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OIL & COLOUR CHEMISTS' ASSOCIATION

CURRENT PUBLICATIONS

Introduction to Paint Technology

The Association's extremely popular book "Introduction to Paint Technology", which forms an excellent introduction to the whole field of surface coatings and related technologies and which has already sold over 16 000 copies, has now been completely revised and updated in a new fourth edition. An important addition in this latest printing is a glossary of most of the chemical and technical terms used in the text: this has been included for the benefit of those readers who require a less superficial knowledge of paint formulation. A brief account of the history and development of chemistry and chemical symbols, formulae and equations is included as an introduction to the glossary itself.

Price: £5.00 (Registered Students of the Association £2.50).

Paint Technology Manuals: Part Seven "Works Practice"

The Association has sponsored the publication of a series of Paint Technology Manuals primarily intended for students and those entering the industry but already acknowledged to be invaluable to the practical man within the industry. "Works Practice" was originally published in the *Journal* as a series of Student Reviews. The volume is concerned with the practical aspects of making paints. In view of the fact that there has been little published material on this topic, a fairly broad coverage is attempted, including factory layout and organisation, paint and media manufacturing processes, legal aspects and safety precautions.

Price: £3.00

Paint Technology Manuals: Part Three "Convertible Coatings"

Part Three of the Association's series of Paint Technology Manuals has been reprinted as a second edition in 1972 and a limited number of copies are still available.

Price: £2.80

Ultraviolet Polymerisation

A volume, bound in limp covers, comprising papers presented at a symposium of the Newcastle Section of the Association in 1975 and subsequently published in the *Journal*.

Price: £5.00

Conference Preprints

The Association organises an international Conference every two years and preprints of the papers presented are prepared for delegates. The complete bound set of papers for both the 1973 and 1975 Conference are still available and offered for sale at £5.00 for each volume.

The 1973 Conference was held at Eastbourne with the theme "Towards 2000" and the bound set of preprints for this Conference includes 16 papers all dealing with various aspects of the surface coatings industry towards the year 2000.

The 1975 Conference, which was held at Scarborough, had as its theme "Performance of surface coatings—does reality match the theory?" and 17 papers were presented.

Many of the papers presented at these two Conferences were later published in various issues of the *Journal of the Oil and Colour Chemists' Association* and back issues are usually available (see below).

The Association's 1977 Conference will be held once again at Eastbourne; further details are given on page 40 of this issue.

History of the Association

As part of its 50th Anniversary celebrations the Association published in 1968 "A Fascinating Story—the History of OCCA 1918-1968". This is an illustrated book comprising 89 pages and bound in hard covers.

Price: £1.50

Journal of the Oil and Colour Chemists' Association

The *Journal of the Oil and Colour Chemists' Association* (*JOCCA*) is taken each month by thousands of chemists, technologists, and other personnel in the paint, printing ink and allied industries, as well as by numerous science libraries and organisations engaged in research and the supply, production and application of surface coatings, throughout the world. Copies of the *Journal* are now distributed each month to more than 80 countries.

Price: £25.00 ($50.00) per year

Back issues

Most back issues from recent years and a considerable number of earlier issues, dating back in some cases to the earliest volumes, are available for purchase from the Association's offices at the current *Journal* cover price. The availability of particular issues can be obtained on request from the Association's offices.

Price: £2.50 ($5.00) each

Consolidated Indexes

Earlier this year the Association published a Consolidated Index, by subject and by author, of all the Transactions and Communications which appeared in the *Journal* during the previous 10 years (January 1966 to December 1975).

This invaluable "quick reference" guide to the literature of the surface coatings industries has been produced in the international A4 size and it can, therefore, be bound with copies of the *Journal*. (Binding facilities for *JOCCA* are available through J. S. Wilson—see page 472 of December 1976 issue.

Copies are still available of the Consolidated Indexes for the years 1918-1945, 1946-1955 and 1956-1965.

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JOURNAL of the
OIL AND COLOUR CHEMISTS' ASSOCIATION

Contents   **Vol. 60 No. 4**   **April 1977**

Transactions and Communications

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

Adhesion and failure of organic coatings*

By W. J. McGill

Department of Materials Science, University of Port Elizabeth, PO Box 1600, Port Elizabeth 6000, South Africa

Summary

The forces acting when a liquid is in contact with the surface of a solid are described. The effects of viscosity and the roughness of the surface on the rate of spreading are considered. The fundamental principles thus established are applied to explain the reasons for various types of adhesion failure.

Keywords

Properties, characteristics, and conditions primarily associated with:

  materials in general

   interfacial tension
   wettability
   surface tension
   contact angle
   viscosity

  dried or cured films

   adhesion

  structures or surfaces being coated

   roughness

La perte d'adherénce des revêtements organiques

Résumé

On décrit les forces qui entrent en vigueur lorsqu'un liquide se trouve en contact avec la surface d'un corps solide. On considère les effets sur la vitesse d'étalement qu'exercent la viscosité du liquide et la rugosité de la surface. Les principes fondamentaux sietablis sont utilisés pour expliquer les raisons pour les divers types de perte d'adhérence.

Haftung und Schäden organischer Beschichtungen

Zusammenfassung

Die Kräfte werden beschrieben, welche bei Berührung einer Flüssigkeit mit der Oberfläche eines Festkörpers in Aktion treten. In Betracht werden die Auswirkungen von Viskosität und Oberflächenrauheit auf die Ausbreitungsgeschwindigkeit gezogen. Die auf diese Weise gefundenen fundamentalen Prinzipien werden zur Erklärung der Ursachen für die verschiedenen Arten von Haftungsfehlern verwandt.

Introduction

If two atomically smooth planar surfaces are brought together in a perfect vacuum they would adhere, at least initially, because of van der Waals' forces acting between atoms in the two surfaces. Interfacial forces based on van der Waals' forces alone, will far exceed the real strength of either the one or the other adhering material, with the result that interfacial separation will never occur when purely mechanical means are used to separate a pair of materials that have achieved complete interfacial contact. Van der Waals' forces are operative over very small distances and for atoms to adhere as suggested above very close contact is essential. Two real surfaces would not adhere if they were simply brought together since surface roughness would prevent the necessary intimate contact being achieved over more than a few isolated points, leading to the formation of a weak boundary layer of air at the interface. The materials would readily part as a result of a break in this weak boundary layer. It is these weak boundary layers which are responsible for the failure of two materials to adhere.

To enable one surface to match the topography of another more closely, most films or coatings on solid surfaces are formed from the fluid state, either from the melt or from solution. The adherence of a film depends critically on the ability of the coating fluid thoroughly to wet the surface rather than on the fundamental nature of intermolecular forces of attraction across the interface. It is, therefore, important to consider the two factors which control wetting *viz.* the thermodynamics and the kinetics of wetting. Most examples of poor adhesive performance result from incomplete wetting caused by failure of the system to attain thermodynamic equilibrium in the time available before the coating sets. Hence, a weak boundary layer is formed which leads to failure of the coating to adhere to the substrate.

Frequently, the most important contribution of groups capable of more energetic interactions with the solid substrate will be their influence in lowering the interfacial free energy of the system and thereby facilitating wetting. Thus improved performance results not so much from improved adhesion as from improved wetting. Mention was made earlier of van der Waals' forces between surfaces being more than sufficient to ensure adherence. This does not imply that other molecular forces do not participate in bonding, but by the time such interaction occurs molecular contact must have been established and van der Waals' forces must already be operative.

Chemisorption or bonding via chemical reaction thus occurs after adhesion is achieved. Furthermore, since it is believed that van der Waals' forces alone are sufficient to prevent interfacial separation, further strengthening of the bond does not have any positive influence on the mechanical strength of the joint. It may, however, increase the permanence of the joint by retarding the destruction of the interfacial region by moisture.

Some aspects of the thermodynamics and the kinetics of wetting may be considered in greater detail. Thermodynamics is concerned with the energy available to bring about interfacial contact between the phases, whilst kinetics deals with the rate of this wetting process.

Thermodynamics of wetting

Contact angle

The effects of intermolecular forces at the interface between the solid and the coating can most easily be considered in terms of the surface energies of the two phases. The surface energy of any phase may be defined in terms of the work necessary to create a surface—i.e. the excess free energy associated with molecules in the surface compared to molecules in the bulk. This surface energy is given the symbol γ which is called surface tension.

A drop of liquid on a smooth surface will have a certain contact angle θ with the surface. Fig. 1 shows the surface tensions operating at the point of contact between liquid, solid, and vapour or the air. When $\theta = 0$ the liquid is said
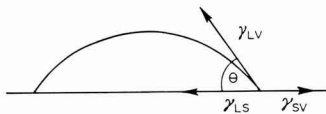

Fig. 1. Surface tensions at edge of drop

to wet completely the solid and will spread freely over the surface at a rate determined by the viscosity of the liquid and surface roughness. When $\theta > 0°$ the liquid is non-spreading. Every liquid wets every solid to some extent i.e. $\theta \neq 180°$. Thus there is always some adhesion between any liquid and solid. Since the tendency for a liquid to spread increases as θ decreases, the contact angle is a useful inverse measure of spreadability or wettability. It can be shown that the energy τ available to bring about wetting is:

$$\tau = \gamma_{LV} \cos \theta$$

and since γ_{LV} is a property solely of the liquid, the property which characterizes the effect of solid-liquid interaction in promoting wetting is $\cos \theta$.

Low and high energy surfaces

In discussing the wetting of surfaces and the thermodynamic approach to adhesion, it is helpful to define two extremes of the specific surface free energies of solids. This subdivision is a matter of convenience and has no exact physical meaning.

(i) *High energy surfaces.* Hard solids have surface free energies ranging from 5000 to 500 ergs cm^{-2}, the higher values being associated with solids of greater hardness and higher melting points. Examples of high surface energy solids are metals, metal oxides, nitrides, silica

and glass, although glass can often be classed as intermediate between high- and low-energy surfaces.

(ii) *Low energy surfaces.* In contrast, soft solids with much lower melting points have surface free energies of less than 100 ergs cm^{-2}. Examples are waxes, most organic polymers, and, in fact, most organic solids. The surface free energies of all liquids (except liquid metals) are less than 100 ergs cm^{-2}.

Because of the comparatively low surface energies of organic and most inorganic liquids they would be expected to spread freely on solids of high surface energy, since this would result in a decrease in the free energy of the system. On the other hand, the surface free energies of liquids and of low energy solids are rather similar, and systems showing non-spreading are most commonly found among such combinations. Whenever a liquid does not spread on a high surface energy solid, it can be shown that an adsorption process has taken place before or during contact of the liquid and solid and, as a result, a coating has been deposited on the surface making it behave like a low energy surface. The phenomena of cissing and crawling in paints and varnishes where the wet film appears to retract around certain areas exposing the surface underneath, are examples of surface contamination. This is most frequently due to a greasy and dusty surface. It often occurs when varnishes are applied over high gloss paint coatings which tend to exude oily constituents. It is also possible for a fluid to spread very rapidly across a clean high energy surface forming an oriented adsorbed monolayer which has a critical surface tension less than that of the liquid itself. The liquid will now exhibit a relatively large contact angle on the high surface energy solid, the surface having been converted into a low energy surface by the oriented monolayer. Such liquids that are unable to spread on their own oriented monolayer are said to be autophobic. This phenomenon has been observed for octanol-1, octanol-2, 2-ethylhexanol-1, trichlorodiphenyl, and tri-o-cresyl phosphate on platinum, stainless steel, glass and fused silica. Another situation which is somewhat akin to this phenomenon will be discussed later where, in a coating comprising a mixture of liquids, one component may be preferentially adsorbed and move across the surface ahead of the bulk of the coating material. If equilibrium is not established before the viscosity increases, i.e. the coating dries, poor adhesion results due to inadequate wetting by the coating fluid.

Another example of poor wetting of a high surface energy solid is found in the application of certain esters to glass or fused silica. Hydrolysis by adsorbed water molecules results in the formation, at the surface, of two hydrolysis products, and the one with the longer average lifetime of adsorption will eventually coat the surface as a close-packed monolayer. If this monolayer has a critical surface tension of wetting which is less than the surface tension of the ester, non-spreading behaviour is observed. In this case the ester is unable to spread on a monolayer of its own hydrolysis product.

If a lacquer used to coat a tin plate contains dispersed oily gel-like particles these may deposit on the tin plate forming nuclei around which the lacquer tends to retract, particularly during stoving operations.

Critical surface tension of wetting

The spreading of liquids on low and high energy solid surfaces has been mentioned, and in this regard a most useful parameter is the critical surface tension of wetting γ_c, which can be used to determine whether a liquid will or will not wet a solid. It has been observed experimentally that, for any

particular solid, a plot of the cosine of the contact angle for each of a homologous series of organic liquids against their surface tension, results in a straight line plot as shown in Fig. 2. This has lead to the useful concept of the critical surface tension of wetting, defined by the intercept of the extra-polated straight line relationship between $\cos \theta$ and γ_{LV} with a line drawn at $\cos \theta = 1$, i.e. at $\theta = 0°$ where complete wetting would occur.
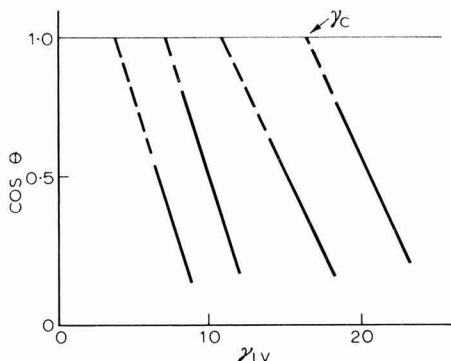

Fig. 2. Critical surface tension of different solids

If instead of a series of homologous liquids a variety of non-homologous liquids are used, the experimental points are found to cluster closely together in a narrow band. The intercept of the lower surface tension side of the band with the line drawn at $\cos \theta = 1$ is now defined as the critical surface tension of the solid. Although the exact position of this intercept can be less precisely determined than with a homo-logous series of liquids it is a much more useful parameter since the critical value obtained is a characteristic of the solid surface only. Clearly, any liquid with a surface tension below γ_c will spread freely across the surface.

Values for the critical surface tension of a number of plasticizer-free polymeric solids are given in Table 1. These values are in agreement with predictions based on surface composition and packing density. Since, for all the polymers listed in the table, γ_c is well below the surface tension of water ($72·8 \times 10^{-3}$ Nm^{-1}), all are hydrophobic.

Table 1

Some values for critical surface tension

Polymer	$\gamma_c \times 10^{-3}$ Nm^{-1} (at 20°C)
Polytetrafluoroethylene	18.5
Polyvinyl fluoride	28
Polyethylene	31
Polystyrene	33
Polyvinyl alcohol	37
Polymethyl methacrylate	39
Polyvinyl chloride	40
Polyhexamethylene adipamide (nylon)	46

With this background most of the spreading properties of liquids on solids can be explained. These can be generalised as follows: every low energy liquid will spread freely on a smooth high energy surface. This is so unless the film adsorbed by the solid is so constituted that it acts as a low energy surface, having a surface tension less than that of the liquid.

Kinetics of wetting

The rate of wetting of a surface depends chiefly on two factors: (i) liquid viscosity and (ii) surface roughnesss, which exerts an effect on wetting through its influence on the resistance to flow.

(i) Viscosity

The rate at which a liquid can spread over the surface of a solid is affected by the energy available to bring about wetting, which is dissipated in overcoming viscous friction within the liquid. It has been proposed that the wetting rate must be a function of $\gamma_{LV}/L\eta$ where η is the liquid viscosity and L is a temperature independent constant. Both θ_{LV} and η are temperature dependent. In the case of coating fluids η is also dependent on time and viscosity will increase with time as setting occurs. Complete wetting must, therefore, occur before the viscosity has increased to a point beyond which spreading becomes difficult.

(ii) Roughness

Surfaces are never smooth, and various kinds of surface irregularity can be distinguished but, generally speaking, surface roughness does not markedly retard the displacement of air which can be achieved with a liquid of sufficiently low surface tension. However, penetration of the fluid into surface pits will also depend on the radii of curvature of the pits, and if pits are small or deep, or of an irregular shape, they may be covered by a viscous fluid without it reaching down to the bottom of the crevice. Penetration into pot shaped pits (Fig. 3) will depend on fluid viscosity, but penetration into inkwell shaped pits is problematical. Improvements in adhesive performance resulting from sand blasting are usually ascribed to a cleansing of the surface and the removal of a weak bound-ary layer, but it has been suggested that such treatment could also have an important influence on the topography of the surface, by replacing sharp edged or deep pits by shallow open structures that can more readily be filled by a fluid. The size and shape of surface interstices is probably an important factor, since adherence in general seems to be strongly dependent on the smallest scale roughness exhibited by the substrate. Entrapped air may be responsible for macroscopic non-wetted areas (where fluid viscosity is high), but it is sug-gested that the entrapment of air in very small interstices is not important, since most organic films are sufficiently per-meable for the permanent gases to diffuse into the bulk coating within a few minutes. Adsorbed water should similarly permeate into the coating with even greater readiness. Wetting rates could be appreciably altered if a film of water several layers thick has to be displaced.
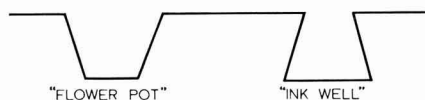

Fig. 3. Surface pits

When void formation is not completely averted its dele-terious effect on adhesion depends on the shape and size of the bubble and on its position. For example, in a horizontal surface carrying a top coating a bubble might rise, depending on fluid viscosity. The effect on film performance of a bubble

in various positions as indicated in Fig. 4 decreases in severity from *a* to *c*. It is sometimes also possible for bubbles to be squeezed out of surface positions with excess fluid when such fluid is displaced along the surface. This is probably the most common method of their removal in adhesive joints.
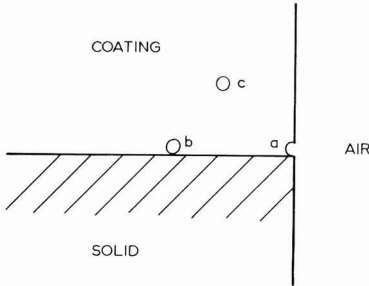

Fig. 4. Bubbles in a film

Virtually all coatings contain a mixture of materials and this complicates the situation as far as wetting is concerned. There are several ways in which the presence of more than one component can influence wetting. A preferentially ad-sorbed component can spread on the interface well ahead of the bulk fluid, leading to a change in surface energy resulting in increased contact angles and a decrease in wetting rates. Phase separation may occur with the more fluid phase wetting the substrate and filling interstices. In time equilibrium must be restored with the more viscous phase. However, where a solvent evaporates wetting rates will decrease as fluid viscosity increases and problems may arise if wetting by the polymer component has not been achieved by the time solvent has been lost to such an extent that a visco-elastic coating fluid has formed. Incomplete wetting by the polymer would lead to local areas where adhesion between coating and substrate was absent, and stress concentrations would develop around these areas if the coating reaches its glass transition tempera-ture before all the solvent has evaporated.

If a surface is rough, but the formation of voids does not occur, a roughness factor can be defined as:

$$r = \cos\phi/\cos\theta$$

where φ is the apparent contact angle on the rough surface. The roughness factor r is the ratio of the real surface area to the apparent geometric area and for carefully machined or ground surfaces has a value of 1·5 to 2·0 or greater. There are several important consequences of surface roughness, its effect on wetting being dependent on the value of the contact angle θ. For $\theta < 90°$ the apparent angle should decrease with surface roughening i.e. the liquid should wet the surface more readily. Most organic liquids exhibit contact angles of less than 90° with clean metal surfaces and the liquid will spread more readily on a roughened surface. Similarly, to obtain the best adhesion on some plastics surfaces, notably polyesters and polyalkylene chlorides, it is advantageous to first carry out blasting with a fine grit to increase r and hence to decrease φ. However, when $\theta > 90°$ as is the case with water on a smooth paraffin surface, surface roughening leads to an increase in φ causing spreading to become more difficult. The problems associated with the inclusion of air at the solid-liquid interface, discussed earlier, should be borne in mind when considering rough surfaces, as such inclusions are one of the major causes of inferior adhesive performance, as will be seen later.

Technology of wetting

There are two general modifications that are commonly used to improve wettability. Either the surface energy of the liquid can be lowered by means of a surfactant or the solid surface can be modified by various treatments. The function of a surfactant is simply to lower the surface tension of the liquid to below the critical surface tension of the solid. The main function of surface pretreatment for metals is to remove surface contaminants which lower the critical surface tension of the solid to below the liquid surface tension and to remove loose or poorly adhering films (oxides) which may act as weak boundary layers. Surface treatment of polymer surfaces is more varied. For polymers, such as polyvinyl chloride and polyethyleneterephthalate where γ_c is close to 40×10^{-3} Nm^{-1}, thorough cleansing of the surface is usually sufficient to ensure good wetting, but polyalkylenes, for which γ_c is of the order of $30–50 \times 10^{-3}$ Nm^{-1}, require oxidation of their surfaces by flaming, high voltage spark discharge, or immersion in concentrated oxidising acids. This treatment increases the critical surface tension of the polymer slightly, but it is claimed that in polyethylene, for example, such treatment results in surface crosslinking and the removal of a weak boundary layer of low molecular mass material. Improved adhesive performance thus results not so much from improved wetting as from the absence of the weak layer.

Strength of adhesive bonds

The strength of joints

The most important problem in the science of adhesion is the strength of the final joint between the two materials. In the surface energy approach as originated by Dupré a hundred years ago, it was assumed that the strength is determined by the molecular attractions between external molecules of the two layers. The work needed to peel a length of ribbon from its base was interpreted as a measure of the intensity of molecular adhesion. This is totally incorrect for a number of reasons. The main reason for the assumption being wrong is the fact that rupture never takes place at the interface betweeen two materials; one of the two materials making up the ad-hesive joint breaks down. Failures exactly along the adherend-coating interface were often postulated in the past, but as far as is known, if they occur at all, they occur so rarely as to be of no practical importance. Whenever a careful examination of the fracture surfaces has been made, it has always been found that a little of one material has adhered to the other surface and vice versa. Another reason why the interpretation is wrong is that a certain amount of deformation of the materials normally occurs before failure of the joint and some of the energy applied was, therefore, dissipated in producing this deformation. In many cases a distinct boundary may not exist, as in polymer coatings applied to polymer substrates where a certain amount of intermixing occurs across the interface. In other instances, the transition zone between adherend and coating is stratified, a stratum of metal oxide being interposed between the metal substrate and a polymeric coating. No sharp frontier exists between the metal and its oxide, firstly because the oxide is nonstoichiometric, and secondly, because the oxide and metal lattices have different lattice parameters and are likely to be distorted for a depth of several atoms on both sides of the imaginary frontier.

Improbability of adhesion failure

Rupture will start at the point where local stress exceeds local strength. Suppose that rupture does start in adhesion, i.e. at a point between a surface atom of the adherend and the coating.

To continue "in adhesion" the crack must extend between the next pair of adherend and coating atoms. Alternatively, the crack may grow by advancing between two atoms of adherend or between two atoms of the coating. If these 3 paths in this two dimensional model are equally probable, the probability of the crack continuing in the phase boundary for 2 atoms is $1/3$ and the probability of it continuing there for $(n + 1)$ atoms is $(1/3)^n$. When $n = 10$ the probability becomes 1 in 59 000 that a phase separation 11 atoms long will occur. This calculation can be refined in a number of ways, all of which decrease the probability of interfacial detachment. If each atom occupies an approximately cubical space there are 3 paths between adherend and adherend and 3 between coating and coating for each path between adherend and coating. Hence the probability of a crack growing along the interface for a distance $(n + 1)$ atoms is $(1/7)^n$. When $n + 1 = 7$ the probability is below 1 in 100 000. A second refinement concerns the molecular nature of polymeric coatings. Since it is easier to separate two molecules of a polymer than to break a chain, any crack which reaches a space between two molecules will advance in this space until a space between two other molecules is reached, and it is clear that the crack will practically never return to the interface. Thirdly, since intermolecular forces between dissimilar materials are greater than those between similar materials, the probability of a break along the paths described above is not equal, but is higher for paths leading into one of the two materials.

Thus, the breaking strength of a joint is not important in proper joints and failure takes place in a material rather than between materials. This does not mean that the various adhesion tests, such as the peel strength test, are meaningless, but what it does mean is that such tests measure adhesive performance in a given situation and not the adherence between two different surfaces.

Adhesive performance

Failure and weak boundary layers

It has been shown that failure in adhesion often occurs close to the phase boundary and is then incorrectly interpreted as "failure in adhesion". Such failure may be due to the presence of a weak boundary layer or to high stress concentrations near the interface. Normally, when two materials "do not stick", it means that a weak boundary layer has been formed at the interface, and there are seven classes of weak boundary layers that can occur, depending on the source of the weak material. Where weak boundary layers are absent, the system is referred to as a proper joint, whilst improper joints contain weak boundary layers. The weakening material in the boundary layer may originate from the following sources:

(i) the air
(ii) the coating
(iii) the adherend
(iv) the air and the coating
(v) the air and the adherend
(vi) the coating and the adherend
(vii) all three phases (air, coating, adherend).

Examples of all these classes of weak boundary layers are known, but only a few examples will be mentioned briefly. Weak boundary layers of the first class are very common and always occur when the coating fluid does not wet the adherend sufficiently leaving air pockets between the two materials after solidification of the coating. A zone of weakness is introduced with the air bubbles acting as points of stress concentration, whilst the true area of contact between coating and adherend is reduced.

When the coating contains impurities soluble in the molten coating or in the coating solution, but insoluble in the solidified coating, these may separate as another phase during solidification, and whenever this phase forms between the adherend and the bulk coating, a weak boundary zone is established. When polyethylene solidifies in contact with certain metal surfaces numerous crystallisation nuclei are formed, leading to the growth of rod-like structures, rejection of low molecular mass material into the bulk, and the formation of a zone of high strength, but on non-nucleating surfaces low molecular mass material is rejected to the interface where it constitutes a zone of weakness.

Impurities on the surface of an adherend frequently act as weak boundary layers. There are many conflicting opinions as to how a particular surface must be cleaned so as to allow a given coating to be bonded to it. It should be remembered that the object of cleaning a surface is twofold: (i) to remove material which may render the surface non-wettable and (ii) to remove material which may lead to the formation of a weak boundary layer—the removal of well adhering surface contaminants is not necessary. For example, Al_2O_3 need not be removed from the surface of aluminium metal for polymer coatings since no polymer can rupture the natural oxide film, but the presence of aluminium powder, which is chemically similar to the bulk adherend, cannot be tolerated. Likewise, the need for painting to be done in a dust free atmosphere is well recognised. Traces of phthalate ester rolling lubricant persist on stainless steel even after repeated abrasion, and are sometimes responsible for poor paint adhesion. If a metal is chemically treated, on drying its surface is covered with a layer of oxide or salt. Abrasion leaves abrasive powder on the surface. Thus pretreatment should be seen, not as a cleaning operation, but as a process during which strong boundary layers are substituted for weak ones. Statements to the effect that it is easier to attach rubber to steel, brass, cast iron and aluminium alloys than to stainless steel, bronzes and magnesium alloys simply mean that satisfactory cleansing methods for the rubber-metal systems in the latter category are not known.

The environment in which a coated article is used can lead to the formation or disappearance of weak boundary layers. For example, a coating may become loose because of the migration of water along the adherend-coating interface, and in this respect it is usually helpful to protect the edges of a coating. Blistering and flaking are well known phenomena, where water or other volatile material is released to the interface from wood, especially from knots in the wood. Zinc and zinc oxide react with the organic acids present in many coating materials to form a layer of friable and water-sensitive soaps at the metal/paint interface. Initially adhesion of the coating is usually satisfactory, but a steady deterioration occurs with time.

Setting

Setting of a coating occurs by one of three main mechanisms: (i) by cooling, (ii) by solvent removal or (iii) chemical reaction. One important condition for the solidification of a coating that will perform well is that the rate of nucleation is large compared to the rate of crystal growth. Under these conditions the film is more likely to be continuous and, therefore, strong than when crystal growth is fast from a few nuclei, since voids are then likely to develop between crystals. Those polymers

that do crystallize do not form separate crystals, but have crystallites linked together via their amorphous surrounds, with the result that polymers form good coatings. There are two main devices for retarding crystal growth in an attempt to improve coatings. One method consists of adding impurities that concentrate at the crystal-liquid boundary, and the other device is to increase fluid viscosity.

Setting of a fluid coating is usually accompanied by a volume decrease. For example, in polyethylene the solid to melt volume ratio may be 0·80 to 0·86 and in polystyrene 0·95. These volume changes may lead to stress concentrations at the interface, or to the formation of voids. Stresses will concentrate around voids and how seriously these effect the film will depend on their position in the film, as indicated earlier. The magnitude of such defects, which lead to the introduction of a weak boundary layer, depends on the stage at which the glass transition temperature is reached during the setting process. If the bulk of the volume contraction occurs before the glass transition temperature is reached, considerable stress relief is possible. Fillers may be used to reduce volume contraction on setting.

Moisture may also enhance or reduce internal stresses in a film, as in the case of wood which can swell or shrink in different environments. The use of rubbery or flexible coatings will facilitate stress relief in these cases.

The most common cause of internal stresses is the difference in the coefficient of thermal expansion between the coating and the base material.

Conclusion

Fluids have low surface energies and will spread freely on high surface energy solids unless contact between the solid and the fluid results in the formation of a low surface energy film on which the fluid cannot spread. Fluid viscosity and surface roughness are the two most important factors in determining the rate at which a fluid will spread across the surface and, since fluid viscosity increases as setting occurs, thermodynamic equilibrium must be achieved before the viscosity becomes too great to allow spreading into crevices or stress relief to occur. Failure in adhesion will not occur in "proper" joints, and a break in the weaker material (usually the coating) will occur under extreme mechanical loads. The failure of coatings to adhere well can be ascribed to the introduction of weak boundary layers. Interfacial separation will not occer. Likewise, the inability to achieve coatings that perform well on certain substrates is due to failure to eliminate weak boundary layers.

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To underline the importance of this viscosity stability in hot melt applications, tests were made using a hot melt adhesive formulation of equal parts of ethylene-vinyl acetate copolymer, paraffin wax and rosin. Gum, wood and hydrogenated wood rosins were compared with Sylvachem products. Blends using SYLVAROS-80 and PRIMAREX-80 showed no inc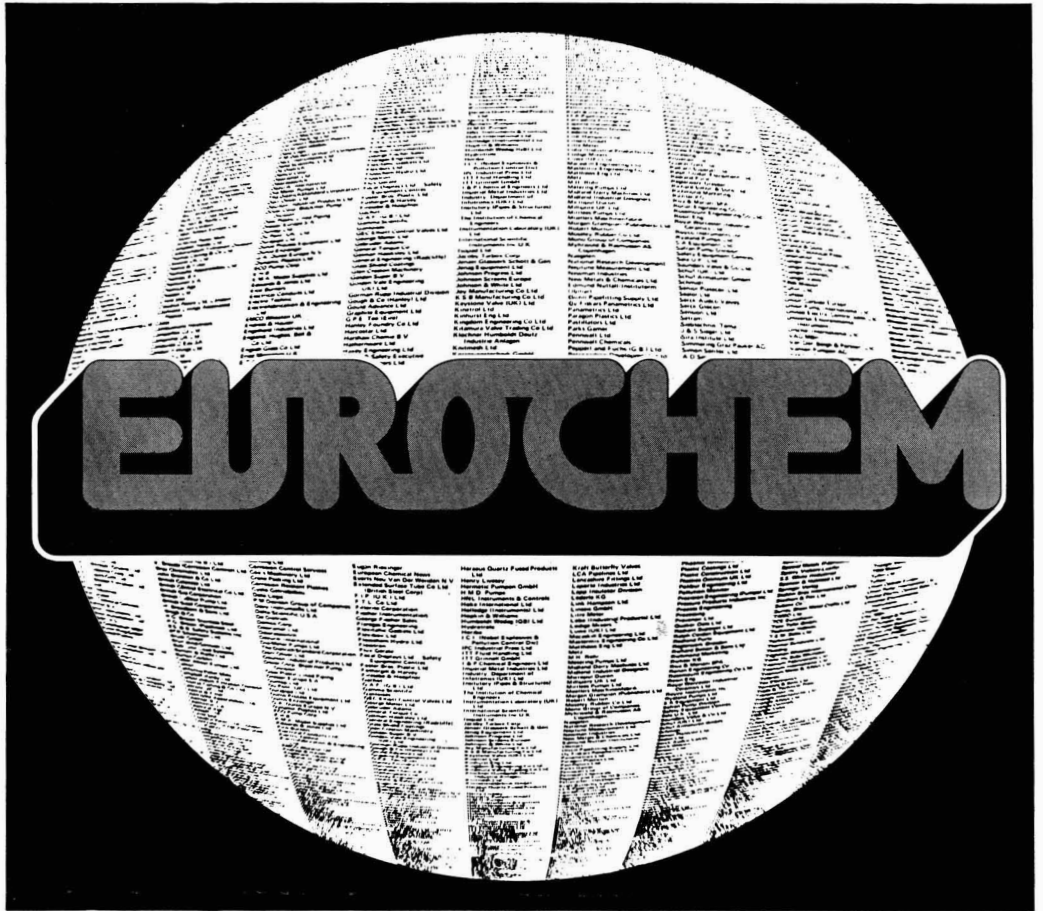rease in viscosity after three days at 200°C, compared with 84-89% increases for gum and wood rosins. After six days, the gum and wood rosin blends had gelled, but the PRIMAREX-80 blend had even lower viscosity than that made with hydrogenated wood rosin.

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Techniques for the investigation of the biodeterioration of paints developed at CSIRO, Australia

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Summary

The work on the formulation of fungus resistant paints carried out by the author and his co-workers at the CSIRO Division of Building Research at Highett, Victoria is summarised and the conclusions which could be drawn from the project are stated.

Keywords

Types and classes of coating and allied products

  fungus resistant paint

Processes and methods primarily associated with analysis, measurement or testing

  accelerated testing
  exposure testing

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

  fungus

Raw materials: biologically active agents

  fungicide

Techniques pour étudier la biodégradation de peintures mises au point par la CSIRO, Australie

Résumé

On donne un résumé des travaux concernant la mise au point des formules de peintures résistantes à végétation mycélienne, effectués par l'auteur et ses collaborateurs à la Division of Building Research, CSIRO à Highett, Victoria, et l'on constate les conclusions que l'on saurait tirer de ce projet.

Von der CSIRO, Australien entwickelte Techniken zur Untersuchung des biologischen Abbaus von Anstrichmitteln

Zusammenfassung

Eine Zusammenfassung der vom Author und seinen Mitarbeitern in der CSIRO Division of Building Research in Highett, Victoria, geleisteten Arbeit zur Entwicklung von Vorschriften für pilzbeständige Anstrichfarben, und die Schlüsse, welche dar aus gezogen werden können.

Introduction

Refs. 1-3

Mould growth on painted surfaces is of frequent occurrence in humid tropical areas, but it can also occur in temperate climates under special conditions[1]. Any description of an assessment technique is not of much use unless the reasons for its development are discussed, its justification is demonstrated and a comparison is made with competing systems of evaluation; or, to put it differently, every method of testing has limitations regarding the forecasts which can be made from the results of the test, and these limitations can be best appreciated if something is known about the development of the method.

Disfigurement by mould growth leads to more frequent redecoration than would otherwise be necessary, and this is expensive. In Australia alone (1970 prices) it is estimated that between Aus. $15 to 30 million in material and labour are spent annually in areas susceptible to mould growth. If the service life of coatings could be increased in these areas by only 10 to 20 per cent by the use of more fungus-resistant paints, considerable savings could be made. No data are available to make an estimate on a world scale, but the problem of disfigurement by mould is bound to become more and more important as the standard of living rises in the large areas of the world which have climates conducive to mould growth.

The economic importance of the production of paints with high fungus resistance is, therefore, evident. One way of increasing the resistance is by incorporating fungicides or fungistatic agents into the formulation. Paint manufacturers are inundated with calls from suppliers offering compounds which are claimed to have the desired effect. How can the user—that is, the paint technologist—judge the veracity of these claims?

It would be desirable, of course, to have a method by which decision could be reached in a few days or weeks about the suitability of a formulation The laboratory procedure of Vicklund and Manowitz[2] has been used for this purpose (VM procedure), but after many years of comparing the forecasts of these tests with actual performance it has become quite clear that there is no worthwhile correlation. The reason for this is obvious and it is astonishing that anyone should have expected a correlation to exist. However active a fungicide may be initially, it can be of practical value only if it is reasonably persistent in the paint film. Yet the stability of the fungicide is not measured by this test at all. Attention to this elementary

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fact would have saved a great deal of disappointment, labour and expense.

When the futility of the original VM test for the fungus resistance of paint in the field became obvious, many variations of the procedure were tried. Some workers abandoned the simple procedure of the VM test altogether and constructed tropical chambers of large sizes, apparently in the belief that the failure of the VM test to predict behaviour in service was due to the unnatural conditions under which mould growth took place. Others tried weathering the paint films in a weatherometer under some arbitrary defined conditions, before exposing them in the test chamber[3]. This procedure was apparently chosen in the belief that if the fungicidal activity was still present after this test, it was proof that the fungicide was still there to impart some fungal resistance. This, of course, is true. However, such a one-point test is of little value and this can be seen quite simply. Suppose that two fungicidal formulations, after exposure in a weatherometer, are found to retain some properties of fungal resistance. The conclusion that both have an equivalent mould resistance is not reliable because one fungicide may be very stable, whereas the other might have largely decomposed, leaving just enough to show some residual resistance to fungus growth. Paints formulated with the less stable compound will have a short service life, whereas coatings which incorporate the other compound will last much longer, and this difference can be found only by analysing for the remaining active compound. Every compound will disappear from the paint film in time, because it must be slightly soluble or volatile in order to enter the body of the developing spore, but the critical point is the rate at which it disappears from the film. It is for this reason that the author recommends an investigation into a fungicide's stability under various climatic conditions as part of the test system to measure its efficiency.

As the VM test proved so unreliable for making forecasts about mould growth on coatings for both exterior and interior use in the field, more and more stress was laid on the method of exposing painted panels at sites favouring profuse mould growth. However, this was also very unsatisfactory for two reasons.

Firstly, panels (15 × 30cm) were exposed and the growth of mould observed, but there was rarely any investigation of the behaviour of the additive used. The fundamental question why mould appeared was rarely asked, and even when the subject was raised, the answer was simply a speculation without much fact to support it. Did the fungicide disappear from the paint film by decomposition, volatilisation or leaching? Was the appearance of mould due to the basic instability of the formulation, or to its adaptation to a new environment? The author believes it is justifiable to describe this method as "hit and miss".

Secondly, nobody had ever seriously bothered to ascertain whether extrapolation from such small panels to large surfaces on houses was justified. The author's trials at Lae and Rabaul in New-Guinea showed that this was not the case. The proposed system of tests for a fungicidal paint will now be described.

Step 1. Testing of a chemical compound for fungicidal activity

Refs. 2, 4, 5

Before any chemical investigation on a compound recommended as a fungicide can be started it has first to be ascertained whether that compound has any activity at all.

For this purpose the VM test[2], the test proposed by Hendey[4] or any of the many proposed variations can be used. Various conclusions can be drawn from the outcome of such a test. For instance, paints containing zinc oxide do not show any appreciable improvement in their fungus resistance if examined with the VM procedure. It might be concluded from this that the addition of zinc oxide to a paint does not increase its mould resistance under any circumstances. Paints containing zinc oxide are reported to have been used with some success in humid tropical areas. More importantly, paints containing zinc oxide have been tested in the dwellings built by the "Housing Commission Victoria" and have been found very useful. The same zinc oxide paints were without effect, however, in the much more favourable conditions for mould growth prevailing in a brewery[5].

If, on the other hand, the tests had been carried out by Hendey's method some activity would have been found: but this, in its turn, does not mean that these formulations would have been effective under all conditions.

Once it is certain that the compound has some fungicidal activity the next step can be taken.

Step 2. Persistence of the active compound in the coating under various climatic conditions

Refs. 6-17

The stability of fungicides has been studied by brushing the paints containing the fungicides and the corresponding blanks on polyethylene-terephthalate polyester films (30 × 15cm) which were attached to both sides of asbestos cement panels and exposed at Lae in New Guinea, facing north at an inclination of 45 degrees. After the desired time of exposure, a specimen was cut off from the film and sent to Melbourne for analysis. In this way, it was possible to observe the same paint film for whatever time was deemed necessary.

The loss of fungicide from the paint film should be studied in the type of paint in which the compound will be used in service. It is not valid to extrapolate, for instance, from the loss of fungicide in a gloss alkyd enamel to the loss from a latex paint. Barium metaborate (BMB) is quickly leached from the latter, but is reasonably stable in the former. Experiments showed that more than 90 per cent BMB was lost at Lae, New-Guinea from a latex paint film in less than 10 months, but there was only a 45 per cent loss from an alkyd gloss enamel in 18 months[6].

An analytical work curve was plotted showing loss of fungicide against time. With the procedure which has just been described, it may take, with a reasonably stable fungicide, two to three years to reach a decision whether the formulation could be useful. However, this part of the investigation can be considerably accelerated by exposing paint films on stainless steel panels in a weatherometer. The degradation of paint films was studied in a xenon arc weatherometer[7] and, in the author's opinion, the conditions used should be as follows: shade temperature 30 to 35°C, relative humidity 75 to 85 per cent, and the percentage spraying time during the total exposure period should be about the same as the percentage rainfall during day-time. Analysis has to be carried out at suitable intervals of, say, one to three weeks, depending on the stability of the compound which is being investigated. To find the factor of acceleration between the weatherometer and the humid tropical climate at Lae, it is advisable to expose in the weatherometer one of the fungicides tested on the site at Lae and compare the disappearance there with the one in the

accelerated test. For instance, trichloromethylthiopthalimide[8] (NTP) would be suitable for this.

Interior paints

From the tests described, it is not possible to draw safe conclusions on the suitability of a formulation for interior decorations. On interior surfaces, of course, losses will not be caused by the radiation of the sun on the paint film. The losses under these conditions may be due to volatilisation, reaction of the fungicide with trace components of the atmosphere, and leaching due to washing of the walls, or heavy condensation. For instance, traces of hydrogen-sulfide (less than 0.03 microgramme per litre) can react with heavy metals, such as mercury to form mercuric sulfide, which produces a stain[9].

In order to gain a better idea of the behaviour of a fungicide in a paint film, its persistence was determined in a fog room at $20°C$, in a constant temperature room at $20°C$ and 65 per cent relative humidity, and in a hot room at $38°C$ and 25 per cent relative humidity. This gives additional characteristics to judge whether a given formulation is likely to be effective in some contemplated environment. For instance, for NTP it has been found that the loss was 5 per cent at $20°C$ after 12 months, but 25 per cent at $38°C$ after the same time. It would, therefore, be wise to avoid the use of this compound in circumstances where the temperature would reach $40°C$ or more.

The analytical method used for the determination of the persistence of a fungicide must be simple. It is pertinent to illustrate what is meant by a simple technique. For instance, it has been proposed by Taylor[10] that the loss of mercury from a paint film should be measured by a radioactive method. This method may be the simplest one for those who have facilities to prepare radioactively tagged compounds and the necessary equipment for carrying out the measurements, but it certainly would not be a simple technique in the average paint manufacturer's laboratory. Two methods have been used to follow analytically the loss of a fungicide from a paint film:

1. If the compound contains a characteristic element or group, for example mercury, zinc, sulfur, a halogen or boric acid, then this is determined. The author has always used micro- or semimicro volumetric methods since these are quickest. For the "liberation" of some of the compounds in the paint films, combustion of the paint film in a Schoeniger oxygen combustion flask is of great use[11].

2. The second method is to extract the effective compound from the paint film with a suitable solvent and determine its ultraviolet spectrum. In this case, however, an extract of a blank paint film which has been exposed to the same conditions as the weathered film should be used for comparison.

The techniques used in the investigations for phenylmercury compounds[9,12,13] pentachlorophenol[14], N-trichloromethyl-thiophthalimide[14], salicylanilide and paratoluenesulfone-amide[15], copper hydroxyquinolate[16] and barium metaborate[17] have been described and probably could serve as models for similar cases.

Step 3. Testing in the field

Ref. 18

The previous two steps make it possible to decide which of the fungicides has a reasonble chance to be effective in a paint formulation. It is now required to demonstrate with field tests that the chosen formulation is adequate. It was concluded from steps 1 and 2 that coatings containing BMB and NTP

should have a satisfactory fungus resistance. Indeed, panels coated with paints containing the two compounds showed a higher fungus resistance than the rest of the formulations which had been tried. However, it was doubted whether an extrapolation from small-scale tests could be made to field applications. The growth of mould depends very much on local environmental conditions, which include food supply, humidity, temperature and combinations of these. On an exposure site these conditions will be the same over large areas, whereas on an actual structure they may change from one small area to another.

It was decided to carry out the tests[18] on two houses—one at Lae and one at Rabaul. Both houses were constructed of weatherboard and had a history of mould growth. The houses were cleaned of mould growth by washing with a dilute hypochlorite solution (approximately two per cent active chlorine) which was hosed off after about half an hour. In order to obtain a representative result, the walls and eaves (the underside of the corrugated galvanised iron roofing) of the houses were painted in a series of strips approximately 0.4m wide using paints A, B, C, D at Lae and paints A, D, E, F at Rabaul. The paints on the strips were varied in a pre-determined random pattern. The mould growth was assessed under the eaves, at the top, middle and bottom of the walls at approximately three monthly intervals for up to two years, after which the assessments were made less frequently, usually at intervals of 7 to 9 months.

The assessments employed a numerical scale of 0 to 9 to indicate the degree of mould growth, 0 meaning mould absent, and 9 total obscuration by the mould. Assessments were judged subjectively. To give an idea what is meant by this numerical side, a photograph of the middle of the scale is shown in Fig. 1.
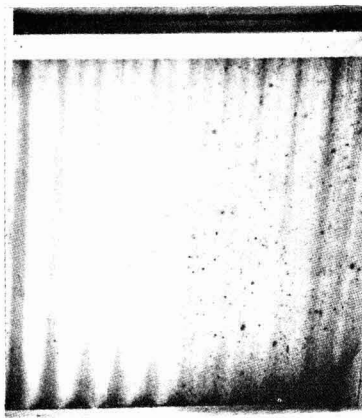

Fig. 1. Mould growth under eaves of test house in Lae. Left, mould rating 0; right, mould rating 5

Table 1 gives the formulation of the paints which were used. The degree of mould growth on the four walls of the house in Lae[5] at the end of 23 months is shown diagrammatically in Table 2.

Assessment rate *1* indicates a probable trace of mould, rating *2* is considered more significant, since it implies that mould is definitely established even if the intensity is still low. Probably, most occupants would like their houses to be cleaned or repainted if this degree of mould growth is reached and, therefore, a rating of *2* or more was considered a failure.

Table 1
Main ingredients (parts by weights) of paints used on the houses at Lae and Rabaul

Paint		Resin* solution	Rutile TiO$_2$	Barium metaborate	N-trichloromethyl-thiophthalimide (% of total paint solids)
Lae:	A	51	32.4	—	—
	B	51	32.4	—	2.5
	C	51	14	14	—
	D	51	14	14	2.5
Rabaul:	A	51	32.4	—	—
	D	51	14	14	2.5
	E	51	18.5	10.5	2.5
	F	51	23.0	7	2.5

*Long soya bean pentaerythritol alkyd solution (70% NVM)

Table 2
Assessment of test strips on house in Lae, 23 months after painting

North-west or street wall

Strip code	C	D	B	A	B	C	A	D	A	B	D	C	D	A	C	B	D	B	A	C	A	D	C	B	C	A	B	D	B	C	D	A
Under eaves	1	0	5	6	6	0	7	0	6	6	0	1	0	6	0	5	0	5	6	0	6	1	2	5	0	7	6	1	6	0	0	6
Wall: Top	3	1	1	5	2	4	5	2	4	1	0	2	0	3	3	1	0	0	4	3	4	1	3	2	4	5	3	2	1	3	1	4
Middle	1	0	w	w	w	w	4	1	3	w	w	w	w	w	w	d	d	0	1	3	1	w	w	w	w	w	w	w	w	w	2	1	0	5
Bottom	0	1	w	w	w	w	3	2	3	w	w	w	w	w	w	d	d	0	2	3	0	w	w	w	w	w	w	w	w	w	2	1	0	4

South-east or rear wall

Strip code	C	D	B	A	B	C	A	D	A	D	C	D	A	C	B	D	B	A	C	A	D	C	B	C	C	A	B	D	B	C	D	A
Under eaves	2	1	6	7	6	0	6	0	—	—	0	0	5	0	3	0	3	5	0	0	0	0	4	3	—	—	—	—	—	—	—	—
Wall: Top	3	0	0	4	0	2	4	0	3	0	1	0	3	1	0	0	0	3	0	2	0	0	1	1	0	1	w	0	1	0	w	1
Middle	1	0	0	d	d	0	2	0	w	w	w	w	w	w	w	0	0	w	w	w	w	w	w	w	w	w	0	0	0	0	0	0	0	1
Bottom	1	0	0	d	d	0	0	0	w	w	w	w	w	w	w	0	0	0	3	0	3	0	1	0	1	1	0	0	0	0	0	0	0

←———————— VERANDA ———————→   ·———————— WATER TANKS ————————·

←—— HWS ON ROOF ——·

South-west or driveway wall

Strip code	C	D	B	A	B	C	A	D	A	B	D	C	D	A	C	B	D	B	A	C	A	D	C	B
Under eaves	0	0	5	6	5	0	6	0	6	0	0	0	0	—	—	—	—	5	5	0	7	0	0	7
Wall: Top	2	0	0	4	0	3	4	0	3	0	0	1	0	2	0	2	0	0	2	1	3	0	2	0
Wall: Middle	0	0	1	w	w	w	w	0	4	0	0	1	0	1	0	1	0	w	w	w	w	w	w	1
Wall: Bottom	0	0	2	w	w	w	w	0	5	0	0	1	0	1	0	0	1	0	4	2	4	1	2	2

←———— BAMBOO BLIND ————·   ·———— WATER TANK ————·   ·———— BAMBOO BLIND ————·

North-east wall

Strip code	..	..	..	C	D	B	A	B	C	A	D	A	B	D	C	D	A	C	B	D	B	A	C	A	D	C	B	C	D
Under eaves	..	..	..	0	0	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	5	1	0
Wall: Top	..	..	..	3	0	1	3	1	3	4	1	3	0	1	2	0	3	2	1	1	0	4	3	4	1	3	0	2	1
Wall: Middle	..	..	..	0	0	4	4	w	1	5	0	4	2	0	1	0	4	1	2	0	w	w	w	w	w	2	2	0	0
Wall: Bottom	..	..	..	0	0	3	3	2	0	4	0	4	2	0	0	0	4	0	3	0	0	4	2	4	0	2	2	0	0

·———— BAMBOO BLIND ————·

Ratings from 0, no mould ; to 7, heavily infested

A—Gloss enamel paint   B—Formulation containing N-trichloromethylthiophthalimide   C—Formulation containing barium metaborate   D—Formulation containing N-trichloromethylthiophthalimide and barium metaborate

w = window   d = door

Table 3
Summary of assessments on house at Lae

Wall	Position on wall	7 months				10 months				13 months				16 months				20 months				23 months			
		A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
NW	Under eaves	4	3	0	0	4.5	2.5	0	0	5	4	0	0	6	4.5	0	0	6	5	0	0	6.3	5.5	0.5	0.25
	Top	0	0	0	0	2.5	0	0	0	2.5	0	0.5	0	3.5	0	1.5	0	3.5	1	2	0.5	4.3	1.4	3	0.8
	Middle	0	0	0	0	0	0	0	0	3	0	1	0	4	1	1	0	3.5	1.5	0	0	3.8	1.5	1	0.3
	Bottom	0	0	0	0	3	0	0	0	3	1	0	0	3	2	0	0	3	2	0	1	3.3	2	0.5	0.8
SE	Under eaves	1	0	0	0	2.7	0.6	0	0	4	2.5	0	0	4.5	4	0	0	4.5	4.5	0	0	4.6	4.4	0.3	0.3
	Top	0	0	0	0	1.3	0	0	0	2.5	0	0	0	2.5	0	0	0	2.5	0	1	0	3	0.3	1	0
	Middle	0	0	0	0	0.4	0	0	0	1	0	0	0	0	0	0	0	1	0	0	0	1	0	0.3	0
	Bottom	0	0	0	0	0.6	0	0	0	1	0	0	.0	1	0	0	0	1	0	0	.0	1.2	0	0.5	0
SW	Under eaves	4	0	0	0	4	0	0	0	4	1.4	0	0	5	2	0	0	6	4	0	0	6	4.4	0	0
	Top	0	0	0	0	1	0	0	0	2	0	0	0	2	0	0	0	3.5	0	1	0	3	0.3	1.5	0
	Middle	0	0	0	0	1.3	0	0	0	2	0	0	0	2.5	0	0	0	2.5	1	0	0	2.5	0.8	0.3	0
	Bottom	0	0	0	0	1	0	0	0	2.5	0	0	0	3	0	0	0	3	0.5	1	0	3.5	0.8	1	0.6
NE	Under eaves	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	1	1	0	0	1	1	0.2	0
	Top	0	0	0	0	1	0	0	0	1	0	0	0	2	0	0	0	2.5	0	1.5	0	3.5	0.5	2.6	0.7
	Middle	0	0	0	0	0	0	0	0	2	1	0	0	3	1	0	0	4	2	0.5	0	4.3	3	0.7	0
	Bottom	0	0	0	0	2.7	0.7	0	0	3.5	2	0	0	2.5	2	0	0	4	1.5	0.5	0	3.8	2	0.6	0

Wall	Position on wall	27 months				32 months				36 months				43 months				47 months				54 months			
NW	Under eaves	6.5	5.6	0.5	0.3	5.5	4.5	1.4	0	5.2	4.7	1.7	0.5	5.5	5	1.8	0.6	6.3	6.1	2.1	1.9	6.4	5.4	2.8	2.6
	Top	4.5	1.4	3.1	1.0	5	2	3	0.6	4.7	2.4	2.7	0.75	5.3	3.6	3.2	1.7	5.2	3.9	3.1	2.4	4.5	3.4	3	3.3
	Middle	3.8	1.5	1.0	0.5	3.5	0.5	0.7	1	3.3	2.5	0.7	1.2	3.6	2.5	1.3	3.2	3.7	2	2	3.7	4.2	4	2.3	4
	Bottom	3.5	2.0	0.3	0.8	3	0.5	0.3	1	3	2.5	0.3	1.2	3	2.5	1	2.5	2.7	2.5	1.3	3.2	3.8	3	2.6	3.5
SE	Under eaves	4.6	4.6	0.3	0	5	3.3	2	1.2	5	4	2	2.6	6	6.4	2.8	3.3	6	7	2	2.8	6.5	5.2	4.1	5.7
	Top	2.8	0.3	0.8	0	2.8	2.4	0.8	0.4	3	2	1	0.5	3.4	1.4	1.6	1	2.9	2	1.8	1.7	3	2.0	1.6	2.0
	Middle	1.0	0	0.3	0	0	0	0.8	0	0	0	0.3	0	0	0.3	0.3	0.5	0	0.3	0	0.3	1	0.7	0	1
	Bottom	1.2	0	0.4	0	1	0	0.3	0	1.1	0	0	0	2	1	0.5	1.5	1	0.3	0.2	0	2.3	1.8	1.1	2
SW	Under eaves	6.0	4.4	0	0	6	5	0.4	0	6.2	5.2	1.2	0.8	7.2	6.6	1.2	1	7.2	6.2	1.8	1.6	6.5	5.4	2	2.4
	Top	3.0	0.3	1.5	0	3	0.2	2	0	3.5	0.5	2.3	0.2	4.7	2.3	3.5	1.3	4.3	2.7	2.7	2	5	3.0	3.8	3
	Middle	2.5	1.0	0.1	0	2	0.9	1.0	0.4	2.5	0.7	1	0.2	3	2	1.3	1.3	2.5	2	0.7	1.2	3.5	2.8	1.7	2
	Bottom	2.8	1.4	1.0	0.5	2.5	1.2	1.2	0.7	2.5	1.4	1	0.5	3.2	1.2	1.4	1	2.2	1.8	1.2	1.2	3.8	1.6	1	2.2
NE	Under eaves	0.8	1.0	0.1	0	1	1	0.3	0.3	1	1	0.3	0.1	1.3	1.3	0.3	0	1.7	1.5	0.9	0.4	4	1.8	1.7	2
	Top	3.5	0.5	2.6	0.7	3.7	0.7	2.1	0.3	4	0.9	2.7	0.7	5	2.5	3.1	0.2	4.3	3.2	3.1	2.0	5	3.3	2.3	2.5
	Middle	4.3	2.3	0.8	0	3.2	1.7	0.7	0.3	3	2	0.7	0.2	3.5	2.5	0.2	0.2	3.5	2.8	1	0.9	5	3.5	2	2.5
	Bottom	4.2	2.2	0.7	0	3.6	2.2	0.7	0.7	2.3	1	0.3	0.5	2.3	1.3	0.1	0.1	2.8	1.7	0.7	0.5	4	3	2.3	2.9

Table 4
Summary of assessments on house at Rabaul

Wall	Position on wall	3.5 months				7 months				11.5 months				17 months				21 months				30 months			
		A	D	E	F	A	D	E	F	A	D	E	F	A	D	E	F	A	D	E	F	A	D	E	F
W	Under eaves	1.7	0	0	0	2.6	0	0	0	4.7	0	0	0.6	6.6	0.8	1.2	2.5	7	2.5	3.0	4.2	6.7	3.0	3.7	4.9
	Top	1	0	0	0	2.7	0	0	0	4.6	0	0	0	5.8	0.8	1	1.5	6.4	2.2	2.4	3.3	6.2	2.7	3	4.8
	Middle	1.5	0	0	0	4	0	0	0	7	0	0	0.8	6.3	1.3	3.3	3.2	6.3	2.3	3.7	4.4	6.5	2.7	3.3	4.8
	Bottom	2	0	0	0	4	0	0	0	6.6	0	0.3	0.5	6.5	1.7	3.7	4.2	6.5	2.2	3.7	5	6.2	2.5	3.3	4.7
S	Under eaves	1.1	0	0	0	2.9	0	0	0	5.6	0	0	0.1	6	0.8	3	4	6.7	3.1	4.5	5.2	7.1	5.1	5.7	6.6
	Top	0.6	0	0	.0	2	0	0	0	4.5	0	0.1	0.1	5	1.5	1.5	2	6.6	2.5	2.5	3	6.7	4.3	4.4	5.6
	Middle	0.3	0	0	0	2.7	0	0	0	6	0	0.5	0.3	6	2.4	3	3.2	6.7	2.8	3.7	4.5	7.5	4.6	5	6
	Bottom	2.3	0	0	0	2.9	0	0	0	6.2	0.4	0.8	1.4	6.5	2.1	3	4	6.7	2.5	3.5	4.8	6.3	4.3	4.6	5.1
E	Under eaves	1.8	0	0	0	2.5	0	0	0	5.6	0	0.6	1	6	1.2	4.5	4.7	7.5	3.2	4.2	5	7.3	4.8	5.4	6
	Top	0.6	0	0	0	1.8	0	0	0	4	0	0	0	6	0.8	2.6	2.8	7	2	3.4	3.3	6	3.2	4.8	5.4
	Middle	0.5	0	0	0	2	0	0	0	4	0	0	0	6	0.7	3.8	3.3	7	1.7	4	4.8	6	3.3	5	5.4
	Bottom	1.5	0	0	0	2.3	0	0	0	5.4	0	0.2	0	6	1	3.2	3.5	6.6	1	3.4	3.8	6	3.4	4.6	5.3
N	Under eaves	1.4	0	0	0	2.8	0	0	0	5.3	0	0	0	6.3	0.3	2.6	3.3	7.2	2.6	4.1	4.9	7.3	3.7	5.3	5.4
	Top	0.4	—	0	0	2.5	—	0	0	5	—	0	0	6.5	—	2.8	2.6	7	—	3.3	3.6	6.7	—	4.7	6.5
	Middle	1.2	0	0	0	2.9	0	0	0	5.5	0	0.7	0.4	6.5	1.7	3.5	3.8	7.3	2	3.7	4.6	7	4	5.1	6.8
	Bottom	1	0	0	0	2.7	0	0	0	5.9	0.6	1.2	0.8	6.5	1.8	3.5	3.5	7.2	2.1	3.6	4.5	7	4	5.4	6.7

To facilitate interpretations of the results of the various assessments, the ratings over each strip have been added up and the sum so obtained divided by the number of strips. For example, on the north-west side there are eight *A* strips with a total rating of 50, or 6.3 per strip. The number 6 is a good indicator of how the section would look if it were painted with coating *A* only. Tables 3 and 4 give the results of the assessments for the houses in Lae and Rabaul.

To obtain a realistic appreciation of the test, it is necessary to show how many strips are included in each section. Clearly, if the number of strips is very small because of the presence of windows and doors, the conclusions which can be drawn are less reliable. It is also necessary to show how the

assessments vary in each section as this in its turn gives an indication as to the change in local environmental conditions favourable to the growth of mould. Tables 5 and 6 show this for the houses in Lae and Rabaul. The conclusions which can be drawn from such an approach are wide ranging.

1. The mould growth may depend, even at the same site, on both the orientation of the wall and the position of the coating on the wall. For example, on the north-west wall formulations *A* and *B* failed (assessment 2) under the eaves after seven months. Altogether, paint *B* does not perform significantly better than *A* in this position. Paint *B* is more fungus resistant, however, than *A* on the other parts of the structure.

Table 5

*Number of painted strips on each wall section at Lae,
and the variation in intensity of mould after 54 months*

| Wall | Position on wall | Total number of strips on section | | | | Paint | | | |
		A	B	C	D	A	B	C	D
NW	Under eaves	8	8	8	8	5,5,6,6,7,7,7,8	5,6,6,6,6,6,6,6	2,2,3,3,3,3,3,3	1,2,2,2,3,3,4,4
	Top	8	8	8	8	4,4,4,4,4,4,5,5	3,3,3,4 4,4,5,5	1,2,2,3,3,4,4,5	1,2,2,3,3,3,3,4,4
	Middle	4	2	3	4	4,4,4,5	3,3	1,3,3	3,3,5,5
	Bottom	4	2	3	4	3,4,4,4	3,3	1,3,3	2,3,4,5
SE	Under eaves	6	5	7	6	4,5,6,8,8,8	3,5,5,5,8	2,3,3,4 4 4,5	3,3,6,6,8,8
	Top	6	4	7	5	0,2,3,3,5,5	0,2,3,3	0,0,2,2.2,3,3	0,2,3,3,3
	Middle	2	3	2	3	0,2	0,0,2	0,0	0,0,3
	Bottom	4	5	5	4	1,2,3,3	1,2,2,2,2	1,1,2,2,2	1,2,2,3
SW	Under eaves	5	5	5	5	5,6,6,8,8	1,6,6,6,8	1,2,2,2,3	1,1,3,3,4
	Top	6	6	6	6	3,5,5,5,6,6	1,3,3,3,5,5	0,4,4,5,5,5	1,2,3,4,5,5
	Middle	2	4	3	5	2,5	0,2,2,3	0,2,3	1,1,2,2,4
	Bottom	3	5	4	4	2,3,5	0,1,1,2,4	0,1,1,2	1,2,2,4
NE	Under eaves	6	6	7	7	3,3,4,4,4,5	0,0,1,2,2,6	1,1,1,2,2,3	1,2,2,2,2,2,3
	Top	6	6	7	7	4,5,5,5,5,6	2,3,3,3,4,5	1 2,2,2,2,3,4	2,2,2,3,3,3,4
	Middle	4	4	6	6 ·	3,5,5,6	2,3 4,5	1,2,2 2,2,3	2,2,2,3,3,3
	Bottom	6	6	7	7	2,4,4,4,5,5	1,2,2,3,5,5	1,2,2,2,3.3,3	2,2,3,3,3,3,4

Table 6

*Number of painted strips on each wall section at Rabaul,
and the variation in intensity of mould after 30 months*

| Wall | Position on wall | Total number of strips on section | | | | Paint | | | |
		A	D	E	F	A	D	E	F
W	Under eaves	3	6	4	6	6,7,7	2,2,3,3,4,4	3,3,4 5	4,4,5,5,5,6
	Top	4	6	5	6	5,6,7,7	2,2,3,3,3,3	2.3,3,3,4	4,4,5,5,5,6
	Middle	3	3	3	5	5,7,7	2,2,4	2,3,4	4,4,5,6,6
	Bottom	4	6	4	6	5,6,7,7	2,2,3,4	3,3,4,5	4,4,4,5,5,6
S	Under eaves	8	8	9	8	7,7,7,7,7,7,7,8	4 5,5,5,5,6,6	4,5,6,6,7,7,7,7,7	5,6,7 7,7,7,7,7
	Top	7	8	7	7	6,6,6,7,7,7,8	4,4,4,4,4,5,5,5	4,4,4,4,4,5,6	5,6,6,6,6,6
	Middle	2	5	2	3	7,8	4,4,5,5,5	4,6	6,6,6
	Bottom	7	8	7	7	6,6,6,6,6,6,8	3,4,4,4,4,5,5,5	3,4,4,5,5,5,6	5,5,5,5,5,5,6
E	Under eaves	6	5	5	6	7,7,7,7,8,8	4,4,5,5,6	5,5,5,6,6	5,5,6,6,7,7
	Top	6	5	5	6	6,6,6,6,6,6	2,3,3,4,4	3,5,5,5,6	5,6,6,6,6,6
	Middle	4	3	4	5	6 6,6,6	2,2,5	3,5,6,6	5,5,5,6,6
	Bottom	6	5	5	6	6,6,6,6,6,6	2,2,4,4,5	3,5,5,5,5	5,5,5,5,6,6
N	Under eaves	10	10	10	10	7,7,7,7,7,7,8,8,8	3,3,3,3,3,4,4,4,5,5	4,5,5,5,5,6,6,6,6	4,5,5,5,5,5,6,7,7
	Top	4	0	7	5	6,7,7,7,	—	4,4,5,5,5,5,5	5,6,6,6,7
	Middle	6	3	7	7	7,7,7,7,7,7	4,4,4	5,5,5,5,5,5,6	5,6,6,7,7,7,7
	Bottom	10	8	10	9	7,7,7,7,7,7,7,7,7,7	4,4,4,4,4,4,4,4	5,5,5,5,5,6,6,6,6	6,6,6,7,7,7,7,7,7

The most suitable paints to combat fungal growth in Lae would be C or D, with the latter being marginally better. Mould growth on nearly all parts of the house could be avoided for 43 to 47 months.

2. In Rabaul, the coatings formulated for fungus resistance all performed well compared with the control paint, each taking three to four times as long to reach the criterion of failure (assessment 2). Reduction of the quantity of BMB by substitution with titanium dioxide produced a corresponding reduction in the fungal resistance of the paints, although the drop in performance between compositions E and F was not as marked as that between D and E.

3. As paints A and D were used in Lae and Rabaul (see Table 1), it is possible to compare their behaviour in the two localities. At the Rabaul house, assessment >2 for both the control and the fungus-resistant paint was reached in a little more than one third of the time it took at Lae; furthermore,

both paints developed higher assessment ratings at Rabaul than at Lae.

The experience at Lae and Rabaul emphasises that care has to be taken of extrapolating results of observations made on one site to another one. At present there is no way of making a reasonable quantitative forecast from the measurements of the environmental variables of the length of time a paint will stay free from mould, or nearly so, at one site if its behaviour is known at another.

Paints for interior surfaces

Refs. 5, 1, 14, 19, 20

The data gathered in Step 2 are also of help in deciding what type of paint could possibly be useful on interior surfaces. It is, however, not feasible to conclude from them with any

Table 7

Composition of paints used in brewery

Paint	Pigments	Latex resin	PVC, %	Cu 8-hydroxy-quinolate	N-trichloro-methylthio-phthalimide	Tetramethyl thiuram disulphide
					% on paint solids	
A (blank)	r.TiO₂			---	---	
B				---	5	
C				5	---	
D	ZnO and r.TiO₂ weight ratio 2 : 1	Vinyl acetate/ acrylate copolymer	25	---		Nil
E				---	5	
F				5	---	
G (blank)	r.TiO₂			---	---	
H				---	5	
I				5	---	
K	ZnO and r.TiO₂ weight ratio 2 : 1	Styrene terpolymer*	25	---	---	Nil
L				—	5	
M				5	—	
N (blank)	r.TiO₂			---	---	
O				---	5	
P				5	---	
R	ZnO and r.TiO₂ weight ratio 1.2 : 1	Vinyl acetate/ acrylate copolymer	40	---	---	Nil
S				---	5	
T				5	---	
U (blank)	r.TiO₂			---	---	
V				---	5	
W				5	---	
X	ZnO and r.TiO₂ weight ratio 1.2 : 1	Styrene terpolymer*	40	—.	---	Nil
Y				---	5	
Z				5	---	
1	ZnO r.TiO)	Styrene terpolymer*	25			---
2			25			4
3			25			8
4	ZnO		40			---
5	r.TiO)		40			4
6			40	Nil	Nil	8
7		Acrylic	40			8
9			40			8
11			40			8
8			40			---
10			40			---
12			40			---

* Lytron 684

certainty how the paint will perform. For this reason, when an approach was made by the management of a brewery for a recommendation for a mould-resistant paints, this was declined until field tests in the brewery had been carried out. An area over a bottle washing machine was chosen (where the conditions for mould growth appeared especially favourable) and some formulations which it was judged would give favourable results[5] were tested there.

1. Paints containing zinc oxide[1]. These, on interior application, would not lose any zinc oxide and had already proved useful on interior application in the dwellings of the "Housing Commission Victoria".

2. Paints containing NTP[14]. These were chosen because the fungicide's persistance in the paint film was high even under very humid conditions.

3. Paints containing copper hydroxyquinolate[19]. Again, the fungicide's persistence was high under very humid conditions

4. Paints containing tetramethyl thiuramdisulfide[20]. This fungicide is lost comparatively quickly under humid conditions; a series of paints with increasing amounts of this compound was therefore tested.

The composition of the paints and their performance can be seen from Table 7 and Figs. 2 and 3. The Figures show clearly how necessary it is to test paints for fungal resistance in an environment which is at least similar to the one in which the chosen formulation will be used. In the present case, zinc oxide paint proved of no value, although the same formulation had shown some effect in the humid tropics and in the dwellings of the "Housing Commission Victoria".
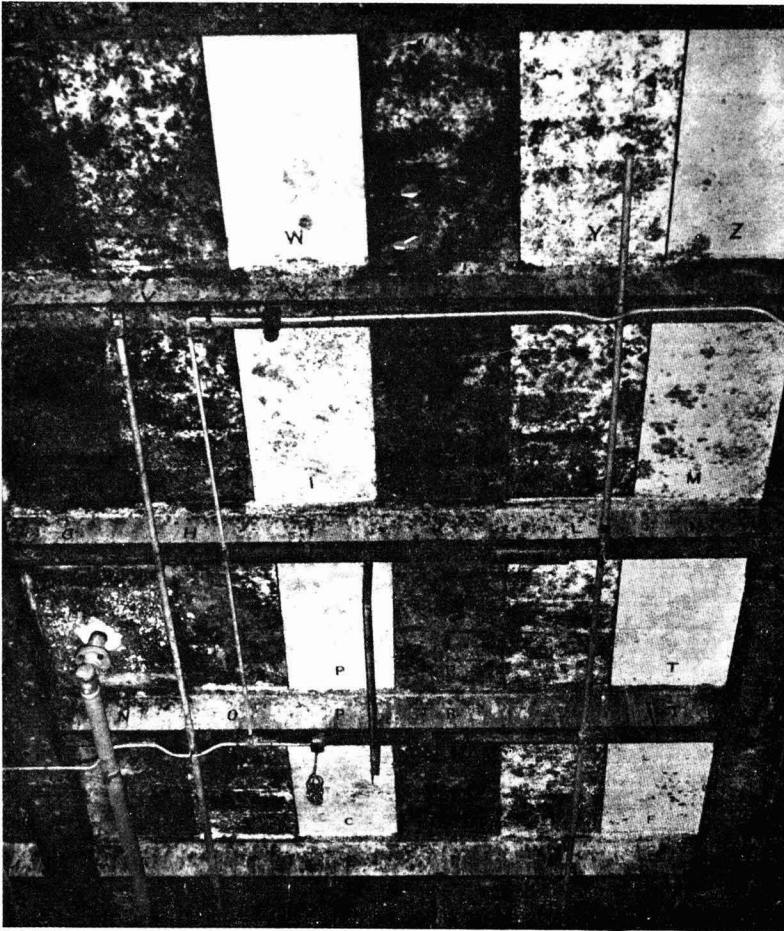
Fig. 2. Test area on ceiling over bottle washing machine in brewery, 17 months after painting with formulations detailed in Table 7 Left to right:

First strip—Blank.   Second strip—Formulations B, O, H, V containing N-trichloromethylthiophthalimide Third strip—Formulations C, P, I, W containing copper 8-hydroxyquinolate.   Fourth strip—Formulations D, R, K, X containing zinc oxide.   Fifth strip—Formulations E, S, L, Y containing zinc oxide and N-trichloromethylthiophthalimide.   Sixth strip—Formulations F, T, M, Z containing zinc oxide and copper 8-hydroxyquinolate.
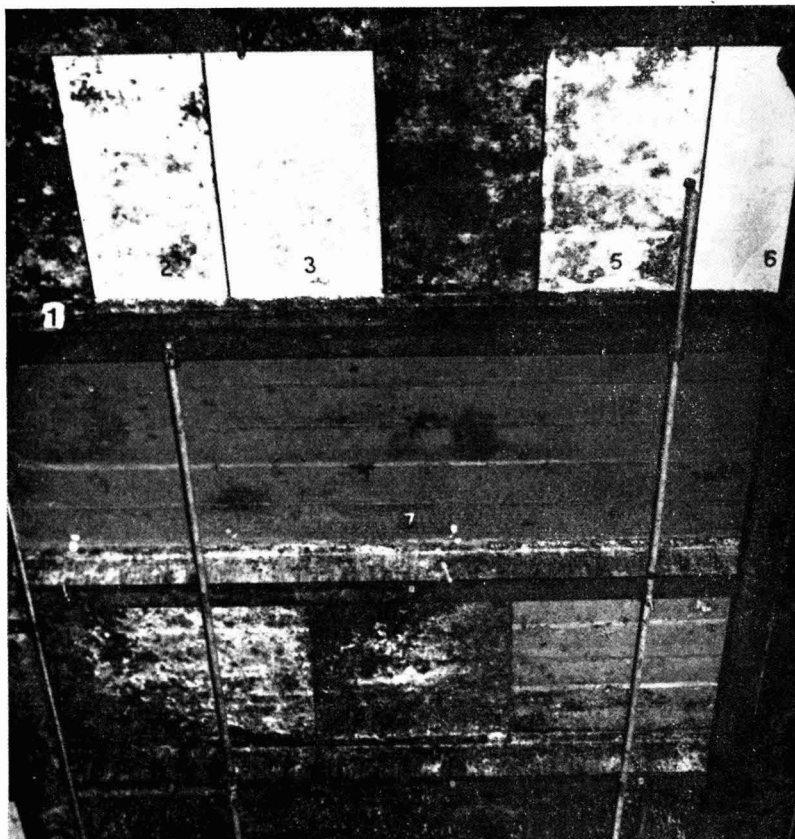
Fig. 3. Test area on ceiling over bottle washing machine in brewery, 17 months after painting

Panels 1 and 4—Formulation containing zinc oxide.   Panel 2—Formulation containing 4% TMTD, PVC 25%.
Panel 3—Formulation containing 8% TMTD, PVC 25%.   Panel 5—Formulation containing 4% TMTD, PVC 40%.
Panel 6—Formulation containing 8% TMTD, PVC 40%.

Paints containing NTP also proved of little value, although its solubility is only of the order of 0.001 per cent and it has been shown to be reasonably effective in a dye house[1]. Paints containing copper 8-hydroxyquinolate and TMTD are worthy of consideration. The first has been used on large areas in the brewery. The only disadvantage, if it is one, which could be noticed was a darkening of the painted surface; the surface darkens evenly (that is, there are no stains) and in the author's opinion this scarcely matters. There are other important observations which have been made in this test and these have been discussed[5]. A summary of possible uses of the data which have been collected on fungicides and fungistats has also been published[21].

The role of the supplier and the paint technologist in the testing of fungicides

Refs. 2, 9, 23, 6, 22-24

It may seem that the outlined schedule of testing is very long drawn out and that it would not be possible for the average paint technologist to do what is here considered desirable.

However, it is the author's belief that the work should be shared between the supplier and the paint technologist. At present, a supplier quotes a laboratory test and some panel exposures, usually of short duration (1 to 2 years) as proof of the usefulness of the compound he recommends as a fungicide. It has been demonstrated that: (a) the persistence of a fungicide in a paint formulation is one of the essential conditions for satisfactory performance, (this by now has been recognised by some workers: for instance, Dr O. Pauli[22] from Bayer AG, after discussion of some of the work at the Division of Building Research in Melbourne, concludes: "The author's personal experience agrees quite accurately with the data given by the Australian authors, and he confirms the importance of analytical control for developing paint fungicides and specific mildew coatings"), and (b) the extrapolation of the results of panel exposures to the actual structures used in service can be very misleading.

Therefore, a supplier who recommends a fungicide should state: 1. Its antifungal activity; this could be done by a laboratory test, such as the Vicklund-Manowitz test; 2. The stability of the fungicide under various climatic conditions; 3. A simple analytical technique for the determination of

residual fungicide in the paint film; 4. A test on a large-scale structure, carried out in the way as described above.

Once these data are known, a paint technologist can then further test the compound in his formulations for the environment in which he wishes to use the paint. A note of warning should be given here. There are four mechanisms by which a fungicide disappears from the paint film:

(i) By reacting with some of the trace ingredients of the air, for example hydrogen sulfide[9], or with one of the components of the paint. Phenylmercury compounds can react not only with free hydrogen sulfide but also with sulfur-containing pigments, like zinc sulfide[23].

(ii) The compound may have a sufficiently high volatility to disappear by evaporation.

(iii) The compound may be decomposed by solar radiation.

(iv) The compound may be leached out by rain and dew. Of course, in most cases all four mechanisms will play a part.

Some workers appear to believe that the stability of a fungicidal compound to leaching can be derived from its degree of water solubility. It is certainly true that a high water solubility (for example greater than 0.001 per cent) might possibly render a compound useless as a fungicide in exterior paints, but this is not necessarily so, as can be seen from the following two examples.

BMB has a water solubility of 0.2 per cent. It proved[6] to be of no value in latex paint if the paint film were exposed to rain, because it was quickly leached out. However, it was effective in latex paints if the paint films were protected from rain. On the other hand, its rate of solution from gloss enamel paints is much smaller, probably due to the reaction of the hydroxyl groups in the alkyd which form weak bonds with it, thus slowing down the rate of leaching by water. It has been shown that gloss alkyd paints containing BMB show a worthwhile fungus resistance.

Zinc oxide has a solubility of less than 0.001 per cent but, nevertheless, it disappears from the chalk layer which forms on the paint film[24]. This could be due to the formation of zinc peroxide or zinc carbonate (each of which has a 14 to 22 times higher solubility than zinc oxide) or to the attack of acidic products formed by weathering of the binder.

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Synthesis of some water-soluble etherified methylolated melamine resins and their use as hardeners for water-soluble alkyd resins

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Summary

Hexamethylol melamine has been prepared and etherified under acid conditions at room temperature by excess methyl or ethyl alcohols or by ethylene glycol monomethyl ether. These etherified methylol melamine precondensates have been used in combination with water-soluble alkyd resins in order to study the effect of the type of the etherified product on the physical properties of a paint film prepared from these combinations. From the values of König pendulum hardness plotted against stoving temperature, it is found that all the melamine formaldehyde resins tested lie nearly within the range of suitable hardness. Only melamine formaldehyde resins etherified with ethyl alcohol give high values of hardness, but they also affect the appearance of the film owing to their incomplete compatability with alkyd resins.

Keywords

Raw materials for coatings: binders (resins, etc)

  alkyd resin
  melamine resin

catalysts, accelerators, inhibitors

  hardeners

La synthèse de certaines résines solubles à l'eau, à base des éthers de méthylol mélamine et leur emploi en tant que durcisseurs de résines alkydes solubles à l'eau

Résumé

On a préparé la hexaméthylol mélamine et l'à éthérifiée sous des conditions acidiques à la température ambiante, au moyens d'un excédent de méthyle ou éthyle alcool ou d'éthylène glycol mono méthyle éther. On a utilisé ces précondensats de méthylol mélamine éthérifiée en combinaison avec des résines alkydes solubles à l'eau, afin d'étudier l'effet qu'exerce le type du produit éthérifié sur les caractéristiques physiques d'un film de peinture à base de ces constituants. A partir des valeurs de la dureté, chiffrée par le pendule König, portées par rapport à la température d'étuvage, on trouve que toutes les résines mélamine formol, qui ont été essayées, se trouvent dedans les limites de dureté convenable. Seule les résines mélamine formol éthérifiées avec l'éthyle alcool donnent des valeurs élevées de dureté, mais en même temps elles exercent une influence nuisible sur l'aspect du film en raison de leur compatibilité incomplète avec les résines alkydes.

Synthese einiger methylolierter Melaminharze und ihre Verwendung als Härter für wasserlösliche Alkydharze

Zusammenfassung

Hexamethylolmelamin wurde unter sauren Bedingungen und bei Zimmertemperatur durch Zusatz eines Überschusses von Me;hyl- oder Äthylalkoholen oder Äthylenglykolmonomethyläther prä- pariert und veräthert. Diese verätherten Methylolmelaminprä- kondensate wurden zusammen mit wasserlöslichen Alkydharzen dazu benutzt, um die Auswirkung des verätherten Produkttyps auf die physikalischen Eigenschaften eines aus diesen Kombinationen erzeugten Anstrichfilms zu studieren. Aus den König Pendel- Härteprüferwerten, aufgetragen gegen die Ofentrocknungstempera- turen wurde gefunden, dass alle geprüften Melamin-Formal- dehydharze beinahe innerhalb der geeigneten Härtegrenzen liegen. Lediglich die mit Äthylalkohol verätherten Melaminformalde- hydharze ergeben hohe Härtewerte, beeinflussen aber auch das Aussehen des Films, weil sie nicht völlig mit Alkydharzen ver- träglich sind.

Introduction

Refs. 1-9

Melamine reacts with formaldehyde under slightly alkaline conditions giving methylol derivatives with up to six methylol groups per molecule. These derivatives readily undergo condensation reactions with the formation of polymeric products. The reactions leading to hexamethylol melamine may be typically expressed as:

where R is CH₃OH, C₂H₅OH or CH₃OCH₂CH₂OH
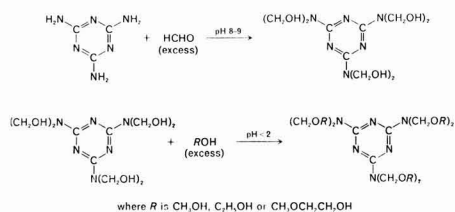
The methylol melamines are most stable at about pH 8–9. In neutral and especially in acid solutions, further condensa- tion takes place with the formation of insoluble resins.

The methylol groups can be protected from premature polymerisation by blocking the methylol groups by etherifica- tion with reactive alcohols, glycols or ethylene glycol ethers[1–5]. Thus, when methylol melamine is allowed to react with alcohol in the presence of an acid, water is split off between alcohol and methylol groups and alkyl ethers of melamine are formed.

The type and amount of alcohol employed in etherification determine the compatibility and solubility characteristics of the product; thus, the use of methanol with methylol melamines usually produces clear water-soluble derivatives; with ethyl alcohol, alkylated resins of limited water solubility are obtained, but with higher alcohols, such as butyl alcohol, hydrophobic alkylated derivatives are produced.

Etherified methylolated melamine could be prepared by two different methods. The first is the continuous one-stage process in which hexamethylol melamine (HMM) is first prepared by precondensing one mole melamine and 6–8 moles of formalin at pH 8–9 at 90°C for a short time (10 minutes). The methylol melamine so formed is directly etherified with the appropriate alcohol under acid conditions to give ethers[1-9]. The second method is the two-stage process in which HMM is first prepared by the above method, the resulting product is separated by filtration, washed well with water, dried and then etherified with the appropriate alcohol under acid conditions at room temperature to give the corresponding ethers[3,8,9].

The water-soluble alkylated melamine precondensates have important industrial applications owing to their capacity to be cured by splitting off alcohol with resins containing hydroxyl or carboxyl groups. They are, therefore, capable of building up high-molecular weight condensation products. One of the most important industrial applications is the use of these water-soluble alkylated melamine precondensates in combination with water-soluble alkyd resins in protective coatings, where water is used as a solvent or diluent instead of the organic solvents. This combination produces a remarkable improvement of the varnish quality. Thus, the lowest baking temperature of a system prepared from an alkyd resin based on trimellitic anhydride and hexakis (methoxy methyl) melamine[6] is 140°C, whilst the water-soluble alkyd resin alone requires a high stoving temperature (220°C) to achieve adequate curing, and this will entail much darkening of the baked film. The reactions taking place during baking are complex and involve both the melamine and the alkyd parts of the mixture.

In this study, an attempt was made to prepare different types of etherified methylol melamine. Thus HMM was etherified under acid conditions at room temperature by methyl, ethyl-alcohol and ethylene glycol monomethyl ether. These etherified methylol melamine precondensates were used in combination with water-soluble alkyd resins in order to study the effect of the type and amount of the etherified product on the physical properties of the mixture and the paint film prepared from the combination.

Experimental

Refs. 10-13

Materials

Melamine was chemically pure. Formalin (30 per cent) was used; its concentration was determined iodometrically[10]. Methyl and ethyl alcohols, and ethylene glycol monomethyl ether were twice distilled. Water-soluble alkyd resins: an alkyd with the following composition was prepared[11]:

	moles
Dehydrated castor oil	1
Glycerol	1
Phthalic anhydride	1.5
Trimellitic anhydride	3.53
Diethylene glycol	6.81

It had the following constants:

Excess hydroxyl	17.8%
Oil length	27.18%
Alkyd constant "K"	1.0136

The properties of the finished alkyd were:

Acid value	46
Hydroxyl value:[12a]	89
Diene number[12b]	17.6
Iodine value (Woburn)	41.25

Experimental method

a) Synthesis of hexamethylol melamine (HMM)

The product was synthesised by heating 1 mole melamine and 8 moles of formalin (30 per cent) at pH 8–9 for a short time to about 90°C. After a clear solution was obtained the reaction mixture was cooled slowly to room temperature at which point a white precipitate began to appear. The latter was then filtered off with suction. The precipitate was repeatedly redispersed in water, washed and filtered until the odour of formalin disappeared, since in the presence of excess formalin, and at elevated temperature, complex products may be formed[13-15]. The product was then dried *in vacuo* to a fine powder giving an HMM yield of 95–100 per cent. It gave the following elemental analysis:

	C	H	N
found	34.5	6.1	25.1
calculated	35.29	5.88	24.1

b) Synthesis of etherified methylolated melamines

The dried HMM was readily etherified by the appropriate alcohol or ethylene glycol monoether at room temperature in the presence of concentrated nitric acid. Thus, 1 mol (30.6g) HMM in powder form was well stirred in 10 moles of the appropriate alcohol in the presence of 10cc conc. HNO_3 at room temperature. It must be emphasised that the nitric acid was added dropwise and that the temperature was not allowed to exceed 30°C. A clear solution was obtained after one to two minutes. After eight minutes the mixture was neutralised with $NaHCO_3$ and the salt removed by filtration. The unreacted alcohols or glycol ethers were removed at 40°C under vacuum, leaving the etherified methylol melamine. The following table represents the elemental analyses of the etherified methylolated melamines, together with their solubility in water.

No	MF resin		C	H	N	O	solubility in water
1	HMM etherified with ethylene glycol monometyl ether.	calc: found:	49.54 49.51	8.23 8.30	12.84 12.80	29.37 29.39	V. Soluble
2	Poly (methoxy methyl) melamine	mixture of hexa-, penta-, and others					V. Soluble
3	Hexakis (methoxy methyl) melamine	calc: found:	46.15 46.16	7.69 7.67	21.53 21.49	24.61 24.38	Soluble
4	Hexakis (ethoxy methyl) melamine	calc: found:	53.16 53.12	8.85 8.75	17.72 17.65	20.27 20.28	limited solubility

The infrared spectra of the etherified methylol melamines are shown in Fig. 1.
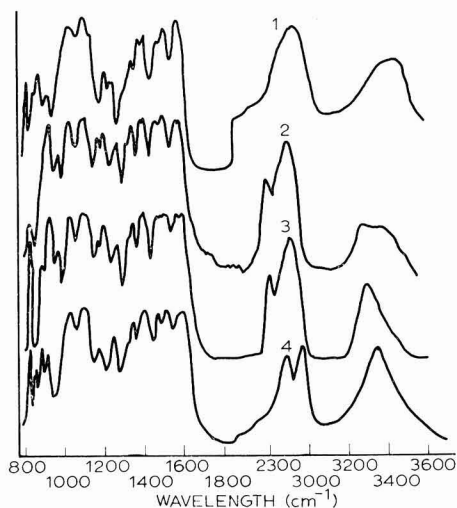
Fig. 1. Infrared spectra of resins 1, 2, 3 and 4

Paint formulation: Ball mill base:

Additive	g
TiO$_2$	70
50%Alkyd resin	110
Antisettling agent: Gel bentone 10% (0.5% on wt of Pigment)	3.5
Wetting agent: Sodium hexametaphosphate (0.2% on wt of Pigment)	0.48
Disperser N	0.48
Silicone oil	0.12

These ingredients were dispersed for 12 hrs. After obtaining the required degree of dispersion the rest of the ingredients were added and mixed thoroughly to have the following specification:

Pigment: binder ratio	1:1
Solid content	60%
Amino resin	30% and 40% respectively.

The alkyd-melamine formaldehyde-resin mixture to be investigated was applied to a glass plate (10 × 15cm).

Results and discussion

Figs 2, 3 and 4 represent the influence of stoving temperature on König pendulum hardness of stoved films prepared from a mixture of water-soluble alkyd resin and MF-resins 1, 2, 3 and 4 respectively. Stoving time was 30, 60 and 90 minutes respectively. The mixtures were prepared using 30% of MF resin by weight and 70% of the alkyd resin. The film thickness varied from 40μm to 60μm.
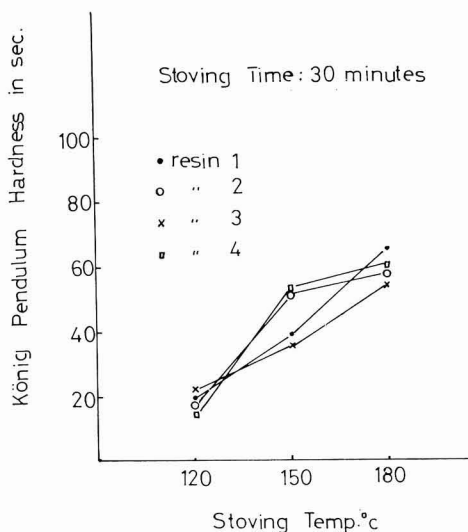
Fig. 2.
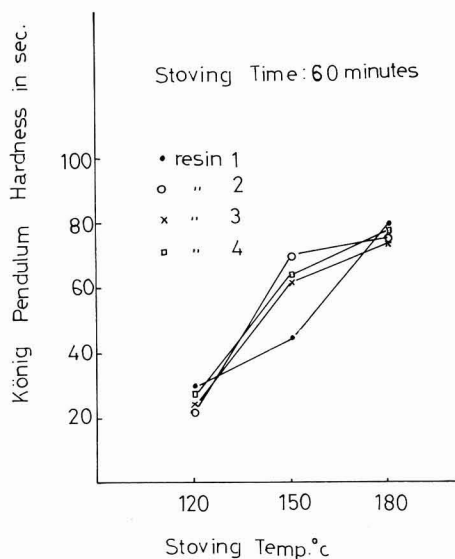
Fig. 3.

The influence of stoving temperature on curing can be estimated by measuring König pendulum hardness as a function of stoving temperature, and in this way it is possible to compare the influence of stoving temperature on curing of different types of MF-alkyd combinations.

On comparing the results shown in Figs. 2, 3 and 4, it was observed that at the lower stoving temperature of 120°C for 30 minutes, resin 3 gave higher values of pendulum hardness in comparison with resins 1, 2 and 4 respectively. At 150°C resin 4 gave the higher values of hardness and this means that resins 1 and 4 require higher stoving temperatures to increase

Fig. 4.

Fig. 5.

of pendulum hardness; at 150°C the hardness of resin 1 increases gradually, but the other three resins show a more remarkable increase in hardness. Resins 2, 3 and 4 did not shows a significant increase in hardness and this means that the reaction is approximately complete at 150°C, but resin 1 show a remarkable increase with increasing stoving tempera-
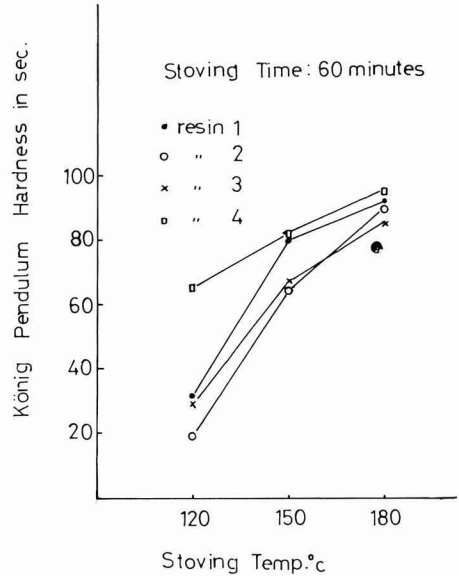
Fig. 6.
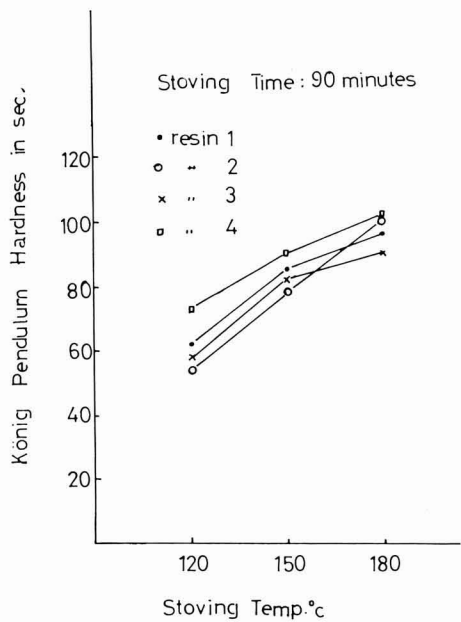
Fig. 7.

Figs. 2-7. The influence of stoving temperature on König pendulum hardness

the degree of curing; this was quite clear at a stoving temperature of 180°C, where resin 1 gave the highest values of pendulum hardness. It was concluded that resin 3 was much more reactive than the other resins tested at the lower stoving temperatures, whilst the others require high stoving temperatures or high stoving times to achieve the adequate curing. From Figs. 3 and 4, at longer stoving times (60, 90 minutes) it was observed that the pendulum hardness continues to rise with an increase of stoving time. Thus, resin 1 at 120°C and stoving times of 60 and 90 minutes shows much higher values

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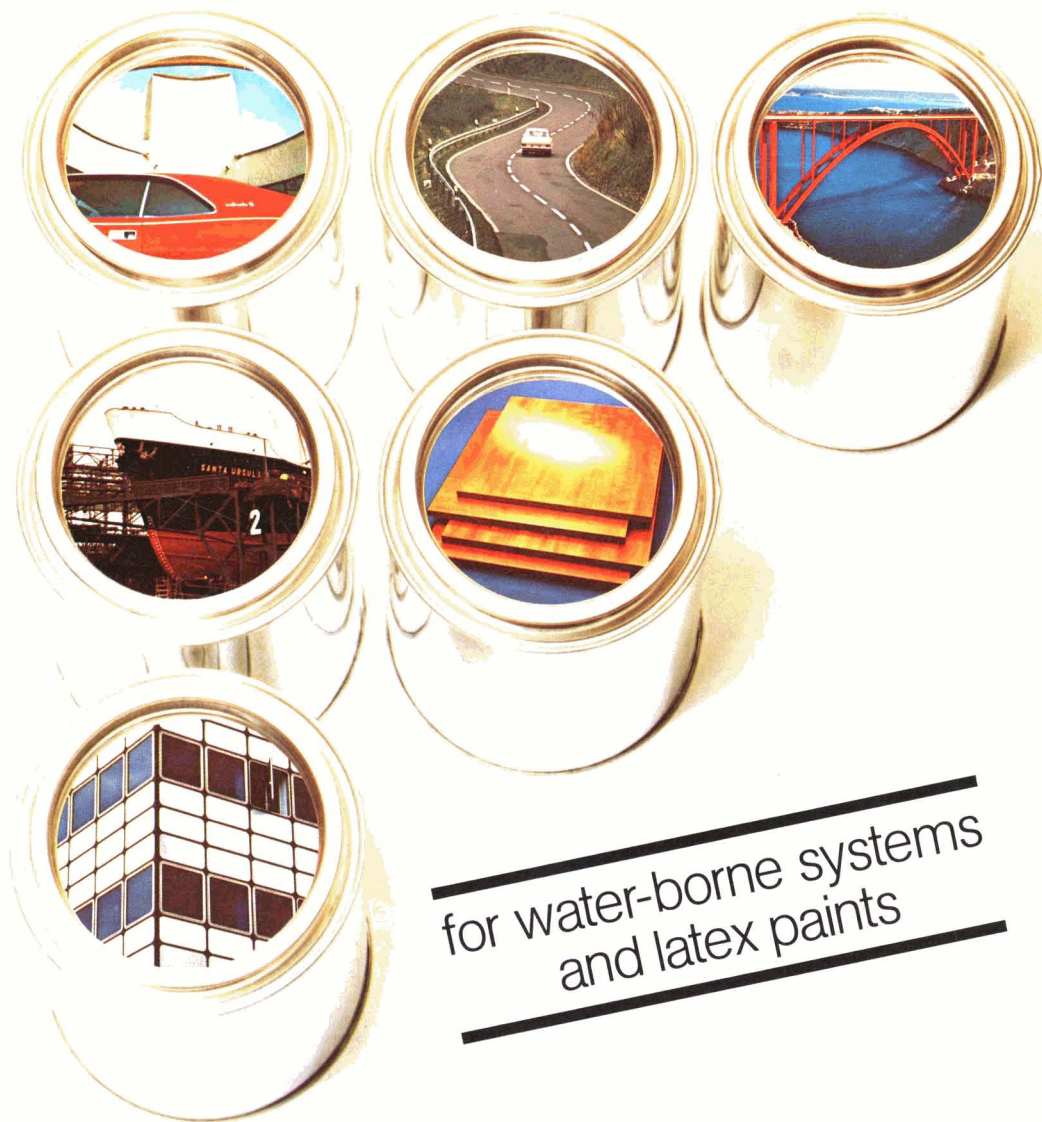
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Hydropalat 1667		☐			Mixture of polyacrylate & special phosphates	0.1 – 0.5%	pigment
Texapon P	Wetting Agent and Dispersing Agent for emulsion paints	☐			Mixture of anionic and non-ionic surfactants.	0.3%	finished paint
Disponil 19 + 20	Wetting agents and stabilizers for emulsion paints: Emulsifiers for pigment preparations: Wetting agents for brush cleaners: Emulsifiers for alkyd resin and nitrocellulose emulsions; Emulsifiers for polymerisation	☐			Low foaming wetting agents	0.1 – 0.5%	finished paint
Disponil 1828		☐			Foam inhibiting wetting agent with synergistic interaction with Dehydran defoamers for optimum foam depressing requirements	0.1 – 0.5%	finished paint
Disponil 21			☐			0.1 – 0.5%	finished paint
Dehydran C	Defoamers and foam inhibitors for emulsion paints and plastic dispersions	☐			Silicone-free	0.1 – 0.7%	finished paint
Dehydran F		☐			Silicone-free	0.1 – 0.7%	finished paint
Dehydran G		☐			Contains small amounts of silicone	0.1 – 0.7%	finished paint
Dehygant B	In-can preservative for emulsion paints	☐			Heterocyclic compound containing nitrogen and halogen	approx. 0.04%	finished paint
Dehygant LFD	Preservatives for in-can preservation of emulsion paints, emulsions, aqueous colour batches			☐	Primarily chloro-acetamide	0.2 – 1.0%	finished paint
Dehygant LFM		☐			Heterocyclic compound containing nitrogen	0.2 – 1.0%	finished paint
Product LA 535	Anti-settling agent for water-borne systems	☐			Amine neutralized polyester	0.2 – 0.6%	finished paint

[1] = in emulsion paints, [2] PVP = Polyvinylpropionate, [3] Shell Chemicals

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- the average or starting dosage.

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- moderate increase of the film thickness
- uniform film thickness
- smooth surface
- better flow
- less flooding and floating
- no pigment settling

It should be mentioned that a combination of PRODUCT LA 535 with PRODUCT VP-LA 671 for water-borne systems (based on amine-neutralized binding agents) is recommendable.

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Flow improvement and a reduction in possible flooding and floating have been observed as positive side-effects.

No negative side-effects have been discovered, provided that the correct dosage of 0.2 – 1.0% is used.

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ture and this means that curing this resin requires high stoving temperatures or long stoving times for completion of the cross-linking reaction.

From Figs. 2, 3 and 4 the effect of stoving time on the degree of curing of the mixtures can be deduced. It is also possible to compare the reactivity of the different types of MF-resins towards condensation with the water-soluble alkyd resin Thus, resin 1 is much more reactive than the other resins at a high stoving temperature of 180°C or a long stoving time, whilst resin 3 is more reactive than the others at the lower stoving temperature of 120°C, that is, they can split off methyl alcohol readily whilst the other resins require higher temperatures or longer stoving times in order to cure and to allow the less volatile by-products to leave the film.

Figs 5, 6 and 7 show the results for a mixture of 40% MF and 60% alkyd resin. It is seen that at the stoving temperature of 120°C and shorter stoving time (30 minutes), resin 1 gave the higher values of pendulum hardness. At 150°C and 180°C and also at 120°C with longer stoving times (60 and 90 minutes) resin 4 gave the higher hardness values. In spite of the greater hardness of resin 4, some roughness appears on the surface of the film most probably due to incomplete compatibility of the MF and the alkyd resins. Finally, it was observed that resin 1 gave higher pendulum hardness than resins 3 and 2 respectively.

Conclusion

Resin 4 gave the greatest hardness, but at the same time it affected the appearance of the film owing to its incompatibility with the alkyd resin. Resins 1 and 3 produced the best film properties, whilst resin 2 lies approximately in the range of suitable hardness. Resins 1, 2 and 3 gave the required

hardness together with good film appearance when used in combination with water soluble alkyd resins and this is due to their complete compatibility with the alkyd resin.

Note: Resins 1 and 2 are readily compatible with the alkyd resin but resin 3 require good milling for good compatibility.

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Porosity of building materials—a collection of published results

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Summary

The pore size distributions of various building materials have been obtained from the published literature and reduced to a common basis to provide an easy comparison. Sources are quoted and form a bibliography of the subject. The primary use is in the study of paint behaviour on porous surfaces and some discussion of this is included, but the data should be of general interest in the field of penetration of liquids into porous solids.

Keywords

Types and classes of coatings and allied products

    primer

    sealer

    masonry finish

Types and classes of structures or surfaces to be coated

    brick

    wood

    concrete

Properties, characteristics and conditions primarily associated with:

    materials in general

        porosity

        permeability

    structures or surfaces being coated

        porosity

La porosité des matériaux de construction—un receuil de résultats cités dans la littérature

Résumé

On a extrait à partir de la littérature les répartitions de la grandeur de pores de divers matériaux de construction, et l'on les a reduit à une base commune en vue d'assurer une comparaison facile. On cite les sources qui constituent une bibliographie du sujet, dont l'emploi principal se trouve dans l'étude du comportement des peintures appliquées aux surfaces poreuses, dont l'article renferme une certaine discussion. Pourtant, les données devraient être d'un intérêt général dans le domaine de la pénétration de liquides dans les solides poreux.

Porasität von Baumaterialien—eine Zusammenstellung veröffentlichter Resultate

Zusammenfassung

Aus veröffentlicher Literatur wurden die Porengrössen-verteilungen in verschiedenen Baumaterialien herausgezogen und wegen leichterer Vergleichbarkeit auf einen gemeinsamen Nenner gebracht. Quellen werden angegeben und bilden eine Bibliographie für das Thema. In erster Linie dient diese Arbeit dem Studium des Verhaltens von Anstrichmitteln auf porösen Oberflächen, und sie enthält auch eine diesbezügliche Besprechung; die Angaben dürften jedoch von allgemeinem Interesse für das Gebiet des Eindringens von Flüssigkeiten in poröse Festkörper sein.

Introduction

The movement of water and other liquids in porous building materials is an important factor in their behaviour and has been extensively studied. It is a function of the effective pore size and configuration (as well as of the properties of the liquid) and the literature contains a large amount of information on pore size distribution, quoted in various units such as volume fraction or percentage, or volume per unit weight, and in different groupings of sizes, or in cumulative distribution diagrams.

A survey of the published literature has been carried out by the library of the Building Research Establishment with particular reference to the substrates used for paint, and covering the period from the 1920s to 1975 (no suitable references were found earlier than 1956). The data have been rationalised by conversion to volume percentage, using quoted densities where necessary, and interpolated to a common set of size ranges.

It is emphasised that the figures for pore size distribution are approximate, and the materials may be highly variable.

Moreover, the measured value of the total porosity depends on the extent to which the finer pores are included and, therefore, on the equipment used. This does not, however, affect the relative abundance of coarse pores in different size ranges, and it is these which largely determine the absorption behaviour of paint.

Definitions

Porosity is here defined as "open porosity", i.e. the volume of pore space accessible from the exterior, expressed as a percentage of the total volume of the material. Surface pores and interconnected internal pores are included, but not internal voids which are completely sealed off.

The *Equivalent Diameter* of a pore is the diameter of a uniform cylindrical pore which would respond in the same way to the test conditions. In practice pores may be highly irregular in shape with variable diameters. Since it is the narrowest part of the pore which determines its behaviour under mercury infiltration, equivalent diameters measured by porosimetry are often systematically too small. The total void

volume may be correctly assessed by the technique but the size distribution will be somewhat artificial. The effect of non-uniform pore diameter on measured pore size distribution has been considered by Hill[10].

Micropores are generally defined as pores with equivalent diameter less than 0.1μm. In cementitious materials, micropores make up an appreciable proportion of the total porosity.

Measurement of porosity

Refs. 21, 29, 1

Whereas microporosity is often measured by gas absorption experiments, the commonest method of determining coarse pores is by mercury porosimetry. Mercury is allowed to infiltrate the sample under gradually increasing pressure; the greater the pressure, the finer are the pores which can be filled. The volume of mercury absorbed at any given pressure can thus be converted into the volume of pore space within a particular pore diameter range. The minimum pore diameter which will admit mercury depends on the instrument used; it may be as small as 2.5nm, but is usually about 10nm. It should be noted that where the entrance to a pore is of smaller diameter than the pore itself, it is this entrance diameter which will be measured by mercury porosimetry. It is for this reason that measured equivalent diameters are often smaller than the actual diameters of the pores. Pores whose entrance diameters are below the minimum value will not be detected.

Total porosity can be calculated from density measurements on oven-dried and water-soaked material. Porosities calculated in this way include micropores but not closed voids; the latter, however, are not common in ceramics or cementitious materials. Alternatively, the total porosity may be taken as the cumulative porosity measured by mercury infiltration not including the finer micropores. The method used to calculate total porosity is indicated in the tables of results.

The method used by De Castro[27] to measure pore size distribution in limestones involves suction desorption of adsorbed water, where the suction pressure determines the maximum diameter of the pores which can be emptied. The method may be considered as liquid penetration in reverse.

The porosity of wood results from the structure of hollow cells of various kinds, 90-95 per cent being the longitudinal fibres, closed at the ends but inter-connected by membrane-covered "pits" in the cell walls. Part of the pore structure is isolated, hence total porosity can be much greater than the pore space accessible to liquids. Pore sizes can be derived from direct microscopic observations or from gas or liquid flow measurements, but these are not in good agreement[29]. Mercury porosimetry has been little used[1]. Swelling liquids

(e.g. water) exhibit a flow behaviour different from that of non-swelling ones (e.g. hydrocarbons).

In softwood the fibres, or "tracheids", are 2-5mm long and of approximately rectangular cross-section, with dimensions of 20-60μm tangentially, but varying radially from similar figures in the earlywood to as little as 4 or 5μm in the latewood. The pore hydraulic radius is found to be in the range 5-10μm and the pit membranes have effective pore sizes of 0.01-0.5μm (gas flow measurements giving the smaller results).

Hardwood fibres are shorter (1-2mm) and their diameters are variable, around 15μm. There are also cells known as pores or vessels of much larger diameter, e.g. in oak 30-500μm. Vessels are made up of elements which, in some species, provide uninterrupted longitudinal flow paths for several metres, but in others the vessels become blocked by resins or other substances. Penetration may then be shallow, but they can absorb relatively large amounts of the thin films of paint in the large open cavities of the cut surfaces.

Adsorption of paints and paint components by porous substrates

Refs. 2, 3, 4

Pore penetration may affect both the ease of application of paints and their subsequent performance or durability. A typical paint consists of a binder, an appropriate solvent or "thinner", and dispersed pigments. These components differ considerably in their intrinsic ability to penetrate a porous substrate. The commonly employed volatile solvents are the relatively low molecular weight hydrocarbons, ketones, alcohols or esters, or water in the case of emulsion paints, capable of penetrating almost all the open pores measurable by the techniques described. However, the solvents will not necessarily penetrate the substrate independently of the molecules in solution. Under zero-head conditions, aqueous solutions may not penetrate pores in a material of high solid/liquid surface tension.

Simple drying-oil binders have fairly low molecular weights and penetrate many porous substrates easily, absorption being sometimes considered beneficial and sometimes undesirable. For polymeric oils and synthetic polymers the ability to penetrate pores will be governed by the effective molecular size in the solvents used. This is difficult to determine, especially at the high concentration of binder normally present, but will differ widely for different binder types. A crude estimate of the pore diameters which some examples of paint binders might be expected to penetrate freely are given below, corresponding to the calculated extended chain lengths of the various types.

Binder type	Molecular weight	Corresponding pore diameter (nm)	(μm)
Epoxy resins (Bisphenol A type) (1)	340–1760	2–10	0.002–0.01
Linseed oil	785	5	0.005
Alkyd resins, long oil type	2000–5000(M$_n$)	10–20	0.01–0.02
Overall range (2)		5–150	0.005–0.015
Chlorinated rubber	150 000–400 000	400–1000	0.4–1.0

Notes: (1) Amine and polyamide hardeners will be within a similar size range, but effective polymer size will increase rapidly as reaction proceeds.

(2) The figures are taken from gel permeation data; the ratio M_w/M_n is usually high (3–8) and hence the effective size of alkyd resins can vary widely.

These estimated sizes are high, especially for the high molecular weight polymers, since the molecules will be more or less tightly coiled, depending on the solvent used. For example, polystyrene of molecular weight (MW) $= 10^6$ has a calculated extended chain length of 2500nm whereas the mean diameter in toluene solution is reported[2] as 100nm. However, in concentrated solutions of such materials, molecular intertwining renders the situation complex and the higher figure may be preferable. On this basis, high molecular weight binders, such as chlorinated rubber, should show much lower penetration into cementitious substrates than other binders. The actual extent of penetration will depend upon such factors as viscosity and rate of loss of solvent.

For the dispersed binders in emulsion paints, particle size rather than molecular weight is the critical factor and will usually be in the range 0.1–1 μm. Penetration of polymer and pigment particles into the finer pores will be slight, and the water phase may be extracted from the film leaving the polymer/pigment phase almost entirely on the surface. A high-viscosity polymeric colloid in the water phase may, however, restrict its absorption. The range of particle size shown by typical pigments is wide, ranging from c 0.2 μm for titanium dioxide to 5–25 μm for many extenders, for example. Even larger particles may be present in textured masonry paints.

Practical consequences of these size distributions are frequently observed. For example, as penetration varies with pore and particle size it may be selective, thus altering the effective composition of the liquid film. Solvent-thinned paints applied to a microporous surface can lose solvent and binder to the substrate leaving an underbound pigment layer at the surface. Similarly, an emulsion paint may lose water with excessively fast drying, and possibly poor film formation. On substrates with relatively large pores, notably bricks, both pigment and binder can penetrate to appreciable depths so that unwanted paint may be almost impossible to remove. Differential absorption can occur on the bands of early and late growth in softwoods.

Sealers used to satisfy the porosity of the substrate before painting should clearly be formulated to provide the correct molecular or particle size for the intended substrates. The application of water to a surface, such as gypsum plaster, can temporarily prevent excessive absorption of the aqueous phase of emulsion paints and make them easier to brush, whereas the use of a soluble polymer of too high a molecular weight as a "size" can produce a layer of unabsorbed material on the surface which assists brushing of subsequent coats but may be a weak layer in the system.

It is commonly believed that penetration into a porous surface is a major factor in achieving good adhesion, but since adhesion is also strongly influenced by the nature of the polymer (polar attraction, good wetting, etc.) penetration may be essential only for coatings of intrinsically low adhesion, or when it permits consolidation of a mechanically weak porous surface. The case against the need for, and value of, penetration of coatings into wood has been made by Gray[3] and Van Loon[4].

The *rate* of penetration of porous solids by liquids is, of course, a function of viscosity and surface tension (Washburn's equation), as well as of pore size.

Results from the literature

Refs. 5-44

The data obtained from references[5-29] either directly or by conversion are set out in the table below. Details of composition, heat treatment, ageing or curing treatment, and density are included if stated in the source documents. An asterisk by the reference indicates that the total porosity of the material was determined by water absorption and has a greater value than would be obtained using mercury alone; this is also reflected in the value of the porosity of equivalent diameter less than 0.1μm. References[30-43] are included for completeness; they contain micropore size distribution data or results which are otherwise unsuitable for tabulation.

Material	Porosity (vol %) in size range (equivalent diameter)						
	Total	<0.1(μm)	0.1–1.0	1.0–10	10–100	100–1000	Reference
Bricks							
Pressed red facing brick							
most porous of batch of 12	32	6	1	9	14	2	14
least porous of batch of 12	30	0	1	8	20	2	
Leicester red wirecut brick							
most porous	25	0	2	15	6	3	14
least porous	23	3	2	13	3	2	
Wirecut Keuper Marl brick							
most porous	24	0	2	16	3	3	11
least porous	23	3	2	13	1	4	
Semi-dry pressed Woolwich Beds brick							
most porous	29	1	2	7	16	3	11
least porous	28	4	1	8	13	2	
London stock (2nd) pressed Wirecut brick							
most porous	36	2	1	24	7	2	11
least porous	30	4	1	21	3	1	
London stock (common) pressed Wirecut brick							
most porous	42	1	8	27	3	3	11
least porous	38	2	4	24	4	4	
London stock (2nd) machine made							
most porous	46	2	4	34	4	2	11
least porous	42	1	4	33	3	1	

| Material | Total | Porosity (vol %) in size range (equivalent diameter) | | | | | Reference |
		$<0.1(\mu m)$	0.1–1.0	1.0–10	10–100	100–1000	
Handmade brick, Gault clay, fires white							
fired at 900°C	38	2	33	1	1	1	12
fired at 1000°C	37	2	33	0	1	1	
fired at 1100°C	36	2	13	19	1	1	
Handmade brick, Gault clay, fires yellow							
fired at 900°C	35	3	30	0	1	1	12
fired at 1000°C	35	1	32	0	1	1	
fired at 1100°C	30	2	25	1	1	1	
Handmade brick, Gault clay, fires red							
fired at 900°C	26	14	10	0	2	0	12
fired at 1000°C	31	10	18	0	1	2	
fired at 1050°C	27	10	17	0	0	0	
fired at 1100°C	37	5	10	20	1	1	
Handmade brick, Grinstead clay							
fired at 900°C	33	30	1	0	1	1	12
fired at 1000°C	26	24	2	0	0	0	
fired at 1050°C	17	12	3	0	1	1	
fired at 1100°C	4	2	0	0	1	1	
Handmade brick, Weald clay							
fired at 900°C	34	14	18	1	0	1	12
fired at 1000°C	28	3	24	0	0	1	
fired at 1050°C	26	2	22	0	0	2	
fired at 1100°C	4	3	0	0	0	1	
Handmade brick, Wadhurst clay from Sussex							
fired at 900°C	34	5	27	2	1	1	12
fired at 1000°C	33	0	28	5	0	0	
fired at 1100°C	21	2	8	8	1	2	
Handmade brick, Wadhurst clay from Kent							
fired at 900°C	31	14	14	2	1	0	12
fired at 1000°C	29	0	22	5	2	0	
fired at 1100°C	23	0	11	7	4	1	
Handmade brick, Wadhurst clay from Sussex							
fired at 900°C	36	12	22	0	1	1	12
fired at 1000°C	34	7	27	0	0	0	
fired at 1100°C	26	1	24	0	1	0	
fired at 1200°C	17	11	15	1	0	0	
Handmade brick, Tunbridge Wells sand from Sussex							
fired at 900°C	34	4	27	2	0	1	12
fired at 1000°C	33	4	18	11	0	0	
fired at 1100°C	32	1	8	23	0	0	
fired at 1200°C	31	1	4	24	1	1	
Handmade bricks, Tunbridge Wells sand from Kent							
fired at 900°C	33	4	9	20	0	0	12
fired at 1000°C	35	3	9	21	0	2	
fired at 1100°C	33	3	3	27	0	0	
fired at 1200°C	32	3	0	28	1	0	
Handmade brick, Gault and Greensand							
fired at 900°C	29	3	6	19	0	1	12
fired at 1000°C	29	1	3	24	0	1	
fired at 1100°C	27	2	0	24	1	0	
fired at 1200°C	22	2	0	12	7	1	
Handmade brick, Ashdown beds, Sussex							
fired at 900°C	36	3	6	25	1	1	12
fired at 1000°C	34	0	5	28	0	1	
fired at 1100°C	35	0	1	32	1	1	
fired at 1200°C	32	3	0	27	0	2	
Handmade brick, Ashdown beds, Kent							
fired at 900°C	43	3	3	15	22	0	
fired at 1000°C	43	3	4	20	16	0	
fired at 1100°C	45	0	2	18	23	2	
fired at 1200°C	43	2	0	16	25	0	
Brick (type unspecified)							
Density 1840 kg m^{-3}	40	0	18	20	2	0	24
Density 1740 kg m^{-3}	26	0	3	21	2	0	
Hard-baked brick	33	0	0	5	28		22

Material	Total	Porosity (vol %) in size range (equivalent diameter)					Reference
		<0.1(μm)	0.1–1.0	1.0–10	10–100	100–1000	
Semi-dry pressed brick							
White Gault clay	49	0	18	21	10		*5,6
Fletton	35	6	13	10	6		
Fletton	37	1	16	13	7		
Fletton	38	2	17	11	7		
Middle lias	33	0	13	8	12		
Middle lias	25	0	8	10	17		
Stiff plastic pressed brick							
Shale	18	2	3	7	6		*5, 6
Shale	31	0	8	12	10		
Shale	15	1	10	3	2		
Shale	32	2	14	8	7		
Shale	38	3	17	8	9		
Shale	27	7	13	8	1		
Shale	21	3	6	3	8		
Plain and pressed wirecut							
London stock	36	2	3	21	9		*5, 6
London stock	42	0	3	29	10		
London stock	43	1	8	29	6		
Glacial clay	41	2	33	4	1		
Glacial clay	41	3	37	1	0		
Glacial clay	41	1	38	0	2		
Glacial clay	37	0	20	16	2		
Weald clay	19	1	7	10	2		
Keuper Marl	40	2	17	20	2		
Keuper Marl	42	0	21	20	1		
Etruria Marl	16	1	8	3	3		
Yellow-firing clinker brick	14	1	4	9	0	0	22
Other ceramic products							
Extruded tile	20	3	10	7	0	0	26
Extruded tile	20	1	6	13	0	0	
Pressed tile	23	2	6	15	0	0	
Pressed tile	21	1	6	14	0	0	
Wall tile							
fired at 800°C	31	15	16	0	0	0	*5, 6
fired at 900°C	31	16	14	0	0	0	
fired at 1000°C	31	7	22	2	0	0	
fired at 1100°C	26	0	16	10	0	0	
fired at 1220°C	14	1	6	8	0	0	
Facade clinker	18	0	3	14	1	0	22
Roof tile	22	0	10	11	1	0	
Roof tile	30	3	25	2	0	0	
Roof tile	26	1	14	9	0	0	
Roof tile	14	1	3	9	1	0	
Roof tile	26	1	16	8	1	0	
Roof tile	23	1	13	8	1	0	
Roof tile	17	1	9	6	1	0	
Roof tile	27	1	15	9	1	1	
Roof tile	23	0	13	9	1	0	
Roof tile	25	0	10	14	1	0	
Roof tile	26	1	10	14	1	0	
Roof tile	26	1	6	19	0	0	
Roof tile	22	1	19	2	0	0	
Roof tile	24	4	18	2	0	0	
Experimental tile							
fired at 900°C	20	5	11	4	0	0	22
fired at 960°C	18	2	9	7	0	0	
fired at 1000°C	16	1	6	9	0	0	
Montmorillonite body							
fired at 800°C	31	8	10	12	1		10
fired at 950°C	27	6	5	15	1		
fired at 1050°C	33	2	7	22	2		
fired at 1150°C	24	2	14	7	4		
Illite body							
fired at 700°C	41	12	20	8	1		10
fired at 100°C	39	8	19	12	0		
fired at 1000°C	24	2	4	16	2		
fired at 1050°C	34	3	10	17	4		
fired at 1100°C	9	1	1	4	3		
fired at 1150°C	43	9	17	9	8		
Kaolinite body							
fired at 600°C	41	16	24	1	0		10
fired at 950°C	37	11	26	0	0		
fired at 995°C	41	13	25	2	1		
fired at 1055°C	38	9	27	2	0		
fired at 1105°C	36	11	24	0	1		
fired at 1150°C	38	5	30	2	1		

Material	Total	$<0.1(\mu m)$	0.1–1.0	1.0–10	10–100	100–1000	Reference
Calcium silicate products							
Sand-lime brick							
most porous of 12	31	9	4	3	9	6	14
least porous of 12	26	7	4	4	7	4	
Calcium silicate—asbestos board							
of density 775 kg m^{-3}	62	23	39	0	0	0	24
Sand-lime							
density 0.4 $\times$ 10^3 kg m^{-3}	80	16	60	4	0	0	19
density 0.6 $\times$ 10^3 kg m^{-3}	70	39	28	2	1	0	
density 0.8 $\times$ 10^3 kg m^{-3}	63	31	29	2	1	0	
density 0.9 $\times$ 10^3 kg m^{-3}	55	36	19	0	0	0	
density 1.2 $\times$ 10^3 kg m^{-3}	43	41	2	0	0	0	
density 1.6 $\times$ 10^3 kg m^{-3}	23	20	1	1	1	0	
density 1.9 $\times$ 10^3 kg m^{-3}	7	5	2	0	0	0	
density 2.1 $\times$ 10^3 kg m^{-3}	0	0	0	0	0	0	
"Cellular concrete"							
density 460 kg/m^3	37	5	18	5	9	0	24
density 510 kg/m^3	36	18	5	3	10	0	
Cementitious products							
Cement paste							
Water content (w/c) 0.3	32	28	2	1	1	0	20
Water content (w/c) 0.45	39	32	6	1	0	0	
Cement paste, carbonated							
Water content (w/c) 0.3	26	20	4	1	1	0	20
Water content (w/c) 0.4	30	22	5	2	1	0	
Water content (w/c) 0.5	32	25	6	1	0	0	
Cement paste w/c 0.4							
aged 1 day	49	22	25	2	0	0	*21
aged 2 days	46	26	19	1	0	0	
aged 3 days	44	31	13	0	0	0	
aged 5 days	42	38	4	0	0	0	
aged 7 days	42	40	2	0	0	0	
aged 28 days	38	36	2	0	0	0	
aged 60 days	37	35	1	0	0	0	
aged 320 days	36	36	0	0	0	0	
Cement paste w/c 0.6							
aged 1 day	55	19	25	10	1	0	*21
aged 2 days	53	22	30	1	0	0	
aged 3 days	51	25	26	0	0	0	
aged 5 days	50	29	21	0	0	0	
aged 7 days	50	33	17	0	0	0	
aged 28 days	49	45	4	0	0	0	
aged 59 days	47	44	3	0	0	0	
aged 318 days	45	42	3	0	0	0	
Cement paste w/c 0.28							
aged 28 days	23	12	10	1	0	0	25
aged 1 year	16	12	4	0	0	0	
Cement paste w/c 0.3							
aged 3 days	20	15	5	0	0	0	
aged 56 days	12	11	1	0	0	0	
Mortar, sand/cement 4:1							
w/c 0.64, before curing	19	3	7	7		2	*13
	23	3	5	9		6	
	19	3	7	7		2	
after curing 64 days							
in CO$_2$	20	1	4	4		11	
at 100% RH	19	6	7	3		3	
at 65% RH	23	3	7	9		4	
Mortar, sand/cement 3:1							
w/c 0.87, before curing	25	2	9	12		2	
	25	2	10	12		2	
	29	4	7	10		8	
after curing 64 days							
in CO$_2$	23	3	5	9		6	
at 100% RH	20	8	10	2		0	
at 65% RH	30	2	5	10		12	
Mortar cured at 100% RH							
1:1 sand/cement, w/c 0.3	17	14	2	1		0	15
2:1 sand/cement, w/c 0.3	24	13	7	3		1	
2:1 sand/cement, w/c 0.35	21	13	7	1		0	
2:1 sand/cement, w/c 0.4	21	14	6	1		0	
Mortar cured at 65% RH							
1:1 sand/cement, w/c 0.3	23	8	14	1		0	
2:1 sand/cement, w/c 0.3	30	10	14	2		3	
2:1 sand/cement, w/c 0.35	27	6	15	6		0	
2:1 sand/cement, w/c 0.4	28	7	18	3		0	

Material		Porosity (vol %) in size range (equivalent diameter)					
	Total	<0.1(μm)	0.1–1.0	1.0–10	10–100	100–1000	Reference
Concrete							
untreated	17	8	5	3	1	0	*23
fired at 620°C	15	6	4	4	1	0	
fired to 620°C wetted and							
cured for 1 day	18	12	2	3	1	0	*23
fired to 620°C wetted and							
cured for 7 days	17	12	3	1	1	0	
Air-entrained concrete w/c 0.5							8 (by
vibrated 5 sec	8	0	0	1	5	1	microscopic
vibrated 30 sec	3.5	0	0	0	3	0.5	examination)
Asbestos-cement							
density 1.78 × 10³ kg m⁻³	33	29	4	0	0	0	28
frost-resistant	37	25	10	1	1	0	16
frost-sensitive	42	31	7	3	1	0	
frost-resistant, weathered	36	26	6	3	1	0	
Stone							
Lime sandstone density 2120 kg m⁻³	24	8	6	2	8	0	24
Limestone	19	0	11	8	0	0	18
Limestone	28	0	3	9	16	0	
Limestone	28	6	20	1	1	0	27
Limestone	14	5	8	1	0	0	
Plaster of paris	38	1	5	29	3	0	9
Plasterboard	65	44	7	7	7	0	24
Mineral wool board	83	0	7	11	65	0	
	72	0	0	0	72	0	
Wood board							
Particle board density 530 kg m⁻³	42	0	6	19	17	0	
Fibreboard							
density 215 kg m⁻³	60	0	0	11	49	0	
density 610 kg m⁻³	61	0	0	25	36	0	
density 870 kg m⁻³	44	2	3	23	16	0	
Masonite fibreboard	26	3	20	3	0	0	9
Wood							
Spruce perpendicular to grain							
density 410 kg m⁻³	53	2	31	16	4	0	24
Pine 530 kg m⁻³	43	3	27	13	0	0	
Soft white pine	72	2	4	35		31	9
Hard maple	38	4	10	13		11	

Void volumns of wood calculated from densities given in reference
17, pp 54-55. Fibre dimensions from reference 7.

Wood	Void volume (%) at 12% moisture content	Mean fibre length (mm)	Mean fibre diameter (μm)
Ash	55	—	—
Birch	51	1.85	20–36
Beech	—	1.2	16–28
Maple	46	—	—
Elm	53	—	—
Red oak	48	—	—
White oak	45	—	—
Douglas fir	63	—	—
Pine	63	3.4	28–42
Spruce	68	3.2	24–34

Mean pore diameters estimated microscopically[29]

Wood	Tracheid lumen (μm)	Bordered pit pore (μm)
Fir	10–20	0.04–0.5
Spruce	10–20	0.02–0.3
Western Hemlock	10–20	0.1 –0.6

The subject of pore structure and materials properties in general was covered by the 1973 *RILEM/ IUPAC* Symposium[44]. Histograms of pore distribution in some common materials are given in Fig. 1.
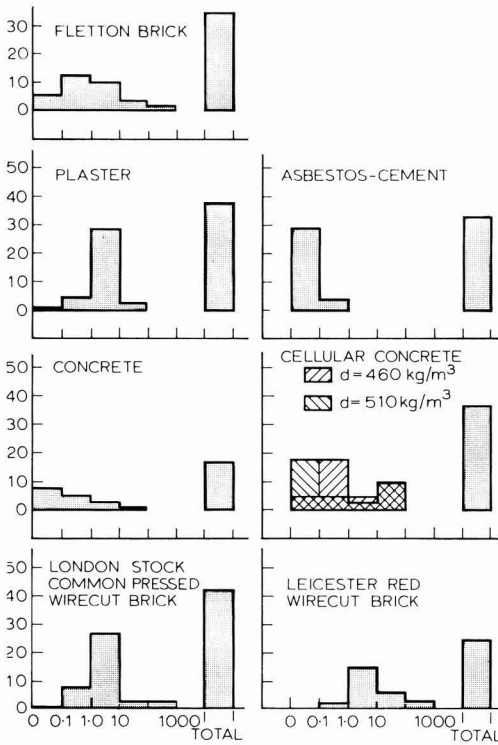

Fig. 1. Histograms of the pore size distributions of some common building materials

Acknowledgment

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Errata

Kinetics of film formation of alkyl silicate zinc-rich coatings

It is regretted that the following errors have occurred in the paper "Kinetics of film formation of alkyl silicate zinc-rich coatings" by T. Ginsberg, C. N. Merriam and L. M. Robeson, published on pages 315 to 321 of the September 1976 issue of the *Journal:*

1. At the end of the summary the words "by a lacquer-type mechanism." should be deleted.

2. Equation 10 on page 318, for " G' " read " G'' ".

3. All values of time on the abcissa in the graphs for Figs. 5, 6, 9–11 should be multiplied by a factor of 10^6. (10^3 seconds is equal to approximately 17 minutes; 10^4 seconds is approximately 2·8 hours and 10^5 seconds approximately 28 hours.)

We apologise to readers for any inconvenience caused.

Next month's issue

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

Development in electropaint coatings *by R. L. Nicolay*

The use of arsenates as reinforcing toxicants in soluble antifouling paints based on cuprous oxide *by V. Rascio, J. J. Caprari, H. J. Chiesa and R. D. Ingeniero*

Liquid polybutadiene resins for surface coatings *by P. Auckett and A. R. Luxton*

Bristol

Smoke emission

A paper was read to the Section on Friday 4 February at the Royal Hotel, Bristol, by Mr K. A. Safe of Vinyl Products Ltd on the subject of smoke emission from polymer and paint films, with Mr Brookes in the Chair.

The Speaker gave a most interesting and informative lecture which was well illustrated by slides detailing the construction and use of the NBS smoke density chamber. The chamber was used to assess the smoke emission from specimens burning under controlled conditions, which could be either in the "smouldering" or "non-flaming" condition or in the "flaming" condition.

The smoke emission was measured by the attenuation of a standard light beam from a source mounted on the base of the chamber and projecting upwards to be collected by a photo electric cell.

The tests were allowed to run until a maximum reading was recorded allowing for the maximum specific optical density to be determined.

The speaker gave examples of the smoke emission from various polymers including vinyl acetate, vinyl acetate/olefin copolymers, SBR *etc.*

Many of those present had questions for the speaker who gave informative answers.

The vote of thanks was given by Mr Lageu and carried unanimously by those present.

J.R.T.

Newcastle

Techniques in research management

The Royal Turks Head Hotel, Newcastle, was the venue for the fifth meeting of the Section on 3 February, 1977, when Mr F. Westwick of Sunderland Polytechnic presented a paper entitled "Some techniques in the management of research". Drawing on many years of industrial experience Mr Westwick delivered an instructive talk which contained a good deal of humour. Specific topics dealt with were the corporate plan, research project proposals and project planning, and in all cases the need for precise definitions of objectives and methods of assessing these were stressed. Following a lively discussion period the Chairman proposed a vote of thanks to the speaker on behalf of the 29 members and visitors present.

T.H.

London

Micro emulsions

An evening meeting of the Section was held on 13 January, 1977 at the "Princess Alice", Romford Road, E.7. when 40 members and guests heard a lecture on "Micro emulsions" from Professor C. Gillberg and Mr K. H. Falklin of Perstorp AB.

In her presentation Professor Gillberg briefly reviewed the history and development of microemulsions. Shulman in the 1940s had first dispersed mixtures of hydrocarbons and water and formed stable single phase systems composed of swollen micelles in non-solvent. In addition to the non-miscible solvents, surfactants had to be added. Anionic surfactants gave microemulsions that were stable over a range of temperatures; typically -18 to $30°C$. Non-ionic stabilised microemulsions existed over a much smaller temperature range. Both "oil in water" and "water in oil" microemulsions could be prepared.

The microemulsions were thermodynamically stable and readily formed when the components were mixed. They reformed after freezing or boiling. There was a rapid exchange between the micelles and the micellar solution. In addition, both the aqueous and the oil phases retained their own particular solubilities.

The parameters involved in formulating stable microemulsions were discussed, the levels of aqueous and hydrocarbon solvents and surfactant required depending on the components involved.

Mr Falklin indicated some of the practical uses the method could be put to in producing resin systems. Alkyd and polyester resin could now be prepared as fully water borne single phase systems instead of the water reducible, amine neutralised and solvent thinned resin solutions currently available.

The greatest difficulty in formulating practical microemulsions was to keep the surfactant level as low as possible. High surfactant levels led to slower drying and softer films than conventionally cast films because of surfactant retention. Their pH stability was often poorer than the water reducible resins and they had a non-Newtonian rheology. The advantages of the microemulsions over current water borne resins were discussed. They had high gloss, were both thermodynamically and mechanically stable and could thus be used to disperse pigments in various milling equipment. Compared with emulsions, little energy was required to prepare them as they readily formed. Flow could be adjusted by the use of different solvents.

A vote of thanks to the lecturers for their interesting and stimulating paper was given by Mr J. A. L. Hawkey.

A.J.N.

Manchester

Organic versus inorganic coatings

On Friday 11 February a meeting was held at the Woodcourt Hotel, Sale, when some 70 members and guests attended to hear a lecture from a section member, Mr J. R. Lyon of Goodlass Wall & Co., entitled "Organic versus inorganic coatings".

Mr Lyon outlined the development of zinc rich silicate coatings of both alkali metal and "ethyl silicate" types and compared their performance with a two pack zinc rich epoxy, which he claimed was the best of the organic based types. With the aid of a large number of slides and some demonstrations reminiscent of David Nixon, he demonstrated the effects of long term weathering compared to some forms of accelerated testing.

The results appeared to show that inorganic coatings were either superb or a complete disaster dependent on formulation and surface preparation.

A very lively question time followed and the vote of thanks, proposed by Mr A. McWilliam, was enthusiastically received.

A.McW.

Ontario

Food pigments

The Ontario Section held its first Technical Session of 1977 on Wednesday 19 January, at the Skyline Hotel, Toronto. Almost 50 members and guests were present for an interesting address by Mr W. Fibiger of Canadian Hoechst Ltd.

Mr Fibiger dealt with a subject becoming more and more of critical significance in the colour industry; that is of the attitude and stance currently being taken by the Canadian Food and Drug Directorate which closely parallels that of the US Food and Drug Administration.

In summary, the talk presented "objections" being forwarded to this controlling body in an effort to modify their stance on the expensive test studies regarding the use of colour pigments and their use in food packaging and plastics.

On 28 January, 1977, a highly successful first Annual Dinner-Dance was held at the "Old Mill" with an attendance of 80 people, despite severely inclement weather.

Editorial

Comments are received from time to time regarding the content of Transactions and Communications in the *Journal*. These are varied in nature, but perhaps the majority are demands either for "more practical papers", or requests for more papers of a "research standard".

Before discussing the papers published during the last few years, it is of interest to refer to the aims of the Association and the content of the *Journal*, as laid down in the "Memorandum and Articles of Association" published in 1962 and amended in 1969. These state under 3 (iii) "To raise the standard of and the scientific, technical and professional knowledge of persons engaged or intending to be engaged in the said industries . . ." and under 3 (viii) "to prepare, edit, translate print, publish, acquire, sell, lend and distribute books, periodicals, pamphlets and papers relating to the primary objects, including reports and proceedings at any meetings of or sponsored by the Association . . .". An amendment to 3 (iv) adds ". . . to publish the results of such research, experiments and scientific work". Clearly, the intentions of the Councils concerned with these Articles were the furtherance of the research and scientific aspects of the subjects covered by the Association.

When selecting papers for publication in the *Journal*, the past and present Honorary Editors have properly kept these objectives in mind. The range of readership of the *Journal* is very wide, both on account of the number of industries covered and the individual preferences of the readers. In the opinion of your present Hon. Editor, it is virtually impossible to please all readers all the time but an attempt has been made, at least, to satisfy most readers sometimes.

The Association does not commission papers, and under the present financial conditions could not do so. The papers published, therefore, depend upon what is received either directly from their authors, or which arise from meetings,

symposia and conferences either from the UK or overseas. Papers of a practical nature would be considered as meeting the requirements of the Articles and there is no bias against them, but they are very seldom received. During the past eight years the number of this type of paper submitted could be counted on the fingers of one hand.

The majority of papers submitted emanate from raw material manufacturers, research organisations and government departments. This distribution applies both to those submitted directly and those arising from meetings, symposia *etc*. The organisers of these events seem to be in the same situation as your Honorary Editor.

During the past eight years over 500 papers have been received, read and assessed from all sources and of these only about 80 have been rejected. None of the latter were practical papers; the main reasons for rejection have been irrelevance to the industries covered by the Association, on topics which have been covered adequately by other sources and a few which contained veiled advertising without disclosing precise information.

Most requests for more practical papers appear to arise from those concerned with paint manufacture. Whilst raw material manufacturers and research organisations undoubtedly employ highly skilled staff with an adequate knowledge of paint technology, their experience does not enable them to advise on many of the day to day problems which arise in paint manufacture. This must come from these manufacturers, if the requests received for more practical papers have been correctly assessed, and as mentioned above, this industry has not been a fruitful source of papers in the past.

The solution lies with our members to write or urge others to write suitable practical papers. Any such papers received will certainly be welcomed.

S. R. FINN

Notes and News

Report of Council Meeting

A meeting of Council took place at the Great Northern Hotel, London, N1 on 23 February 1977, with the President, Mr A. T. S. Rudram in the chair. There were 19 members of Council present.

The Annual Report of the Council for 1976 was approved, together with the Agenda for the Annual General Meeting which will take place on 18 June 1977. Reports were received on the arrangements for the Council Reunion Dinner in October 1977 and for the Diamond Jubilee celebrations 11-12 May 1978.

It was pointed out that congratulatory messages to the Association in the form of advertisements in the May 1978 issue of the Journal would be welcome from both raw material suppliers and paint and printing ink manufacturers. All members were asked to bring this matter particularly to the attention of their own organisations and details of advertising facilities would be supplied from the Association's offices.

It was reported that the "Official Guide" and season admission tickets to OCCA-29 Exhibition had been sent to all members of the Association earlier in the month and that late applications were still being received. The March issue of the *Journal*, containing up-to-date information, would be posted to members early in March.

Mr Mitchell commented that the Manchester Section had arranged a joint travel group for members attached to the Section and that already the party totalled more than 90. The Council felt that this was an excellent way in which Sections could participate in the Exhibition and asked other Sections to follow the example set by the Manchester Section Committee.

Arrangements had been made at OCCA-29 for the Committee to hold an informal luncheon to which principal officers of other societies, government departments, *etc* would be invited and the response had been extremely good. It was intended to hold a formal luncheon for which applications for tickets could be made by exhibitors and visitors in one of the two restaurants at Alexandra Palace on the opening day of OCCA-30, which would take place from 18-21 April 1978.

It was unanimously agreed that any member whose subscription was three months in arrear would not receive the April issue of the *Journal* and would not be entitled to copies of the *Journal* published during the period of arrears.'

Details were given of the present position in respect of the Paint Technology manuals and other publications. The position in respect of the Conference papers

was explained. Two of the papers mentioned in the November issue of the *Journal* would not now be given, *ie* those by Professor Bainbridge and Dr van der Hauw. However, the SLF had nominated a paper by Dr S. Haagenrud, and in addition two papers had been offered by Mr Hardisty of Bath University and Mr Parrish of Ward Blenkinsop & Co., bringing the total number of Conference papers to 14.

The Jordan Award Committee had considered the applications received and had awarded the 1976 prize to J. C. Reid for his paper "A fracture mechanic's approach to lacquer cracking" which appeared in the August 1976 issue of the *Journal*.

It was agreed to send a congratulatory message to Her Majesty the Queen on the occasion of the Silver Jubilee of her accession to the throne.

Dr G. P. Parfitt had agreed to present a paper which would be designated as the Association's contribution to the FATIPEC Congress which will be taking place in Budapest 4-9 June 1978.

Other matters dealt with included the representation of the Association on a BSI committee, the increase in rent on Priory House, an amendment to the London Section rules and Section Reports.

There being no other business, the President thanked members for their attendance and declared the meeting closed at 3.58 pm.

West Riding Section

Dinner and Dance

The Annual Ladies' Evening, was held as usual at the Crown Hotel, Harrogate on the last Friday in November; the Guest of Honour was Mr M. J. Levete, Director of the Paintmakers Association, who replied on behalf of the guests and ladies, to a toast of welcome by the Chairman, Mr P. Bartrum.

The opportunity was taken by the Chairman to present the Chairman's Golf cup to the 1976 winner Mr T. Wood, who also received a silver goblet as a permanent reminder of his success. For the second time a lucky ticket number draw was arranged, the fortunate winner of which was Mrs M. Booth who will receive a weekend for two at a hotel in the Falcon Hotel Group.

The Committee would like to thank all the Section members and guests for combining to make this function a very friendly and successful event, despite one or two hiccoughs!

Group photo of members and guests at the West Riding Section's Dinner and Dance.

The Chairman's table was well supported by Chairmen from Manchester Section—Mr J. E. Mitchell, Hull Section—Mr T. W. Wilkinson, Midlands Section—Mr R. J. King, Newcastle Section—Mr K. V. Hodgson, and London Section—Mr J. T. Tooke-Kirby, accompanied by their ladies.

Home made wines and the effect of alcohol on the body system

A meeting of the Section was held on Tuesday 14 December at the Mansion Hotel, Leeds. The speaker was the Chairman, Mr P. Bartrum, who delivered the traditional "Chairman's lecture".

Very appropriately for the time of year, Mr Bartrum chose as his subject, "Home made wines and the effect of alcohol on the body system". He clearly had considerable practical experience and gave an excellent exposition on the subject, containing lots of valuable tips for the budding winemaker. The success of the evening, however, was guaranteed since he had promised to produce some samples for consumer evaluation, and there were few who could resist such an offer. The occasion was made a Ladies' Evening, which also helped to create an excellent turnout.

Your reporter can vouch for the fact that all the brews offered were excellent. This opinion was shared by Mr T. Wright who succeeded in proposing a very lucid vote of thanks.

R.A.C.C.

Cape Section

New Branch

The inaugural meeting of the Eastern Cape Branch of the Association was held on 19 January and was attended by some 25 people. Mr G. Warman was in the Chair and was addressed by the Vice-President of the South African Division, Mr D. Pienaar. A proposal for a branch to be formed was put to the meeting, seconded and carried. The following provisional Committee members were elected:

Mr A. Price
Mr L. Hagemann
Mr H. Potgieter
Mr D. Lindsay
Mr E. Snow
Mr D. Bett
Mr R. Meyer

The Branch is awaiting approval from Council. Those interested in joining the Branch should contact the acting Honorary Secretary of the Branch, Mr A. Price.

Forthcoming Events

Details are given of Association meetings in the United Kingdom and Ireland up to the end of the month following publication and in other parts of the world up to the end of the second month following publication.

April

Friday 1 April

Midlands Section—Trent Valley Branch: Annual General Meeting, followed by Buffet Dance at Cross Keys Inn, Turnditch, at 7.30 pm.

Tuesday 12 April

West Riding Section: Annual General Meeting to be held at the Griffin Hotel, Bear Lane, Leeds commencing at 7.30 pm.

Thursday 14 April

Newcastle Section: Annual General Meeting at Belle Vue Hotel, Low Fell, Gateshead.

Scottish Section: AGM followed by a Ladies Evening to be held at the Beacon's Hotel, 7 Park Terrace, Glasgow G3 at 6.00 pm.

Thursday 21 April

Thames Valley: Annual General Meeting and talk on "Furniture" by Mr L. E. D. Baskerville of Parker Knoll Ltd (Ladies invited) to be held at the Beaconsfield Crest Motel (White Hart), AylesburyEnd, Beaconsfield, Bucks at 6.30 for 7.00 pm.

Midlands Section: Annual General Meeting to be held at Birmingham Chamber of Commerce and Industry, Harbourne Road, Edgbaston B.16 at 6.30 for 7.00 pm.

London Section: Annual General Meeting.

Friday 29 April

Bristol Section: Annual General Meeting to be held at the Royal Hotel, Bristol at 7.15 pm.

Irish Section: Annual General Meeting to be held at the Clarence Hotel, Dublin at 8.00 pm.

May

Monday 2 May

Hull Section: Laides' Evening "Pottery, colour and decoration" by Mr A. Simkin-Blythe Colours Ltd, to be held at the "Haven Inn", Barrow Haven, Lincs.

News of Members

Mr W. Moffatt, an Ordinary Member attached to the London Section, has been appointed Deputy Director of the Paint-makers Association of Great Britain Limited who have recently moved to Alembic House, 93 Albert Embankment, London SE1 7TY.

Mr H. G. Clayton, an Associate Member of the Manchester Section, has been appointed Divisional Manager of the Plastics and Additives Division of Ciba-Geigy (Japan) Ltd. Mr Clayton will relinquish his present responsibilities at the end of March and be based mainly in Basle, Switzerland for a period of preparation for his new position in Japan, which he takes up in September.

Mr H. G. Clayton who has been appointed Divisional Manager for Ciba-Geigy (Japan) Ltd

He first joined Ciba-Geigy in 1959 from Monsanto as a sales representative in London for pigments and some aspects of plastics, moving to Manchester in 1961.

Mr I. S. Moll (a former Chairman of the Manchester Section and a Fellow in the Professional Grade) has changed his address to 3 Charlton Manor, Charlton Marshall, Blandford Forum, Dorset. Mr Moll will remain as a Member of the Manchester Section.

The announcement of the death of Mr J. H. Grimshaw on 14 March was noted with regret. Mr Grimshaw, a former Chairman of Horace Cory & Co. Ltd., was a Member of the Association for many years.

Register of Members

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

Ordinary Members

BAIRD, NIGEL DAVID, LRIC, Craig & Rose Ltd, 172 Leith Walk, Edinburgh EH6 5EB.   (*Scottish Section, Eastern Branch*)

ENG, KAREN, MSc, Birkjogterrasserne 413E, 3520 Farum, Denmark.   (*General Overseas*)

EVANS, RONALD ARTHUR, 56 Harewood Road, Norden, Rochdale, Lancs.   (*Midlands Section, Trent Valley Branch*)

HANSEN, CHARLES, MSc, Scandinavian Paint & Printing Ink Research Institute, Odensegade 14, 2100 Copenhagen, Denmark.   (*General Overseas*)

KAPOOR, ASHOR KUMAR, BSc, 9 Clement Gardens, Hayes, Middlesex.   (*London*)

NURRISH, CHRISTOPHER MICHAEL, PO Box 252, Kasselvlei 7533, Cape Town, South Africa.   (*Cape*)

RUSSELL, FREDERICK CHARLES, 39 Dale View Avenue, London E4 6PJ   (*London*)

Associate Members

FRANKLIN, PETER, 16 Glen Drive, Stoke Bishop, Bristol BS9 1SB.   (*Bristol*)

HAMMOND, FRANCIS WALTER, 40 Millands Road, Thankerton, By Biggar, Lanarkshire.   (*Scottish*)

WALTON, KEITH ANTHONY, Lancashire Solvents Ltd, 295 Liverpool Road, Cadishead.   (*West Riding*)

WILLIAMS, ROBERT BOWEN, 14 Mossop Drive, West End, Langtoft, Peterborough PE6 9LY.   (*West Riding*)

Professional grade

At a meeting of the Professional Grade Committee held on 23 February 1977, the following Ordinary Members of the Association were admitted to the categories shown. The Section to which each Member is attached is shown in brackets.

Fellow

John George Nixon Smith (*Newcastle*)

Associate

David Walter Norbury Clayton (*Manchester*)

Thomas Hackney (*Auckland*)

John Henry McFetridge (*Wellington*)

Andrew Wilson Provan (*Wellington*)

Frederick Charles Russell (*London*)

Review

Physical chemistry of surfaces

By A. W. Adamson,

London: Wiley & Sons, 1976.

Third Edition. Pp. xviii + 698

Adamson's "Physical chemistry of surfaces" is a well known and much respected text book intended principally for college courses, of which previous editions have appeared in 1960 and 1967. It has many merits. In the first place, it is eminently readable, and theoretical concepts are lucidly presented. The book is about basics, without detailed development, so if reference to Wilhelmy's method for surface tension is required, it is there; but if a thorough-going discussion of adhesion fundamentals is necessary, it is not, though a reasonable sketch of surface energetics is given, divided between two chapters, one of which is concerned with contact angles. The stability of emulsions is discussed, but no account is given of coalescence phenomena in drying emulsion films. Thus, whilst

the subject is broadly relevant to coatings technology, the treatment is suggestive, not detailed. Polymers appear only briefly in an account of Zisman's method for the measurement of contact angles and in the adsorption of polymers by solids. On the other hand, the final chapter on the adsorption of gases by solids is detailed.

In this new edition, the layout of the second edition has been followed with some additions, described as relating to a more molecular approach. In chapter 2, a novelty is the thermo-dynamics of monolayers; in chapter 4, the thermodynamics of the electrocapillarity effect; in chapter 5, additions to the study of surface structure (photoelectron spectroscopy for example); in chapter 6, anomalous water; in chapter 7 potential distortion model for the solid/liquid interface; in chapter 8, nucleation and crystal growth (a completely new chapter); in chapter 9, surface area from negative adsorption; in chapter 10, tertiary oil recovery.

Provided the book is looked upon as providing basic concepts, it is of real use as background reading for the coatings technologist.

J. L. PROSSER

Eastbourne Conference 16-19 June 1977

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

Registrations

The closing date for registration for the Conference was given as 1 April 1977 primarily for the benefit of the Hotel managements who would be in a position to let any accommodation not taken by that date. Registrations have been received from delegates in the United Kingdom and several overseas countries.

Applications can still be accepted, and delegates are reminded that VAT (8 per cent at the time of going to press) applies to all registrations. Copies of the full programme of technical and social events and registration forms can be obtained from the Association's offices (Tel: 01-908 1086; Telex: 922670).

Preprints

Preprints of the papers are now being prepared and it is expected that these, together with details of accommodation, badges, programmes etc., will be sent to those who have registered at the beginning of June. It is a feature of the Association's Conference that preprints are sent out well in advance of the function, in order that delegates can read them before the Conference, at which lecturers illustrate their topics, but do not read their papers in their entirety. This allows for a much longer discussion period than at any other conferences and has proved of immense value to those attending previous Association Conferences.

Dates and times of sessions

As a result of several requests after the last Association Conference, this year the Conference dates include a weekend to make it easier for delegates to arrange to attend. The Conference assembles on the evening of Thursday 16 June when, in accordance with its usual tradition of hospitality, the Association will hold a reception for all those attending this function, which will be followed by a meeting of the lecturers and chairmen of the sessions. The conference sessions (which this year comprise 14 papers) will be held as follows:

Friday 17 June (9.30 am–12.30 pm)

Chairman: C. N. Finlay, ATSC (Hon. Research and Development Officer, OCCA).

Mr Parrish (Ward Blenkinsop) "Ultra Violet polymerisation".

Mr J. A. Seiner (P.P.G. Industries, USA) "Microvoid coatings—material and energy savers".

Dr S. Haagenrud (SLF) "Atmospheric corrosion testing of metallised, metallised and painted, and painted steel".

Dr A. O. Christie (International Paint Co.) "Recent developments in anti-foulings".

Friday 17 June (2.30 pm–4.30 pm)

Chairman: Dr L. Valentine, FTSC (Director of Research and Development, Berger Jenson & Nicholson Ltd and a former member of Council).

Mr M. A. Glaser (Dexter Corporation, USA). "Conserving human resources through innovation".

Mr J. G. Balfour (BTP Tioxide Ltd). "The cost of flocculation".

Professor K. Hamann and Dr G. Joppien (Research Institute for Pigments and Paints, Stuttgart). "Layer structures of absorbed polymers at pigment/solution interfaces and their influence on the dispersion stability of pigments in paints".

Saturday 18 June (9.30 am–12.30 pm)

Chairman: Dr F. M. Smith, FTSC (President, Paint Research Association and a Vice-President of OCCA).

Mr D. J. T. Howe (Consultant to the Paintmakers Association). "The paint industry in a situation of diminishing availability of raw materials".

Dr J. L. Mondt (Hoechst AG, Germany). "Binders without environmental pollution and with good penetration properties on the basis of acrylic emulsions with very fine particle sizes".

Mr A. F. Sherwood and Mr T. R. Bullett (Paint Research Association). "Save

your paint, your money and your substrate."

Professor W. Funke (University of Stuttgart). "Possible uses of reactive microgels in paint formulation".

Saturday 18 June (2.00 pm–4.00 pm)

Chairman: Mr A. G. Holt, FTSC (ICI Ltd, Paints Division and a former Chairman of the Thames Valley Section and former Vice-President of OCCA).

Mr K. Winterbottom, Mr N. S. Moss and Mr D. J. R. Massy (Ciba-Geigy Plastics & Additives Co). "A study of the effects of thiol modification of alkyd resins on their ease of cure with amino-plasts".

Mr R. W. Kay (HM Factory Inspectorate). "Labelling of dangerous substances and preparations in the EEC".

Mr Hardisty (Bath University) "Analysis of the constant-rate period of ink drying".

Social events

A full range of social events has been organised for the delegates and their families at the Conference, including a golf tournament, table tennis, coach tours, Ladies' talks, and a theatre party.

There will be an informal reception for all delegates at lunchtime on Friday and a Civic Reception will be held, at which the Mayor and Mayoress of Eastbourne will welcome the delegates, on the evening of the same day. The Association's Dinner and Dance will be the closing function of the Conference on the Saturday night. Further details of the social programme are given in the Conference programme leaflet, available from the Association's offices.

A view of the promenade at Eastbourne

OCCA Anniversary

Diamond Jubilee

In May 1978 the Association will celebrate the sixtieth anniversary of its foundation and it is felt that Members (and others who wish to take part in the celebrations) would like to have as much notice as possible of the dates. Following the pattern successfully used at the Association's Fiftieth Anniversary in 1968, the main events will be on two consecutive days. On the evening of Thursday 11 May it is planned to hold at a City Livery Hall a Commemorative Lecture, followed by a Dinner to which Past Presidents, Past Honorary Officers of the Association, Honorary Members and the surviving Founder Member will be invited as guests. On Friday 12 May the Association's Dinner and Dance will be held at the Savoy Hotel, London WC2 and Presidents of other societies, together with their ladies, will be invited to attend.

PRELIMINARY ANNOUNCEMENT

OCCA-30

THE ASSOCIATION'S THIRTIETH ANNUAL TECHNICAL EXHIBITION

WILL TAKE PLACE AT

ALEXANDRA PALACE
LONDON N22

ON

18-21 APRIL, 1978

Invitations to exhibit will be despatched in June. Companies which have not previously exhibited and wish to receive a copy of the invitation should contact the Director & Secretary of the Association as soon as possible.

OIL AND COLOUR CHEMISTS' ASSOCIATION, PRIORY HOUSE, 967 HARROW ROAD, WEMBLEY, MIDDLESEX HA0 2SF, ENGLAND   -   -   -   *Telephone :* 01-908 1086   *Telex :* 922670

Optional Professional Grade for Ordinary Members

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

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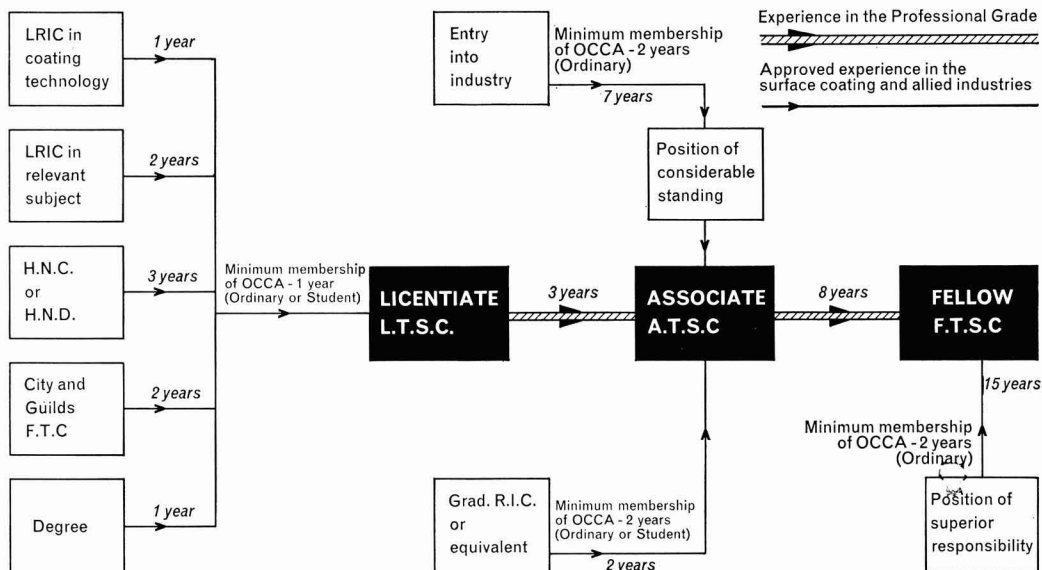
Note: At present there is no restriction on Students up to 21; between 21 and 25 a certificate from the employer or college confirming the course being taken is required.

Regulations for admission to the Professional Grade

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

A. Licentiate

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

2. Shall have attained the age of 22.

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

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

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

OR (d) Shall have passed Higher National Certificate or Higher National Diploma with three years' approved experience in the science or technology of coatings since qualifying, but two years' approved prequalification 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 Licentiateship, have practised the science or technology of coatings for not less than three years.

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

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

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

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

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

C. Associate, not already a Licentiate

EITHER

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

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

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

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

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

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

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

OR

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

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

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

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

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

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

D. Fellow

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

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

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

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

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

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

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

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

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

The fees payable with applications are as fellows:

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

Application

Completed application forms should be returned, together with the appropriate remittance, to the Director & Secretary at the Association's offices (except in the case of those Members attached to the Auckland,

South African and Wellington Sections who should address their forms to their Section Hon. Secretaries).

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

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

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

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

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

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

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

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

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

Length: Text should be approximately 5 000 words.

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

Information Received

Ciba-Geigy modernises phthalocyanine production

Ciba-Geigy is investing £2.5 million in its UK pigments operation with the extension and modernisation of phthalocyanine production at Paisley, Scotland. The new plant, which will come on stream in the second half of 1978 has been designed by the company's own engineering department at Paisley. The plant will incorporate new process technology developed at Paisley, which it is believed will provide the basis for the development of new products and more efficient production, whilst ensuring consistency of product quality.

Berger successful in South Africa

It has been announced that the production line trials of South Africa's first wide coil coating line in the Transvaal have been run successfully using a Berger silicone modified polyester system. This was achieved by a close three-way liaison between the company's UK laboratories at Chadwell Heath, Essex, Berger S.A. and the Iron and Steel Corporation of South Africa (ISCOR). ISCOR envisage a first year production of 10-12 000 tonnes, eventually rising to over 50 000 tonnes, adding a very real new dimension to the coil coating industry in South Africa.

Kiwi Products takes over safety equipment business

It has been announced that responsibility for manufacturing and marketing the complete Alan Walker & Partner range of industrial protective clothing and associated pressure ventilation equipment has been taken over by Kiwi Products Limited of Dartford. The product range provides complete safety protection to process operators, research workers, technicians and engineers in the nuclear, chemical and other related industries, or wherever a hostile environment exists.

Change of name

K. W. Revai Chemicals Ltd has announced that its name is to be changed with effect from 1 February 1977 to KWR Chemicals Ltd. The change is solely for the convenience of customers and suppliers and in every other respect the business remains unchanged.

Swale coatings now manufactured in Canada and USA

Arrangements have now been concluded between Swale Chemicals Ltd and Technical Coatings Co. for the manufacture and marketing of Swale coatings for packaging materials throughout Canada and the USA. To maintain identical worldwide standards, the raw materials used in North America will be unchanged from those already used elsewhere by Swale companies.

New plant

Schelde Chemie NV (a joint venture of the Bayer and Ciba-Geigy chemical groups) has decided to erect its first plant at Brunsbuettel, Schleswig-Holstein, German Federal Republic on a site some 120 acres in an area within an existing industrial zone. It will accommodate plant producing several thousand tons annually of anthrquinone, its mono and diamino derivatives and aminoaphtholsulfonic acids as dye precursors for the dyestuffs industry. The first installations is planned to go on stream at the end of 1979.
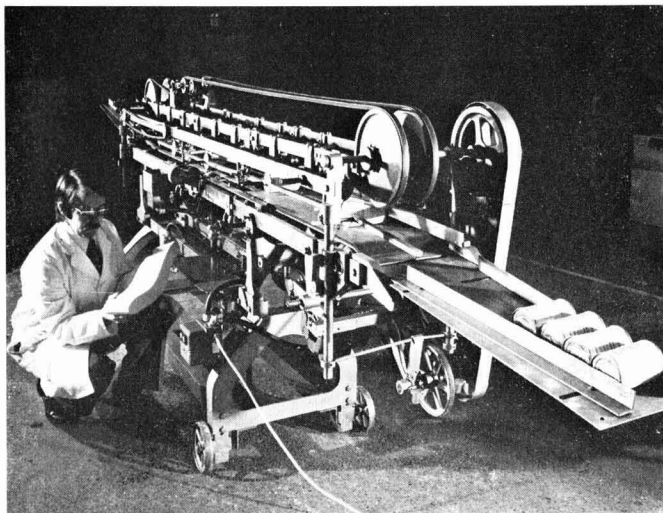
The latest Mateer-Burt labelling machine from Neumo

Expansion at Perkin Elmer Ltd

Perkin Elmer Ltd, a leading UK manufacturer of analytical instruments, have recently completed an extension to their factory at Llantrisant, South Wales which doubles the factory space available. Perkin Elmer specialise in arange of infrared, ultraviolet and fluorescence spectrophotometers, gas chromatographs and nuclear magnetic resonance spectrometers.

Total service

The Kent Chemical Co. Ltd, a member of the Phonotas Group of companies and one of the UK's leading contract chemical formulating, manufacturing and packaging companies have announced a new simplified "total service" for their customers greatly reducing the administrative and invoicing costs. They have also appointed Phillips & Hind Associates as their Public Relations Consultants.

New products

New anti-foam agent

Theo Goldsmchidt have announced a new anti-foam agent called Polymekon 1488 designed for use in the manufacturing of high gloss acrylic emulsion paints. The product, a 20 per cent emulsion of a modified silicone oil, is claimed to be effective both during the production of the paint and its application, without affecting the gloss finish of the paint.

Mini-Z Electro thermometer

Channel Electronics (Sussex) Ltd have announced a new simple operation thermometer called "The Mini-Z Electro thermometer" which incorporates modern thermistor technology to provide rapid and accurate readings of temperature. The instrument is said to be invaluable to laboratory technicians, engineers, research workers *etc.* both in the workshop and in the field.

Improved wrap-around labeller

Neumo of Newhaven have announced their latest Mateer-Burt high speed, automatic, roll-through labelling machine, capable of labelling metal, glass, plastics and spiral-wound containers at rates of 500 a minute.

Suprapal AP 20

BASF have announced their new range of the Suprapal AP resins which are styrene-maleic copolymers (alcohol-soluble hard resins with high melting points) with applications in rapid drying, nonyellowing and water-resistant coatings for paper and film and in printing inks for use either as sole binders or together with cellulose nitrate.

Corrosion-resistant valves

Durco Process Equipment Ltd have announced a new range of Durco G4 sleeveline valves with applications throughout the process industries for the control of liquids, gases, vapours, slurries and sterile services. Suitable for operation at pressures of 720 psi and vacuum to 1 micron, these valves have been proven in service in the USA and on the Continent when handling hydrofluoric acid and anhydrous HCl, pickle liquor, phosgene, chlorine, vinyl chloride and many other chemicals and mixtures. A major feature of the G4 valve range is the reverse lip PTFE diaphragm seal around the stem of the valve. It provides a static seal against leakage to atmosphere, or on vacuum service, against air leakage to the valve.

New range of impregnating varnishes

Three new cost-saving impregnating varnishes have been developed by Hadfields Industrial Division of Bestobell Paints Ltd. The products, now being launched, are isophthalic polyesters, with flash points greater than 32 C, capable of withstanding temperatures up to and

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including class F (155°C) continuously, and up to class H (180°C) intermittently. This new range of impregnating varnishes has been developed specifically to reduce operating costs by reducing varnish/solvent usage, improving performance and reducing storage problems and fire risks.
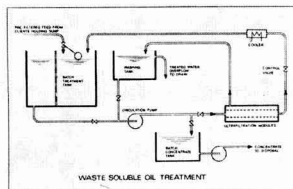
A schematic representation of the new system

New waste oil disposal system

Paterson Candy International Ltd, Reverse Osmosis Division, have developed a new economical system for disposal of soluble oil emulsion wastes. The system, ultra-filtration, does not require the addition of any chemicals and works by separating the waste into oil concentrate and water which is clean enough to discharge to sewers. The oil concentrate is reduced to about one tenth of the original solution volume, and although still about 50 per cent water, can be stored and tankered to waste cheaply, can be burnt in gas or oil fired incinerators and, in many instances, can be accepted by reclamation companies for refining.

New stencil systems

Many screen printers from the London area were recently invited to Stericol's new stencil making premises to see the latest techniques involved in screen stencil production. On show was a new


Adhesion properties of the new Alphastar photostencil film being demonstrated

automatic screen stretcher capable of tensioning pieces of mesh up to 8×3 metres permitting an average of ten large frames to be stretched at a time. The

equipment was complemented by additional pneumatic stretchers and a full range of photographic facilities was demonstrated.

Mr G. West, Sales Manager of Autotype International gave an illustrated lecture on the benefits of Alphastar, the new indirect photostencil with the very wide exposure latitude, and which is composed of pre-sensitised blue pigmented gelatine emulsion coated on to an optically clear 0.05mm polyester base of high dimensional stability. It has the benefit of simple processing combined with excellent adhesion to mesh, rapid washout and protective "Pro-Kote" to prevent blocking even at high humidities. Alphastar has been designed for use with paper or plastics and the edge definition is very sharp.
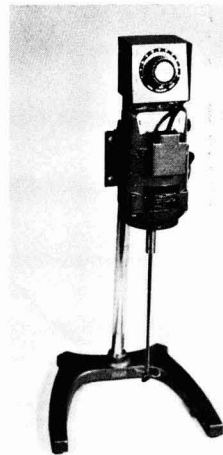
New Voss S8/CB Stirer which incorporates giving speed control from Voss Instruments Limited

New level controller

Goring Kerr Controls Division have announced a new level detector and indicator for use in liquids and solids contained in tanks, containers, hoppers, silos, barrels *etc*. The system, using bridge measurement techniques in a remote controlled unit, is intended for controlling the filling or emptying of any container, and can be used to sound alarms in the event of incorrect or danger situations occurring.

With the exception of the output plug-in relay, which provides electrical isolation, the equipment is entirely solid state offering high reliability.

Conferences, courses etc.

Polymer symposium

Polytechnic of the South Bank, Department of Chemistry and Polymer Technology is to hold a three-day Seminar on Developments in Condensation Polymers commencing 24 May 1977 in Room 248 at the Polytechnic.

International Colour Association

Color 77 will be held on the Campus of Rensselaer Polytechnic Institute, Troy, New York, 10-15 July, 1977.

Corrosion meeting

The Institute of Corrosion Science and Technology, Midland Branch will hold a two-day meeting on 2-3 May 1977 at the Emgas Regional Training Centre, Waverley Street, Long Eaton, Nottingham. "A second short course in external corrosion and protection of buried pipelines."

Colour courses

Instrumental Colour Systems Ltd will hold a Colour Course on 3-6 May, 1977 at 13 Bone Lane, Newbury, Berkshire on "Colour Technology".

Varnishes and paints congress

XIVth FATIPEC Congress organised by Hungarian Chemical Society will be held on 4-9 June 1978 in Budapest, Hungary, on "Recent progress in the production, processing and properties of varnishes and paints".

Filtration course

A refresher course on Laboratory Filtration organised by the Filtration Society will be held on 23 March 1977 at The Regent Centre Hotel, Carburton Street, London W.1.

Mildew symposium

The Paint Research Institute is organising a symposium on "Mildew vulnerability" to be held at Battelle Memorial Institute, Columbus, Ohio on 16-17 May, 1977.

Literature

Airmix spray equipment test

After being approached by Kremlin Spray Painting Equipment Ltd, the Paint Research Association at Teddington have published a report on the new Kremlin Airmix Spray equipment. The conclusions of the report were that the automatic airmix gun reduced bounce back and overspray considerably thus saving on the amount of paint used and improving conditions for operators.
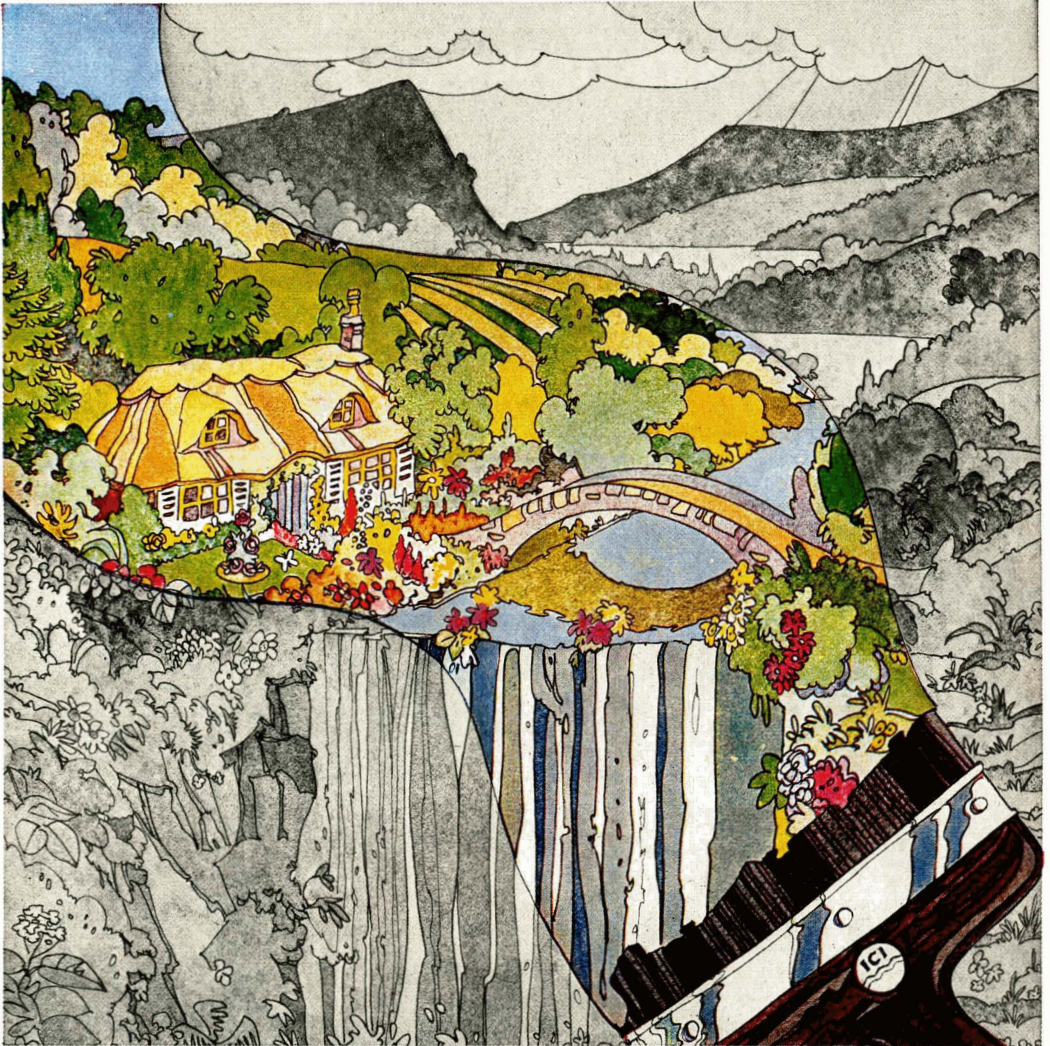
European paint industry profile

Information Research Limited have issued a News Release entitled "Profile of the European Paint Industry" which identifies major paint makers in each of the national markets, and gives comparisons of sales levels, market shares and number of employees. Recent changes in the industry are commented upon and the most significant national and international acquisitions in recent years are listed.

Resin guide

Cray Valley Products Ltd. have published their 1977 United Kingdom Resin Guide which lists the various types of resins, their suggested uses and their reference codes.

Solvents booklets

Esso Chemicals Limited, Solvents Division, have announced that they will be publishing a revised version of their brochure "Esso solvents at a glance" in April, and they have also published a booklet "Solvents, society and safety" which is about hazards to the users of the solvents.

Protect your environment with Proxel CRL.

Looking at the water from which paint can grow

A tin of water-based paint that doesn't contain a totally effective in-can preservative can escalate into quite a nightmare. Gassing, loss of viscosity, fouling odours, modification of pH and coagulation of the latex are all the results of in-can degradation.

Dow has done something about it. We spent years researching antimicrobials for paint. Correlating laboratory data with field results. Comparing our bactericides with our competitors' on a stringent cost-performance basis.

Carrying out tests on our clients' paints. Painstakingly developing Dowicil *75, the high water soluble preservative that stops in-can degradation before it starts. And concentrations from 0,05 to 0,15% are all you need.

It could mean the difference between a good paint and a lost reputation.

Our Technical Service and Development Department will be pleased to supply you with further information.

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a) Heathrow House, Bath Road, Hounslow TW5 9QY. Tel: 759 2600.

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Please attach this coupon to your letterheading, stating your name and send to one of the addresses above for further details of Dowicil 75.

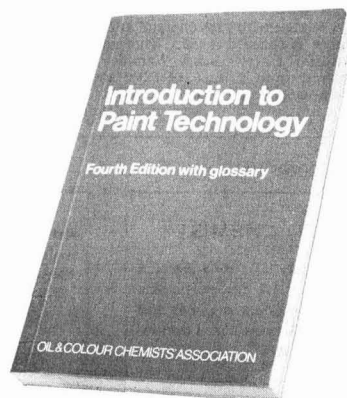## Dowicil *75
Helps keep paint, paint.

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Contents include:

1. Origins and Development of Paint Technology

Science and empiricism. What is paint technology? Paint origins. Pigment, Vehicle, Paint. Synthetic Resins—early history. Film formers. Molecular structure and size. Polymerisation. Mechanical bonding. Thinners. Types of drying mechanism. Physic of paint technology. Paint formulation. Paint systems. Nomenclature.

2. Oils

Drying oils. Semi-drying oils. Non-drying oils. Chemical structure of fatty acids Drying rate. *Drying oils:* Linseed oil. Stand oils. Tung oil. Soya bean oil. *Semi-drying oils:* Dehydrated castor oil. Tall oil. Tobacco seed oil. Safflower seed oil. Sunflower seed oil. Poppy seed oil. *Non-drying oils:* Castor oil. Coconut oil.

3. Natural and Synthetic Resins

Natural resins: Run gum. Damar resin. Rosin. *Synthetic resins:* Alkyd resins. Manufacture of alkyd vehicles. Phenolic resins. Vinyl resins. Vinyl polymers and copolymers. Solvent soluble vinyl resins. Vinyl chloride dispersions. Styrene containing resins. Polyester resins. Urea resins. Melamine resins. Epoxy resins. Epoxy/pitch media. Polyurethane resins. Acrylic resins. Silicone resins. Coumarone resins Petroleum resins. Chlorinated rubber. Non-aqueous dispersions.

4. Resins as Media for Paints

Oleoresinous media: Alkyd resins as media. Cellulose lacquers and media. Solvents for cellulose lacquers. Manufacture of lacquers. Other solvent-soluble, film-forming high polymers. *Spirit varnishes.* Solvent and driers: solvents, driers. *Some uses of clear finishes.* insulating varnishes, wood finishing by cellulose lacquer. Water-based paints for industrial use.

5. Pigments and Extenders

Dispersion and wetting: wetting, wetting agents. *Inorganic Pigments:* white pigments: titanium dioxide, antimony oxide, zinc oxide, lithopone, white lead, zinc phosphate. Extenders: barytes, blanc fixe, whiting, precipitated chalk, silica, china clay bentonite, slate powder, mica, asbestine, talc. Black pigments: carbon blacks, vegetable (lamp) black, bone and drop blacks. Metallic pigments: aluminium, bronze powders, zinc. Oxides of lead: red lead. Natural oxides of iron: red oxides, ochres, siennas, umbers, micaceous oxide of iron. Chemically prepared oxides of iron: yellow hydrated oxides, reds and browns, black oxide. Chrome pigments: lead chromes, zinc chromes, zinc tetroxychromate, stronium chromate. Blue pigments: prussian blue, ultramarine blue, Green pigments: chrome (Brunswick) green. Flooding and floating. Cadmium pigments. Nickel titanate. *Organic pigments:* classification of organic pigments: pigment dyestuffs, toners, lakes. Chemical classification: azo pigments, alkali blue or reflex blue, phthalocyanine pigments, phthalocyanine blues, phthalocyanine greens, vat colours, idanthrone blue, quinacridone pigments, dioxazine pigments. *Luminescent pigments. Testing of pigments:* staining power or tinting strength. Opacity or hiding power. Oil absorption Water-soluble matter. Lightfastness. Chemical constitution. Purity. Conditions of exposure, measurement of lightfastness. *Pigment hazards:* toxicity, dust.

6. Decorative and Structural Paints

Types of decorative and structural paints. Sealers. Primers: primers for wood, primers for alkaline and porous surfaces, primers for iron and steel, the mechanism of corrosion, protective mechanism of paint coatings, metal cleaning and pretreatment, blast primers, etch (or wash) primers, zinc-rich primers, zinc silicate primers, zinc phosphate primers, zinc chrome primers, red oxide/zinc chrome primers, red lead/ linseed oil primers, calcium plumbate primers, primers for galvanised surfaces.

Undercoats, fillers and stoppers: stoppers, fillers, undercoats. *Finishes:* alkyd-based finishes. 'Non-drip' or thixotropic finishes, semi-gloss and eggshell finishes, oleoresinous finishes, finishes for structural work, chlorinated rubber finishes, epoxy-resin finishes, epoxy ester finishes, vinyl resin finishes, masonry paints. *Emulsion paints:* nature of emulsions, preparation of polymer emulsions, homopolymers and copolymers, manufacture of emulsion paints, additives, properties and uses of vinyl emulsion paints, acrylic emulsions.

7. Industrial Stoving and Cold-curing Finishes, including Marine Finishes

Industrial finishes. Table of media used for various purposes, alkyds, alkyd/amino combinations, epoxy and epoxy ester resins, epoxy/pitch combinations epoxy/ acrylamide acrylic resins, hydroxylated acrylic/amino resins, hydroxylated acrylic, isocyanate resins, thermoplastic acrylic resins, cellulose finishes, polyurethane finishes, vinyl resin finishes, plastisols and organosol finishes, chlorinated rubber finishes, polyester finishes, non-aqueous dispersion finishes, phenolic resin finishes, water-thinnable finishes, solicone resins, zinc silicate finishes, oil-free polyester finishes. *Stoving Equipment:* convection, infrared radiation, induction, dielectric heating. U.V. curing, electron beam curing. *Paint application:* padding, spraying, airless spraying, electrostatic spraying, hot spray technique, dipping, 'roto-dip' process, flow coating, curtain coating, roller coating, silk screen method, vacuum and pressure impregnation, electro-deposition, powder coatings, strip coating, aerosol spraying.

8. Paint Manufacture and Hazards

Paint milling: function of paint mills. General principles of paint mills. *Types of mill:* premixers, mixers for pastes, mixers for slurries, paddle mixers, high speed mixers. Dispersing mills. Dispersing mills requiring premixers. Triple roll mills, single roll mills, colloid mills, the sand mill, sealed sand mill, the 'Dyno' mill. Dispersing mills, direct charge: the ball mill, the attritor mill, high speed dispersers, the kady mill. Thinning mixers. Straining. Filling. *Health and fire hazards:* toxicity, pigments, resins, solvents, fire, other fire risks.

9. Common Defects of Varnishes and Paints

Varnishes: bloom, blushing, pinholing and cissing, silking. *Paints:* blistering, checking, cissing, crawling, dirt collection during drying, flotation, livering, pinholing, pigment sedimentation, rivelling, sagging, curtaining and tears, silking, skinning.

10. Paint Testing

Liquid paint: viscosity, brushability, colour measurement, colour matching, lightfastness, opacity, drying time. *The dried film:* adhesion and elasticity, hardness, gloss, film thickness, wet and dry, fineness of grind, water resistance, humidity resistance, salt spray resistance, durability, weatherometers.

Glossary—Appendices—Index

Copies of this book are available at £5.00 each (prepayment only), post free by surface mail, from:

OIL AND COLOUR CHEMISTS' ASSOCIATION, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF.

CLASSIFIED ADVERTISEMENTS

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PIGMENT CHEMIST

Unusual opportunity for young pigment chemist to live in USA and participate in growth of independent pigment and flush producer. Interviews in London, late April. Reply to:

Pope Chemical Corporation,
33 Sixth Avenue, Paterson,
New Jersey 07524, USA.

SITUATIONS WANTED

Paint Technologist, 32, with wide experience in formulation, testing and manufacture of modern industrial paints, seeks opportunity in overseas. Languages: fluent German, English and some Spanish. Box No. 439.

SYMPOSIUM

Colour Group Symposium

Colour: Art, Design, Science and Industry

To be held at the Royal College of Art in the Gulbenkian Hall on Monday and Tuesday 25-26 April 1977.

Enquiries to: Miss Audrey M. Mitchell, Hayward Mitchell and Pavey Limited,

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Retired member of the Association wishes to dispose of copies of JOCCA 1948–76 (less one copy March 1956) unbound. £10.00 o.n.o. Box No. 437.

BOOKS WANTED

Books Wanted: Overseas student particularly wishes to obtain complete set of the Paint Technology Manuals Parts I-VII. Please state in reply whether the copies of Parts I-III are the first or second edition and the price required. Box No. 435.

ANNOUNCEMENT

OCCA-30

will be held at

Alexandra Palace London, N22

on

18-21 April, 1978

Companies wishing to exhibit should contact the Director & Secretary at the address on the Contents page to receive an Invitation to Exhibit.

BOOK ORDER FORM

To: The Director and Secretary,
Oil & Colour Chemists' Association,
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Date..

Please send me copies of the books as listed below (see page 77 of this issue for titles and prices):

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