resin; dry film thickness 27 μm
- D. White paint on epoxy resin; dry film thickness 20 μm

1. Some typical infra-red-spectra (Fig. 1) of various thermo-setting paints indicate that the spectral range between 6

* Presented at the 1973 Eastbourne Conference.

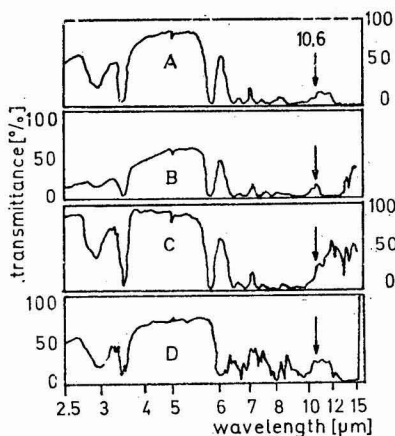


Fig. 1. Infra-red-spectra of various thermostetting paints

In the near infra-red, however, there are not only considerable differences in transmission (for example 15 per cent for the red paint B, 86 per cent for the clear varnish C, measured at 2.5 μm wave-length), but also important reflection losses. The latter may reach a maximum of 50 per cent in the case of high pigmentation with titanium dioxide¹.

2. Conventional infra-red sources can be described by the Planck equation for a black-body and derived from this equation by Wien's displacement law and the Stefan Boltzmann equation. It follows that, using a thermal radiation source having its emission maximum in the previously cited wave-length range from 6 to 12 μm, the temperature of the source would lie between 470°K and 240°K corresponding to 200°C and -30°C (see Fig. 2).

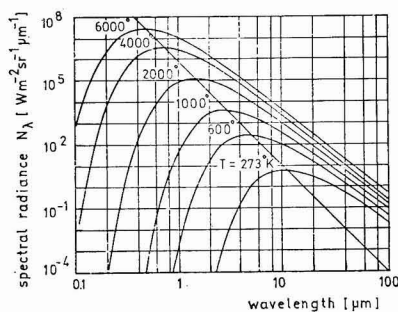


Fig. 2. Spectral radiance N_{λ} of a black-body at the absolute temperature T shown on each curve

The diagonal line, intersecting the curves at their maxima, shows Wien's displacement law²

3. Thus, in the most favourable case, at a maximum temperature of 200°C on the surface of the infra-red source and assuming a theoretical thermal equilibrium, the temperature of the paint could reach not more than 200°C because even with the best methods of focusing the radiation, the temperature of the irradiated object would not be higher than that of the source. The total power emitted per square centimetre would reach a maximum of 0.3 W. For a rapid heating, and hence hardening of coatings, temperatures of about 300°C for short periods and,

depending on coating and substrate, power density levels of 1–10W cm⁻², are necessary.

4. At present, the only radiation-source in the medium infra-red suitable for hardening coatings and offering high power and an almost unlimited power-density, is the CO₂ laser. This commercially available iraser, which emits at a wavelength of 10.6 μm, gives a higher continuous-wave output combined with a higher efficiency (theoretically up to 40 per cent of the pumping energy) than any other iraser or laser.

Again, with reference to Fig. 1, the uniformity of the transmission curves at the point of the emission of the CO₂ laser can be seen.

The losses of radiation energy by reflection amount to about 5 per cent only, irrespective of the pigmentation, thus permitting up to 90 per cent of the incident radiation power to be transformed into heat. These facts reveal the significant possibility of the CO₂ laser being able to compete successfully with conventional infra-red sources, where special hardening conditions are required.

Table I shows some characteristic data of such conventional infra-red sources in comparison to those of a CO₂ laser.

Table I
Characteristic data of some infra-red sources

	λ_{\max} (μm)	H_{\max} (W cm ⁻²)	P (10 ³ W)
Low-temperature infra-red radiator (473° K)	6	0,3	1–10
Quartz-halogen lamp (2854° K)	1	10 ²	1–5
CO ₂ laser (CW)	10,6	10 ⁸	0,1–2

λ_{\max} wave-length of maximum emission

H_{\max} greatest irradiation power-density achievable

P total radiation power

The power-output of a single CO₂ laser is low, compared with other infra-red sources, but as its power-density cannot be attained by any conventional means, the CO₂ laser is generally used for cutting and drilling metallic or ceramic materials, when the highest accuracy is required. Hardening organic coatings with a CO₂ laser still seems to be contradictory, however, because an extremely well-focused CO₂ laser beam shows considerable disadvantages in this field of application, where enlargement of the beam would be of more interest.

The acceleration of the cross-linking reaction in thermostetting resins by the use of such an intensive infra-red source is economical only if the radiation power applied to the paint system can be regulated. Without control, the least change in absorption (for example, varying film thickness) would cause either insufficient cross-linking or thermal decomposition of the organic substance. Control of the intensity during irradiation can be achieved either by pulsed operation of the CO₂ laser or by continuous variation of the pumping power. With the aid of a device for measuring temperature without contact, it is possible to construct an automatic control-unit for the temperature of the coating.

To irradiate larger areas with the CO₂ laser beam, the time control is combined with a spatial control determining the direction of the electromagnetic wave. To enlarge the cross-section of the beam with the aid of lenses or equivalent

mirror systems would be simple and elegant but this method cannot be applied for the following reasons.

The far-field mode-pattern of the CO₂ laser is neither constant nor uniform. An enlarged projection would therefore lead to great local differences in temperature due to the poor heat conductivity of synthetic resins.

Fig. 3 shows some of the principal far-field mode-patterns of a He-Ne gas laser. Similar intensity distributions can be observed with a CO₂ laser (the mode-pattern of an iraser is difficult to record due to the lack of suitable apparatus).

today would be destroyed by the high power densities or because most known scanning devices are too inefficient³. In practice, a simple scanning with metal mirrors is feasible. The operating band-width, when using the most elaborate equipment, can be extended to a maximum of 1kHz, which is quite sufficient for the CO₂ laser when curing paint films.

Experimental

The first attempts to harden organic coatings with a CO₂ laser were made in 1969. The results were so promising that in

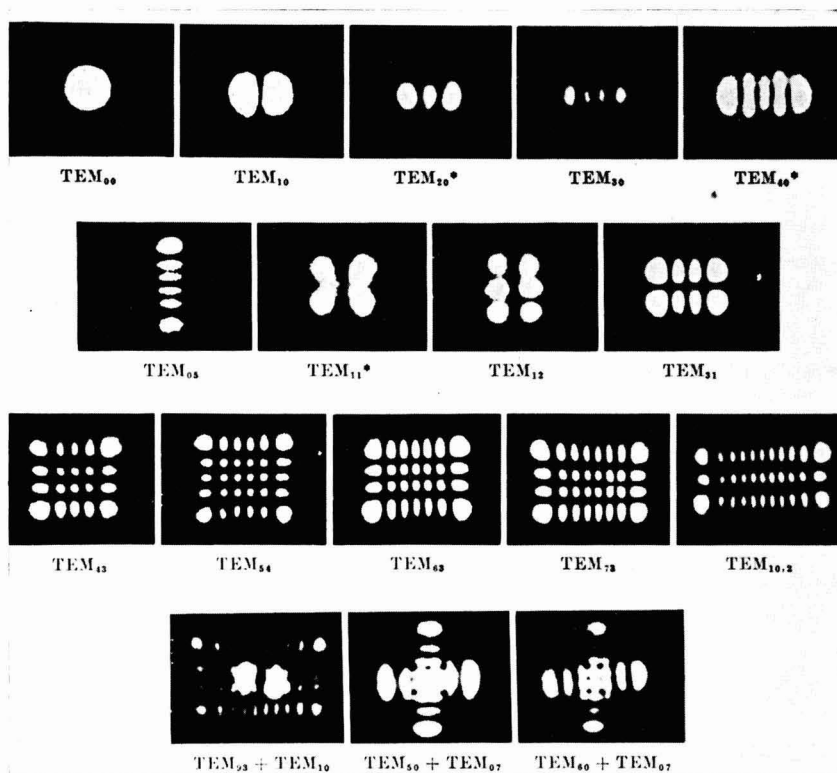


Fig. 3. Far-field mode-patterns of a He-Ne gas laser³

The low total power of a CO₂ laser is best exploited when each part of the coated surface is irradiated for a very short time to absorb the minimum amount of radiation-energy necessary for the acceleration of the crosslinking reaction. Thus, the energy loss by heating the substrate which, unlike the coating, usually has an enormous heat capacity, is considerably reduced. This means that the area is best scanned with a slightly focused beam of diameter 10mm, each part being exposed several times to the maximum temperature for a very short time interval.

An electromagnetic wave has to be deflected through reciprocal reaction with matter. Unfortunately, the methods applicable to electro-optics in the visible range cannot be applied to the CO₂ laser, partly because the materials used

the same year a patent⁴ covering the process was filed. Since then, a series of tests has been carried out using a CO₂ laser of 100W theoretical output, in co-operation⁵ with the Institute of Physics at the University of Graz.

The arrangement to irradiate flat surface areas is shown in Figs. 4 and 5. Temperature regulation was achieved by modulating the scanning speed of the CO₂ laser beam.

The beam leaves the CO₂ laser (1), passes first through the optical system (2) (3) and the beam splitter (4), and after being reflected at two fixed (9) and one moving mirror (10) it scans over the surface of the sample (11). The temperature of the coating is controlled by means of an infra-red thermometer (7) and the feedback loop, consisting of the control

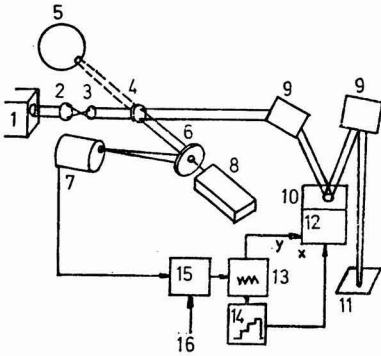


Fig. 4. Schematic diagram of equipment used to irradiate flat samples

- 1 CO₂ laser
- 2,3 Germanium optics
- 4 beam splitter
- 5 power monitor
- 6 concave mirror
- 7 infra-red thermometer
- 8 He-Ne laser
- 9 fixed mirror
- 10 moving mirror
- 11 sample
- 12 mirror drive
- 13,14 programmer unit
- 15 control amplifier
- 16 temperature adjustment

amplifier (15), the sawtooth and staircase generators (13) (14) and the mirror drive unit (12). The equipment is completed by the power monitor (5) and the He-Ne laser (8), which serves as an indicator for the invisible infra-red beam.

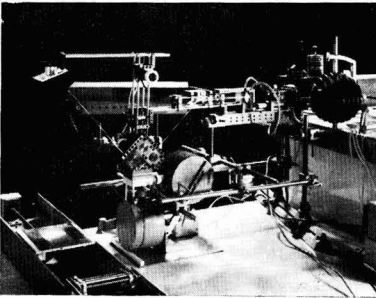


Fig. 5. Practical arrangement to irradiate flat samples

The power-output of the disposable CO₂ laser amounted to 70W. The irradiation power density, just sufficient to cure the organic coating in a short time, lay between 1 and 10Wcm⁻², and was largely dependent upon the heat-capacity and heat conductivity of the substrates (usually steel panels but also plates of wood and glass). Thus the surface areas of the coated samples were limited from about 7 to 70cm². The ideal film-thickness of each hardened organic coating, usually about 30 μm, was calculated from the corresponding infra-red spectra. In practice, the applied film, still containing solvents, required a uniform heating without severe temperature gradients. This was best realised on metallic substrates as the decreasing intensity of radiation within the

film was nearly compensated by the reflection of the transmitted radiation at the metal surface.

An industrial enamel, normally stoved at 100°C for 30 minutes, could be cured within 30 seconds, without any flash-off time being necessary. The peak temperatures during the irradiation were 300°C, the paint film was faultless and of excellent quality.

In those cases where the samples were smaller than the diameter of the unfocused CO₂ laser beam, the modified arrangement shown in Figs. 6 and 7 was used.

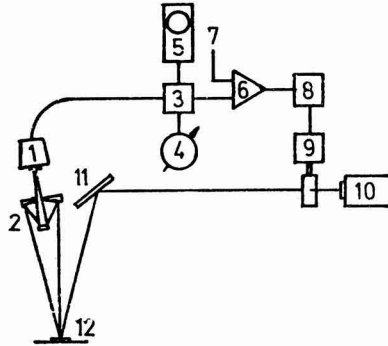


Fig. 6. Schematic diagram of the apparatus used for irradiating small samples

- 1 infra-red thermometer
- 2 Cassegrain telescope
- 3 measuring amplifier
- 4 recorder
- 5 oscilloscope
- 6 control amplifier
- 7 temperature adjustment
- 8 power amplifier
- 9 actuating magnet
- 10 CO₂ laser
- 11 mirror
- 12 sample

The intensity-modulation was achieved by the actuating magnet (9). The CO₂ laser beam was directed on the sample (12) via the fixed mirror (11); due to the smallness of the object, a telescope (2) had to be used in front of the temperature measuring device.

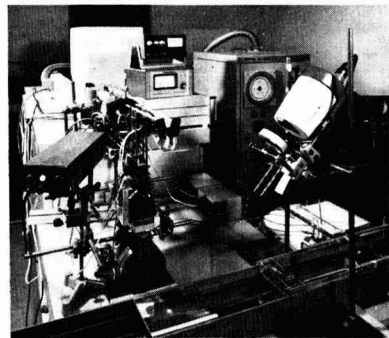


Fig. 7. Arrangement for curing small samples

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The temperature schedule used with this equipment to cure an epoxy resin film is shown in Fig. 8. By far the greater part of the irradiation time necessary was used to evaporate the solvents at a low temperature. The cross-linking reaction in this example only took four seconds.

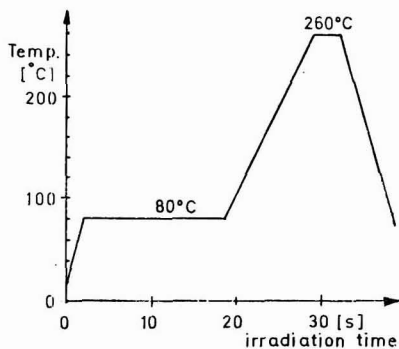


Fig. 8. Temperature schedule for curing an epoxy resin

Conclusions and general outlook

Summing up the experience gained from laboratory work, the following advantages over conventional infra-red sources are noted.

The time necessary to harden organic coatings can be considerably reduced, but depends upon the nature of solvents and substrates involved.

The energy input is precisely controlled in time and space, and can be adjusted with practically no time-lag. Thus, the film-forming reaction is effected by a temperature-time programme specially adapted to the paint system in question. By means of additional optical equipment, not only plane objects but also spatial ones can be irradiated.

Local differences in the heat conductivity and heat capacity of the substrate are compensated by modulation of the intensity of the laser beam during scanning (broadening by deflecting with a mirror).

Since air does not absorb electromagnetic radiation of $10.6\mu\text{m}$ wavelength (see Fig. 9), the laser can be placed at a greater distance from the object. The hazard of the explosion of solvent vapours is greatly reduced.

Discussion at Eastbourne Conference

DR U. ZORLL asked whether the greater versatility of the iraser system's application in the paint field was not primarily an engineering problem. In the electron beam curing system, the beam had to be deflected magnetically for scanning a sufficient surface area of the paint film to be hardened. Thus, for the carbon dioxide laser, a similar effect might be brought about by a rotating mirror system.

DR H. D. HANUS replied that it was a matter of cost. A carbon dioxide laser would have cost almost £10,000, and it was difficult to convince the research department to buy

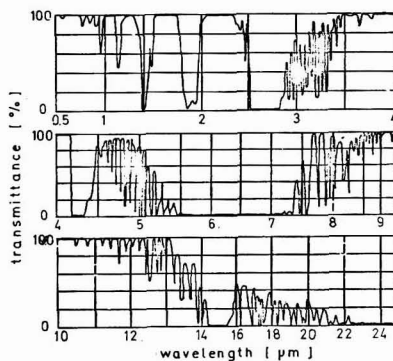


Fig. 9. Transmission spectrum of air²

At present, the main disadvantage of the method described in this paper is the fact that the time to harden an organic coating depends above all on the average irradiation-power density per unit area during the irradiation time. The relatively low total power output and the still high purchase price of commonly available CO_2 lasers only permit the curing of coatings on small surface areas, such as on components for the optical and electronic industry. For this application the rate of curing, the ability to harden in close proximity to heat-sensitive materials, the gain of efficiency by pulsed operation, the reduced risk of explosion and the compactness of the installation may be decisive for the choice of a CO_2 laser.

It is to be expected that more efficient and less expensive irasers will appear on the market in the near future⁶. This will justify continuing the "towards 2000" experiments into the hardening of organic coatings with irasers; a great many problems of theoretical or practical interest are still waiting to be overcome.

[Received 6 February 1973]

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another one more versatile in its application. There had been a considerable development in CO_2 -lasers during the last five to ten years, but the authors had the impression that this was for military use in the United States, and they could not get one. There are already very powerful lasers on the market but with rather astronomical prices. It was an engineering problem, and the authors were dependent on engineers as well as people who would take the courage to begin with this new method.

MR J. S. BOROKY said that lasers used in microrecording on plastics had to be carefully controlled against extensive surface effects. He asked what the practical limits were in

controlling surface damage for the authors' process. Lasers used in microrecording had to work with a beam intensity so low that two subsequent letters, or digits, were not affected by melting.

DR HANUS agreed that, generally, lasers were used in focussed beams to cut metals and plastic, and here the problem was to enlarge the beam or to let it scan. Until now, they had only tried to harden coatings on metallic surfaces, and were just beginning to use plastics. They did not encounter serious difficulties when hardening coatings even on plastics because it was not the whole plastic substrate which was being heated as would occur in a normal oven, but only the surface. Even if the surface were slightly distorted, this would improve the inter-facial and the intercoat-adhesion between the plastic support and the varnish itself. Mr Boroky was quite right when he said that the laser beam had to attack the plastic support, but until now the authors had not found any harmful effects.

MR A. R. H. TAWN asked the authors to confirm that they were dealing with a beam of a lower quantum energy than those used for these other purposes. The problem was diminished because of the lower quantum energy radiation.

DR HANUS agreed.

DR E. LANDSTADTER added that they were using power density levels of one or two watts per square centimetre. For drilling and cutting, much higher power density levels were used, up to a million watts per square centimetre.

MR A. G. NORTH said that, when trying to decide between the many alternative radiation systems which were available, it seemed that one should take due notice of the so-called "energy crisis"—the problem of supplying enough energy in a few years' time. There were many curing processes currently talked about (electron beam, ultra-violet, infra-red, glow discharge and so forth), and it seemed that electron-beam was by far the most efficient in terms of the cure of coatings for a given quantity of original electrical energy input. It was difficult to make comparisons, because one was often curing different sorts of coatings. Mr North asked the authors whether they had compared electrical efficiencies, that is the initial electrical input compared with the final quantity of cured coating.

DR LANDSTADTER answered that one had to spend much more energy in any film-forming reaction than was really needed for the chemical reaction itself. This was why he felt that the overall efficiency of the carbon dioxide laser was very good. One could reach, theoretically, 40 per cent efficiency based on electrical input to radiation output, and as radiation was absorbed, or could be absorbed nearly totally in the coating, there were only negligible reflectance losses, and absorption losses in the air. In practice, one could get 20 to 25 per cent efficiency for a high power carbon dioxide laser, and up to 90 per cent of the output was transferred to heat within the film. This was quite comparable with electron beam curing.

DR HANUS added that, generally, in the paint industry one always thought of large areas. His firm was concerned mainly with car finishing and priming, and although the laser could be of use in the car industry, the authors were far from that stage of development in practice. At the present time, the laser would be of use only over very small areas where there was no other method available for curing the film. A very large unit might be used in a coil coating installa-

tion in connection with common heating installations so that, after a certain flash-off time using conventional equipment, the laser would be used for the very last cross-link curing reactions. The losses in terms of electrical energy would be more or less compensated for by the gain in space inside the factory. This application, too, was in the future, and depended on the development of lasers. Dr Hanus stressed that, at the present time, only very small surface areas could be cured.

DR D. J. MURRAY commented that the present paper had discussed the use of infra-red lasers. He asked the authors to comment on the possible applicability of lasers emitting in the ultra-violet, or even visible, regions of the spectrum.

DR LANDSTADTER said that lasers in the visible range, which had been known since 1960, were not very useful for this kind of application because they had very bad efficiency. The efficiency of a laser in the visible range was about 0.1 per cent, or even less, and the efficiency of a carbon dioxide laser was the greatest of all lasers known. One could not afford to spend such enormous electric energy and get out only 0.1 per cent efficiency, and this was the reason for not using lasers in a visible range. In the ultra-violet range, it might be useful for photo-chemical reactions but when only producing heat, as the authors were doing, the carbon dioxide laser was the only laser on the market worth considering.

MR TAWN commented that this seemed to come back very firmly to Mr North's point.

DR HANUS added that there was a considerable difference in absorption in the near or far infra-red regions which had not yet been explained. It was pointed out in the paper that, for a wavelength of 10.6 micrometres, the absorption was almost independent of the binders and pigments used, which was another argument in favour of the carbon dioxide laser instead of some other laser.

PROF. W. FUNKE asked whether it was possible to apply infra-red laser curing to very small areas like those which were involved in the preparation of electronic circuits or printing letters with photopolymerisable polymers. He asked what were the smallest dimensions which might be cured without too much heat conduction to the surrounding areas not to be cured.

DR HANUS said that this was a very good question but rather difficult to answer because with a laser there was no new process; it was a simple heating, absorption, and cross linking process absorbing electromagnetic energy and converting it into heat. There was no special polymerisation unless induced by heat. They had started the work trying to harden monomers to polymers, and there had been no curing at all.

MR P. FINK-JENSEN asked what were the smallest dimensions which could be cured by this new method; was the lowest dimension a millimetre, or less than that.

DR LANDSTADTER replied that they had not tried to focus the beam at the limits, but he thought there were no limits, down to several micrometres. The limits were then caused by diffraction and although they did not try to harden coatings on one square micrometre, nevertheless, in principle it was possible. A limit might be the heat conductivity of

the resin and of the substrate which was being coated; to go below this limit would give blurred edges.

DR HANUS reminded Prof. Funke that they had discussed earlier the possibility of testing films on very small surface areas, and the authors were really quite happy to find testing methods for an area of two or three square centimetres. They had no intention to go down to even two square millimetres, because it was not possible to test the paint film.

MR FINK-JENSEN said that the authors had been

comparing the infra-red laser's action with that of ordinary lamps. He asked what comparison the authors could make with longer wave lengths, with microwaves for example, which were also produced by an electrical method and where the energy could be controlled very efficiently. This is to say, what comparison was there between the use of microwaves and the laser beam.

DR LANDSTADTER said that he had no experience of microwave curing, and could not, therefore, make a comparison.

The American paint industry Present trends and future possibilities*

By F. Armitage

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Summary

This paper deals mainly with the current trends in the American industry, but consideration is given to the numbers of British Patents issued during the years 1961 to 1970. That a high proportion of these patents, emanate from American and German sources is very evident, and the patents' probable effect on British industry is discussed.

The current position of paints for the principal outlets, trade and industrial, is outlined, and the probable future for trends in the types of media used in their formulation discussed. The future

developments in water-based paints, powder coatings, non-aqueous dispersions and so forth are considered, as well as the possible effect of anti-pollution legislation on solvent-based paints.

The future prospects for curing by means of an electron beam, ultra-violet and induction heating techniques are discussed as well as possible trends for automotive paint, coil coating and wood finishing. Some consideration is given to the economics of paint manufacture in America and the probable influence of American practice and investment in Europe.

Keywords

Specifications, standards and regulations

patents
specifications

L'industrie de peintures aux Etats Unis. Les tendances actuelles et les possibilités à l'avenir

Résumé

Cet article traite largement des tendances actuelles de l'industrie de peintures aux Etats Unis, mais on considère également la prolifération des brevets délivrés en Grande Bretagne entre les années 1961 et 1970. Il est évident qu'une proportion élevée de ces brevets a émané des sources américaines ou allemandes. On discute les effets éventuels de ces tendances sur l'industrie britannique. On trace les grandes lignes de la situation actuelle en ce qui concerne les peintures destinées aux débouchés principaux; peintures industrielles ou celles pour le peintre-artisan, et l'on discute les tendances vraisemblables à l'égard des types de milieu destinés à être utilisés parmi les constituants de ces peintures. On considère les développements à l'avenir dans les domaines de peintures à base de l'eau, revêtements en poudre, les dispersions

non aqueuse etc., de même que les effets éventuels suscités par la législation pour diminuer la pollution provoquée lors de l'emploi des peintures à base de solvants.

On discute les perspectives à l'avenir des techniques de durcissement au moyen des faisceaux d'électrons, de rayons ultra violet, et de rechauffage par induction, de même que les tendances éventuelles dans le domaine de peintures pour automobiles, de revêtements en continu, et des finitions pour bois. On donne quelque considération aux facteurs financiers de la fabrication de peintures aux Etats Unis et également à l'influence éventuelle de la pratique et les investissements américains en Europe.

Die Amerikanische Lackindustrie—gegenwärtige Strömungen und künftige Möglichkeiten

Zusammenfassung

Dieser Vortrag befasst sich in der Hauptsache mit den laufenden Strömungen in der amerikanischen Lackindustrie, jedoch werden auch die zahlreichen, während der Jahre 1961 bis 1970 ausgegebenen Britischen Patente in Betracht gezogen. Es ist ganz offensichtlich, dass ein hoher Prozentsatz dieser Patente aus amerikanischen und deutschen Quellen stammt; es wird besprochen, wie sich dies auf die britische Industrie aller Voraussicht nach auswirken wird.

Die gegenwärtige Geschäftslage für die Hauptabsatzgebiete, d.h. für Maler- und Industrielacke, wird umrissen, und die voraussichtlichen zukünftigen Strömungen in der Art der in Rezepturen benutzten Bindemitteltypen wird besprochen. Die künftigen

Entwicklungen auf den Gebieten von wassergetragenen Lacken, Pulverlacken, nichtwässrigen Dispersionen, etc., werden ebenso betrachtet, wie die Auswirkung von Antipollutionsgesetzgebung im Bezug auf lösungsmittelhaltige Lacke.

Besprochen werden ebenfalls die künftigen Aussichten für das Härten mit Elektronenstrahlen-, Ultraviolet- und Induktionsbeheizungstechniken, wie auch mögliche Entwicklungen auf den die Autolackierung, Bandlackierung und Holzlackierung betreffenden Gebieten. Aufmerksamkeit wird auch den die amerikanische Lackindustrie betreffenden wirtschaftlichen Gesichtspunkten und dem wahrscheinlichen Einfluss von amerikanischen Praktiken und Investitionen in Europa geschenkt.

Американская красочная промышленность. Современные тенденции и будущие возможности

Резюме

Статья описывает главным образом текущие направления в американской промышленности, уделяя в то же время внимание британским патентам опубликованным с 1961-го до 1970-го года. Тот факт что большая пропорция этих патентов исходит из американских и немецких источников весьма очевиден и обсуждается возможное влияние этих патентов на британскую промышленность.

Обозревается настоящее положение красок для главного спроса (торговля и промышленность) и обсуждаются возможные будущие тенденции в типах сред применяемых в их формуляции. Рассматривается будущее развитие водяных красок, порошко-

вых покрытий, безводных дисперсий и т. п. и также возможный эффект противокоррозийных мер на красках основанных на растворителях.

Обсуждаются будущие перспективы сушки при помощи электронных лучей и техники ультрафиолетового и индуктивного нагревания и также возможные тенденции в самоиндуктивных красках, спиральных покрытиях и окрашивании дерева. Уделяется внимание экономике красочной промышленности в Америке и возможному влиянию американской практики и капиталовложения в Европе.

* Presented at the 1973 Eastbourne Conference.

Introduction

American paint sales are divided into trade and industrial sales, and the trade sales group comprises about 86 per cent architectural coatings, which are essentially interior and exterior paints for houses and buildings. The remaining 14 per cent include automotive refinishing paints, traffic paints and some marine paints for pleasure boats. For convenience of presentation architectural paints have been isolated. These are applied manually by brush, roller-coater or spray-gun and have included the 14 per cent of non-architectural paints in the section of the paper entitled "Industrial paints". Figures quoted in gallons refer, of course, to American gallons.

During the past ten years, total paint sales¹ rose from 623 million gallons (\$1,750 million) to 874 million gallons (\$2,831 million) in 1971. Neglecting annual fluctuations, the production of architectural paints appears to have shown an overall decrease from 45 per cent to 42 per cent (of all paint sales) on a volume/volume basis. How much this proportion will change in the next twenty or thirty years depends on several factors, as will become apparent in the following sections where recent developments and current trends are discussed.

Architectural paints

Markets

Less than 10 per cent of these paints is used on buildings other than private dwellings, and perhaps 80 per cent is used for repainting rather than for the painting of new structures. This may indicate that the proportion of architectural paints out of total paint sales is not going to change very much in the future, although the increasing use of pre-coated wood sidings and internal panelling, and of pre-coated aluminium sidings may tend to cause a decrease of this figure gradually below the present 42 per cent. The amount of repainting will depend, apart from fluctuations in the national economy, mainly on the numbers of occupied houses and apartment buildings. Fig. 1 shows the increase in the numbers of conventional dwellings compared with the rise in population since 1900.²

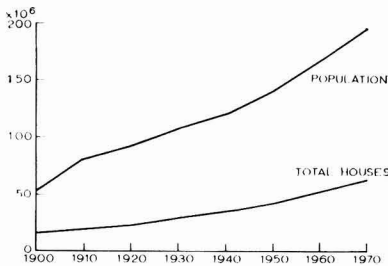


Fig. 1. Increase in the population and total number of houses in USA since 1900

Fig. 2 shows the annual construction of conventional units since 1960, and the manufacture since 1965 of (a) mobile homes and (b) factory-produced single family units. Mobile homes are based mainly on pre-coated aluminium; and industrialised houses, mainly on timber or plywood,³ there being little or no progress in the use of steel, concrete or plastic for this purpose. It is noticeable that mobile homes

and factory-produced houses together now amount to 30 per cent of all homes built in 1971.

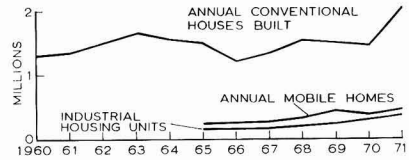


Fig. 2. Types of houses built in USA since 1960

The rate of growth of the population is expected to decrease considerably during the coming years,⁴ as a result of an increase in the numbers of married women seeking paid employment outside the home, better availability of contraceptive drugs and abortion, and rising levels of education and later marriages. Against these factors, increasing affluence should lead to more frequent replacement of slum property, and the production of second homes for urban families—a trend already apparent.

It has been estimated that for new houses of the conventional type, 30-35 per cent of exterior surfaces are of wood or wood products, 40-45 per cent are of brick, stone or stucco, and about 25 per cent are of aluminium, although the last figure includes repairs to older houses. Less than 10 per cent may be of asbestos shingles.

Incorporation of the numbers of mobile homes and industrialised houses into the total numbers of new houses will tend to show increases in both wood and wood-products, and in aluminium, at the expense of other materials during future years depending on the rate of growth of these types of dwellings in relation to the building of conventional houses. The mobile home appears to be a specifically American development; it is defined as a vehicular portable structure built on a chassis designed to be used without a permanent foundation as a year-round dwelling, when connected to utilities more than 8ft wide and more than 34ft long, and weighing over 4,500lb. Available parking land is often pleasantly landscaped and equipped with the necessary facilities, in country neighbourhoods. In 1971 pre-coated aluminium for residential sidings and mobile homes already accounted for 50 per cent of all aluminium coated strip, including that used for repairs and maintenance; the proportion used for mobile homes being somewhat larger than that used for sidings.

It goes without saying that incorporation of pre-coated materials into any type of house will tend to increase the period of time before repainting becomes necessary because the baked finish has superior outside durability, and over the years this factor will tend to reduce the total amount of repainting which would have been carried out if the houses did not include such materials in their construction (although in any one year this effect will be marginal).

Technology

The do-it-yourself market has developed more in the USA than in other countries, partly because of high labour costs, and the home-occupier may be faced with a bewildering display of diverse products in a large paint-store or super-market department. The paints will be formulated for application to a wide variety of substrates for specific locations, including interior floors and ceilings, and exterior

patios, roofs and swimming pools as well as for the more typical areas of wood, masonry and aluminium comprising the bulk of the construction. Perhaps half a dozen of the major companies will be offering latex wall-paints in three different qualities at three different prices. The automatic colour dispenser for producing required shades of paint has, of course, been in common use for many years. Besides the sales of paints in cans, 240 million paint aerosol packs were sold in 1971.

The main trend over the past 20 or so years, has been an increase in latex paint sales, which in 1971 represented 65-70 per cent of all interior paints, and 52-55 per cent of all exterior paints, on a volume basis, depending on whether or not aerosol paints or other products of lesser importance are included.¹

Most inside latex paints are based on vinyl acetate polymers or copolymers, which continue to increase at the expense of styrene/butadiene-based latex paints. For outside application most latex paints are based on straight acrylics, although some may include aromatic modification and, no doubt, some vinyl acetate copolymer latices are used. Ethylene/vinyl acetate copolymers do not so far appear to be substantial competitors either for inside or outside use. The ratio of all interior paint usage to outside usage is about 1.7 to 1.0—including both latex and solvent-based types.

A continuous increase in the sales of latex paints and a fairly slow decrease in solvent-based paints must be anticipated during the next several years. Whether or not the latter will eventually be eliminated entirely, depends to a large extent upon whether or not a water-based, high-gloss paint can be produced, and upon whether or not such a product would have acceptable outside durability. The author feels entitled to assume that during the next twenty years, this long sought-after material, with performance equal to that of a conventional alkyd paint, will become available, made from a polymer latex, from a water-soluble resin, or from a combination of the two. Already some 12 per cent of inside latex paints are of the semi-gloss variety, which are now well established. However, it should be noted that a fair amount of external painting is carried out in very cold weather, for which, at present, latex paints are unsuitable.

Latex paints

Many problems arose before these paints gained public acceptance for outside application to wood and plywood, in particular the extremes of climatic conditions prevalent throughout the United States. In general, it was found that the earlier types would allow transmission of water through the paint film, causing expansion and contraction of the wood substrate with changes in temperature and humidity, thus causing film failure by checking and cracking. Ingress of moisture also caused solubilisation of the coloured substances in such substrates as cedar and redwood, which substances eventually came to the paint surface as unsightly stains. Staining by surfactant leaching in dark-coloured paints was another early problem.

Improved emulsion polymers, methods of pigmentation and selection of thickener and surfactant system, were ultimately to eliminate these faults, especially when the paints were applied over a solvent-based oil or alkyd primer—on new wood. Latex primers now perform as well as solvent-based primers under normal conditions of application—and even better in some respects.

Fume-staining was originally caused by the presence of mercurial fungicides which react with hydrogen sulphide in the atmosphere above certain geographical areas, and was prevented by the elimination of the mercury (which, in any case, is now widely prohibited for quite different reasons).

With so much repainting being carried out, it became necessary to supply paints capable of performing satisfactorily on chalking paint surfaces, and this was accomplished by emulsifying into the paint a proportion of oil or alkyd resin, which in turn involved the incorporation of a satisfactory system of driers in order to retain the quick recoatability of the product. It is not too difficult to visualise the time when polymeric emulsions are produced with built-in properties for penetration in and adhesion to chalky surfaces.

Mildew formation on paint films in the hot, humid southern areas of Louisiana and the Gulf Coast has always been a serious problem with all paints, and, in general, latex paints are less susceptible than oil-based paints. Nevertheless, protective precautions must be taken. The formulation of the primer itself is a factor contributing to mildew resistance. Many hundreds of proprietary mildewicides have been examined by the industry, including the mercurials and arsenicals now prohibited. Many have failed because of their relative ineffectiveness; some have shown instability in the can; some have caused staining of the paint film on exposure; and some are too expensive to produce in the amounts required to give protection. For totally exposed films, a controlled degree of chalking is very helpful, but this cannot be obtained on unexposed areas. Zinc oxide, as part of the pigment in top-coats, is effective and is often used.

For outside application, it is important that a sufficiently thick top-coat be brushed on to give proper hiding and protection, and, in the past three or four years, latex paints have been developed with built-in brush-drag, which prevents the painter from over-spreading the material simply because the controlled rheology makes over-spreading physically difficult.⁵ The advent of a one-coat latex paint involved this principle. The procedure differs from that employed for thixotropic gel paints where the application of relatively thick coats depends more on the skill of the painter.

A recent development introduced by PPG Industries⁶ relies on the production of hiding power by incorporation of spherical voids in the paint. These microscopic voids may be obtained in a variety of ways, and this paint, when properly formulated, can reduce the amount of titanium dioxide required. The system is also applicable to solvent-based paints. PPG presented a paper at last year's FATIPEC conference in which it was said that the original inspiration arose from observation of the whiteness of snow, where microvoids of air are entrapped within crystalline water structure. The authors suggested that their paper "opens up opportunities for a decade of research," and it is perhaps too early to judge whether or not this interesting development will have a really important role to play in paint formulation of the future.

It may be interesting to consider patents in the field of polymer latices and latex paints in general over the past several years. The numbers of British patents published each year up to March 1970 are shown in Table I, the numbers relating to the year in which the patent was first filed, either in the UK or in the country of origin, when the specification was filed under Convention. British patents have been chosen because one can see the comparative activity between

companies from different countries when all are filing on common ground. Table 1 covers specifications concerned with the preparation of straight-chain polymer emulsions where these are recommended for use in paints on hard substrates, and does not include those patents where the products described are useful especially as adhesives, or in coatings for paper or fabric. About 20 per cent of the patents are concerned with modifications to latex paints as such, including surfactants and thickeners particularly.

Table 1
British patents filed on straight-chain polymer emulsions for use in paints on hard substrates

Application year	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	Totals
Total patents	10	16	25	16	25	23	30	17	16	2	180
By UK companies	2	6	9	4	6	4	5	3	4	1	44
By US companies	4	3	11	6	13	7	9	7	7	1	68
By German companies	3	3	3	4	5	6	10	5	3	—	42

Thus almost 40 per cent of these patents have been secured by American companies, of which Du Pont and Celanese Coatings have some 30 per cent of total American-owned patents between them. Bayer, BASF and Hoechst between them, have about 70 per cent of German-owned patents. Of those held by British companies, ICI and Dunlop own some 45 per cent between them.

Vinyl acetate is by far the most frequently mentioned of the monomers exemplified in these patents, with acrylates or methacrylates in second place.

Solvent-based paints

Paint manufacturers have been concerned during the past year or so about proposed legislation to control the amount of lead permitted in products used in or on houses. A maximum of 0.06 per cent lead by weight of dried film is suggested, and this seems to be an excessively low requirement. The paint industry anticipating the possibility of this figure being universally applied by statute law, has undertaken a massive programme of reformulation, which have involved extensive changes in drier combinations. Following the earlier programme devoted to changes in industrial paint solvent blends as a result of "Rule 66" type legislation, the present concern about lead is a burden on the industry, and whilst this burden has been for the most part conscientiously accepted, it has inhibited technical work in other, more profitable directions. The lead problem arose, apparently, because of the incidence of "pica" among infants, particularly in run-down and neglected city areas, where children were found to be eating flaking and peeling paints, some of which paint was many years old and contained lead pigment.

A recurrent problem in northern states has been intercoat peeling on inverted horizontal surfaces, such as may be found under the eaves of houses and car-ports, and is related to the peculiar climatic conditions which may occur in winter, especially round the Great Lakes area.

In general, technological advances in solvent-based decorative paints have been understandably neglected in the face of the growing importance of latex paints, but the manufacture of oil-modified alkyd resin media has received attention, in terms of alcoholysis catalysis and the improvement of reactor output.

An interesting development in alkyd resin technology, leading to reduced reaction times and improved colour, has been described.⁷ This is a batch process generally applicable to esterification reactions which are carried out in presence of solvent, and is, of course, not confined to those alkyds used in architectural finishes. A portion of the mixed ingredients from the main reactor is continuously removed to an auxiliary heat-exchanger, in the form of a thin-film evaporator, which is maintained at a somewhat higher

temperature than the main batch, and where the water of esterification and solvent are removed as the products of esterification are returned continuously to the bulk reactor.

Industrial paints

The total industrial paint market, including automotive refinishing paints and traffic paints, stood at 504 million gallons (\$1,490 million) in 1971, compared with 370 million gallons (\$1,340 million) for architectural paints. Paints for industry may be divided into several more or less well-defined end-uses, some of which will be separately examined later. The most important single factor affecting the use of industrial paints has been the legislation prohibiting atmospheric pollution by certain solvents and solvent combinations, which originated in California, and was followed by corresponding legislation in other States. This has given particular impetus to the use of solventless finishes, powder coatings and water-based paints, all of which, however, were being manufactured prior to the anti-pollution laws. Non-aqueous dispersions, lately introduced, involve new techniques for their manufacture. From water-based coatings there evolved electrodeposition; a new method of application at the time of its commercialisation, and one which is still less than ten years old.

As an alternative to the use of these coatings, many industrial paint consumers have installed solvent incinerators,⁸ or other means of preventing atmospheric pollution from, for example, baking oven fumes. Thermal incinerators, or so-called "after-burners", require careful engineering to cope efficiently with a wide variety of organic emissions, which may include decomposition products of the paint medium. Already, demands by industrial coaters are such that fuel supplies in some areas are becoming a problem. Chemical scrubbers or water scrubbers, used less frequently than after-burners, also involve sophisticated engineering and must overcome, in the case of water-scrubbers, air pollution without running into the danger of river pollution.

A feature of much of the literature in the past five to ten years, concerning newer types of finish and methods of application, has been the over-optimistic forecasts about the future of individual developments, usually propagated by companies with a vested interest in a particular line of work, and indifferent to, or unaware of, parallel developments in potentially competitive products.

One method of cure recently shown to be commercially advantageous is UV curing, and electron beam curing has been the subject of considerable interest. Induction heating also should not be overlooked as a future development.

Water-based finishes

In 1968 these paints amounted to 5 to 10 per cent of all industrial finishes, and Rogers⁹ has suggested a figure of 45 per cent for 1975, an estimate which might seem to be quite unrealistic, although there is little doubt that there will be growth in this area in various fields of application such as conventional spray, electrodeposition, and probably roller coating. Electrodeposition may already account for up to 90 per cent of water-based coating application, and a separate look at this process will not be out of place.

Electrodeposition

Fig. 3 shows the commercial development in terms of tank capacity in use, in each successive year since 1966.¹⁰ By 1971 electrocoating had reached about 2 per cent of all industrial finishing on a dollar basis—progress by no means insignificant having regard to its present limitations as a baked primer or one-coat finish on metallic objects, and to the relatively high capital cost of equipment.

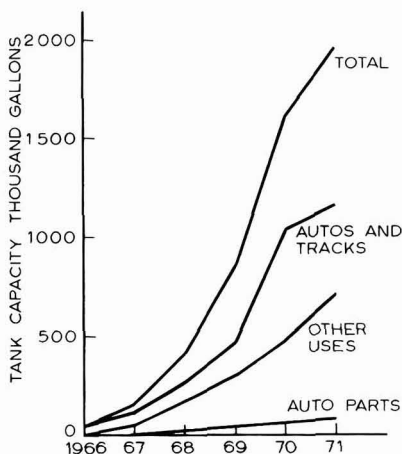


Fig. 3. Production of paint for electrodeposition in terms of production tank capacity

Rate of growth in the future will depend in part upon the extent to which the automotive industry choose to increase the 1972 figure of 15 per cent of American car-bodies receiving these primers.¹¹ Progress in (a) use of two-coat systems, (b) manufacture of air-drying products, (c) application to coil-

coating and (d) cathodic deposition (all of which are scarcely beyond the laboratory or pilot-plant stage at present) will give a boost to the rate of growth generally.

Table 2 shows the numbers of British patents on electrodeposition, arranged in the same manner as those in Table 1.

Judging by the present state of development of electrodeposition, it appears unlikely that the peak years of 1965 and 1966 will ever again be equalled in terms of patent activity in this field. Out of the total number of patents, about 55 per cent describe resinous binders, and 45 per cent describe other aspects of the process, such as pigments and paint compositions, metal pretreatment, pH control, electrical and mechanical operations and so forth. The largest American interest is represented by the Ford Motor Corporation with 42 patents and by PPG with 18.

One of the most useful innovations described in later patents is the ultrafiltration process, already used fairly extensively on a commercial scale. Although capital cost for a complete system is relatively high, a considerable economy of running costs may be introduced, depending on how much paint is normally lost in the final rinse when operating without the ultrafiltration unit. It has been found in some plants that paint losses may be as much as 20 to 25 per cent.

A dozen or so patents have been concerned with deposition at the cathode, and US companies are actively examining such coatings, which may reduce the discolouration which often occurs on steel or copper anodes. In some cases, improved throwing power has been claimed too.

Perhaps the most notable trend in the commercial use of resinous media for anodic deposition, especially for one-coat finishes of light colours on aluminium and steel, has been the widespread use of thermosetting acrylics and oil-free polyesters.

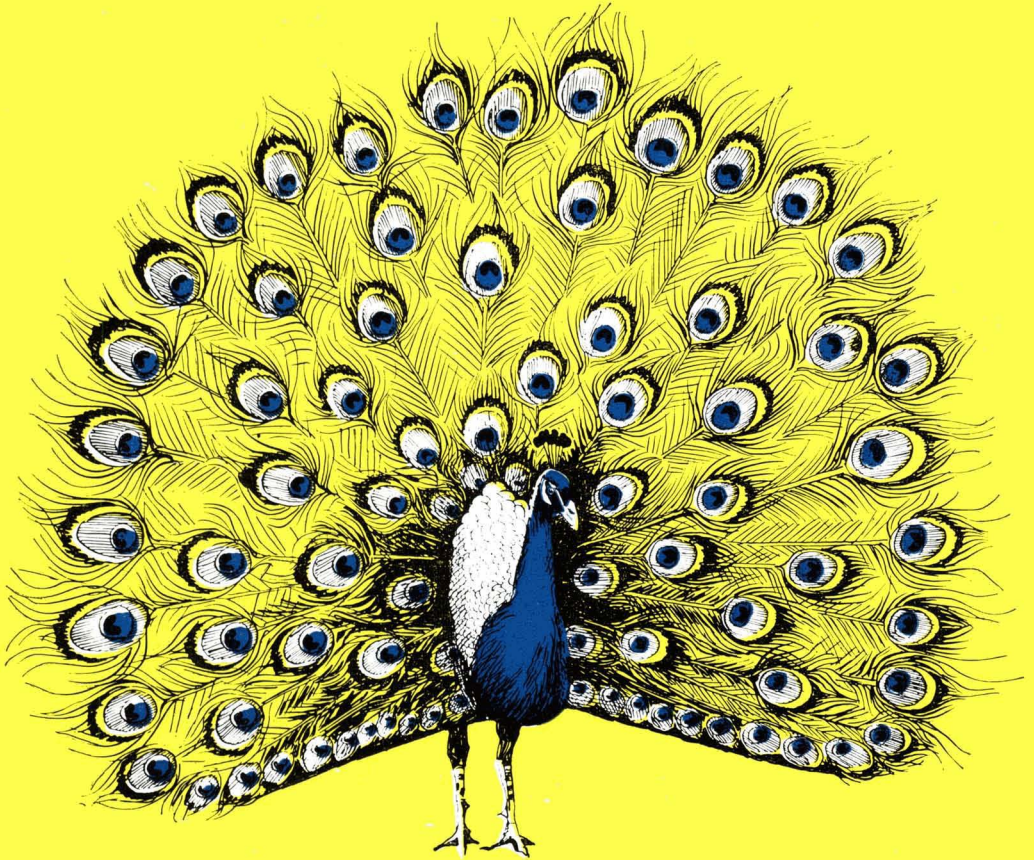
Powder coatings

Levinson¹² estimates total sales in North America of powder coatings to be about 30 million lb, excluding polyethylene used for carpet-backing, and suggests a figure of less than 10 per cent of the industrial market by 1976. Rogers,⁹ on the other hand, has guessed 20 per cent of the US industrial market by 1975. Child's⁹ projection of about 11 per cent by 1980 is more in line with Levinson's figure, and several estimates of 50 per cent or more by 1980 appear to be wildly exaggerated, and even 50 per cent of baked finishes on metal is hardly likely to be achieved, especially considering the competition from water-based materials.

Some observers have been optimistic about the use of powder coatings on motor-car bodies, but so far this application is only in the experimental stage, and it is often overlook-

Table 2
British electrodeposition patents filed since 1960

Application year	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	Totals
Total patents	2	2	10	31	25	64	65	46	39	37	7	2	330
By UK companies	—	—	4	15	12	23	13	3	8	3	1	—	82
By US companies	—	1	5	11	11	21	23	14	11	17	4	1	119
By German companies	—	—	1	5	1	17	14	10	10	7	—	—	65



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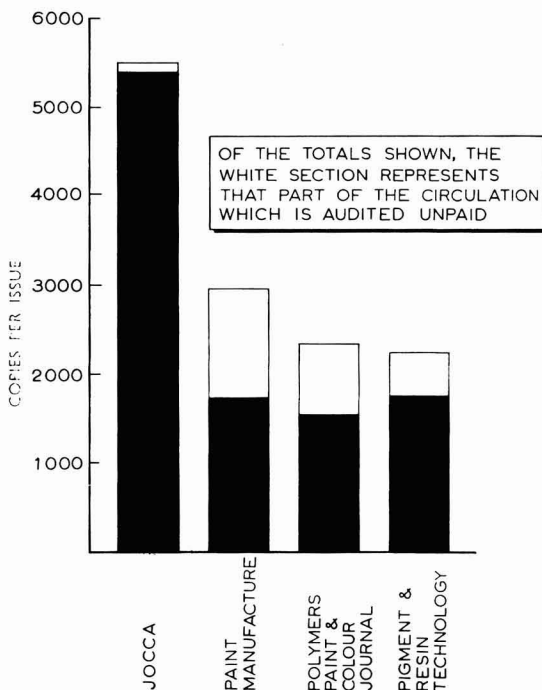


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ed that the finishing of automobiles represents only about 13 per cent of the industrial paint market.

Table 3 shows the numbers of British patents concerned with powder coating since 1960. As with the patents on electrodeposition, about 55 per cent are concerned essentially with resins and the remainder with equipment. As may be expected, most of those patents describing fluid-bed application were filed prior to 1964 and those concerning electrostatic spray equipment were filed after 1964. In the resin field, appreciably more patents have covered the use of epoxy resins, but an emphasis in the future on acrylics, and polyester and polyurethane powders may be anticipated where commercial usage is, as yet, negligible.

Table 3
British patents on powder coatings filed since 1960

Application year	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	Totals
Total patents	6	9	13	19	19	11	12	14	17	12	4	1	137
By UK companies	—	—	4	2	4	—	1	4	6	1	—	—	22
By US companies	3	4	6	5	9	4	5	2	1	1	1	—	41
By German companies	—	1	1	6	3	3	2	3	3	6	2	—	30

It is interesting to note that at least seven of the above patents have been concerned with the coating of metal strip or wire.

Non-aqueous dispersions

These materials have begun to find industrial usage within the past twelve months, particularly in the automotive field. In some ways they resemble the organosols employed in coil-coating but, of course, the non-aqueous dispersion vehicles are formed by polymerisation or copolymerisation in an organic liquid, whereas organosols are formed by dispersion of preformed polymer powders (particularly polyvinyl chloride polymers) in the liquid medium. Non-aqueous dispersions, in their most common form, are copolymers of acrylic and methacrylic ester monomers, and may be thermoplastic or thermosetting. They represent an advance over solution acrylic lacquers or paints, in so far as they have an appreciably higher solids content at spray viscosity. It is too early to say how these materials will develop in the future, but it is safe to say that competition from both water-based coatings and powder coatings will detract from the commercial importance which they might otherwise have achieved.

The record of British patent activity differs from that of other products and processes mentioned. Not only has relatively low interest been displayed in them, but also filing is lower by overseas companies than by British companies—more correctly by one British company, ICI Ltd., who have secured all but one of the 28 patents.

Table 4
British patents on non-aqueous dispersions filed since 1960

Application year	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	Totals
Total patents	5	7	1	3	4	6	6	10	6	1	1	50
By UK companies	4	3	1	3	3	5	4	3	—	1	1	28
By US companies	1	4	—	1	1	—	—	2	2	—	1	12
By German companies	—	—	—	—	—	—	—	2	—	—	—	2

Balm Paints of Australia holds nine patents, no doubt arising from its association with ICI. The limited American interest is represented by Du Pont, Rohm & Haas and Celanese Coatings, all of whom have filed more extensively in the United States. It is reported that ICI has sold its know-how to more than one American company, and has secured US patents corresponding to its British ones.

Methods of curing

An important element of equipment used in industrial paint plants is the baking oven, which is usually heated by gas or infra-red lamps. Gas ovens are often excessively long and

uneconomical in terms of floor space, unavoidable with conventional baking finishes.

Induction heating has been proposed for the curing of finishes applied to continuous metal strip, and already has some commercial application. The strip is passed through an induction coil, electric currents are generated in the strip, the metal temperature rises, the heat generated passes on to the coating, which cures from the lower layers upwards. This system tends to avoid the problem of "solvent popping", and ensures through-curing of the film. Not all of the problems associated with this development have been solved, especially those encountered in the curing of paints on aluminium. No doubt this method will be limited to flat metal stock, and will not be applied to wood or to plastics, so that although it may increase in popularity, its ultimate level of usage will never be more than a small proportion of all industrial types of curing.

UV curing, especially for wood finishes, has been practised for some years in continental Europe, but hardly at all in the UK or in the United States. Unsaturated polyester/monomer based wood fillers have been used mostly, but clear top-coats have also been applied. Within the past twelve months, commercialisation in the American furniture industry has begun. It has been claimed by J. J. Crowley¹³ of the O'Brien Corporation that sixteen lines were operating last July, and that new lines in excess of one per month would be installed. The present limitations of UV curing are probably likely to limit this method of cure to its use on furniture and interior panelling, and even in that field it may be supposed that the resin types suitable for UV poly-

merisation will make slow progress in the face of competition from the well-established nitrocellulose or cold-curing urea and melamine resins.

Electron beam curing represents a rather unique situation in so far as publicity on the subject has been very considerable during the past two or three years, and patent activity, as indicated by British publications, has been nearly three times as great as that concerned with UV curing. In spite of this, commercialisation is noticeably less than is the case with UV curing, not only in Europe, but also in the United States where, at the time of writing, only one line is thought to be operating (for the curing of coatings on plastic automobile parts). Table 5 shows the numbers of British patents issued over the past ten years. The figures refer only to the use of electron beam curing of coatings on rigid substrates, and do not include the use of the system for cross-linking plastic sheets or articles, but do include equipment and its modification, which amount to about twenty per cent of the total.

Table 5
British patents filed since 1960 on electron beam curing

Application year	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970	Totals
Total patents	2	1	2	1	2	14	17	12	16	32	2	101
By UK companies	—	—	—	—	—	1	4	1	1	6	—	13
By US companies	—	1	2	—	1	12	12	9	9	23	1	70
By German companies ..	—	—	—	—	1	1	—	2	1	—	1	6

No less than forty-two of these patents were filed by the Ford Motor Company which company also figured prominently in the electrodeposition field. In three cases Ford coupled the process of electrodeposition with that of electron beam curing. Some patents (not by Ford) disclose curing of coatings on metal strip, and there are several patents covering UV curing (or part-curing) followed by electron beam curing, or UV or electron beam curing as alternatives, with the same resinous binder.

Levinson¹⁴ has compared the technology, speed of cure and economics of UV and electron beam curing, and suggests that by 1975 sales of UV cured coatings will be \$5.8 million and for electron beam cured materials \$2.4 million, which together amount to less than 0.5 per cent of the expected total industrial sales. It is a little difficult to foresee any significant break-through for radiation curing during the next twenty years or so, judging by experience so far, although electron beam curing of finishes on plastics may show some progress. In terms of capital cost of equipment, Levinson quotes figures of \$20,000 to \$50,000 for UV, and ten times these figures for electron beam; but the latter does have advantages, at present, of curing more quickly and of curing pigmented products.

Automotive paints

The automotive industry in the United States utilises about 13 per cent of industrial paints on both a volume and dollar basis. The refinishing and repair of automobiles represents about 7 per cent by volume, or 11 per cent on a dollar basis. Since 1950 annual production of passenger cars has varied between 6.5 and 9.5 millions, the latter figure being reached in 1965 and in 1971. The production of buses and trucks also fluctuated over the same period, reaching a peak of 2.3 millions in 1971. Fig. 4 shows separately the increases

in registered passenger cars and commercial vehicles since 1950¹⁵. The rate of increase of new passenger cars alone was almost three times the rate of growth of the population over the same 20 year period.

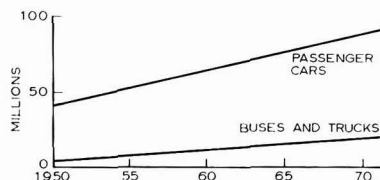


Fig. 4. The number of registered vehicles in the USA since 1950

General Motors, Ford, and Chrysler between them produce some 80 per cent of American cars in the approximate proportions of 60 per cent, 25 per cent and 15 per cent

respectively. Ford has its own paint plant with a captive capacity of some 15 million gallons, and Chrysler too produces some of its own paints. These three companies have many foreign plants, and their collective influence in Europe is well known; in the UK alone nearly 50 per cent of automotive production is American owned.

Since 1960, or slightly earlier, the types of paint finish have changed from those based on nitrocellulose or baked alkyd/melamine resins, to top-coats based on thermoplastic or thermosetting acrylic resins on a high proportion of new cars. It has already been mentioned that very recently non-aqueous dispersion type acrylics have been applied to some cars. The introduction of the electrodeposition of primers in the early 1960s was a small revolution in the surface-coating industry. It was initiated in the United States by Ford, PPG Industries and Glidden.

Besides the interest in non-aqueous dispersions, work is being undertaken by the major companies on both powder coatings and water-based finishes. It would be premature to anticipate which of these will ultimately become the most popular, but perhaps water-based top-coats have the greatest potential, considering their flexibility of application, cost and compliance with pollution regulations.

Of particular interest to the paint industry is the increasing use of plastics¹⁶ in the average American passenger car, which now amounts to 100lb per car, having almost trebled in the past ten years. Most rigid plastic parts are relatively small, for example nameplates, fan shrouds, air-deflectors, control knobs, lamp lenses and so on; larger parts are radiator grills, front-end panels and instrument panels. The total plastics content, includes flexible cushioning and plasticised pvc covering material. Moulded reinforced plastic parts in 1970 were based on about 30lb unsaturated polyester/monomer compositions, and 12lb ABS polymer per car.

Polyolefin mouldings accounted for another 12lb¹⁷. Some mouldings are part of the outside of the car, and may now include reinforced nylon.

Several automotive manufacturers have extensive plastics component moulding departments, and it has been estimated that the average content of all types of plastic in the mass-produced passenger car will be three times the present figure of 100lb by 1980. As a result of the incursion of plastics, not only in the automotive but also in furniture and other industrial products, the painting of rigid mouldings has become an important part of the industry's development programme. The use of electron beam curing by the Ford company is an illustration of one method of ensuring good adhesion, at least on ABS plastic.

For refinishing, quick-drying alkyd resin-based materials are mostly employed, and also acrylic lacquers, which may be modified with nitrocellulose or cellulose acetate butyrate. The third most important type is based on a monomer-modified alkyd medium, first introduced more than ten years ago. It is not uncommon to blend automotive finishes with small amounts of polyisocyanates before application to improve the properties of the film.

Coil coatings

Fig. 5 shows the amount of aluminium and steel strip in thousands of millions of square feet coated each year since 1962; the average rate of increase has been about 17 per cent per year; the 25 million gallons of paint used represents some 5 per cent on a volume basis, or 6.5 per cent on a dollar basis, of industrial paints in 1971¹.

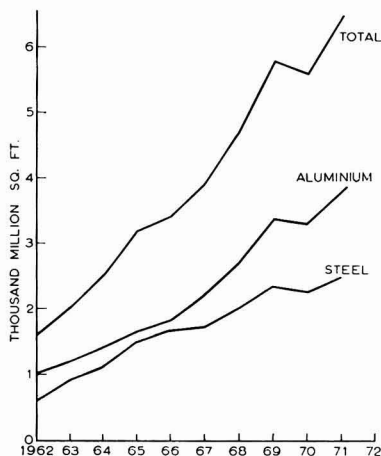


Fig. 5. Area of aluminium and steel strip coated each year since 1962

Building products as a whole utilise some 70 per cent of the total of precoated aluminium, mainly for mobile homes (29 per cent) and residential sidings (23 per cent). Can manufacturers take about 18.5 per cent. Of precoated steel, building products take about 60 per cent (less than 1 per cent being for residential sidings); the next largest usage embraces furniture, home and office fixtures and office equipment, which, taken together, represent about 7.5 per cent. Thus the coated steel is more widely distributed

among end-users than is the case with aluminium¹⁸. The total amount of both metals used for all types of domestic appliance is no more than 2 per cent, and there appears to be scope for expansion in this area.

The formulation of coil coatings used today is based mainly on thermosetting acrylic media, followed by the old-established alkyd MF systems, and probably both of these are likely to decrease with increasing competition from oil-free polyesters, silicone polyesters and pvc plastisols. Fluorocarbon polymers have not shown the growth expected when they were first introduced three to four years ago, and their future is still a matter for speculation.

Papers presented at a National Coil Coaters Association meeting ten years ago by various technically interested parties in the coil-coating field discussed the possibilities of operating lines at 1,000ft min⁻¹ with evident optimism, but the average speed today is still below 300ft min⁻¹ with a maximum, for reverse roller-coating of paint, at not much more than 450ft min⁻¹.

Very high speeds have been obtained in the case of steel strapping up to half an inch wide, where a 6in coil is first slit into 12 narrow widths, and the black paint applied by electrodeposition, at no more than 0.2ml thick.

For normal wide strip coating, suggestions have been made, and experiments carried out, for the application of resinous powders by different methods, and for the application of primers by electrodeposition. Water-based top-coats applied by normal roller coating are of current interest, and are expected to be used commercially in the not too distant future. Increased speed of cure, perhaps leading to increased line speed, has been the subject of semi-commercial trials using the Ford Electrocrete (electron beam) system, but the future of this process remains uncertain.

Wood finishing

The wood-finishing industry primarily involves the finishing of furniture, which accounts for about 10 per cent of industrial paint business on a volume basis, or 6 per cent on a dollar basis, and factory-finished timber which accounts for about half the furniture coating business.

The furniture industry is considerably more fragmented than the paint industry and comprises some five thousand companies, of which two-thirds employ less than twenty people. Nitrocellulose remains the most important basis for furniture finishes, followed by cold-hardened urea/formaldehyde and melamine/formaldehyde resins. In an earlier section the growth of UV-cured unsaturated polyesters has been mentioned.

The growth of plastics in furniture is a feature of both the wood and automotive industry, and most of the larger companies have their own moulding departments. A total of 800 million lb of plastics was said to have been used in 1970, of which by far the largest item was pvc covering; flexible polyurethane foam cushioning also represents a considerable proportion. In the case of rigid plastic, nearly half (125 million lb) of the high impact polystyrene was made injection moulded, with perhaps 55 million lb of foam polyurethane and 40 million lb of unsaturated polyester made by casting (a more flexible and economic process than injection moulding)¹⁹.

Most of the plastic has been used for decorative curved pieces common to reproduction style furniture in general, and after suitable finishing is indistinguishable from the wood with which it is incorporated. Lately, rigid polyurethane foam has been used for structural pieces; the density of this material can be varied from 2 to 50 lb ft⁻³ with increasing strength. Wood or fibre board remains a relatively inexpensive substance for straight flat pieces, which form the bulk of modern furniture.

The factory prefinishing of wood or wood products for modular housing introduces the same labour-saving costs over traditional on-site painting that are inherent in metal coil-coating. Baking up to 120°C for short periods can be used, and catalysed thermosetting acrylic latex coatings have been proposed for top-coats²⁰.

Raw material changes

Changes in types of paint used for different types of application, are reflected in changes in the resinous paint binder, for the most part, and published figures show some interesting comparisons in respect of rate of change for some important materials. Fig. 6 shows how the use of natural triglyceride oil, oil-modified alkyd resins, acrylic resins and polyvinyl acetate has changed since 1965. Each point on the graph represents the ratio of dry weight of resin to total volume of paint produced each year, that is the weight of resin (or oil) in millions of pounds, divided by the volume of paint in millions of gallons²¹. The trends illustrated are as accurate as available statistics will allow, and it may be noted that, for example, "acrylic" resins undoubtedly include a minor proportion of styrene or vinyl toluene although, in the main, they comprise copolymers of acrylic and methacrylic esters. Polyvinyl acetate resins, on the other hand, include minor proportions of plasticising monomers, some of which are acrylic types. The oil-modified alkyd resins are not defined according to oil length, but there is little doubt that the average content of combined oil or fatty acids will have decreased over the period. Oil-free polyesters are not included.

The dotted curve in Fig. 6 relates to all types of oil used (drying or otherwise), either alone or in combination with resinous materials, including that used in alkyds.

Thus the amount of oil used in the "average" can of paint has been reduced by about 45 per cent in the six years under review, and the amount of alkyd by some 15 per cent; this is consistent with the rise in consumption of acrylics and polyvinyl acetate. Epoxy resins and polyurethanes, currently used at less than 100 million lb per annum, have also shown a continuous increase.

Acrylics and vinyl acetate copolymer emulsions have displaced both oils and alkyds in architectural paints, and solvent-based acrylic polymers have also had outstanding success in industrial paints, particularly for automobiles, metal strip and appliances. It is to be expected that the use of

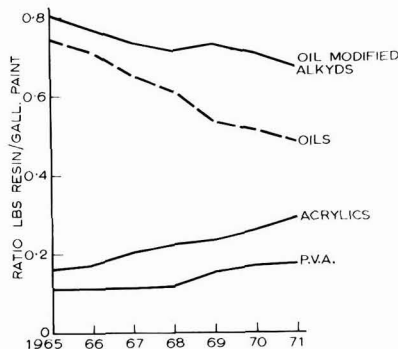


Fig. 6. Variation of the amounts of certain raw materials used per year

acrylics will continue to rise at a greater rate than polyvinyl acetate, especially when powder coatings and water-based paints become established in the industrial field.

Table 6 gives the numbers of British patents published since 1960 on the subject of thermosetting acrylic resins, the criterion for "acrylic" being that the acrylic (or methacrylic) monomer be more than 50 per cent of the specified addition polymer (whether an additional crosslinking or a modifying resin is used or not) according to the main claim of the patent. From this survey are excluded air-drying latex polymers, non-aqueous dispersions, and polymers for radiation curing. The total patents comprise 144 solvent-based resins, and 65 water-based resins, and of the latter, 33 were recommended for electrodeposition, and were previously included in Table 2.

The total published British patents from Tables 1-6 are arranged in Fig. 7 and amount to some 780 (eliminating the

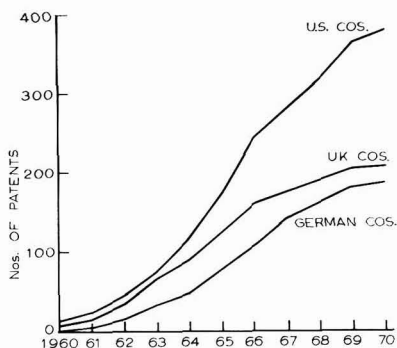


Fig. 7. Variation in the numbers of British patents filed in the years 1960 to 1970 from the data in Tables 1-6 (COS = companies)

Table 6
British patents published since 1960 on acrylic resins

Application year	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	Totals
Total patents	6	16	22	23	28	36	30	26	14	8	209
By UK companies	2	3	5	2	2	5	9	3	1	—	32
By US companies	3	11	5	12	12	12	11	11	6	3	86
By German companies	—	—	6	5	6	16	9	6	4	4	56

33 electrodeposition cases from Table 6). Fig. 7 shows the accumulated patents secured by British, American and German companies in these areas of paint technology.

A survey of all patents covering paints, resins, raw materials and methods of application indicates similar domination by the combined forces of America and Germany (with the Americans having, in general, the most influence) in other countries of Europe. On the other hand, patents filed in the United States over the same broad field, show only 10 to 15 per cent ownership by foreign companies.

Economics

As in many other countries, the American paint industry is very fragmented, with something like 1,500 companies in business. Surveys indicate that smaller companies consistently operate at lower profit margins than larger companies²² and a recent analysis by Bewley²³ shows that overall profitability of the industry is well below the average for American industry in general. This difference is even more marked if one considers net profits per employee, when inefficient use of manpower becomes apparent—perhaps typical of all countries, and endemic to the type of operations carried out, and the structure of the industry.

Figures published by Kline¹ show that from 1958 to 1968 the ratio of production workers to total employees fell from 60 per cent to 55 per cent, in which period the average hourly earnings of production workers rose 3.8 per cent whilst the average annual gallons per man-hour rose by 2.6 per cent. Greater use of high-speed dispersion techniques and continuous sand mills contributed to this modest advance, and although refinements and modifications of such equipment have taken place, there does not appear to be any fundamentally new method of dispersion in sight.

Between 1961 and 1971 average annual volume increase was about 3 per cent for trade sales and about 5 per cent for industrial paints. On a dollar basis, the annual increase was about 5.5 per cent over the same period for all paints manufactured, rather less than the rate of increase of the gross national product. There is no reason for believing that this modest rate of growth will not continue in the foreseeable future.

Fifteen companies account for 40 to 45 per cent of total sales, no single company having a share of more than about 10 per cent. The top four, Sherwin-Williams, Du Pont, PPG Industries and Glidden in that order, account for about 25 per cent of the total. Sherwin-Williams has a pigment and chemical division and important can-manufacturing units, although paint sales account for more than 60 per cent of total income, mostly through over two thousand owned or rented paint stores. In the case of Du Pont, only 4 to 5 per cent of the total are sales of paint products; PPG Industries sells about 17 per cent of its total output in the form of resins and paints; and Glidden's paint sales represent about 22 per cent of the total sales of SMC Corporation, the parent company.

In the past five years some 80 paint companies have been bought up by larger organisations, and this consolidation is expected to continue, perhaps at an accelerating pace. Paint formulation and methods of application, especially in the industrial field, have now reached such a state of sophistication, that a larger proportion of paint production falling into the hands of the larger companies may be expected, because they are better equipped to acquire the

essential technical personnel and instrumentation required for successful operations.

Influence in Europe

Although there is some American investment in European paint manufacture as such, it does not amount to a very significant proportion. The high proportion of American-owned patents in European countries relates essentially to the American ownership of European industrial paint users. American ownership is especially prevalent in the automotive industry, but also concerns many companies producing farm equipment, office machinery, domestic appliances, and so forth. The licensing of patents and/or technical know-how to European paint companies is often involved, therefore, so that products matching those used in the United States may be formulated. American influence is not only restricted to those paint manufacturers supplying American subsidiaries; a good deal of American know-how is bought by companies in Britain and continental Europe, because they choose to improve their technical competence in this way rather than by investing money in research and development work for themselves. An example is the recent spate of American licensing in the field of coil coatings.

When speaking of "American know-how," reference is, obviously, to the know-how of certain large American-based companies, with the necessary research and development facilities for the commercialisation of new and improved products, and sufficiently orientated towards the European market to be able to profit from licensing activity. The enlargement of the EEC may well increase American interest and influence, but it is equally possible that the continued growth of such European companies as Shell, AKZO, Bayer, BASF, Hoechst and ICI, especially where this involves investment in paint manufacture, may do something to alter the trend in the next five to ten years, and this could happen independently from any changes in the status of the user industries. It seems unlikely that, short of some untoward catastrophe, American interest in Europe as a whole will decline. The possibility of individual European governments choosing to limit American investment in national economies is another matter, but such decisions will certainly require careful thought because irreparable damage could be done.

Many politicians and professional economists see nothing but advantage in the encouragement of American investment generally, and certainly the paint industry itself must acknowledge technological advances which might not otherwise have occurred.

[Received 21 March 1973]

Acknowledgments

Acknowledgments are due mainly to those mentioned in the paper, from whom the author has quoted relevant observations and statistics, but helpful material from colleagues in the Sherwin-Williams Company has also been used on occasion.

The author's qualified predictions about the future do not occur with any noticeable frequency but, such as they are, may be attributed only to the author himself, unless otherwise stated.

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Discussion at Eastbourne Conference

DR L. VALENTINE asked if Mr Armitage were Research Director and had to concentrate on only one route towards pollution-free coatings, would he select water-based coatings, non-aqueous dispersions (NADs), high solids coatings or powders.

MR F. ARMITAGE replied that it would have to be water-based coatings. Both water-based coatings and powder coatings had been used commercially for more than 20 years in the industrial field. More recently, the use of both had accelerated because of new application methods—in the case of water-based materials by the electrodeposition, and with powder coatings by electrostatic spray. If thinking were restricted to industrial finishes, powder coatings were unsuitable for air-dry finishes, including among others, automotive refinishes. They were also unsuitable for wood and plastic finishes, which cut down their potential considerably. There was no such restriction with water-based finishes. Non-aqueous dispersions represented a technological advance of great interest, and had involved very sophisticated development. They might be less restricted than powder coatings in their potential usage, but might ultimately conflict with anti-pollution laws in the States in some areas. They were a relatively new development, and it was the author's opinion that, in terms of eventual importance, they would always be behind water-based coatings. High-solids coatings—those with less than 20 per cent of solvent, already typified by pvc plastisols—had certainly become of greater interest because of clean-air legislation, and would include older-established materials which incorporated a reactive solvent such as unsaturated polyester/styrene types or cold-catalysed epoxy types. If high-solids materials, thinned with water, could be produced, then this might be the best compromise.

MR G. R. SIDDLE asked whether, in view of the projected shortages of oil-based chemicals for surface coatings, Mr Armitage knew of any research efforts directed towards vegetable oils (and other products) to improve the yield or to discover new varieties.

MR ARMITAGE apologised and said that he did not.

MR G. WILLISON asked if the American regulations on solvent contamination of the atmosphere took any heed of the emission of resin-decomposition products during stoving operations.

MR ARMITAGE said that if the decomposition products included proscribed materials then technically the legislation took heed of them, but the legislation was concerned with amounts allowed into the atmosphere, and in the ordinary way the decomposition products of resinous materials were very small in relation to the total amount of solvent evaporated. In the case of powder coatings, where decomposition products might be of the order of, say, 3 per cent, it was the author's understanding that, even in Los Angeles, so long as the emissions did not exceed 3lb per hr there would be no problem—that is, 3lb per hr from one unit. For larger amounts it would be necessary to find out whether the emission was permissible—probably such decomposition products would be non-exempt.

DR M. L. ELLINGER commented that in the paper the advantage of cathodic electrodeposition was pointed out in respect of improved colour on steel substrates. There seemed to be some evidence that, whilst substrate iron dissolution was avoided, a certain inherent discolouration of the binder occurred (yellowing) and, therefore, the main advantage of cathodic deposition versus the anodic methods was perhaps the greatly improved corrosion and salt spray resistance.

MR ARMITAGE agreed that one of the points made in respect of cathodic deposition was improved corrosion resistance over steel. With anodic deposition, he thought, every binder was subject to yellowing, and indeed one could now get good whites with anodic deposition. He thought this had not been achieved on copper, which was a difficult substrate anyway.

MR M. HESS mentioned the presence of amines in water-based paints, which are also pollutants.

MR ARMITAGE answered that amines were present in very small amounts, but he was not aware that they had raised problems in terms of air-pollution. It might be that they had to be considered in respect of water-pollution, but he was not sure about that.

MR R. J. WOODBRIDGE asked Mr Armitage whether he could give any estimate of the relative size of the "good-better-best" sectors of the retail latex paint market, and any trends in these sectors.

MR ARMITAGE replied that he could not really say, but one might presume that the cheaper grades—or cheaper grades marketed by larger companies who were perhaps not in this field previously—would tend to attract more total business in decorative paints to the larger companies.

MR J. M. RACKHAM said that whilst the lecture was entitled "The American paint industry, present trends and future possibilities" would Mr Armitage like to extend his comments to the European scene, where the pollution requirements and climatic conditions could be quite different from the USA.

MR ARMITAGE replied that anti-pollution laws in the States varied considerably from one area to another, those in Los Angeles being more stringent than those in other cities or States, simply because Los Angeles was in a unique location, coupled with a high u/v incidence. It also had the highest concentration of automobiles, from which oxides of nitrogen were exhausted, which catalysed the photolytic

degradation of some solvent vapours. In other industrial areas, of course, sulfur dioxide and/or particulate carbonaceous materials were the chief offenders. With regard to the latter, he was sure that European countries already had legislation to reduce pollution. With regard to vapour emission from paint-using plants, he did not doubt that Europe was watching the position, and one could only speculate that some areas might need special legislation but it was his guess that whatever might be introduced, it would be less widespread and less severe than it was in many of the American States or cities.

Control of automotive emission was another matter again; motor vehicles made in the States by 1975 had to reduce emission of both nitrogen oxides and unsaturated hydrocarbons, either by engine modification or by catalytic exhaust burners. Petrol should also be free of lead additives, so far as one could judge. It might seem reasonable to suppose that continued increase in the concentration of automobiles in European large cities, might encourage similar legislation.

Next month's issue

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

Relations with the developing countries by *A. T. S. Rudram*

The challenge of metal finishing by *G. Isserlis*

The role of coatings in corrosion prevention—future trends by *V. Ashworth and R. P. M. Proctor*

Electrochemical activity of conductive extenders for zinc rich coatings by *V. P. Simpson and F. A. Simko*

Reviews

Advances in electrophoretic paint deposition 1971-72

Bibliographies in Paint Technology No. 21 By R. H. Chandler

R. H. Chandler Ltd., pp. 80. Price £5 (\$15)

Quite apart from its recognised advantages as a method for the application of paints, particularly corrosion-inhibiting primers, interest in paint application by electrodeposition has been further stimulated by the fact that it causes considerably less atmospheric pollution.

The present volume of 80 pages is the fifth in the series on electropainting and opens with a discussion of some of the theoretical aspects of electrodeposition based on papers published in the period under review. Particular attention is paid to defects such as pinholing and lifting (caused by gassing), anodic processes such as oxidation and neutralisation/coagulation, and the influence of molecular weight on film properties. The influence of the type of resin and pigment as well as the value of pretreatment is also examined. Other topics under discussion are throwing power and the technique of bath control by ultrafiltration. The latter technique has made major advances in the last couple of years and is becoming an established procedure.

The interesting discussion section is followed by 189 literature references. Among these are the 19 papers dealing with the reactions in electrodeposition and presented in 1971 at the Los Angeles meeting of the Organic Coatings Division of the American Chemical Society, the 21 papers read at the "Electropaint 71" conference in London, and the 16 papers presented at the "Electropainting for the seventies" conference in London in 1972.

There are brief descriptions of the painting schedules and plant employed in 44 installations covering a wide range of products from car bodies to computer components. The final section, containing abstracts of 192 patents, will be found very valuable and could save a lot of time at the Patent Office.

This bibliography maintains the high standard of earlier volumes and is a valuable addition to literature on electropainting.

W. M. MORGANS

Progress in polymer science Japan

**Minoru Imoto and Shigeharu Onogi (Editors)
Tokyo, Kodansha Ltd., and
New York and London John Wiley & Sons**

Vol. I. 1971 pp. xii + 520. Price £11.05

Vol. II. 1971 pp. ix + 379. Price £8.15

An analysis of the papers published since 1970 in three of the major polymer review series shows the following distribution by source:

Source (per cent)	UK 12	W. Europe 16	N. America 51
Source (per cent)	Japan 16	Eastern bloc 2	Australia 3

One can hardly say that this indicates a strong bias against papers of Japanese origin, but there can be little doubt that much Japanese work nevertheless remains inaccessible to western scientists. This at least is the justification expressed by the editors for a new review series wholly devoted to reviews by Japanese authors of work conducted for the most part in Japan. With the objective of bringing Japanese work to the attention of western scientists so clearly stated, it would not have been surprising to find less than full credit being given to the work in western laboratories, but, as far as this reviewer can judge, the Japanese authors have been scrupulously fair and numerous papers of western origin are cited.

Volumes 1 and 2 are dated 1971 but some delay in publication is to be presumed since they did not reach the British public until the end of 1972. One hopes that this will not recur, for secondary sources decrease sharply in value as they fall behind the times.

The contents of these volumes will be of interest to all general polymer scientists though few of the more specialised contributions are likely to be read by those whose activities are confined to the field of surface coatings. In the reviewer's opinion, the following papers are likely to be of most interest to readers of this Journal.

In Volume 1:

Otsu, Structure and reactivity of vinyl monomers in radical polymerisation (68 pp).

Tazuke, Effects of metal salts on radical polymerisation (80 pp).

Osaki and Einaga, Viscoelastic properties of concentrated polymer solutions (56 pp).

In Volume 2:

Iwatsuki and Yamashita, Radical alternating copolymerisations (48 pp).

Nozakura and Inaki, Radical polymerisation of internal olefines (62 pp).

Onogi and Asada, Rheo-optical studies of high polymers (68 pp).

The standard of presentation is extremely high, and the editors appear to have been wholly successful in eliminating the rather quaint phrasology often found in the English writings of Japanese authors. If the present standard is maintained in substance as well as presentation, the series will be highly prized.

A. R. H. TAWN

Information Received

Bayer build a third waste water treatment plant

Bayer AG has started constructing another fully biological waste water treatment plant at its Krefeld-Uerdingen factory beside the Rhine. With this joint waste water treatment plant (final capacity of 135,000m³ of waste water per day) and the Dornagen project between the Erdoelchemie GmbH and Bayer AG (100,000m³ per day), all Bayer factories on the Rhine will be equipped with fully biological plants for the treatment of industrial waste water by 1975 at the latest. The total costs for the Uerdingen plant, including the necessary biological sewers, amount to some 55 million DM. About 7 million DM are needed each year for the running of the plant.

Production of AEI paints transferred to IPC

An agreement has been signed by The International Paint Company Limited and the General Electric Company Limited whereby the production of industrial and decorative paints by The Micanite & Insulators Company Limited (AEI PAINTS), a GEC Company, is to be transferred to The International Paint Company. The move is part of a strategy to expand the traditional business of The Micanite & Insulators Company Limited as major UK suppliers to the Electrical Industry of mica products and other insulating varnishes and materials, and to enable the concentration of overall resources into the company's main-line activities.

Paints and varnishes in Europe

The Chemical department of the METRA group will have completed soon its three year survey of the European (former EEC countries and the UK) markets for paint and varnishes. Building and "do-it-yourself" represent 52 per cent of the market, the other main end-users being the automotive industry (10 per cent), automotive repairing (8 per cent) wood and furniture, metal products and marine equipment. Besides this sector of the market, the survey covers distribution channels, production and application techniques, raw materials and new products.

Statistics for the dyestuffs and pigments industries

A new statutory quarterly inquiry into the sales of the dyestuffs' and pigments' industries, designed to provide up-to-date statistical information for the industry as well as for the Government, has been launched by the Business Statistics Office.

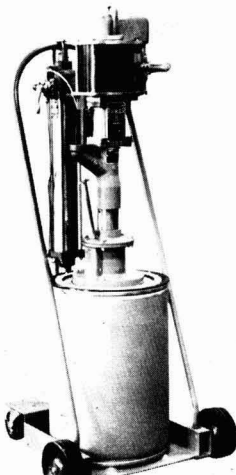
The product headings on the inquiry form have been compiled after consultation between the Department of Trade and Industry, the Chemical Industries Association and the British Colour Makers' Association.

Forms will be sent to approximately 50 establishments in the industry—all those employing 25 people or more. The first return covers the second quarter of 1973, and replaces the existing quarterly inquiry into colours, and the monthly collection of statistics, previously undertaken by the Dyestuffs Office, which have been discontinued.

New products

Transfer pump for lithographic inks

A new 30 gallon pressure pump primer has been developed by Lincoln St. Louis, Division of McNeil Corporation, for the transfer of lithographic inks used in commercial litho work on metal, plastic and glass containers. The unit is adaptable to materials of medium and high viscosity. It aids pump priming action, eliminates manual pump handling, and enables the user to buy larger quantities at lower costs.



Lincoln Engineering transfer pump

Polyurethane elastomers for textile and foam coating

A range of polyurethane elastomeric resins for coating of flexible substrates is now

available from Synthetic Resins Limited, following extensive application trials. Developed primarily for use with textiles with direct-coating or transfer-coating techniques, the resins are not only suitable for producing synthetic leathercloth and coatings for pvc and self-skinned polyurethane foam mouldings, but they have also been shown to have considerable potential on application to pre-foamed and in-situ chemically foamed pvc.

A new low-odour ink from Coates

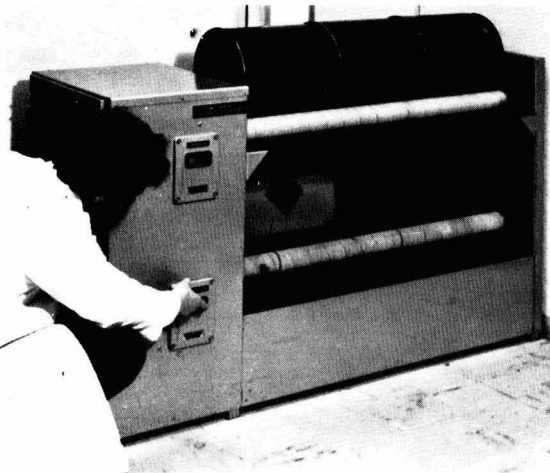
The latest addition to the range of litho inks manufactured by Coates Brothers Inks Ltd is CLT FRESH. Although basically an oil based system, with the machine properties to be expected from a conventional ink, it has been formulated to give an odour level that has previously not been attainable with any system other than water miscible inks. In addition, CLT FRESH achieves its final odour level rapidly and with very little airing.

Carsons and Hadfields rationalise range of wood primers

Carson Paripan Ltd and Hadfields (Merton) Ltd have rationalised their range of four wood primers down to two products. The range, which offered pink and white wood primers specifically for interior or exterior use, now comprises one Pink Wood Primer and one White Wood Primer, both specially formulated by the Carsons/Hadfields research and development team to give optimum performances under either exterior or interior conditions.

Sharples two-tier ball mill

A two-tier ball mill has been introduced by Sharples Engineering Co. (Bamber Bridge) Ltd. for the mixing and dispersal of materials such as chemicals, powders, colour pigments and paint resins. Designed for efficient batch processing, the unit is fitted with independent tier drives which enable one tier to remain in operation whilst the other is unloaded and reloaded.



Two tier ball mill available from Sharples Engineering

New products (continued)

Methylated urea resins

Monsanto has introduced three new grades of high-solid methylated urea resins—Resimene X-970, X-975, X-980—for high speed printing, wood finishing and interior-grade industrial coatings. These new products complement the Monsanto range of high-solid amino resins.

Universal colour dispersions

A range of "A-line" universal pigment dispersions has recently been introduced in the UK by Bee Chemical Company (UK) Ltd. The company claims that these dispersions are unique, for the following reasons. Firstly, the basic composition is declared (100 per cent methacrylate resin pigment, and a glycol ether high flash point solvent) and, secondly, the dispersions are designed for both tinting and to be used as the sole colours. A complete range of industrial enamels may be formulated from one dispersion.

Literature

New publication on ethoxylated amine chemistry

Armour Hess Chemicals Limited has announced the publication of a booklet entitled "Ethomcens Ethoduomeens Ethomids Ethoquads." This has been written to provide an up-to-date reference work on the company's wide range of ethoxylated cationic and ethoxylated non-ionic chemicals. It covers hundreds of applications in many industries and provides a detailed synopsis of the applications of ethoxylated chemicals. Copies are freely available from the Harrogate Office of Armour Hess Chemicals Limited.

Shandon spectrophotometer

Shandon Southern Instruments has recently produced a full colour leaflet on its new Atomic Absorption Spectrophotometer A3400. Contents include chart traces for lead, nickel, tellurium and cadmium and technical descriptions of the monochromator, burner and spray chamber.

Conference, courses, symposia

GDCh Fachgruppe conference

The fortieth conference of the Gesellschaft Deutscher Chemiker Fachgruppe "Anstrichstoffe und Pigmente" will be held from 9 to 12 October 1973 at Bad Neuenahr, West Germany.

Course at Manchester Polytechnic

During the 1973/74 Session, a course will be held at the Manchester Polytechnic entitled "Chemical technology with special reference to polymers and surface coatings," which is a HNC endorsement subject (for LRIC purposes) and which will enable candidates to obtain part of the qualifications for Associateship of the Society of Dyers and Colourists.

PRA Training Seminars

The Paint Research Association will be holding two training seminars on pigment dispersion (25-26 September 1973) and recent advances in analytical techniques (9-10 October 1973).

Section Proceedings

South African

Transvaal Branch

Internal pipeline coatings with particular reference to powders

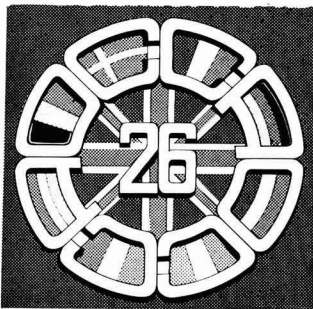
An interesting review of developments in pipeline coating materials was presented by Mr M. A. Brett, of Michael A. Brett and Partners, at the Sunnyside Park Hotel on 14 June 1973.

Mr Brett stressed that it was poor practice in days of ever increasing repair and maintenance costs to select a system that had given average satisfactory past performance at a known cost without investigating the merits of a slightly higher initial capital outlay for better end-maintenance and longer pipeline life. Bitumen, coal tar, enamel, concrete, epoxy resin linings, galvanised finishes and epoxy powder coatings were outlined, and Mr Brett gave some most useful guide-lines which the designer should follow when selecting the type of lining material for use. The advantages of epoxy powder linings over other types of material were dealt with in detail, and the plant necessary was described.

It appeared that in South Africa, nearly 80 per cent of all coated lines were still based on spun bitumen. The balance of coating usage was split between concrete and liquid epoxy resin type materials on an even basis. The epoxy powder materials at this stage, though being used on very small reticulation work in chemical plants, and so forth and on one major project to date, could not yet claim any noticeable percentage of the market. However, it was confidently to be expected that epoxy powder coatings would become specified more and more with a resultant more competitive cost. With the introduction of powder coating would come the opportunity for pipeline owners and operators to obtain longer life-times for coatings, better through-put and longer maintenance-free periods.

The vote of thanks proposed by Mr Delerette was carried with acclamation.

P.A.J.G.



OCCA-26 Exhibition

The European Economic Community's forum for technical display and discussion in the surface coatings industries

23-26 April 1974

As already announced in the August issue of the *Journal*, OCCA 26 will take place at the Empire Hall, Olympia, London, from 23 to 26 April 1974.

Invitation to Exhibit

Invitations to Exhibit were despatched in July to those organisations in UK and abroad who have exhibited at previous Exhibitions or have requested information on the 1974 Exhibition. Any organisation which has not received an Invitation to Exhibit, but wishes to do so, should apply at once to the Director & Secretary of the Association at the Association's offices. *The closing date for applications to exhibit is 3 November 1973.*

International character

The Exhibition, which has long been known as the forum for technical display and discussion for the surface coatings industries, in 1973 attracted visitors from more than 50 overseas countries, and there was direct contribution by exhibitors from 14 overseas countries. The motif chosen for this year's Exhibition shows the flags of the enlarged European Economic Community and, by converging on the flag of the UK, symbolises the welcome extended for many years to exhibitors and visitors not only from these countries but from farther afield to the OCCA Exhibitions in London, one of the capital cities of the European Economic Community. To further the aim of a truly international character, the Exhibition is widely advertised in technical journals both at home and in 18 technical journals overseas. Furthermore, it has been the practice for many years to issue information cards in six languages (English, French, German, Italian, Spanish and Russian) and these are widely distributed to firms and individuals in many countries. Interpreters are available at the Exhibition without charge to help both exhibitors and visitors alike.

Hours of opening

On this occasion the Exhibition Committee has decided to dispense with the Monday opening and to concentrate on four full days as follows:

Tuesday 23 April	..	09.30	to	18.00hrs
Wednesday 24 April	..	09.30	to	18.00hrs
Thursday 25 April	..	09.30	to	18.00hrs
Friday 26 April	..	09.30	to	16.00hrs

Exhibition Dinner

Following the success of the Exhibition Dinner on the opening day in 1973, the Committee has decided to hold a Dinner at the Savoy Hotel, London WC2 on Tuesday 23 April at 19.00 for 19.30hrs. At the request of some exhibitors a cash bar will be made available after the function for those visitors wishing to use this facility. Full details of the Dinner will be announced in this *Journal* from time to time and an application form for tickets will be enclosed in each copy of the *Official Guide*.

Official Guide

The *Official Guide* will be prepared well in advance of the dates of the Exhibition so that copies can be circulated widely, both to members and non-members, thus allowing visitors an opportunity to plan their itineraries. As well as maintaining the Exhibition's unique position as a purely technical display, manned by technical personnel, the Exhibition Committee has for many years followed the successful policy of encouraging visitors in this way, and by making no charge for admission so that the maximum flow of communication between exhibitors and visitors can take place.

Aims of the Exhibition

The Exhibition Committee wishes the aims of the Exhibition as stated in the Invitation to Exhibit, to be as well known as possible and accordingly these are reproduced below.

The aim of the Exhibition is the presentation of technical advances in those industries supplying the paint, varnish, printing ink, colour, linoleum and other allied industries. The technical advances may relate to: new products, new knowledge relating to existing products and their uses, or in suitable cases, existing knowledge which is not generally available in the consuming industries.

The Committee stipulates that exhibitors present a technical theme—that is display in a technical manner the technical developments in raw materials, plant or apparatus illustrated by experimental evidence. It is essential that a technically or scientifically trained person, who has full knowledge of the products displayed, be available on the stand throughout the official hours of opening.

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

Charge to Exhibitors

The OCCA Exhibitions have for many years been planned to keep costs as low as possible for exhibitors. The charge (which includes stand space, floor, walls, muslin ceiling, fascia with coloured felts and pine trims, and painted name plaque), will be £110 (plus Value Added Tax) per unit of 4.32m², and exhibitors receive a free supply of *Official Guides*, six language cards, badges, folders, and so forth. Since there is no charge made for admission to the Exhibition, no "special facility" tickets are issued for distribution by exhibitors. Each visitor is given a copy of the *Official Guide*, together with a folder for technical literature, showing the location of the stands, upon arrival at the hall.

Exhibitors can, if they wish, choose to have their name plaque rendered in distinguished colours and to have superimposed their trade mark at additional cost. Each year the colours chosen for the felts of the fascia have been selected to integrate with the motif chosen for the particular Exhibition, and it has been the custom to have one colour on all fascias north to south, and another on all those fascias which run east to west in the hall. Samples of the felts chosen are sent to each exhibitor and it has been a feature of the Exhibition in recent years that many have incorporated these colours into the design of their interior stand fittings.

Travel Agents

The Wayfarers Travel Agency Ltd., Cranfield House, 97/107 Southampton Row, London WC1B 4BQ., will be allocated a stand adjacent to the OCCA Information Centre at the Exhibition and will be prepared to advise on, and arrange, hotel accommodation and travel facilities to the Exhibition. They will also be able to make theatre ticket reservations for the evenings of the Exhibition.

Please address all enquiries to The Wayfarers Travel Agency AT THE ADDRESS SHOWN ABOVE, and not to the Association.

Report of Council Meeting

A meeting of the Council was held at the Great Northern Hotel, London N1, on 11 July when twenty-eight members of Council were present. The President, Mr L. H. Silver, took the chair.

The President extended a welcome to all new members of Council, both at home and overseas.

The dates for the Council meetings, the Council Reunion Dinner, the Association's Dinner Dance and the Annual General Meeting 1974 were discussed and agreed as follows:

- 17 October: Council meeting followed by reunion dinner
- 26 February 1974: Council meeting
- 4 April 1974: Council meeting
- 23 April: OCCA 26-Exhibition
- 31 May 1974: Association's Dinner Dance

The Annual General Meeting will take place either in late June or in the first part of September 1974.

The appointment of members of Council for the forthcoming session and the representation of the Association on other organisations was agreed.

Reports were received on the Eastbourne Conference and the Annual General Meeting, which took place during the

Conference. A full report on the proceedings of the Annual General Meeting appeared in the August issue of the *Journal*.

It was further reported that a meeting of the Liaison Committee took place at the Eastbourne Conference which was attended by representatives of all four Societies. As a result of this meeting, it was agreed to recommend to the governing bodies of the four societies that a working party be set up to explore the position of close liaison between societies. The Council appointed the President and Mr A. R. H. Tawn, with Mr D. S. Newton as an alternative representative, to represent the Association on the working party which would have to refer its recommendations but would have no power to bind the Association without reference to Council.

A report was also made on the 1973 Exhibition which had been an outstanding success, and a report appeared in the July issue of the *Journal*.

The arrangements for the 1974 Exhibition were briefly discussed, and Council agreed to the booking of the Empire Hall for 1976. Council wishes it to be widely known that the Association's next three exhibitions will take place in April 1974, April 1975 and April 1976, all at the Empire Hall, Olympia, London.

Information was received by the Council concerning the number of Members whose

1973 subscription had not yet been received and whose names would be removed from the Register of Members in accordance with the Articles.

Council was pleased to learn that sale of Part 7 of the Manuals "Works Practice" were still progressing satisfactorily. The papers, together with the discussions, from the Eastbourne Conference will be published in the September/December issues of the *Journal*.

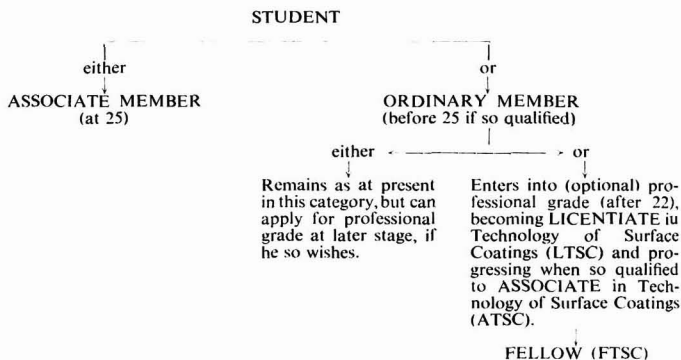
Council received reports from the Jordan Award Committee and the Professional Grade Committee, and took particular note that at least one Polytechnic intended to organise courses which would help young Members reading for licentiate-ship.

Council received information from the various Sections, and was pleased to accept an offer by Dr W. Carr (CIBA-GEIGY Ltd.) to present a paper on behalf of the Association at the forthcoming convention of the Federation of Societies for Paint Technology in November, thus ensuring that an Association paper would be presented at each of the other three societies' conferences in the next session.

There being no other business, the President thanked all members for their attendances and declared the meeting closed at 3.44 p.m.

Professional Grade for Ordinary Members

The innovation of the Professional Grade has proved to be most successful, as evidenced by the impressive list of names in the December issue of the *Journal*. As stated when the Grade was introduced, the main emphasis is on younger Members at the Licentiate level, and the following diagram shows the suggested progression of a Student (up to 25 years of age).



Note: At present there is no restriction on Students up to 21; between 21 and 25 a certificate from employer or college confirming the course being taken is required. For the convenience of potential applicants, full regulations for admission are shown below.

Regulations for admission to the Professional Grade

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

A. Licentiate

1. Shall be an Ordinary Member of the Association and have been an Ordinary Member or Student of the Association for not less than one year.
2. Shall have attained the age of 22.

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

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

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

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

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

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

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

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

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

B. Associate, being already a Licentiate

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

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

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

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

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

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

C. Associate, not already a Licentiate

EITHER

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

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

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

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

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

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

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

OR

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

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

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

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

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

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

D. Fellow

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

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

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

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

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

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

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

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

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

The fees payable with applications are as follows:

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

Application

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

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

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

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

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

The dissertation should be preceded by a short summary and commence with a

brief introduction and some account of the current state of knowledge. Where practicable it should follow the general format of a paper in *JOCCA*.

The dissertation may be a review of a subject, a theoretical treatment, descriptive of practical work or a combination of these. It must indicate that the candidate has a

reasonably wide and up-to-date knowledge of his chosen subject and understands the basic scientific principles underlying it, and that he is able to think critically and constructively.

Where practical work is described, some attempt should be made to draw theoretical conclusions or to form some provisional

hypothesis, together with an outline of what further work would be required to confirm the views put forward or further to advance the knowledge of the subject.

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

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

Length: Text should be approximately 5,000 words.

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

Optional Professional Grade for Ordinary Members

The Professional Grade Committee has issued a further list of admissions to the Professional Grade. The full list showing the Sections to which the Members are attached is given below.

Fellow in the Technology of Surface Coatings (FTSC)

Brooks, Leo James (*London*)
Jolly, Anthony Charles (*Manchester*)
Moll, Ivor Stuart D'anvers (*Manchester*)
Piggott, Kenneth Elliot (*South African*)

Associate in the Technology of Surface Coatings (ATSC)

Calder, Robert Malcolm (*Auckland*)
Formanek, Leopold
(*General Overseas—Czechoslovakia*)
Spargo, Robert (*Auckland*)

Register of Members

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

Ordinary Members

BOULTER, COLIN JOHN, Fishbun Printing Ink Co. Ltd., 94 St. Albans Road, Watford, Herts. (*London*)
BYRNS, ARTHUR ROBIN, "3 Sisters," Berrydel Avenue, Somerset West, CP South Africa. (*South African*)
CLAUSEN, HANS CHRISTIAN, 301 Acutt Avenue, Durban North, Natal, South Africa. (*South African*)
COUGHLAN, THOMAS NOEL, "Ashleaf," Iona Road, Mayfield, Cork, Ireland. (*Irish*)
DAVIS, CECIL EWART, 14 Seymour Gardens, Surbiton, Surrey, KT5 8QE. (*London*)
DUMVILLE, JOHN ALFRED, Worsdall Chemical Co. Ltd., Sole Street, Cobham, Kent. (*London*)
FANTHOM, ROBERT STEPHEN, BIP Chemicals Ltd., Popes Lane, Oldbury, Warley, Worcs. (*Midlands*)
FROHNSDORFF, COLIN HERBERT, BSc, MSc, Bradbury Wilkinson & Co. Ltd., New Malden, Surrey. (*London*)
GROVER, COLIN DAVID, BSc, 31 Melody Road, Biggin Hill, Westerham, Kent. (*London*)
HACKETT, PHILIP PATRICK, 9 Glenwood Close, Maidstone, Kent. (*London*)
HAMILTON, ALEXANDER JOHN FOX, 18 Ridlands Rise, Limpsfield Chart, Surrey. (*London*)
HARRISON, MARTIN ROY, BSc, 9 Almond Close, Crawley, Sussex, RH11 8ED. (*London*)
JAMES, THOMAS GERARD, 16 Wellmount Park, Dublin, 11. (*Irish*)
JARMANY, HENRY, PhD, Research Department Crown Paints, Darwen, Lancs. (*Manchester*)
KNEISSL, UDO, 22 3rd Street, Roodepoort-North (Tvl) South Africa. (*South African*)
LANDRETH-SMITH, IAN NIGEL, 27 St. Clair Avenue, Port of Spain, Trinidad, West Indies. (*General Overseas*)
LOCKYER, DENNIS BRIAN, 105, Leipoldt Street, Ridgeway, Johannesburg, South Africa. (*South African*)
MORGAN, PETER WILLIAM, 16 Upton Road, Bexley Heath, Kent, DA7HAQ. (*London*)
MCCLEMENT, DAVID ALEXANDER, 2 Torphin Place, Kirkcaldy, KY26JG, Scotland. (*Scottish*)
MCCRAE, JAMES MCGEACHIE, PhD, BSc, ARIC, 9 Merrick View, Stewarton, Ayrshire, Scotland. (*Scottish*)

MC ELWEE, ANGUS DAVID, BSc, 51 Forest Drive, Kloof, South Africa. (*South African*)
NIEMANDT, ANTHONY PHILIP, ProLux Paints, Box 3704, Alroag, Alberton, South Africa. (*South African*)
PECK, ROBIN ARTHUR, Reeves & Sons Ltd., Lincoln Road, Enfield, Middx. (*London*)
PHILLIPS, JOHN ROWLAND, 21 Old House Road, Balsham, Cambs. (*Manchester*)
POTGIETER, HARTHMAN ECKHARDT, BSc, PO Box 9099, Port Elizabeth, South Africa. (*South African*)
SCHONE, HANS-JOACHIM, Talse Bay Paints, PO Box 65, Strand, Cape, South Africa. (*South African*)
SINGER, IVOR, BSc, Tioxide International Ltd., 10 Stratton Street, London, W1. (*London*)
SMITH, BRIAN JAMES, LRIC, 48 Chiltern End, Westrees Park, Ashford, Kent. (*London*)
TANNER, ANTHONY EDWARD, 57 Wood Street, Mitcham Junction, Surrey. (*London*)
TAYLOR, RICHARD ANTHONY JOHN, LRIC, 27 Barton Road, Sutton-at-Hone, Kent. (*London*)
TONON, JUAN CARLOS, Aristobulo del Valle 7400, Sante Fe, Argentina. (*General Overseas*)
RAYNER, ALBERT HENRY, 15 Boughton Avenue, Hayes, Bromley, Kent, BR2 7PL. (*London*)
ROBINSON, ROBERT GRANT, BSc 45 Howick Road, Blenheim, New Zealand. (*Wellington*)
WILLIAMS-WYNN, David Ernest Arthur, PhD, MSc, FRIC, 15 Melrose Circle, Westville, Natal. (*South African*)

Associate Members

KIERSANDT, ROLF, 101 Buxton Heights, Firdale Avenue, Tamboerskloof, South Africa. (*South African*)

Registered Students

HITCHINS, CHRISTOPHER ROBERT, c/o W. G. Hitchins, PO Box 13, Renwick, New Zealand. (*Wellington*)
LANGLEY, MICHAEL CHARLES, Polycell Products, PO Box 3744, Airole, South Africa. (*South African*)
LYNCH, GERARD PAUL, 87 Todholm Terrace, Paisley, Scotland. (*Scottish*)
ROSS, PETER ROBERT, 12 Gullane House, Shetland Road, Bow, E3. (*London*)

News of Members

Dr R. H. Leach, an Ordinary Member attached to the London Section, has been appointed director responsible for special projects and development for Fishburn Printing Ink Company Limited. Dr Leach was previously operations director for the company.



Dr R. H. Leach

Mr R. L. Sorensen, an Ordinary Member attached to the General Overseas Section, has been appointed Director of Corporate Development for Printing Developments Incorporated, the graphic arts marketing subsidiary of Time Incorporated, New York.

Mr J. A. Banks, an Ordinary Member attached to the Manchester Section, has been appointed Manager of the Plastics Division of Victor Wolf Limited. He will be responsible for both the commercial and the technical activities of this new division, with emphasis on the pvc industry.



Mr J. A. Banks

Mr B. Green, an Ordinary Member previously attached to the London Section but now attached to the Overseas Section, has returned to Trinidad to take up an appointment as Senior Chemist with Sissons Paints Limited, a subsidiary of the McPherson Group for which Mr Green has been working in England.

He was awarded the London Section's prize for Paint Technology for the 1971-72 session and has recently been awarded a certificate from the East Ham College of Technology for "Industrial administration and works organisation for chemists."

Newcastle Section

The British Titan Cup

The twelfth annual tournament for the British Titan Cup was played on Saturday 30 June 1973 over the Hexham Golf Course. The competition, a four ball better ball against bogey, was won jointly by A. Bridgewood of Laporte Industries Limited and H. Fuller of Tioxide International Limited. The matches were played

in dry and sunny conditions although, as is often the case at Hexham, the wind was a little naughty.

The cup was presented by the Newcastle Section Vice-Chairman, Mr K. V. Hodgson, who also took part in the competition. A friendly stapleford competition held during the afternoon was won by J. G. Bell and J. Rankin.



Mr A. Bridgewood (left) and Mr H. Fuller, joint winners of this year's British Titan Cup

Reunion Dinner for past and present Members of Council

Council has decided this year to hold a Reunion Dinner for those Members who have served on Council at any time, in place of the biennial Past Presidents' Dinner. Notices were despatched at the end of July to all those known to have served on Council. The Dinner will take place on Wednesday 17 October 1973 at the Cafe Royal, 68 Regent Street, London W1, at 6.30 for 7.00 p.m., and informal dress will be worn.

The price of the ticket, to include drinks at the reception, dinner, wines and liqueurs, will be £6.00 (inclusive of VAT). Past Presidents, Past Honorary Officers, Honorary Members and Founder Member have been invited as guests of the Association, as they would have been invited to a biennial Dinner. All other past and present Members of Council must send the necessary remittance with their completed application form. Any Member with service on Council, who has not received an application form and wishes to do so, should write to the Director & Secretary at the Association's offices.

Forthcoming Events

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

September

Tuesday 11 September

West Riding Section: "Radiation Curing" by Mr A. G. North of Cray Valley Products, to be held at the Griffin Hotel, Leeds at 7.30 p.m.

Tuesday 18 September

Manchester Section: Symposium on "Wallcoverings" at the University of Manchester Institute of Science and Technology, Sackville Street, Manchester.

Friday 21 September

Irish Section: "Pollution, its causes and effects" A speaker from the Institute for Industrial Research and Standards, to be held at the Clarence Hotel, Dublin at 8 p.m.

Midlands Section: Ladies Evening 7.00 p.m. Westbourne Suite, Botanical Gardens, Birmingham.

Scottish Section: Wine and Cheese Party, at a venue to be announced.

Wednesday 26 September

Manchester Section—Student Group: "Powder coatings" by Mr N. H. Seymour of Sterling Varnish Co. Ltd. to be held at the Manchester Literary and Philosophical Society at 4.30 p.m.

Thursday 27 September

London Section: Chairman's lecture, Great Northern Hotel, King's Cross. This will be a forum on the future of the London Section.

Thames Valley Section: "Modern developments in Europe on wood-finishing" by Herr Anskinovitch and Dr Schwarz of Glasurit, to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks. at 7.00 p.m.

Friday 28 September

Bristol Section: Ladies Evening. "Colour in the home" by Mr R. G. Stay, Berger Paints Ltd. to be held at the Royal Hotel, Bristol, at 7.15 p.m.

Midlands Section: "Recent developments in radiation curing" D. R. Bailey (Donald Macpherson & Co. Ltd.) to be held in the Birmingham Chamber of Commerce and Industry, PO Box 30, 75 Harborne Road, Birmingham B15 3DH at 6.30 p.m.

October

Monday 1 October

Hull Section: "Polyacrylates in emulsion paints" by a speaker from Allied Colloids, to be held at the Dorchester Hotel, Beverley Road, Hull at 7.00 p.m.

Thursday 4 October

Newcastle Section: "Painting of wooden joinery," A. F. Sherwood, Paint Research Station to be held at the Royal Turks Head Hotel, Newcastle.

Thames Valley Section—Student Group: "Aerosols" by Mr Southby of Aerosols International Ltd., Downmill Road, Bracknell, to be held in the main Lecture Theatre, Slough College at 4 p.m.

Friday 5 October

Hull Section: The Annual Dinner/Dance will be held at Cave Castle, South Cave, Hull.

Saturday 6 October

Scottish Section—Eastern Branch, and Student Group: Joint Meeting on "Dispersions of titanium dioxide in modern paint making" by Mr Derek Craig of Toxide International Ltd., in the Lady Nairn Hotel, Willowbrae Road, Edinburgh, at 10.30 a.m., followed by lunch and the annual skittles match at the Abercorn Inn.

Tuesday 9 October

Manchester Section: Joint Meeting with the North Western Branch of the Institute of Printing. "Change in printing ink technology and the influence of Europe" by Mr G. Whitfield, Mander Kidd (UK) Ltd., at the Cottons Hotel, Manchester Road, Knutsford, at 7.00 p.m.

West Riding Section: "The performance of wood primers" by Mr P. Whiteley of Building Research Station, to be held at the Griffin Hotel, Leeds, at 7.30 p.m.

Thursday 11 October

Midlands Section—Trent Valley Branch: "Paint manufacturing techniques" by Mr B. L. Lucas, Joseph Mason & Co. Ltd., Derby. Venue to be announced later.

Scottish Section: Visit to Planetarium of Glasgow College of Nautical Sciences.

Tuesday 16 October

London Section: "Some aspects of technical training" by Mr G. Birtles, at the Great Northern Hotel, King's Cross at 7.00 p.m.

Wednesday 17 October

Manchester Section—Student Group: "Instrumental colour measurement" by Mr Bravay of Berger Paints, to be held at the Manchester Literary and Philosophical Society at 4.30 p.m.

Scottish Section—Eastern Branch: "Advances in Polymers" by Dr I. Soutar, Heriot Watt University, Edinburgh, to be held at the Carlton Hotel, North Bridge, Edinburgh, at 7.30 p.m.

Thursday 18 October

London Section—Southern Branch: "Problems in the painting of yachts" by a speaker from Campell & Nicholson Ltd., at the Pendragon Hotel, Southsea, at 7.00 p.m.

Friday 19 October

Irish Section: "The use of extenders in titanium dioxide" by Mr M. Hart, Croxton & Garry, to be held at the Clarence Hotel, Dublin, at 8 p.m.

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

Midlands Section: "The current status and role of amino resins in surface coatings" by R. McD. Barrett BIP Chemicals Ltd., to be held in the Birmingham Chamber of Commerce and Industry, PO Box 30, 75 Harborne Road, Birmingham B15 3DH, at 6.30 p.m.

Thursday 25 October

Thames Valley Section: "Printing inks in the seventies" by Mr G. H. Hutchinson, Croda Polymers Ltd., at the Beech Tree Hotel, Beaconsfield, at 7.00 p.m.

Friday 26 October

Bristol Section: "The testing and performance of flame retardant paints" by Mr F. C. Adams of the Building Research Establishment, Fire Research Station, to be held at the Royal Hotel, Bristol, at 7.15 p.m.

Programme for the 1973-74 Session

London Section, Southern Branch

1973

Thursday 18 October

"Problems in the painting of yachts" by a speaker from Camper & Nicholson Ltd., to be held at the Pendragon Hotel, Southsea, at 7.00 p.m.

Thursday 22 November

"Web offset printing" (including a film) by Mr J. D. Freeman, of the News Centre, Portsmouth, to be held at the Pendragon Hotel, Southsea, at 7.00 p.m.

1974

Tuesday 19 February

"Wall and ceiling decoration" by Mr J. T. Ikey, Iotex Products (Decorations) Ltd., to be held at the Pendragon Hotel, Southsea, at 7.00 p.m.

Tuesday 18 March

"Commercial brewing practice" by Mr D. Thomasson, Whitbread Wessex Ltd., to be held at the Pendragon Hotel, Southsea, at 7.00 p.m.

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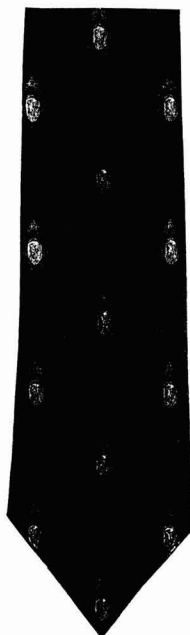
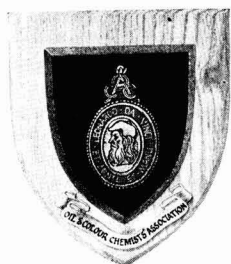
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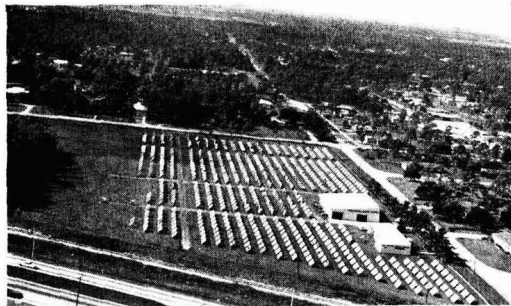
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