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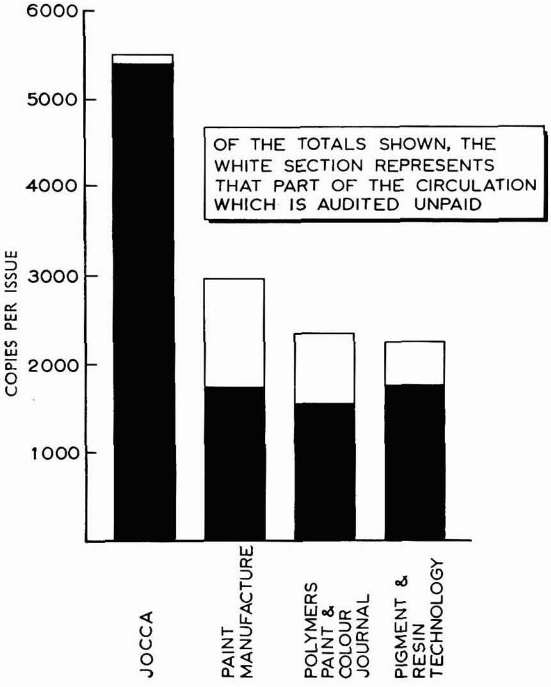

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Contents **Vol. 56 No. 6** **June 1973**

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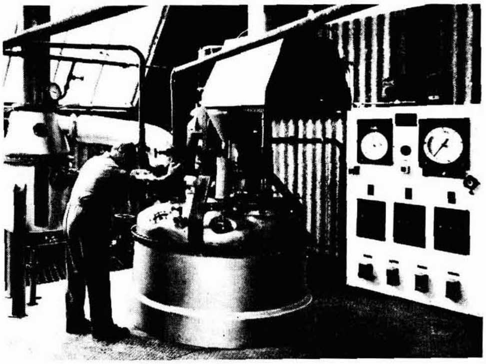

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Transactions and Communications

Micro-organisms, the environment and materials*

By D. Allsopp, H. O. W. Eggins and B. S. Hollingsworth

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Summary

Biodeterioration is defined and examples given of major types. The main principles involved in biodeterioration studies are outlined, and the importance of ecological studies is stressed, particularly in relation to micro-environments. The need for forward planning is emphasised, and economic factors are discussed.

Keywords

Process and methods primarily associated with service or utility

biodegradation

Miscellaneous

micro-organism
pollution

Micro-organismes, l'environnement, et matériaux

Résumé

On donne une définition de la biodétérioration, de même que des exemples des types importants de ce phénomène. On trace les grandes lignes des principes fondamantaux de la biodétérioration, et l'on souligne l'importance des études écologiques, surtout en ce qui concerne les micro-environnements. On fait ressortir la nécessité de la planification pour l'avenir, et l'on discute les facteurs économiques.

Mikroorganismen, Umgebung und Materialien

Zusammenfassung

Biologisches Verderben wird definiert, und Beispiele der wichtigeren Arten werden gegeben. Die hauptsächlichen bei solchen Untersuchungen in Frage kommenden Prinzipien werden umrissen; die Wichtigkeit ecologischer Untersuchungen, insbesondere im Bezug auf die Mikroumgebung, wird betont. Auf die Notwendigkeit vorauszuplanen wird hingewiesen, und wirtschaftliche Faktoren werden besprochen.

Микро-организмы, окружающая среда и материалы

Резюме

Определяется биодетериорация и даются примеры главных типов детериорации. Обсуждаются главные принципы связанные с изучением биодетериорации и подчеркивается важность экологических исследований, в особенности по отношению к окружающей микро-обстановке. Подчеркивается необходимость будущего планирования и обсуждаются экономические факторы.

Introduction

The text of this paper covers, perhaps, a little more than the title suggests in that it is an attempt to outline the main principles involved in biodeterioration studies, and thus organisms other than true micro-organisms are mentioned. It is felt that this is a logical approach for, having established basic ideas concerning the attack on materials by organisms generally, microbiological aspects, and the microbiology of paint and paint films in particular, can be more logically and easily discussed.

As mentioned by Professor Hughes in the previous paper,[1] interactions of organisms and materials can be traced back through history. The historic and notable cases are augmented by the types of attack which are common knowledge, the rotting of timber, insect attack on furniture, moulding of stored food being familiar to all. Many cases of biological attack fall under the heading of biodeterioration, which may be defined as "any undesirable change in the properties of materials of economic importance brought about by the normal vital activities of living organisms." As previously indicated, this definition not only includes micro-organisms but also higher organisms such as molluscs, crustaceans, insects, birds and mammals. Thus, biodeterioration can be considered as pragmatically negative in effect, this being a useful shorthand way of saying that it is not generally welcome in man's economy.

A term often confused with biodeterioration is biodegradation. Although literally meaning decay caused by organisms, this latter term should be used where the results of decay are pragmatically positive or generally useful to man, for instance where a waste material is treated biologically to provide a more useful or acceptable material, as in the case of town waste composting or the production of protein by fungal growth on waste materials.

Types of biological attack

It is useful to classify attacks into main recognised types, although the effects of a biological attack on a material may be varied and several.

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*Paper presented at the Manchester Section's 1972 symposium on "Paint performance and the microbiological environment."

Fouling or soiling

In this instance, it is the presence of the organism, its body or excreta which is objectionable rather than its activities in deteriorating the material. An accretion of fouling organisms such as barnacles, sponges and weed on ships leads to slow speed and increased fuel consumption; the growth of dark-sporing fungi on soap particles clinging to plastic shower curtains is unpleasant aesthetically and necessitates cleaning.

The aesthetic factor is of great importance here. Bird droppings on buildings are of little satisfaction, except perhaps to the birds; and the disfiguring algal films to be seen on painted walls in the tropics are of satisfaction to no one.

Mechanical deterioration

Physical damage to a material by organisms not using it as food falls in this category. Examples are rats gnawing lead piping or electrical cables, and insects tunelling through wood and paint films to provide space in which to lay eggs. Decorative plastic films are not immune; termites can attack these most sucessfully.

Chemical assimilatory deterioration

Here, the material is used as a nutrient-source by the organisms. This is a very common type of deterioration. The utilisation of oils in paint by fungi, the growth of bacteria and fungi on stored food, eating of stored grain by rodents are all examples of this type of deterioration. It is, perhaps, the most readily understood type of deterioration.

Chemical dissimilatory deterioration

This type of deterioration often coincides with the former ones as it covers decay and damage caused by substances liberated from organisms. An instance of this type occurring alone is the etching of optical lenses by acids liberated by fungi; the fungi living not on the glass, but on dirt on the lenses or nearby.

One of the ways in which these different types of decay have been considered in a unified way is by the comparison of aspects of biodeterioration and pathology. The impairment of normal function of a subject, and the reaction of the subject to a noxious agent in human, animal and plant pathology can be compared with biodeterioration cases. The systematics of pathology and biodeterioration can also be compared and listed under equivalent headings. These exercises, whilst being rather academic, do indicate aspects of the underlying unity of biodeterioration.

Another unified approach to biodeterioration is that of ecology, the study of the interaction of organisms and their habitat or environment. Thus, substrates (materials), organisms and environments, all intimately connected with biodeterioration, are also the fundamentals of ecological work. It could be assumed, therefore, that ecological studies have always gone forward hand in hand with studies of biodeterioration. This, however, has not been so in the past, for biodeterioration is a very practical science and often the emergency of a particular situation has demanded that a partial approach to a problem only be attempted, despite this being contrary to good scientific practice.

Fundamentals, such as details of environments, distribution of micronutrients and deteriogen propagules, have often been disregarded, but this attitude cannot continue if more effective and subtle means of control are to be developed.

Ecology

There are basically three types of problem within biodeterioration in which ecology has an important role to play. The first is fundamental, being concerned with predicting the susceptibility of a material to attack by various organisms for known environmental conditions. This can be summarised by the question "Will it rot and, if so, when?"

The second problem concerns the accurate assessment of that colonisation and decay of materials which has been caused by deteriogens, and the successful distinguishing of deteriogens from associated non-deteriogens. This involves, mapping the actual case history of a deteriorated material. It is common to have many organisms present in a deteriorated material. Some will be responsible for the attack, others will be merely contaminants or secondary colonisers living on the by-products of the real deteriogens. It is essential to distinguish the real deteriogens if the third problem is to be overcome efficiently and economically.

This third problem involves the design of specific preventive or remedial treatments which will be effective against predicted populations of susceptible deteriogens.

All these three areas of interest depend upon an accurate knowledge of the distribution of potential deteriogens, not only on a global scale, but also within specific man-made environments. Even where global surveys may be carried out, care must be taken to ensure that the survey is made by trained workers to avoid errors due to variations in the macroscopic appearance of deteriogens. Very little is known concerning such distributions, particularly among the fungi. This is not only a failure of biologists; surprisingly little is also known concerning precise conditions of a particular substrate. It is common to find reference to average temperatures, humidities and hours of light, but such information is usually concerned with the air surrounding a material, rather than with the surface or the interior of a material, which is what really concerns the deteriogens.

In practice, the collection of averages is often all that can be done, but attempts should be made to relate these to the range of variations which may occur, and not speak of average conditions as the usual conditions.

The significance of the interface

The study of the biological implications of growth at interfaces is long overdue. Most growth, especially the reproductive phase of growth, and development of micro-organisms occurs at an interface (consider the formation of dark fungal spores on a paint film). Spores destined for wind dispersal are formed at the surface, not deep down within the material. Leaving aside chemical protection, little is known concerning the purely physical properties of surfaces which may render the material less liable to attack. Factors such as susceptibility for attachment, water holding, encouragement of condensation, and heat and light reflectance need to be studied in relation to microbial ecology, together with changes in these factors, which undoubtedly occur when a microbial colony becomes established. That is, the microclimates of uncolonised and colonised surfaces should be studied.

Micro-environments

When a substrate is considered in this way, on the surface or in depth, it becomes clear that a whole series of micro-environments must be considered. Each will have its own temperature and humidity patterns, nutrient requirements and possibly associated organisms and secreted products. Averages in such situations have relatively little meaning when considering the activities of deteriogens within these substrates. Often, in practice, equilibrium is never reached between the substrate and the surrounding air. Thus, if a piece of painted exposed timber in a particular climatic situation is considered, information regarding average temperatures and humidities in the locality will have little meaning unless attempts are made to relate them to effects at the surface. For example, it is very difficult to find out the precise effects that insolation, that is heating due to the sun, have on a piece of wood, for the surface and internal conditions will fluctuate very markedly, to such an extent that they will bear little correlation to the general air conditions. It is, however, these surfaces and internal conditions which are of the greatest significance in determining the organisms which may be present and able to grow. In such a situation, therefore, it is not surprising that it is possible to isolate a complete temperature spectrum of fungal deteriogens, up to those able to live and cause decay up to around 50°C. Thus, within a substrate there is a population of deteriogens able to grow as the temperature changes, diurnally, seasonally and at various depths. The isolation of one organism at one temperature does not mean that it is the only organism to be considered. When considering case histories, there are several pitfalls open to the investigator. The major one, which is apparent when a deteriorated material is presented for examination, is that an attempt is being made to ascertain at one point in time processes which have gone on before and have no doubt varied.

The work done on a material to isolate organisms at the final stages of decay may only give a partial picture of the range of colonisers. For the work to be of greatest value, an ecological study over a period of time is required; this is of particular relevance where biocides are employed to establish such factors as the fate of the biocide, its effect on different colonisers and its possible detoxification and eventual breakdown. In these times when concern is being shown regarding the effects on chemicals being released into the environment, a true ecological approach to such studies becomes the best practical method for the study of the ultimate fate of biocides. It is, undoubtedly, a very time-consuming approach, but it is one which is becoming increasingly necessary.

Concerning the study of distribution or organisms, it is important to determine not only where different organisms are to be found, but also whether or not an organism varies in its ability to colonise and decay a particular substrate. This would help in the design of test techniques and lead to a more logical choice of test organisms. The numbers of different organisms which exist necessitates that only a few representative samples be chosen for test work and, this being so, samples should be chosen with the utmost care to ensure that the results are really meaningful. Another factor here is that of the inter-relationships of organisms. Usually, isolated toxonomic groups are used for test work, but in nature organisms are usually associated. The implications of these associations (for example of fungi and nematode worms, fungi and insects, bacteria and fungi) in respect of their deteriogenic potential have yet to be thoroughly investigated.

It is to be hoped that the use of ecological studies will continue to increase as a basis for the study of biodeterioration; for test techniques and for biocide development. This approach may not show an immediate return on research investment, but it is hoped that, as biodeterioration is now sufficiently advanced as a subject in its own right, a more long term view can be taken. Ecology is an essential part of the extremely practical science of biodeterioration and deserves due prominence. Techniques of investigation need to be further developed to present answers in the ecological field meaningful to those in the forefront of deterioration prevention. A serious and well planned approach to the prevention of biodeterioration could enhance dramatically the pattern of growth and achievement of developing countries, particularly in regard to their food problems and technological advancement, whereas in the more developed countries such prevention can lead to greater economic efficiency.

Waste

Thoughts on wastage lead to ideas of conservation. Often a narrow view is taken of this topic, by considering only the more natural aspects of man's environment, such as forests and rural areas. These aspects are, of course, important but if they are to be conserved a wider view must be taken. The less raw materials are used up, the more they have chance to re-generate, or the more the chance of substitutes developing. It is in this area that biodeterioration control and applied biodegradation have a part to play, the one slowing down the rates of wastage of materials and the other processing and re-cycling wastes and low-value by-products.

Economics

As biodeterioration is studied, it becomes more and more apparent that it is limited with economic aspects. As standards become more exacting, so biodeterioration becomes more important, for small flaws in a highly processed material due to microbial activity are much less acceptable than the same flaws in a raw material. One maggot in a large bag of fruit is quite probably acceptable, but the same fruit processed into a can of pie filling at four times the price would certainly be rejected due to the presence of the same maggot even if dead and harmless in itself. In a similar manner, a small amount of microbial growth in a can of modern paint at a modern price would lead to its rapid rejection.

In developing countries, where the supply of materials generally is more critical often than in developed countries, and often where conditions for decay are more favourable due to poor storage and the climate itself, losses due to biodeterioration are very marked and very costly.

It is known that the losses due to biodeterioration can be very large, but here, as in the case of the identification of biodeterioration itself, there is a great problem in assessment of losses. It is often necessary for a problem to be assessed accurately in cash terms before action is taken. Statistics for many types of losses are probably on record, but until they are recognised as biodeterioration and then listed as financial records, separate from other losses (due to corrosion, bad handling and so forth), little co-ordinated effort can be made to alleviate the situation.

[Received 26 January 1973

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J. Oil Col. Chem. Assoc. 1973, 56, 241-246

Some general laboratory techniques employed in the study of surface colonisation of materials by soil micro-fungi*

By B. S. Hollingsworth, H. O. W. Eggins and D. Allsopp

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Summary

Biodeterioration is briefly defined and classified. Susceptibility of materials to biological attack is discussed, together with the problems of recognition and identification of biological colonisation of materials. Techniques for examination and identification of materials undergoing surface colonisation are described, followed by an objective review of some general isolation techniques employed in biodeterioration investigations. Perfusion colonisation isolation techniques are described and discussed, together with some laboratory test procedures for the evaluation of colonisation.

Keywords

Processes and methods primarily associated with analysis, measurement or testing
test procedure

Miscellaneous
aerobic organism
biodeterioration

Quelques techniques générales de laboratoire utilisées lors des études sur la colonisation des surfaces de matériaux par les micro-organismes mycéliens de sol

Résumé

On offre une définition briève de la biodétérioration et l'on la catalogue. On discute à la fois la susceptibilité des matériaux à l'attaque biologique, et les problèmes à l'égard de la carácterisation et l'identification de la colonisation biologique de matériaux. On décrit les techniques pour étudier et pour caractériser les matériaux dont les surfaces sont susceptibles à être colonisées, suivi par une revue objective de quelques techniques générales d'isolation. On décrit et discute les techniques de perfusion, de colonisation, et d'isolation, de même que quelques méthodes d'essai de laboratoire pour l'évaluation de colonisation.

Einige allgemeine beim Studium der Kolonisation von Bodenmikropilzen auf Oberflächen von Materialien benutzte Laboratoriums techniken

Zusammenfassung

Biologisches Verderben wird kurz definiert und klassifiziert, Empfindlichkeit von Stoffen gegen biologischen Angriff wird besprochen ebenso wie die Probleme des Erkennens und der Identifizierung biologischer Kolonisation auf Materialien. Methoden zur Prüfung und Identifizierung von Stoffen, auf deren Oberflächen Kolonisation vorkommt, werden beschrieben. Anschliessend werden einige allgemeine Isolierungstechniken zur Untersuchung biologischen Verderbens objektiv betrachtet. Perfusionskolonisations-Isoliertechniken werden beschrieben und besprochen, ebenso wie einige Laboratoriumsprüfmethoden zur Bestimmung des Ausmasses der Kolonisation.

Некоторые общие лабораторные приемы применяемые в изучении колонизации материалов почвенной микроплесенью

Резюме

Биодетериорация кратко определяется и классифицируется. Обсуждается восприимчивость материалов к биологическим атакам и также проблемы опознания и идентификации биологической колонизации материалов. Описываются технологические приемы для анализа и опознавания материалов подвергаемых поверхностной колонизации, после чего следует объективный обзор некоторых общих технических приемов изоляции, применяемых в исследовании биодетериорации. Описывается и обсуждается техника окропляемой изоляции колонизации и также некоторые лабораторные испытания для оценки колонизации.

Introduction

The study of the surface colonisation of materials by micro-organisms may be regarded as the starting point for all further studies in biodeterioration, since it is generally at the surface of materials that the attack is first recognised. It is not, however, necessarily the site at which the problem of biodeterioration really lies.

Biodeterioration[1] of materials is generally accepted as being "any undesirable changes in the properties of a material, caused by the vital activities of organisms". It can be appreciated from this definition that the field of biodeterioration is vast and it is for this reason that the present paper will be limited to the specific field of mycology, although some techniques discussed may indeed be adapted for use in other fields of study.

Biodeterioration may be classified into three major divisions.[1] A material may undergo mechanical damage such as the gnawing action of insects and rodents on non-nutritive materials. Secondly, a material may be attacked chemically, in two ways. An organism may utilise the material as a nutritive source or, alternatively, the organisms may excrete

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*Paper presented at the Manchester Section's symposium on "Paint performance and the microbiological environment."

metabolic products which are injurious to the material. Finally, the function of a specific material may be impaired by the physical presence of an organism, such as the clogging of oil pipelines by bacteria and fungi.

In this paper only the second category of this broad classification will be considered.

Susceptibility to biological attack

Although the subject of biodeterioration spans vast areas of biology, clearly not all materials are necessarily susceptible to biological attack. It might be asked why some organic materials are not susceptible to attack biologically. The reasons for a material not being colonised by micro-organisms may be summarised as follows.

The material may be rendered inaccessible to the micro-organism by, for example, a cannning process. Essential requirements for growth of the organism may be absent; such as water, a substance required by all living things for their growth. The environment in which a material is situated may be toxic to any organism ordinarily capable of attacking the material. The damaging agents, such as enzymes, may be inactivated by, for example, extremes of temperature, which effectively denature the enzymes. The chemical and/or physical nature of the material may be such that it is not suitable, in that particular form, for biological colonisation, such as a substituent terminal group or the branching of aliphatic chains. In addition, substituent groups which do not allow enzyme approach to the site of attack can delay, if not totally prevent, biological colonisation. Finally, a material may be free from biological attack if no organism exists which is able to attack it. The last two points may be confused and can often be identical. It must be pointed out that extreme caution must be taken in making absolute statements as to the susceptibility of a material to biodeterioration, since there might easily exist an organism which is, in fact, capable of colonising a material previously thought to be completely invulnerable to attack.

It has been asked whether or not such an ecological condition as a biologically inert material surface can exist under ideal microbiological conditions.[2]

Materials exposed to a humid tropical environment (which many biologists consider to be an almost ideal microbiological environment) become highly contaminated with foreign matter and micro-organisms on their surfaces, so quickly that the property of so-called inert surfaces, such as certain inorganic materials and plastics, can be questioned. Specific elements other than those of a climate, such as condensable organic volatile matter, apparently interact to provide a proper medium for microbial colonisation. Results suggest that the build-up of layers by condensation of water vapour and enrichment of this condensate with the organic matter present in the atmosphere, exerts a very large influence on microbial colonisation of the surface of a material. Similar results are shown by Tribe[3] who achieved growth on totally inorganic media after taking considerable precautions to remove any organic nutrient. Paint films and similar coatings are clearly susceptible to this situation.

Identification

Having established that many, if not most, material surfaces may be vulnerable to biological attack, given the right set of conditions, it can be appreciated how important the initial recognition of any microbial colonisation is, especially when considering the economic aspects of biodeterioration.[4] It is a fact that, although the problem of biodeterioration has been realised by some people for a long period of time, it is only in recent years that the full significance of microbial colonisation of materials has been realised by many non-biologists and indeed by some biologists. Now the situation is rapidly improving, with many more people becoming aware of the fact that a dirty mark on a particular surface may, in fact, be the first visual sign of microbial attack of that surface, and something more is necessary than simply wiping away the mark. Put into its simplest terms, biodeterioration occurs only when the appropriate organism or organisms, the appropriate material and micronutrients, and the appropriate environment are all present at the same time; and its control may be accomplished by altering one of these variables adversely for the organism responsible for the attack.

Initially, the problem must be fully recognised when considering any biological attack of the surface of a material. A particular attack might appear as a form of biodeterioration; but the problem could have been physically or chemically initiated, with the micro-organisms moving in at a later point along the chain of events occurring at the surface of the material.

In order to solve the problem of whether or not the organism observed is directly, indirectly, or not at all responsible for the deterioration of a material, the postulates of Koch[5] may be modified for the particular situation.

Firstly, the symptoms should be recognised and identified. The procedure is then as follows. Isolate the organism thought to be responsible for the attack into a pure culture. Inoculate this organism from the pure culture on to the original material which is known to be free from any symptoms, and determine whether or not the same symptoms appear. Re-isolate the organism after a period of incubation, and finally identify it with the original organism, comparing the symptoms produced.

The "symptoms" of biodeterioration vary considerably from the very simple to the vastly complex, and steps must be taken to ensure that no contaminants are isolated in error; at the same time, the postulates must not be followed blindly because, although biodeterioration has some similarities to pathological situations in theory, there are some differences.

The following example illustrates the care required when making studies of material surfaces colonised by fungi. The predominant species isolated and identified at the time of examination of the material may not be the organism which was responsible for the initial attack of the surface. The primary attack may have been due to a species which was less predominant or even absent at the time of examination, but was, in fact, predominant at the time of initial attack, which took place before it was realised that biodeterioration was occurring.

Once it is realised that a particular surface is undergoing, or has undergone, microbial colonisation, the first procedure is to observe this biodeterioration closely and to identify the organisms present.

Microscopes

A very simple and easily used technique for this initial observation is described by Lloyd.[6] This technique utilises transparent adhesive tape. An impression is made by pressing the tape lightly, sticky side down, on to the surface of the material being examined. This impression is then mounted in an appropriate stain on a microscope slide and examined under low and high magnification for any evidence of microbial growth. The technique is easily used for the examination of a wide range of material surfaces, such as textiles, paper, wood, plaster, paint and plastics. It is usually possible to identify morphological characteristics, which would be destroyed by transfer of the organisms to a microscope slide by the usual microbiological methods. The particular advantage of this technique is that fragile microbial structures remain in the same positions on the tape, and this facilitates identification of the organisms involved. Not only does the technique aid identification but it also produces good specimens for photographic purposes if required.

This technique offers a more useful tool for use in biodeterioration than do the usual microbiological sampling methods, which frequently have their origins in clinical microbiology.[7]

Having discussed this relatively simple and easy to use technique the other end of the scale may be considered, namely the very highly sophisticated technique of electron microscopy.

The scanning electron microscope is now becoming more widely available as a research tool for use by the biologist, and this instrument can be used, of course, to investigate the surface of any material undergoing or suspected of undergoing biological attack. There are, however, certain difficulties which are mainly due to the inexperience of biologists in interpreting what is actually seen on the screen or photograph. This is because the enormous magnification obtained when using this instrument has not been obtainable in the past, using the ordinary light microscope. It is important, therefore, that the worker takes great care when using this instrument, and does not work with magnifications unfamiliar to him (that is, to begin with the magnifications more usually reserved for visible-light microscopes).

Incubation techniques

A method of sampling, used quite extensively in hospitals and other places where hygiene is of the utmost importance, is the "Agar sausage" technique, which can be utilised for the sampling of surfaces undergoing biodeterioration. The apparatus consists of sterile agar enclosed in a case in the shape of a sausage. The end is cut with a sterile knife, giving a completely sterile surface which can be pressed on to the surface being examined. The resultant growth after a period of incubation is then examined, and identification is carried out.

When faced with a material which is suspected of being susceptable to biological attack, techniques are required which determine, at any one point in time, the actively growing fungi on a particular substrate. An indication is required, too, of the frequency of fungi and their reaction with one another, and with the substrate.

Numerous standard techniques are available, most of which utilise soil as the infecting agent. Soil is used because it contains a high concentration of micro-organisms in spore form and as fragmented hyphae. Moreover, there is usually a wide range of species present, any one of which may attack a particular material surface under the correct specific conditions for that organism.[4]

The dilution plate technique is widely used in microbiology, and may be modified for use in studies of biodeterioration. The modification is simply to employ an agar medium which has the material under investigation incorporated into it as the sole carbon source. For example, paper may be ball milled to offer a cellulose substrate in finely divided form as the major carbon source, thus omitting any other carbon source, such as glucose, from the medium but maintaining all other vital nutrients and trace elements essential to support growth of the organisms. This medium will then selectively isolate, in the first instance, those species which actively utilise the material as a nutritive source, and eventually the secondary colonisers will move from the soil, utilising the nutrients provided for them by the emzymatic activity of the original fungal colonisers.

In this technique, a suspension of soil in sterile distilled water is made up from a known weight of soil in a known volume of water, and from this initial dilution further dilutions are made by taking small known volumes of the original, and transferring them to a further known volume of sterile distilled water. When the appropriate dilutions have been obtained, small samples are pipetted into sterile Petri dishes, covered with the agar medium already described here, and incubated at the appropriate temperature.

The results obtained from the dilution plate technique must be regarded with extreme caution since this particular technique favours the isolation of species freely sporulating in the soil. In the mechanical separation of soil particles by shaking, spores are more easily washed clear into suspension than are the hyphae. In addition, spore masses are more easily split into numerous individual units, each of which is capable of developing into its own colony, whilst the mycelium is filamentous by nature, is usually interwoven, and is, therefore, more resistant to fragmentation. Mycelium will, consequently, be recorded with less frequency when the colony counts are carried out after a period of incubation. Thus, a rather spurious result will be obtained, and this must be recognised in any analysis of results obtained using this technique. The dilution plate technique offers little information regarding the micro-habitats of soil and its organisms since the soil structure is physically destroyed by the procedures. The colonies have developed from spores or the odd fragment of mycelium washed off the soil, and their distribution on the agar plates is probably totally distorted in comparison with the space relationships which these organisms may have in the natural soil.

Since the limitations of the dilution plate technique have been realised, many workers have attempted to use different techniques which overcome the problems discussed above.

Waksman[8] developed a method of directly inoculating soil particles on to agar plates. Mycelium which, developed within twenty-four hours from the time when the soil was inoculated on to the agar medium, was thought to come from the mycelium in the soil since the spores could not develop such a bulk of mycelium in so short a time. This method, too, can be modified for the study of biodeterioration of materials, again by incorporating the material into the agar as the sole carbon source in order to isolate selectively those species able to attack the material directly.

This method does not incur the problems encountered with the previous techniques which favoured primarily the more freely sporulating fungi. However, a few problems still remain. The short incubation period tends to favour, and consequently selectively isolate, those organisms which grow better in enriched media. These organisms will grow over any slower-growing organisms, mask their existence, and prevent their isolation. In addition, the possible excretion of metabolic products can inhibit the growth and development of other species normally capable of attacking the material. In this way, it can be seen that a true spectrum of the fungi and their relationship with each other and the material substrate will not be obtained.

A modification of the Warcup plate technique[9] may be employed, again using agar medium incorporating the material in finely divided form. Here, soil particles are placed in the sterile Petri dish and the agar is poured over the soil, ensuring that all the particles are covered before the agar sets. For this technique, the problem of selectively isolating freely sporulating species is removed. The problem of fast-growing species overgrowing the slower ones is also removed because an oxygen gradient is set up which allows the slower-growing species to compete more easily.

All the above three standard isolation techniques, which can be modified to suit the requirements of the workers studying biodeterioration, have one important disadvantage in that isolation of fungi with the ability to attack materials is carried out under conditions which are far removed from the natural habitat, and which could quite easily lead to very erroneous results and conclusions.

Immersion technique

Chesters[10] attempted to negate these problems, and a modification of his original technique can be used to study the biological attack on a material. Here, the substrate, in the form of ammended agar as in the previous techniques, is placed in immersion tubes which are actually buried in the soil, rather than placing the soil on or in the agar. This technique attempts to isolate actively-growing mycelium from soil by introducing the substrate to the natural soil and the micro-organisms present therein. The immersion tube consists of a tube containing the substrate from which capillary tubes lead to the soil outside. The actively-growing mycelium will grow up these tubes into the agar. After a period of incubation, a sample of the agar can be taken, and plated out to identify the fungi colonising it.

The introduction of this technique was an important step forward in terms of new thought and approach to the real problems associated with soil fungi. The method does, however, have certain disadvantages. The fungi must be capable of growing into the agar to such a depth as to be isolated in the agar core which is ultimately plated out. This implies that the fungi must be able to grow with the low oxygen concentration which occurs in the agar. In addition, a film of water will cover the glassware, and so this method really selectively isolates fungi which thrive in very wet anaerobic conditions.

Agar

The preceding techniques, although quite useful in the study of biodeterioration of materials caused by the micro-organisms in the soil, in addition to having their individual drawbacks already discussed, all utilise a modified agar medium. The fact that agar is used is a distinct disadvantage when considering the biodeterioration of materials, since the material is very selective. It has a relative humidity of approximately 100 per cent, which means that there is probably 96 to 97 per cent water present. This situation is not very conducive to the isolation of some fungi which prefer less moisture, and these conditions are very far removed from those encountered in natural habitats. As a result, even though the material under investigation is incorporated into the medium, only those fungi are selected which are able to attack the material under very specific conditions of high relative humidity and low oxygen concentration. Another factor which must be taken into consideration is that the material itself, being finely divided, is in a very different form from that which occurs in practice.

The logical progression is towards a technique which does not entail the use of an agar medium as the substrate for initial colonisation, which overcomes the numerous problems already encountered with the previous techniques, but which still permits the study of the colonisation of materials "in situ".

Screened substrate technique

One technique which may be considered as a great advance in this study is the screened substrate technique.[11] Here, the material under investigation is used for direct colonisation by soil micro-organisms.

It may be argued that it is adequate simply to place the material in the soil and leave it for a period, eventually removing it, plating small pieces of it on to agar to culture, and then identifying the organisms responsible for any attack. The major disadvantage of the procedure is the difficulty in separating the deteriogen from adhering soil; this makes subsequent isolation of contaminants a real danger and must be avoided at all cost if a true picture is to be obtained.

In the screened substrate technique, the material in the form of short strips is placed against the side of a glass tube, where it is screened from direct contamination by the soil. This screening is achieved by means of a layer of inert glass fibre woven fabric. The fabric is attached to the glass tube by means of glass fibre adhesive tape which is heat- and water-resistant. In this way, the material is completely covered and screened from the soil particles, thus avoiding contamination by fungi which are not actively growing on the material, whilst allowing colonisation by fungi which readily utilise the material as a nutrient source.

This particular technique can be applied usefully to paint films and other coatings, ensuring that they are carried on a biologically inert material to avoid spurious results.

After a period of incubation, the tube is removed from the soil in which it has been buried, and the screen removed, great care being taken to maintain asceptic conditions and avoid contamination of the material by any soil particles adhering to the screening fabric. The material is then cut up into small pieces, again taking the usual asceptic precautions, and placed on agar medium, preferably containing the material in finely divided form. In this way, isolation and identification of the actual organisms responsible for any biological attack of the material is obtained.

This technique does, however, have the slight disadvantage in that there is no constant supply of nutrients to the material. The only nutrients present are those which remain after soaking the material in a nutrient solution prior to burial, and those already present in the soil. Usually, any nutrient on the material will rapidly diffuse into the surrounding soil by capillarity. Moreover, there is no removal of microbial metabolic products excreted by the fungal colonisers, any of which products might inhibit growth or development of certain other species which could otherwise attack the material. This is important since leaching is a process which can commonly occur in the natural habitat, and will influence biological attack. Thus, once again, the complete spectrum of colonisation cannot be obtained.

Perfusion

An improvement on the above technique is the addition of a constant supply of nutrients to the material by running a fibre glass wick from an ancillary nutrient reservoir, which can for convenience be inside the glass tube, to the material itself. Here, a model system of what actually occurs in nature is very nearly obtained.

This modification has led to the development of "perfusion" colonisation techniques[12] which get even closer to those conditions which can occur in natural habitats. The continuous perfusion system offers maintained standard predetermined micro-environments.

Basically the system consists of the slow, controlled perfusion of supplementary nutrients along a woven glass fibre sleeving material, which is able to transport these nutrients in solution by capillarity. The nutrients pass from the reservoir to the material substrate which is being examined, and then away from the colonisation site along a glass fibre "tail wick." In this way, there is a continuous supply of fresh ancilliary nutrients to the substrate, and at the same time the stale nutrients, together with any undesirable waste metabolic products, are removed from the site of biological attack.

The flow of nutrients is maintained by evaporation occurring at the tail wick, and this causes fresh supply of nutrients to be "pulled" along the wick from the reservoir by capillarity. If the material is porous, it can be included in the perfusion chain (for example, paper and cotton textiles), whilst other non-porous materials, such as paint films or similar coatings, must be laid on top of the glass fibre wick.

As already stated, it is possible, using this system, to maintain a constant micro-environment with regard to nutrients. This is unobtainable when the usual microbiological cultural methods are employed. The agar plate, for example, not only becomes depleted of nutrients as the fungi grow, but metabolites build up and are not removed from the site of attack. Moreover, there is an aeration gradient through the layer of agar.

With the continuous supply of fresh nutrients to the system, in addition to the removal of possibly injurious metabolic products, a micro-environment is set up which is more conducive to biological attack of the material in question and to the maintenance of any growth occurring.

The perfusion technique is extremely versatile and can be used not only as an accelerated test for the susceptability of a particular material to biological attack, but also for nutritional and other physiological experiments. These experiments include the effects of various biocides, which may or may not be incorporated in or on to the material, by using either soil inocula or pure and mixed cultures of specific micro-organisms. In conjunction with biocide investigations, the perfusion system is capable of running over long periods of time with proper control, whilst the usual agar plate can normally only be used over a short period of about two to three weeks.

Observation

The first stage in the colonisation of a hitherto infection-free surface is germination of propagules, which can include fungal spores. The physiology of this process differs from that of mere increase in size of the established colony, and thus merits separate investigation. Techniques associated with studies of this kind are usually simple, involving direct observation. They are often quantitative, as well as qualitative, because counts of viable and non-viable spores can easily be made. Spore suspensions of known concentrations are prepared from established colonies of known age, and inoculated on to sterile films of agar or strips of treated materials on microscope slides kept in sterile Petri dishes. Observation can be made aseptically by this means, and frequent checks made. The short times often involved in spore germination adds to the usefulness of this technique.

When carrying out controlled studies of the biodeterioration of a material, it is not sufficient simply to isolate and identify the organisms responsible for the deterioration; quantitative data are required to evaluate the degree to which any deterioration has occurred at any particular time during the investigation.

The degree of deterioration may be estimated either by primary or by secondary measurements. An example of primary measurement is the loss in tensile strength of a material or loss of colour from a painted surface, whilst secondary measurements include loss of weight, spore counts from painted surfaces and enzyme production by the deteriogenic organism (for example, cellulase production in the case of cellulytic fungi).

Many of the techniques described in this paper rely upon colony growth as an indication of microbial vigour. Another mark of microbial activity is the respiration of the organism, usually measured as oxygen uptake or carbon dioxide evolution. By manometric methods, such as the Warburg constant volume respirometer, such activity can be measured accurately. The test is sensitive, and is especially useful for an investigation into the effects of low levels of inhibitory substances on a microbial population in liquid culture.

Conclusions

Although many additional laboratory techniques exist, and occur in scientific literature, this paper describes a few which are intended to give an initial insight into the problems involved when undertaking any study into the biodeterioration of materials. No single technique can, necessarily, be employed for all materials, and those techniques chosen for a particular study must be decided upon after all the factors associated with the particular materials under investigation have been carefully considered.

It must be realised that no one technique will give a complete picture of what is occurring at the site of biological attack, but the picture can be built up piece by piece from the results obtained from a wide range of experiments into the ecological aspects of biodeterioration.

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Effects of timber micro-organisms on paint performance*

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Summary

The ways in which various lignicolous micro-organisms can affect paint performance are discussed. Bacterial attack of floated logs can result in increased absorbency so that, if used as preservative-treated exterior joinery, such timber may absorb wood preservative constituents in sufficient amounts to impair the performance of painted finishes.

"Blue-stain" fungi can develop in painted, softwood joinery causing paint discoloration and, eventually, breakdown of the paint film. It is concluded that fungal infection does not necessarily stem from previously blue-stained wood, but that it can occur, in addition, as a result of direct colonisation of the paint film in service.

The two different types of decay fungi which attack painted wood are discussed briefly. The role of the wood as a water reservoir supplying the moisture required for fungal growth is stressed, and the extent to which wood preservatives and paint films can offer mutual protection is indicated.

Keywords

Types and classes of structures to be coated
timber

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

Miscellaneous
micro-organism

L'effet des micro-organismes de bois sur le rendement des peintures

Résumé

On discute la façon suivant laquelle les micro-organismes peuvent influencer le rendement des peintures. L'attaque bactérienne sur les bûches transportées par flottage peut aboutir à une augmentation de leur capacité d'absorbance, de sorte que si l'on se servait de ce bois pour en fabriquer de la menuiserie extérieure traitée au produit préservateur, de tels bois pourraient absorber les constituants due produit préservateur à tel point qu'ils compromettraient le rendement des peintures y appliquées ensuite.

La vegetation mycélienne "blue-stain" peuvent croitre dans la menuiserie en bois tendre peint et elle peut provoquer un changement de teinte de la peinture, et enfin la désintégration due feuil de peinture. On conclut qu'une infection mycélienne n'est pas forcément issu du bois préalablement teinte au bleu, mais pourrait également le résultat d'une colonisation directe du feuil de peinture lors de sa durée en service.

On discute brièvement les deux différents types de pourriture mycélienne auxquelles les bois peints sont assujetis. On souligne le rôle du bois en tant que réservoirs d'eau qui fournissent l'humidité nécessaire à assurer la croissance mycélienne, et l'on indique à quel point les produits préservateurs de bois et les feuils de peintures peuvent s'offrir une dégre de protection mutuelle.

Auswirkung von Mikroorganismen im Holz auf das Verhalten von Anstrichmitteln

Zusammenfassung

Besprechung auf welche Weise verschiedene auf Holz gedeihende Mikroorganismen das Verhalten von Anstrichmitteln beeinflussen können. Bakterienangriff geflösster Klötze kann zu erhöhter Saugfähigkeit führen, sodass solches Holz, wenn es als mit Schutzmittel behandeltes Bauholz im Freien benutzt wird, Bestandteile von Holzschutzmitteln in genügend grosser Menge absorbieren kann, um die Leistung einer Lackierung nachteilig zu beeinflussen.

"Blaufäule"—Pilze können sich mit resultierender Lackverfärbung in gestrichenem, weichen Bauholz entwickeln und schliesslich Zerstörung des Lackfilms verursachen. Es wird geschlossen, dass Pilzinfektion nicht notwendigerweise von vorangegangener Infizierung des Holzes mit Blaufäule herrührt, sondern auch als das Ergebnis direkter Kolonisierung während des Gebrauchs auf dem Anstrichfilm vorkommen kann.

Die beiden verschiedenen Typs zerstörender Pilze, welche gestrichenes Holz angreifen, werden kurz besprochen. Die vom Holz als Wasserreservoir für das Pilzwachstum notwendige Feuchtigkeit gespielte Rolle wird betont, und das Ausmass, in welchem Holzschutzmittel und Lackfilm gemeinsam Schutz bieten können, wird angegeben.

Влияние микро-организмов в дереве на рабочие характеристики красок

Резюме

Обсуждаются процессы при помощи которых различные деревянистые микро-организмы могут повлиять на рабочие характеристики красок. Разрушающее действие бактерий на плавучие бревна может вызвать повышенное поглощение и если они применяются для консервированных наружных столярных изделий, такое дерево может поглотить составные элементы консервирующего средства в достаточном количестве для того чтобы ухудшить рабочие характеристики красочных покрытий.

«Синяя плесень» может образоваться в окрашенных хвойных столярных изделиях, вызывая потерю цвета в краске и в конце концов разрушение красочной пленки. Делается вывод что заражение плесенью не является обязательно результатом предыдущего заражения дерева синей плесенью, но может также иметь место в результате непосредственной колонизации красочной пленки в служебных условиях.

Следует краткое обсуждение этих двух различных типов разрушающей плесени влияющей на окрашенное дерево. Подчеркивается роль дерева как водяного резервуара снабжающего влагу необходимую для роста плесени и указывается степень до которой консервирующие средства и красочные пленки могут предоставить взаимную друг другу защиту.

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Introduction

Several groups of micro-organisms affect the performance of paint and other finishes used for the protection and decoration of those wooden structures and building components which, either as a result of exterior employment or for other reasons, are exposed to moisture. The manner in which wood can serve as a substrate for the growth of these organisms and the changes which the organisms can cause in the wood in relation to the effects upon paint performance are, in the main, best considered in relation to particular types of micro-organism.

Bacteria

Suolahti and Wallen[1] showed, in laboratory studies on variable permeability of pine, that wood stored in water becomes more permeable as a result of bacterial activity. Later, it was discovered[2] that similar processes occurred when logs were transported or stored in water in the course of normal commercial handling prior to conversion at the sawmill. These findings have been confirmed and elaborated on by other workers and have been recorded in review papers.[3, 4] When permeable timber is treated with preservatives, unusually large amounts of the preservative are absorbed and this can lead to paint failure if the solvents employed have not been lost by evaporation before the paint is applied. There may be worse trouble if water-repellent waxes and resins are incorporated in the wood preservative. When these materials are present in the wood in excessive amounts they can interact with the paint causing a lack of gloss in top-coats or, at worst, complete failure of the hardening process.[5]

The growth of the bacteria and the resultant increase in permeability is restricted to sapwood. Hence, it can be inferred that bacteria utilise the contents of cells which are readily available in sapwood but not present in heartwood. Confirmation of this is the observation that the staining fungi, which primarily depend upon cell contents for their nourishment, do not readily colonise the depleted sapwood of floated wood.[6] Suolahti and Wallen[1] showed, in addition, that bacteria readily attack pectin, a constituent of the membrane which closes the pits in the walls between adjacent wood tracheids. More recently, workers have demonstrated that bacterial attack of the membrane is visible under the electron microscope, and it has been shown[7] too that the membrane, together with its thickened central "torus," can be completely lost. The cells of the rays are attacked too, and the overall effect is for pathways to be opened up in the wood for relatively unrestricted movement of liquids. This results in an increase in dry wood permeability of more than fifty times that of normal dried wood.[8]

Eventually, bacteria might attack the wood substance itself; losses of general strength properties in the order of ten to fifteen per cent have been recorded for wood which had been stored in water for the unusually long period of three years.[9] This strength loss is insignificant, however, in relation to the natural strength variation within a timber species, so it is unlikely that the bacterial weakening of the wood substrate plays any significant part in causing paint performance failures.

Blue-stain fungi

Unless suitable precautions are taken between the felling of a tree and the drying of the sawn timber, the sapwood of joinery softwoods is liable to discoloration caused by the growth of "blue-stain" fungi. As already indicated, these organisms utilise residual wood cell contents as their food and, although they disfigure the wood, they do not weaken it appreciably.[10] It is generally supposed that the use of stained timber as joinery material entails the considerable risk that, if the wood is moistened in service, the fungus will resume growth and may colonise surface finishes. The visible sequence is that paint films become discoloured, then the fungus forms fruiting pustules which break through the paint, increasing the discoloration and contributing to the eventual break-up of the paint film.

The fungi which commonly cause the most stain in softwood logs and sawn timber, species of *Ceratocystis* and *Leptographium*, have not been recorded as causing paint discoloration or damage, and there is a consensus of opinion that, although other fungi—species of *Cladosporium*, *Alternaria*, *Stemphylium* and so on—sometimes occur, the most important cause of the damage to surface finishes in the northern hemisphere is *Pullularia pullulans*.[11] *P. pullulans* is variable in appearance and there are indications that it is really a group of species,[12] members of which grow in soil and on dead pine needles[13] as well as being widespread on other plant debris and also on healthy broad-leaved trees.[14] The fungus is relatively unimportant as a staining fungus in timber prior to completion of drying,[15] possibly because at summer temperatures it grows much more slowly than competing species of staining fungi. It seems unlikely, therefore, that the initial painting of wood already infected by blue-stain fungi is the major cause of paint infection.

Butin[16] suggested that *Pullularia* colonised either via breaks in surface finishes or by wood fibres occasionally projecting through the finish. Observations have recently been made at the Princes Risborough Laboratory on pine sapwood test panels prepared by the Paint Research Station. These panels were immersed for three minutes in a water repellent grade of preservative containing five per cent of pentachlorophenol prior to being painted with various three-coat paint systems. They were then exposed horizontally out of doors on a rural site for an eight-month period which included the winter of 1970/71. Samples were kept in polythene bags after removal from the test site, and both the wood and the undercoat paint were demonstrably moist when observations were made. Even at magnifications of ×40 areas, the mechanical breakage of the paint film was visible only at the corners of the central machined slot and at the corners of the panels themselves. Elsewhere, *Pullularia* had colonised the apparently unbroken paint film but had not penetrated into the wood. Indeed, at many of the points of observation, even in those regions where pustules were being formed, the fungus was confined to the upper zones of the undercoat; penetration of the fungus to the paint/wood interface was observed at one point only. It may be noted in passing that, although the presence of the fungicide had prevented colonisation of the wood beneath intact areas of paint film, in the regions where the paint film had broken mechanically the fungus had already penetrated into and discoloured the surface layers of the wood.

These observations supplement a body of evidence which tends to show that colonisation of intact paint surfaces may be a major source of "blue stain in service". After spore germination, the penetration of fungus by mechanical means assisted in some instances by enzyme action, is indicated.[11]

Another possible mode of infection and colonisation deserves consideration. Initial sources of infection are so widespread that it is possible, even in urban areas, for spores of *Pullularia* to be deposited on bare wood surfaces during manufacturing processes. The development of these spores ought to be prevented by the lethal effects of paint solvents, but there does not appear to be any relevant experimental evidence to support this theory.

The presence of *Pullularia* on painted metal surfaces indicates that its growth in paint is not directly dependent on nourishment obtained from wood, although the fungus can utilise cell contents. Initial attack on paint films is often confined to those regions which lie over sapwood; this may relate to the greater ease of penetration of moisture into sapwood, but it seems likely, too, that water-soluble wood components diffuse from the wood into the paint, and so encourage growth of the fungus. Moreover, there are indications[11] that in certain circumstances the fungus can utilise wood cell-wall components.

Decay fungi

Duncan[17] drew attention to the relatively minor problem of the presence of soft-rot fungi in weathered wood surfaces, and their relation to paint failures. These fungi utilise cellulose, but their attack is restricted by the low levels of available nitrogenous nutrients.[10] Thus, their effect in joinery materials is to cause marked weakening of the extreme surface without affecting the underlying wood, so that failures upon repainting may be failures of the wood rather than of the paint.

In contrast to the soft-rot fungi, the wood-destroying *Basidiomycetes*, some of which attack the lignin as well as the celulose of the cell wall, are not greatly restricted by the low levels of nitrogenous nutrients in wood.[10] Decay of the wood is clearly recognisable, and the resulting loss of or damage to paint films is unlikely to be regarded as a paint failure. However, there are other, more subtle, interactions between the paint, the wood substrate and decay fungi (as well as other micro-organisms) which are not so easily recognised.

Interactions

Recent problems of decay in exterior painted joinery in Britain,[18] whilst appearing to indicate that three-coat paint systems are no longer affording the same degree of protection, are better regarded as pointers to the greater demands now being made on the protection afforded by paint. Change in the designs and uses of both joinery and buildings plays its part.[19] One significant factor which has not received much attention is that the joints in modern cheap joinery are not fully sealed against moisture at the time of manufacture and that glues are sometimes used which are not moisture resistant. In service, in response to seasonal changes in atmospheric humidity, differential movements occur in the joint where end grain abuts on to side grain. This leads to rupture of the paint film and, if the underlying joint is not effectively sealed, opens up a direct pathway for entry of water into the joint. The water then causes progressive moistening of wood in the region of the joint by uptake through exposed end grain. The process is facilitated if part of the joint is formed from sapwood, heartwood being much less permeable. Joints on lower rails have been shown to be the most likely sites for high moisture content in in-service joinery.[20]

Whilst intact, three-coat paint systems protect exposed woodwork against the entry of liquid water, and also retard loss of moisture already present in the wood.[21] These effects are important because micro-organisms and wood-rotting *Basidiomycetes* are all dependent upon moisture and cannot develop in dry wood (at moisture contents below twenty per cent). On the other hand, at moisture contents markedly above twenty per cent, not only is the wood at risk from fungal decay but it may serve also as a moisture reservoir maintaining conditions suitable for the development of *Pullularia* in the paint itself. Failure to recognise these factors may lead to misinterpretation of effects. Fungal discoloration of paint on fascia boards closing the edges of flat roofs in comparatively new buildings has been reported recently as a paint defect. In certain cases it was possible to show that this was in reality a building design failure. The omission of a vapour barrier and insulation behind the boarding had permitted condensation of moisture from the atmosphere within the building on to the reverse side of the fascia boards. The moisture had passed through the wood and promoted conditions suitable for fungal growth in the paint.

Wood preservatives can be used to prevent decay of timber liable to become moist in service. Possible explanations have already been given as to why such treatments do not necessarily protect overlying paint against staining by *Pullularia*; certain preservatives containing fluoride are reported to do so,[22] but these are not in general use in this country. In contrast, protection of pentachlorophenol-type preservatives by intact paint films can be inferred from those observations made here on the PRA test panels. The protective action of paint, in preventing loss of water-soluble preservatives, is a contributory basis for accepting the suitability of dip/diffusion treatments for exterior joinery.[23]

Exterior joinery includes movable parts which should fit closely into their fixed surrounds; hence, the swelling and shrinkage which accompanies uptake or loss of moisture is detrimental. To minimise this "movement", water repellents are often incorporated into joinery preservative formulations. The side effects of applying such treatments to timber attacked by bacteria have already been discussed. Nevertheless, effective water repellents will give protection to paint films by reducing breaks caused by differential movements at joints and by reducing the likelihood of the wood's moisture content reaching a level high enough to support fungal growth.[21]

Conclusions

Whilst problems associated with the increased permeability of ponded wood following bacterial attack have been fully explored, uncertainty exists as to the sequences of events which lead eventually to the discoloration of paint by staining fungi. In general, the interactions between paint and the wood substrate are complex and are not always easy to assess in relation to the biological problems associated with joinery materials.

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Water repellent preservative finishes*

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Summary

This paper deals with the development of water repellent finishes which are used to preserve the natural appearance of wood, including tests developed to assess them. The anatomy of wood is outlined in so far as this affects performance on exterior weathering. The exterior durability of clear resinous finishes (varnishes) is compared with that of water repellent finishes.

Keywords

Types and classes of coating and allied products
water repellent preservative

Types and classes of structures or surfaces to be coated
timber

Process and methods associated with service or utility
biodegradation

Finitions preservatrices hydrofuges

Résumé

Cet article trait du developpement des produits hydrofuges dont on se sert pour conserver l'apparence originale des bois et il renferme aussi les essais mis au point pour les apprecier. On decrit dans une maniere generale la nature des bois au point de vue de son influence sur sa resistance aux intemperies. On fait une comparaison, a l'egard de leur durabilite a l'exterieure, des vernis et des finitions hydrofuges.

Wasserabstossende Schutzüberzüge

Zusammenfassung

In dieser Abhandlung wird die Entwicklung von wasserabstosenden Überzugsmitteln, wie sie zur Bewahrung des natürlichen Aussehens von Holz gebräuchlich sind, behandelt; inbegriffen sind auch Prüfmethoden zu deren Bewertung. Die Anatomie des Holzes wird besprochen soweit diese seine Wetterbeständigkeit beeinflusst. Die Dauerhaftigkeit im Freien von Harze enthaltenden Klarlacken wird mit der von wasserabstossenden Schutzüberzügen verglichen.

Водоупорные консервирующие покрытия

Резюме

Статья описывает развитие водоупорных покрытий применяемых для консервации натурального облика дерева и испытания для их оценки. Обсуждается анатомия дерева поскольку она влияет на рабочую характеристику древесины в условиях наружного выветривания. Сравнивается сопротивление к действию атмосферы прозрачных смольных покрытий (лаков) и водоупорных покрытий.

Introduction

Timber is recognised as a versatile and attractive building material. Practically everybody likes the natural appearance of wood. In spite of modern, man-made alternatives, it still remains one of the most beautiful of all materials. Its appearance, warmth to the touch, ability to be worked with simple, inexpensive tools, and the wide range of colour, grain patterns, and so forth, make it quite unique in both the exterior and interior fields of building and decoration.

In order to understand why different species of wood possess such widely differing characteristics it is necessary to understand a little about wood structure.

Anatomy

Trees are divided into two main classes, hardwoods (broad-leaved trees) and softwoods (conifers—needle shaped leaves) (Fig. 1). The method of growth is identical for both classes, food being made by the respiration of oxygen and carbon dioxide from the air and by water from the earth. These compounds are used to make sugars and starches which, in turn are synthesised into wood. A general section of a tree stem is given in Fig. 2. The three outer layers of bark, phloem and cambium are present for protection, for food transport and as growing zones, respectively. All new wood cells come from the cambium; a single layer of cells only, and these growth areas are shown in Fig. 3.

Xylem (wood) consists mainly of fibres, vessels, parenchyma and rays. The functions of the differing types of cell vary from hardwood to softwood. In most temperate woods (both hard and soft), annual growth rings are visible on a sectional view of a tree-stem (Fig. 2 represents a five-year-old stem. These growth rings are made up from the larger cells formed early in the year when the growth rate is at a maximum, and represents the softer part of the wood. Latewood is more dense and, therefore, harder.

The outer growth rings are called sapwood and the inner ones heartwood. The former acts as a food storage and water transfer zone from roots to leaves, whereas the latter constitutes an inactive strength zone.

In both hardwoods and softwoods, the fibres constitute the main strength element, and in softwood it is via the fibres that the sap is transferred. "Pits" in the walls of wood fibres enable sap to pass from one cavity to another. Vessels are only present in hardwoods and are often referred to as "pores." They vary considerably in size, and are large enough

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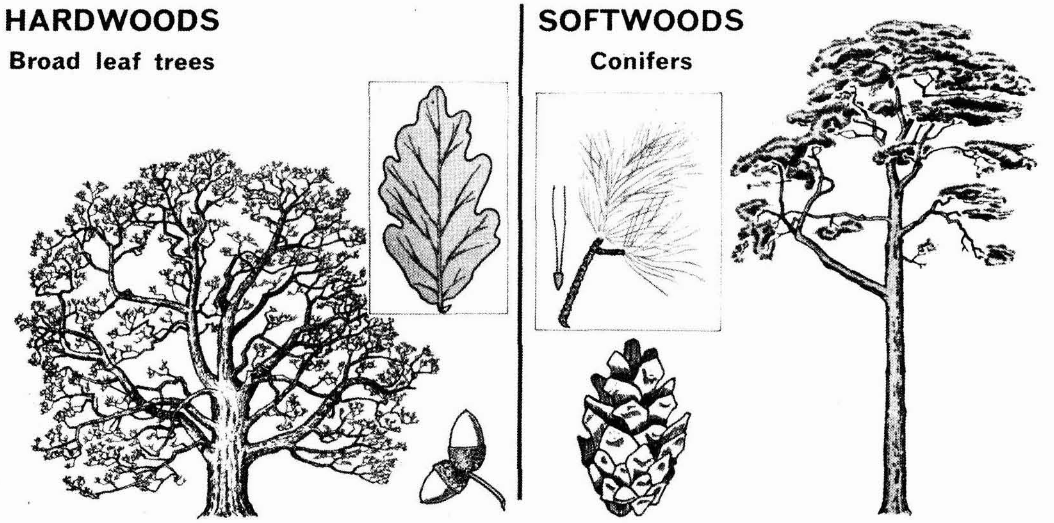

Fig. 1. Classes of tree

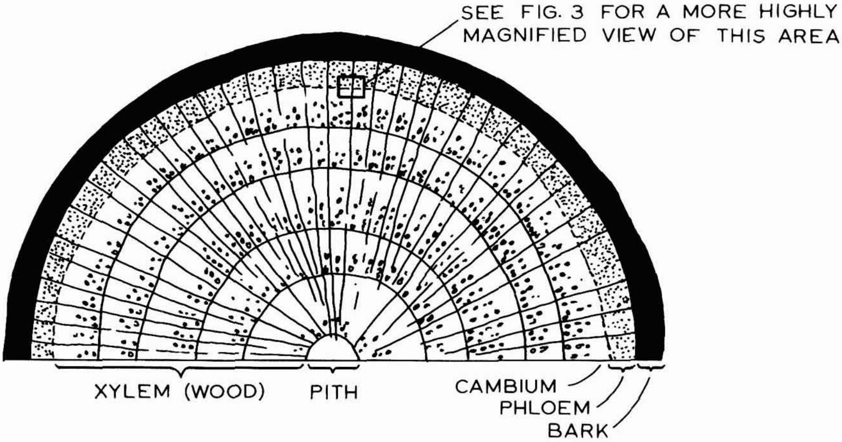

Fig. 2. Transverse section of a five-year-old stem

to be visible to the naked eye in some species. They comprise of large cells with open ends set one above the other, and continue as open passages for quite long distances. Vessels in the outer sapwood conduct water from the soil to the leaves, but those in the inner sapwood and heartwood zones are not active in this way. They are often filled with a froth-like ingrowth (tyloses).

The rays are strips of cells that extend in a radial direction and, in the sapwood areas, transport food made in the leaves. The width of these rays varies from 2 to 50 cells. Parenchyma is a food storage area. A general view of the arrangement of tissues in a hardwood is shown in Fig. 4.

All the cells in wood are cemented together by a thin layer called the middle lamella. This layer can be dissolved by certain chemicals permitting the fibres to be separated as is done in paper making. This brief summary of the anatomical structure of timber explains the wide differences in appearance between species, which can result from the various proportions of differing cell formations. There is, however, another factor which exerts an even greater effect on appearance, and also on performance. This factor is the direction of cut. Three main possibilities exist because the surface being looked at could have been cut:

(a) transversely, (at right angles to the line of growth) so that the ends of cells are evident (end grain),

(b) radially, (more or less parallel to the radius of the stem) when the rays appear as transverse bands on a plank (sometimes referred to as quarter sawn),

(c) tangentially, when the cut is more or less tangential to a growth ring, and the ends of the rays will be visible, (sometimes referred to as flat sawn).

A diagram of these cuts, with reference to general structure, is shown in Fig. 5.

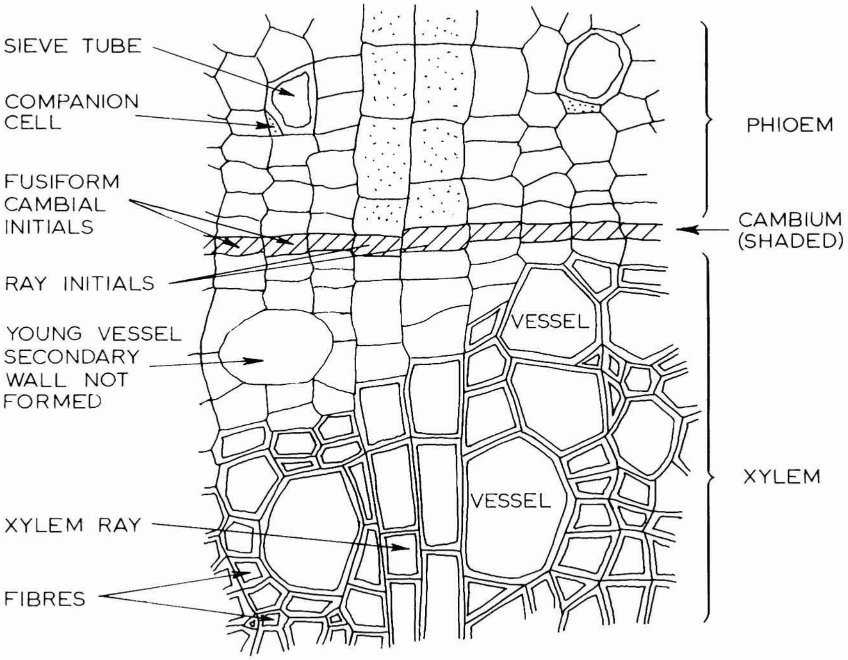

Fig. 3. Details of the stem anatomy showing an enlarged view of the rectangle in Fig. 2

Each cambium initial produces cells in more or less radial rows, the radial arrangement becoming irregular as larger cells (for example vessel elements) push smaller ones out of place. Ray initials form only ray cells; fusiform initials form all other types of cell

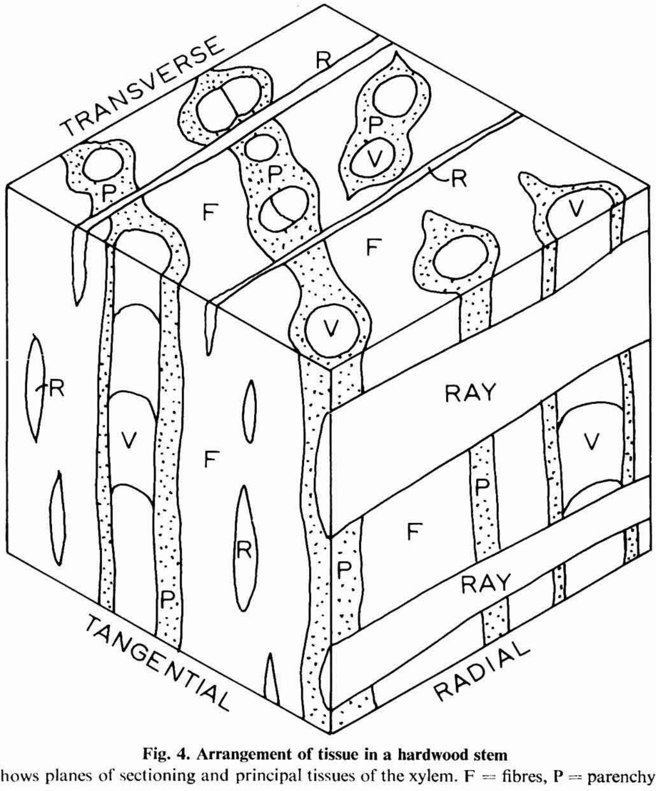

Fig. 4. Arrangement of tissue in a hardwood stem

The cube of hardwood shows planes of sectioning and principal tissues of the xylem. F = fibres, P = parenchyma, R = ray, V = vessel

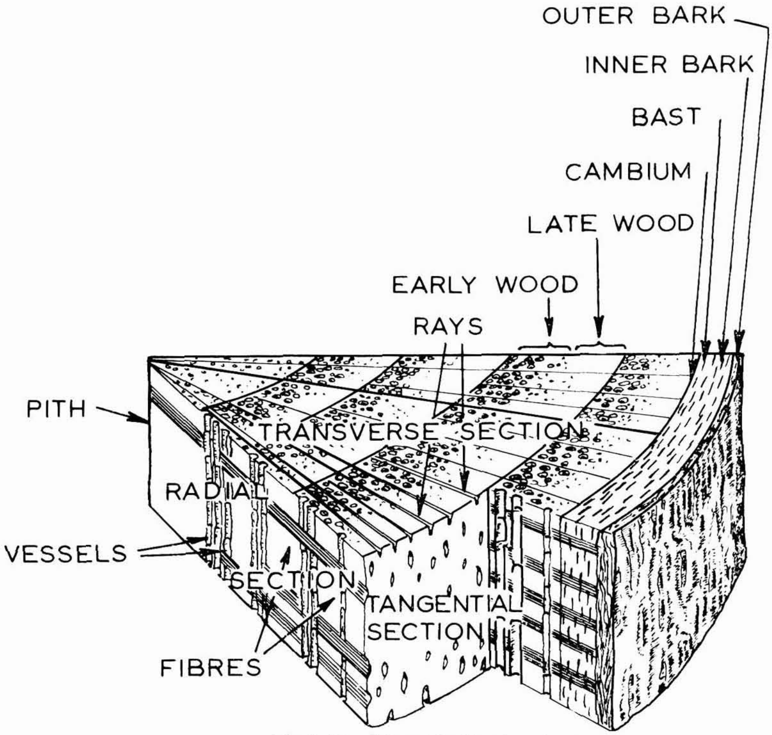

Fig. 5. Effect of possible directions of cut

The direction of cut will modify the physical and mechanical properties of a piece of wood. As far as anatomy is concerned, the type of cell and its chemical make-up will have a significant effect on durability. Generally speaking, sapwood is much less durable than heartwood and, in the log, it is wetter. In softwood trees, a 50mm core of sapwood is quite normal, and in a log 300mm in diameter, this represents 56 per cent of the total volume (which reduces to 30 per cent for a log of diameter 600mm and 20 per cent for a log of diameter 900mm). This factor is very significant today, when the modern forestry policy (many more smaller, faster growing, trees) is borne in mind.

Durability

It is worth emphasising that the term "durable," when applied to timber, refers to its ability to withstand fungal and insect attack. It does not imply that the appearance will not change on exterior exposure, nor does it imply that the surface degradation which timber undergoes when exposed to the weather will be any less severe than that exhibited by a non-durable species. All too often, a particular species is specified on the basis of its being a "durable species," and the specifier is very surprised when this appearance is not maintained on exposure. It is fairly true to say that practically every species of timber will weather to the same standard pale grey if left exposed outside. This definition is quite different from what is usually meant by the durability of a finish, which refers to the maintenance of surface integrity. In other works, in the case of timber, durability refers to strength retention, even if the appearance is altered, whereas clear finish durability refers not only to breakdown (loss of strength) of the material, but also to its ability to maintain the original appearance of the substrate.

Wood possesses excellent inherent durability characteristics and will last for many years unless subjected to abnormal conditions, when microbiological activity can take place. This high durability is exemplified by the discovery, in a Viking grave at Oseberg in Norway, of an extremely beautiful ship which was found almost intact after it had been buried for 1,100 years, whilst all that remains of a similar ship at Sutton Hoo in England is a selection of rivets and an impression in the soil.

The Norwegian vessel had been preserved because biological decomposition is retarded in cold climates; wood may spend one third of its lifetime in a deep freeze.

The chemical composition of wood (both sapwood and heartwood) will affect durability, too. Wood cells consist, essentially, of cellulose and lignin together with small amounts of resin, sugars, extractives, and so forth. Cellulose has the general formula $(C_6H_{10}0_5)_n$, and the following chemicals are believed to build up to form cellulose[1]:

$C + H_20 \rightarrow CH_20$ (formaldehyde)

$2CH_20 \rightarrow C_2H_40_2$ (acetic acid)

$3CH_20 \rightarrow C_3H_60_3$ (lactic acid)

$6CH_20 \rightarrow C_6H_{12}0_6$ (glucose)

$n(C_6H_{12}0_6) - n\ H_20 \rightarrow (C_6H_{10}0_5)_n$ (cellulose)

About 40 per cent to 50 per cent of the dry weight of wood is α (pure) cellulose.[2] The cellulose molecule is characterised by its shape, which is very long and narrow. In addition to cellulose, quite large percentages of hemicelluloses are present in wood. These compounds are similar, chemically, to cellulose, but have much shorter chain lengths and more readily hydrolysed chains. In addition, some 20 per cent to 35 per cent (by weight) of lignin is present. This is a dark brown substance which is hard and brittle, and it is the lignin which is removed in the chemical degradation of wood for paper making. It is, however, the small percentages of "extractives" which are present in the cells which often exert the greatest effect on durability. These "extractive" chemicals are, essentially, either phenolic or tannic in nature, and their presence renders a particular species toxic to both fungi and insects, making it "durable." They do not make a species immune from attack, merely resistant to it.

In order to bring about the decay of timber, a wood destroying fungus must be present in it under the particular conditions conducive to that fungus' growth. Wood destroying fungi require for growth four favourable conditions—enough food, a suitable temperature, and a supply of water and oxygen (air). Food and water are always present in wood, particularly in sapwood. Fungi will grow at normal temperatures (15° to 30°C), but will lie dormant for many months in cold weather. The controlling factor, therefore, in resisting fungal attack is moisture content. For a moisture content above approximately 20 per cent, fungi will continue to grow through their natural cycle: spore-hyphae-mycelium-fruiting body-spore. A rather higher moisture content, of about 26 per cent to 30 per cent (fibre saturation point), is generally required for the inception of vigorous fungal attack.

The most prevalent types of fungal attack are from "wet rot" and "dry rot". (These are really misleading terms as they refer only to the final stage of decay.) Of the two, the more prevalent, wet rot (*Coniophora Cerebella*), involves fine hyphae which, almost immediately, turn brown or almost black. Wood affected by wet rot will split longitudinally and, in some places, laterally; the "cubic" appearance of dry rot is seldom absent. Heavily infected timber can be powdered between the fingers. Dry rot (*Merulius lachrymans*) does not occur on external surfaces. Its presence is shown by the appearance of a white, fluffy, growth or of a grey-white felt with yellow or lilac patches. Strands of hyphae are capable of penetrating mortar, and will cross steel and concrete to reach unaffected areas. (This factor renders dry rot rather unique because the strands will spread—and infest—timber which is outside the actual area of high moisture content needed to initiate growth.) In the final stages of attack, the timber exhibits cubical cracking and checking.

The "blue stain" fungus has been described by Savory,[3] and is not, therefore, being dealt with in this paper. Conditions for the survival of the blue stain fungi are the same as those described above, and if conditions are very bad, then either form of attack can occur.

Sapwood, particularly of the highly porous type, is the least durable part of a tree. It is sometimes slightly lighter in colour than heartwood, but if it is free from defects it has similar density and strength characteristics, but being rich in food materials makes it attractive to both wood-rotting fungi and insect pests. If timber is tangentially cut, it can consist entirely of sapwood, whereas if it is more than 50mm wide and radially cut only one side is likely to be sapwood.

The best way of preventing decay is by good design and the avoidance of conditions under which the fungi can exist. As an added insurance, however, it is possible to treat timber with a solution of a chemical toxic to the attacking agent. These toxic solutions fall into three main classes—tar oils, organic solvent based preservatives, and water borne preservatives. The chemicals used include creosote and tar oils, chlorinated phenols and their derivatives, organo-metallic compounds, and inorganic derivatives of naphthenic acid, and copper, chromium and arsenic salts. It must be emphasised that these preservative solutions, although toxic to micro-biological organisms, are not designed to provide protection against weathering or surface degradation.

Surface degradation

Even if no biological attack has taken place, surface degradation due to climatic conditions can, and will, occur. The resistance of wood to atmospheric, light and climatic attack has been studied. The resultant breakdown has been found to be, initially, almost completely superficial, and to take a very long time to develop. Borgin[4] suggests that surface degradation is caused by fractures in areas of high stress concentrations, and that due to continuous swelling and shrinking, this failure occurs at a relatively early stage. This process is followed, eventually, by breakdown of the surface fibres, although this stage may take hundreds of years before it affects the wood structurally. At an intermediate stage the fibres (other than those on the surface) remain intact, although there is considerable attack on the middle lamella, which is composed essentially of lignin. Both these types of breakdown are accentuated by purely mechanical means (shrinkage and swelling) as the interiors of very old timber show no signs of such stress breakdown. Borgin[4] stated that, contrary to popular belief, photochemical reactions are of little significance because the self protecting process takes place quite rapidly. After only a few years, the surface is protected from light by the development of a thin surface layer, usually of silver grey cells which absorb and reflect chemically active ultra-violet and visible light. Wood cells are, normally, almost transparent to light, allowing their penetration to cause photochemical reactions which, in turn, breaks down the cells.

These findings are extremely important when it is realised that even so called "penetrating finishes" penetrate only a few cells deep into a wooden surface.[5] This minimum penetration, allied to the fact that, in a degraded surface, the cementing bond between fibres will have been weakened, is probably the reason for varnish like materials (which dry to a hard, comparatively, brittle film) being generally inferior to the more elastic, comparatively non-drying, water repellent finishes.

Substrate variability

The reasons for surface variation due to anatomical features of particular species, and to direction of cut have already been described. An important aspect of substrate variability exists in the presence of tyloses in heartwood. These very often completely prevent the passage of liquids through the heartwood cells and this has a very significant effect on reducing the uptake of preservative solution during pressure or vacuum impregnation. Fortunately, the tyloses themselves are high in extractive content, thus rendering heartwood much less susceptible than softwood to microbiological attack.

Surface variability can have a very marked effect on the life of a finish. Tests have shown that sawn timber will "hold" a preservative or water repellent finish much better than planed timber. When the latter is thoroughly sanded several investigations have found decreased adhesion—probably due to the presence of wood flour in the scratches on the surface. Surface fibres are known to have a very important bearing on the durability of applied finishes. During planing these fibres are often crushed down and the same is true of the harder heartwood bands. When the wood is subsequently wetted and swelling and shrinkage occurs, this compression is released. Several instances of liquid water penetration through films by means of protruding fibres ("wicking" action) have been proved and Butin[6] has suggested that blue stain infection can occur through a sound varnish film via protruding surface fibres.

Water repellent finishes

It has been necessary to provide all the background information given above in order to put into perspective the problem of formulating a suitable clear or natural finish for timber. Anatomical variations, direction of cut, porosity, extent of weathering, even the smoothness of the surface are all variables for which allowance has to be made. The most acceptable material today is a water repellent finish. This class of coating has been developed primarily because the earlier solution to the problem, varnish, has been found, over the years, to be far from satisfactory.

Varnish, either semi-glossy or glossy, should represent the theoretically ideal finish for a timber surface; it beautifies the appearance, provides a glossy or semi-glossy finish which is easy to wipe clean, and precludes the use of timber containing shakes, bad knots, sap stain and other fungal agents. What varnish does not do, however, is to maintain either its own or its immediate substrate's chemical and mechanical integrity when exposed to exterior weathering for any significant period. A minimum of three coats, and preferably four, are essential if the film is to remain reasonably intact in every aspect and position for about two years. The main disadvantage of varnish is that when breakdown does occur, the affected areas become discoloured around the flaking varnish, and the job of complete renovation becomes so expensive that it is economically unacceptable.

As a result of these defects, another range of materials (grouped together as "water repellent finishes") has emerged. These may be clear, "natural" materials (lightly pigmented materials designed to enhance the original or weathered appearance of the wood surface), or coloured materials, which are used to provide special effects. They both work by impregnating the surface layers of the timber with a water repellent compound which prevents water from wetting and penetrating the substrate. Although they are pigmented, they usually allow the natural grain pattern to be seen. They also contain a preservative element which, if the first coat is dipped, flow coated or flooded on with a brush, will impart quite a considerable degree of preservation to the surface and any exposed end grain. (Uptake of a solution via end grain is many times larger than lateral uptake, but the converse is true of timber movement which is 20 to 30 times greater laterally than it is longitudinally; it is this property which causes timber joints to open when subjected to alternate wetting and drying.) Maintenance and restoration of these materials is simple because scraping is unnecessary; all that is needed is the removal of surface dirt and the application of a further coat, or coats.

The differences, therefore, between these two groups of products are considerable. Water repellent finishes occupy the position they do today because of the very considerable amount of work which has been carried out to develop them, and their range now covers a multitude of compositions.

The theoretical requirements of a water repellent finish are that it should:

(a) be reasonably slow drying to facilitate maximum penetration,

(b) possess a degree of preservative activity,

(c) possess a degree of water repellency—not only from the point of view of shedding liquid water, but also to provide a degree of timber stabilisation,

(d) show good colour retention,

(e) have low dirt retention properties,

(f) break down by erosion with consequent freedom from cracking and flaking, and

(g) be available in an attractive colour range, preferably of a semi-transparent nature so that the natural grain or figure of the wood will show through and the material does not become just a cheap "paint".

The original water repellent finish designed to match these properties was that developed in 1957 by the United States Department of Agriculture, Forest Products Laboratory,[3] and usually known as the Madison Formula. The basic ingredients of this material are given in Table 1.

Table 1

Composition of the original Madison Formula on a percentage weight basis

Composition	Grade for		
	Cedar	Light Redwood	Dark Redwood
Paraffin wax	2.5	2.5	2.6
Zinc stearate	0.3	0.3	0.3
Turpentine or paint thinner	16.3	15.9	18.4
Pentachlorophenol concentrate*	12.0	11.7	12.2
Boiled linseed oil	57.6	56.2	58.1
Burnt sienna in oil .. .. Spec TT-P-381 Colour 3B	6.9	13.4	2.3
Raw umber in oil .. .. Spec TT-P-381 Colour 3D	4.4	—	1.5
Indian red oxide .. .. Spec TT-P-381 Colour 6B	—	—	4.6
	100	100	100

*40 per cent by weight of P.C.P. in an industrial solvent

A five US gallon batch of finish contains approximately 950gm (1.9lb) of pentachlorophenol, which confers the preservative action, and the pigment present decreases photochemical attack on the timber surface. It is not present, however, in a sufficiently high percentage to obscure the grain.

The disadvantages of the Madison Formula were that, in the United Kingdom, it proved to be impractical because of the slow drying rate, had poor application properties, and was highly dirt retentive. Its use was, therefore, restricted to areas unlikely to be subjected to any physical contact and, in the case of windows, only to use with non-opening lights.

The possibilities for water repellent finishes were most fully appreciated in Northern and Western Europe (Scandinavia, Denmark, Holland, Germany and France), and it was here that work was concentrated to formulate suitable commercial materials. The result has been a range of products of widely differing chemical composition and appearance, but which have become very widely used. In Denmark, the consumption of water repellent finishes is over two litres per head of the population, whilst the total paint consumption (7.25 litres per head) is almost identical to that in the United Kingdom. In Germany, production is about 15 million litres per annum, and is rising by up to 20 per cent per annum. Growth in the United Kingdom will continue to rise, but it is unlikely that (during the next five years) consumption will rise to the level on the Continent. One factor, however, should not be disregarded. Growing evidence is being accumulated[9] which shows that even good quality paint films will allow water vapour to pass through them at a faster rate than they later let it diffuse out. Thus, there is, in a warm, wet summer, a serious possibility of "tanking" of window frames where the moisture content of the wood can continue to rise (via an intact paint film) to dangerously high levels. Water repellent finishes "breathe" more easily than paints, and, once the psychological attitude "we must have white paint" is overcome, their usage may very well rise steeply.

Test methods

Very little published information is available on the results of research work on the assessment of the quality of these products, and there are no widely accepted methods for their testing or for standardisation of their performance. With the absence of such standards, accelerated testing methods are unlikely to be reliable because the parameters affecting performance are not properly known, and because any correlation between accelerated weathering and exterior durability has not yet been established.

The basic difficulties, when drawing up suitable quantitative test methods for water repellent finishes, are (a) the non-availability of methods for determining film thickness in order to standardise test methods, (b) substrate variations leading to patchy absorption, with consequent colour variations, (c) the many factors involved in colour change (darkening of medium, bleaching or greying of substrate change of colour of pigment on exposure), (d) the fact that these finishes are, essentially, not film forming products in the accepted "paint" sense and, therefore, "film" tests are inapplicable.

From the required properties of a water repellent finish, the following emerge as possible performance tests:

1. Drying time
2. Visibility (or otherwise) of grain
3. Gloss characteristics
4. Pigment retention on weathering
5. Cleanliness on weathering
6. General appearance before and during exposure
7. Water repellency

An obvious problem is what is to be used as a test substrate. For practical reasons, the material must obviously be wood in its natural rather than its reconstituted form (hardboard, chipboard, etc). Two factors lead towards one species, Western red cedar (*Thuja plicata*); it is practically free from knots, shakes and other structural defects, and it is the most popular timber for use in the cladding industry (an industry using large quantities of water repellent finishes). Western red cedar and Californian redwood (*Sequoia*) are the only commercially available softwoods which are classified as "durable". The comparatively uniform structure of Western red cedar, however, usually outweighs the fact that it may not be the most demanding of all substrates. A number of tests on other species have shown, in fact, that the ranking on exterior durability of twenty products tested on Western red cedar and other species is similar. In many instances (for example, if suitability for application to window cills is the predominant aspect of a particular testing series) other species are used to evaluate products, but Western red cedar is still used as the main control.

The method of exposing test panels is important. It is customary in the United Kingdom to accelerate paint testing by exposing panels inclined at 45° and facing south, but with water repellent finishes this can prove misleading. Many finishes, including those of the Madison type, contain oils and wax-like substances, and dirt deposition at 45° is increased to such an extent that it both negates any assessment of the appearance and also provides a very efficient screen against ultra-violet light, protecting the film from breakdown.[10] Panels are, therefore, usually exposed vertically with the ends sealed to prevent liquid water ingress, and with the lower ends of the panels raised above the weathering rack by the use of brass eyelets.

Tests for 1, 2, 3 and 5 of the properties already enumerated can be carried out using standard paint testing apparatus and terms. Any assessment of pigment retention must be a subjective one since, concurrently with the loss of colour or darkening of the pigment, there might be a counterbalancing, or additional colour change, of the medium or of the wood itself. Usually pigment retention is assessed by the use of a reference panel retained in the laboratory, but a very considerable degree of "expertise" is necessary to ensure that only loss of colour of the film is taken into account.

Exactly similar reservations apply to any assessment of appearance. All efforts carried out by the Timber Research and Development Association (TRADA) to quantify colour and appearance changes have been unsuccessful and, therefore, general descriptive terms have had to be used for assessments.

One field, however, where a successful test method has been evolved is that of water repellency. From 1964 to 1966 a large number of experiments were carried out using the contact angle of a water droplet on a panel as a measure of the panel's water repellency. When the finish was first applied, this was found to be a very successful method, but as the panel aged the consequent surface degradation, allied to the presence of embedded dirt, caused wide variation to occur. Development of some other method became essential, and work on this subject culminated with the issuing of a TRADA Research Report, WT/RR/2 "TRADA Tentative Standard Test for Water Repellency of Finishes". In this test, a panel (the sides, end, and back of which are protected by suitable shielding techniques) is subjected to a water spray for a given number of hours. The panels are mounted on a rotating disc and pass before the controlled water spray twice every minute. During calibration of the test, a period of 22 hours was found to be optimum, and the more obvious sources of variability (timber variation, moisture content of panels before spraying, methods of end and back sealing and methods of surface drying the panels after spraying) were assessed and found to exert little influence on the results. The method gives reproducible results, and by its use it is now possible to measure any decline in water repellent properties which occur during the natural weathering of test panels. The test gives a direct comparison of the water repellency of materials, and is applicable to the measurement of water penetration through other material finish systems.

Inter-relationship of properties during exposure

The actual role of water repellency in a film is a property whose limitations are not clear, although recent work by Bantis[11] has tended to clarify the role of water repellents in the protection of timber. Bantis has shown that water repellent treatment does confer dimensional stability, and that its effect on other properties, such as adhesion and weathering, is probably minimal.

The four main properties which could be expected to show some interdependence are pigment retention, cleanliness, appearance, water repellency. In a major survey of water repellent finishes carried out at TRADA[10], the results shown in Table 2 were obtained after eighteen months' vertical exposure:

Table 2

The results of an exposure test on water repellent finishes

	Classification, per cent		
	Below average	Average	Good
Pigment retention	23	36	41
Cleanliness	6	37	57
Appearance	23	46	31
Water repellency	12	31	57

Unfortunately, the materials which achieved a particular classification in respect of one property did not have the same classification for the others, and no evidence of any significant correlation between water repellency, cleanliness and pigment retention could be found. It was found, however, that those materials which retained their appearance after exposure (that is, had "good" assessment) did, in fact, have high levels of water repellency, but the converse was certainly not true. In many instances, water repellency had remained at a very high level but the appearance of the product had deteriorated badly. It is in this fact that the basic differences between water repellent finishes and paint are most obviously emphasised in that it is quite possible for a water repellent finish to be almost as effective, practically, after eighteen months' exposure, as it was when originally applied, but its appearance will have degenerated to such an extent that recoating will be necessary.

Conclusions

The author considers that water repellent finishes are the most useful materials available today for the protection and decoration of wood to give a clear or "natural" finish. They are able to cope with the many variables associated with the exterior finishing of timber. They are economical, not only in the first instance, but also when maintenance is necessary because they break down by erosion and, therefore, only need a clean-down before recoating. They do not bring out the grain patterns and so forth as well as varnishes and, in selective, sheltered, areas where regular maintenance is possible (such as hardwood front doors), this latter material can be used. Water repellent finishes are, in some cases, preferable to paint, although they lack the filling properties and opacity of paint.

Testing methods for these products are very difficult to standardise and quantify, particularly for those properties which come under the general heading of "appearance". Their water repellency (measured by the weight of an actual water uptake over a given period) can now be measured. Unlike paint, the appearance of a water repellent finish after weathering is not always a guide to the continuing efficiency of the material, which may still be high despite a degraded appearance.

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Accelerated yellowing tests for white architectural enamels*

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Summary

The colour changes occurring in three accelerated yellowing tests applied to a number of white architectural enamels were compared with the colour changes resulting from exposure of the enamels in three household kitchens. The accelerated tests were exposure to sulfur dioxide for 24 hours, exposure to ammonia for 24 hours, and being contained in a black, lightfast envelope for 60 days. The results of the accelerated tests correlate well with the results of the kitchen exposures.

Keywords

Processes and methods primarily associated with analysis, measurement and testing

accelerated testing

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

yellowing

Binders etc.

alkyd resin

Les essais de jaunissement accélérés sur peintures-émail blanches pour intérieures de bâtiments

Résumé

On a fait comparer les altérations de couleur provoquées au cours de trois essais de jaunissement accélérés qui ont été effectués sur une série de peintures-émail blanches auprès des altérations de couleur mises en évidence lors de l'exposition de ces peintures-émail dans trois cuisines domestiques. Les essais accélérés comprenaient; l'exposition à l'anhydride sulfureux pour 24 heures; l'exposition à l'ammoniaque pour 24 heures; et la conservation dans une enveloppe noire et obscure pour 60 jours. Les résultats des assais accélérés s'accordent bien avec les résultats des expositions sur les cuisines.

Kurzprüfungen auf Vergilbung von weissen für architektonische Zwecke bestimmten Emaillelacken

Zusammenfassung

Eine Anzahl weisser architektonischer Emaillelacke wurde auf ihre Farbtonveränderungen hin drei beschleunigten Vergilbungs-Kurzprüfungsmethoden unterworfen und mit den Veränderungen derselben, ausgesetzt in drei Haushaltküchen, verglichen. Die Kurzprüfungen bestanden aus Schwefeldioxid-Exponierung während 24 Std., Amoniakexponierung während 24 Std. und Aufbewahrung in einem schwarzen, lichtdichten Kouvert während 60 Tagen. Die Resultate der Kurzprüfungen stimmen gut mit den in den Küchenversuchen erhaltenen Ergebnissen überein.

Ускоренные испытания желтения белых архитектурных эмалей

Резюме

Делается сравнение между изменением цвета в трех ускоренных испытаниях на желтение, проведенных с рядом белых архитектурных эмалей и изменением цвета в результате выдержки этих эмалей в трех домашних кухнях. Ускоренные испытания включали выдержку в двуокиси серы на протяжении 24-х часов, выдержку в аммиаке на протяжении 24-х часов и заключение в черной светоустойчивой оболочке в течение 60-ти дней. Результаты ускоренных испытаний хорошо согласуются с результатами испытаний на кухне.

Introduction

The yellowing of white paint films on ageing, particularly indoors, is of considerable importance. Under ordinary domestic conditions, the result of such yellowing is merely to cause an unpleasant appearance; but under certain service conditions, such as those obtaining to space ships and submarines, the yellowing has a depressing psychological effect. HM Australian Navy, particularly the submarine arm, has shown considerable interest in the problem of yellowing. As a result, the study was begun with an assessment of those accelerated test methods used for the measurement of yellowing.

The Baltimore Society of the US Federation of Societies for Paint Technology has made a study of accelerated yellowing tests[1]. It was concluded, among other things, that for alkyd enamels, exposure in a dark cabinet, exposure to ammonia vapour, exposure to elevated temperature, and exposure to elevated temperature and high humidity produced test results in good agreement with long normal exposure. In a study of the chemistry of yellowing of oils and alkyds, Jonas[2] claimed to have shown that the addition of catalysts, which promote vinyl polymerisation, reduce yellowing. He claimed that the addition of organic peroxides or hydroperoxides, to a concentration of 2 per cent by weight, effectively inhibits yellowing. Chandhok and Gupta have comprehensively reviewed the literature of yellowing[3], and also carried out work on architectural enamels[4]. They concluded that direct sunlight often bleaches yellowed films, and that the nature of the oxidation and polymerisation catalysts in paints (driers) is important. Manganese driers in particular

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should be avoided. The ammonia test for producing accelerated yellowing was the subject of lively controversy in 1966[5]. The Greater London Council (England) use this test for approval purposes, but Wahlin and Sunderland criticised the test on fundamental grounds[6]. The UK Paint Research Station considered that the test was useful, if not perfect[7]. Newfield[8], of the Mare Island US Navy Paint Laboratory, studied the yellowing of alkyd enamels particularly in relation to their use aboard submarines, and found that tobacco smoke promoted yellowing.

Different chemical types of paint films yellow for different reasons. The mechanism of yellowing of polyurethane paints, for example, is different from that of alkyd paints, and factors which accelerate the yellowing of the former do not necessarily accelerate the yellowing of the latter. Traditionally, the paint industry has believed in the four statements below.

1. Yellowing is greater, the greater the degree of chemical unsaturation of the base resin[9].
2. Choice of driers is important. (Manganese is known to cause yellowing in many systems.)
3. Contaminants, such as the vapour of decomposed fats and oils, tobacco smoke, and so forth, promote yellowing.
4. Darkness promotes yellowing.

Practical problems arising from yellowing include the discoloration of walls shielded from light (by pictures, furniture, etc). The discoloration is often more severe in kitchens subject to contamination, or in enclosed spaces, such as submarines or space craft, which are subject to a recirculatory ventilation system. Yellowing of painted surfaces is reported to have a depressing effect on personnel. The US Navy is believed to have alleviated the problem by using a light green paint in submarines, thus making yellowing less noticeable. The Royal Navy, however, uses a white epoxy-polyamide paint. Other areas which cause problems include the interior roofs of trains, trams and buses.

Standard tests for yellowing

The following standard tests for yellowing have been published:

1. ASTM D 1543-63 (Reapproved 1969) "Colour change of white architectural enamels". In this test, panels coated with the test enamels are exposed in the dark to dry sulfur dioxide for 24 hours. Colour measurements are made before and after exposure to determine the colour change.
2. Canadian Government Test Method, 1-GP-71 Method 120.2, 13 June 1958. In this test, coated panels are exposed to the vapour of concentrated ammonium hydroxide for 18 hours. The yellowness of the enamel before and after exposure is calculated by reflectance measurements.

Experimental work

Eleven paints, some of known composition, were tested for yellowing characteristics by exposure to ammonia, exposure to sulfur dioxide, and by being contained in light-fast envelopes. The paints were also tested for resistance to yellowing under normal interior exposure in domestic kitchens.

Eleven paints were used, seven of which were produced commercially, the other four being made in the laboratory. The code and formulation details of each paint are given in Table 1.

Table 1

Code number and formulation details of paints

Code	Formulation details
C1	Safflower/tall oil fatty acid, pentaerythritol (PE) phthalate alkyd: 63% oil, 34% PE phthalate. Titanium dioxide: 4.06 lb gall^{-1} Napthenate drier: 3.5% v/v Mineral turpentine
C2	Soya/tall oil fatty acid, pentaerythritol (PE) phthalate alkyd: 63% oil, 34% PE phthalate Titanium dioxide: 3.45 lb gall^{-1} Naphthenate drier: 3.5% v/v Mineral turpentine: 23%
C3	Safflower, pentaerythritol phthalate alkyd: 60% oil. No other details provided
C4	Safflower, pentaerythritol phthalate alkyd: 67% oil, 3.36 lb gall^{-1} Soya pentaerythritol phthalate alkyd: 65%, 2.63 lb gall^{-1} Rutile titanium dioxide: 4.00 lb gall^{-1}
C5	Safflower pentaerythritol phthalate alkyd: 67% oil, 6.05 lb gall^{-1} Rutile titanium dioxide: 4.15 lb gall^{-1}
C6	Polyurethane enamel (one pack). No other details available
C7	Soya pentaerythritol phthalate alkyd; 63% fatty acid. No other details available
P1	54% soya pentaerythritol phthalate alkyd; 64% oil 30% rutile titanium dioxide 14.5% white spirit
P2	54% safflower pentaerythritol phthalate alkyd; 67% oil 30% rutile titanium dioxide 14.5% white spirit
P3	54% linseed phthalate alkyd; 70% oil 30% rutile titanium dioxide 14.5% white spirit
P4	58% mixed drying oil alkyd; 70% oil 28% rutile titanium dioxide 13.5% white spirit

C = Commercial product
P = Laboratory prepared formulation

Test methods

The paints to be tested were applied by brush to 6in by 4in sealed hardboard panels. Three coats, each having a thickness of about 25 microns, were applied to all of the panels with a 24 hour drying time between coats. The tests were conducted after the top coat had been drying for at least 5 days.

Colour differences were measured on a MEECO (Manufacturing Engineers and Equipment Company) "Colormaster" tristimulus colorimeter. The colour of each panel was measured immediately before and after exposure.

The colour changes which occurred were calculated (from the data obtained from the colorimeter) using the Modified Adams Chromatic Value System developed by Glasser and Troy[10]. (This is the system recommended by the manufacturer of the colorimeter.) The units of colour change obtained by this system are a close approximation to NBS units.

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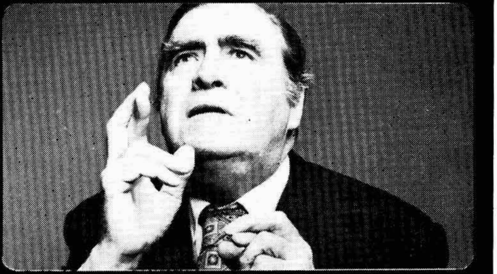

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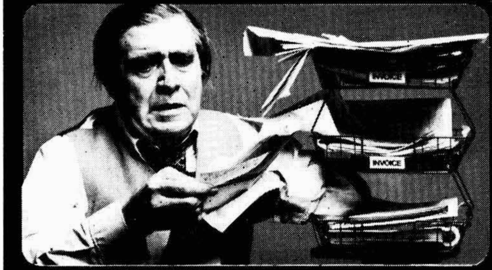

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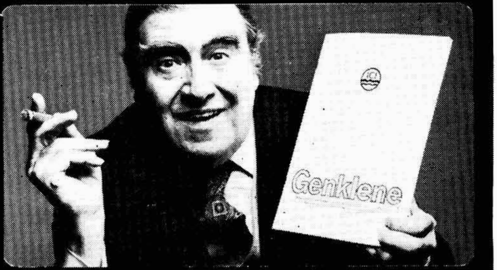

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Exposure to ammonia

Panels coated with the test enamels were suspended from rods in a black cabinet with a capacity of about 5 gallons (11in side cube). A 100ml beaker containing 75ml concentrated ammonia solution (specific gravity 0.88, or density 880kg m^{-3}) was placed at the centre of the base of the cabinet. The panels were removed from the sealed cabinet after 24 hours.

Exposure to sulfur dioxide

Panels coated with the test enamels were suspended from rods in the cabinet used for the ammonia test. Dried sulfur dioxide was passed through the cabinet. After 24 hours the panels were removed. A diagram of the apparatus used is shown in Fig. 1.

Dark exposure

Panels coated with the test enamels were placed in black polythene, light-tight envelopes and stored in a room, at 20°C ± 2° for 60 days, before examination.

Natural interior exposures

Three sets of panels (one panel for each paint) were attached to a wall, out of direct sunlight in three different kitchens. They were examined after 100 days.

Results

The colour changes obtained are recorded in Table 2.

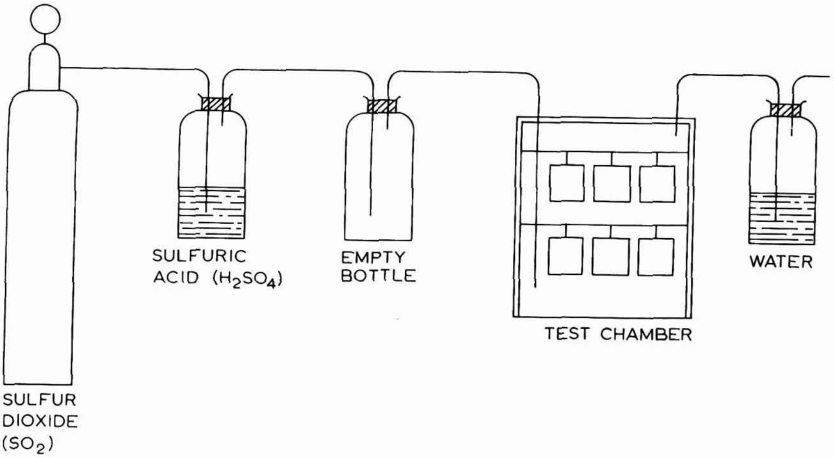

Fig. 1. Sulfur dioxide test apparatus

Table 2
Colour change values (E)

Test	Kitchen I	Kitchen II	Kitchen III	NH_3 (I)	NH_3 (II)	NH_3(III)	NH_3(IV)	So_2 (I)	SO_2 (II)	SO_2 (III)	Dark
Age of panels prior to exposure	7 days	7 days	7 days	5 days	6 days	9 days	10 days	8 days	9 days	10 days	7 days
Code											
C1	1.97	1.70	3.78	5.54	6.10	6.16	7.42	4.05	3.62	3.95	2.02
C2	2.46	1.60	4.65	6.95	6.65	6.90	7.32	4.44	3.70	4.62	2.02
C3	2.78	1.96	4.84	6.90	7.31	7.72	7.30	5.98	4.44	5.90	2.22
C4	2.58	2.12	4.43	5.71	6.23	6.24	7.07	3.09	3.31	3.66	2.28
C5	2.60	1.96	4.41	5.80	6.59	6.73	6.68	6.35	4.84	6.35	2.02
C6	1.63	1.52	4.20	4.74	5.25	5.90	5.00	14.04	12.08	14.08	2.38
C7	3.27	1.73	5.40	6.79	7.79	7.85	7.49	5.40	4.04	5.12	2.25
P1	3.81	2.82	6.76	6.34	7.21	7.43	7.59	9.66	7.60	8.86	3.14
P2	4.11	3.08	6.66	7.52	8.51	8.78	8.99	10.03	7.82	9.52	3.20
P3	5.45	2.84	7.37	10.07	10.50	10.70	11.01	13.50	11.03	12.08	3.91
P4	4.54	3.04	6.59	8.26	8.13	8.74	8.92	12.05	11.01	12.03	2.90

Discussion

Relationship between natural and accelerated colour change conditions.

The colour changes recorded for each paint exposed in kitchen I were compared with the colour changes recorded for the same paint in kitchens II and III and that used for the accelerated tests. The correlation coefficients for these comparisons were calculated[11], and are recorded in Table 3. The values of the correlation coefficients are 0.845 or greater and fall therefore, within the ±0.1 per cent significance limits. From these results, it can be concluded that a correlation between the natural exposures and the accelerated exposures is both likely and significant. Regression lines[12] were fitted for each comparison, and are shown along the plots of data in Figs. 2 to 11. In addition, the parameters for the regression equations are recorded in Table 3.

All paints used in this work were based on long oil alkyd resins except for paint C6, which is based on a polyurethane-alkyd resin. Because of this difference, it was decided that the data relating to paint C6 should be excluded from the statistical treatment. However, inspection of the colour change values for paint C6 shows that, for the kitchen exposures and the ammonia test, this paint exhibited the least colour change (except for kitchen III where it is second

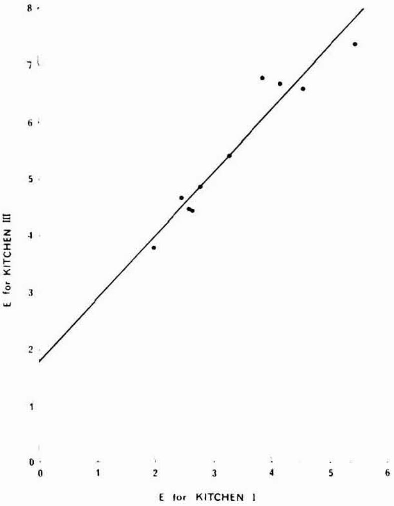

Fig. 3. Comparison of colour change between kitchen I and kitchen III

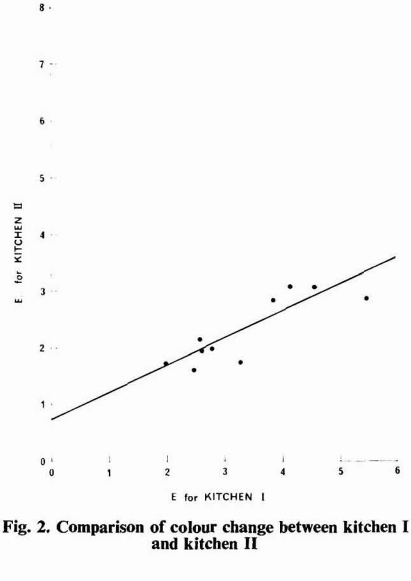

Fig. 2. Comparison of colour change between kitchen I and kitchen II

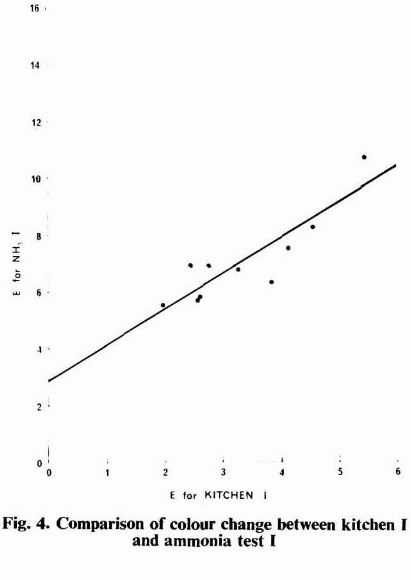

Fig. 4. Comparison of colour change between kitchen I and ammonia test I

Table 3

Statistical parameters relating the colour change (E) for each experiment to the exposure in kitchen I

	Experiments related to that in kitchen I (K_1)									
Parameter	K_1-K_2	K_1-K_3	K_1-SO_2(I)	K_1-SO_2(II)	K_1-SO_2(III)	K_1-NH_3(I)	K_1-NH_3(II)	K_1-NH_3(III)	K_1-NH_3(IV)	K_1-dark
r	0.845	0.961	0.948	0.941	0.947	0.883	0.929	0.940	0.898	0.941
b	0.457	1.097	3.190	2.656	2.918	1.241	1.122	1.194	1.095	0.561
a	0.752	1.808	−3.182	−2.735	−2.482	2.888	3.735	3.715	4.317	0.713

r = correlation coefficient. b = slope of regression line. a = constant of regression line

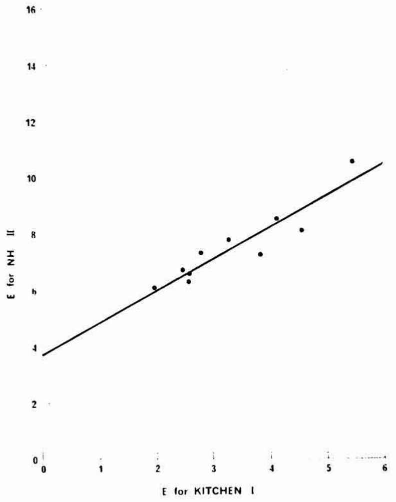

Fig. 5. Comparison of colour change between kitchen I and ammonia test II

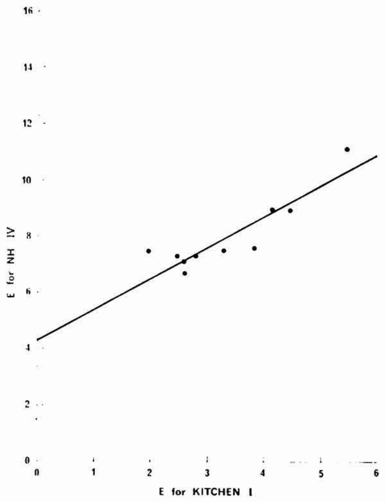

Fig. 7. Comparison of colour change between kitchen I and ammonia test IV

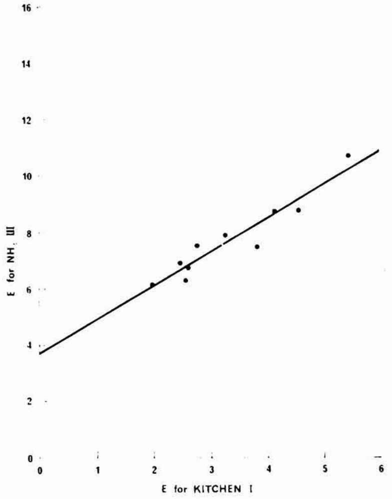

Fig. 6. Comparison of colour change between kitchen I and ammonia test III

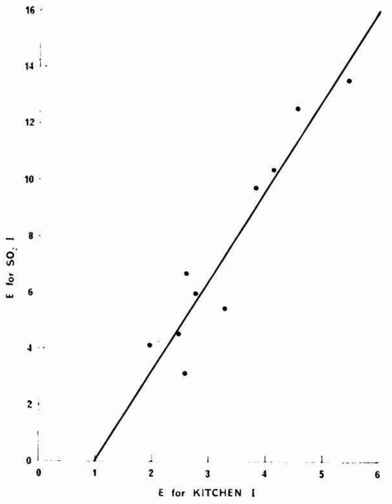

Fig. 8. Comparison of colour change between kitchen I and sulfur dioxide test I

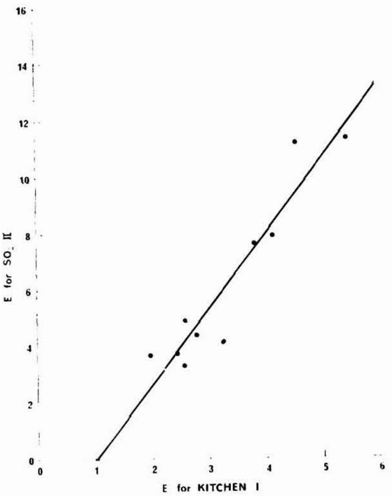

Fig. 9. Comparison of colour change between kitchen I and sulfur dioxide test II

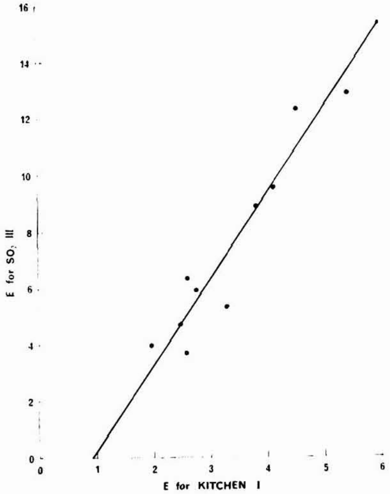

Fig. 10. Comparison of colour change between kitchen I and sulfur dioxide test III

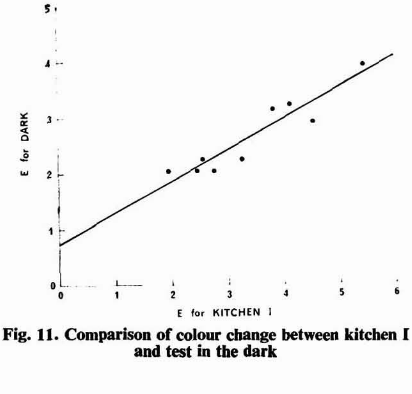

Fig. 11. Comparison of colour change between kitchen I and test in the dark

to least), but for the sulfur dioxide test it exhibited the greatest colour change. For the test in the dark, paint C6 exhibited the seventh lowest colour change. This indicates that the ammonia test may be valid for comparing the relative degrees of colour change between long oil alkyd based paints and polyurethane alkyd based paints, whilst the sulfur dioxide test, and possibly the test in the dark, is unlikely to be valid for such a comparison.

Consideration of results

The existing accelerated yellowing tests are based on exposure to sulfur dioxide or ammonia, whilst the other commonly used test is to keep panels in the dark for one to two months. The advantage of tests based on the exposure to either of the gases over the test in the dark is that the time required to achieve a significant colour change is much less than that required using the test in the dark.

There are conflicting reports regarding the validity of the ammonia test. In 1950, the Baltimore Paint & Varnish Production Club[1] claimed that excellent agreement had been obtained between ammonia exposure and kitchen exposures of various soya alkyd and linseed alkyd paints. Later work carried out by Chaplin and Fish[5] did not confirm the observations of the Baltimore Club. In discussions of the work of Chaplin and Fish both by Sunderland *et al.*[6] and by O'Neill and Brett[7], it was indicated that they too had obtained satisfactory correlation between natural interior exposures and ammonia exposures, although experimental data were not quoted. The results reported here for alkyd enamels support the view that colour change caused by exposure to ammonia can be related to colour change by natural interior exposure.

The ASTM method for accelerated colour change of white architectural enamels requires an exposure of the paint under test to sulfur dioxide for 24 hours. The experimental data from which this method is derived have not been published, so that a comparison between the original data and the data given here cannot be made. The results of this work, however, do confirm that this is a valid test method.

The change in the colour of white paints when kept in the dark has been investigated by many workers and found to give good correlation with colour changes observed under natural interior conditions. These results are confirmed, but the rate of colour change is similar to that observed in practice, and hence the test is not an accelerated one.

Dependence of degree of yellowing on formulation of paints

Detailed information regarding the formulation of most of the paints used for this work is not available; the effects of variation in formulation on yellowing characteristics cannot be determined. Virtually complete formulation details are known for the paints P1, P2 and P3 based on soya alkyd, safflower alkyd and linseed alkyd respectively. The tendency for paint P1 to show the least colour change and paint P3 to show the greatest colour change of these three paints is consistent with the view that vegetable oils yellow in proportion to the degree of their unsaturation[9].

Further work

The Royal Australian Navy uses white epoxy enamels, some of which are known to yellow significantly on most of the interior surfaces of its submarines. The authors, therefore, intend to study the yellowing of these materials in order to develop a suitable accelerated yellowing test. Such a test could be used for evaluating both materials currently available and new formulations designed to resist yellowing.

Conclusions

The results of exposure in three kitchens for 100 days show that there can be a wide variation in the actual colour changes which occur for a given paint. The results indicate, however, that accelerated tests can provide useful information about the relative resistance of various paints to colour change. It is doubtful that the keeping of a paint film in the dark is useful as an accelerated colour change test, because the rate of colour change observed in the test is similar to that in practice.

It is considered that both the ammonia test and the sulfur dioxide test could be used successfully to predict the relative resistance to colour change of white alkyd enamels. The ammonia test is preferred by the authors because of the higher toxicity of sulfur dioxide.

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The formulation of radiation curable paints

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Summary

The radiation curing of paints offers a process whereby coatings can be cured at an extremely fast rate and solvent-free paints can be used. In order to gain these advantages, however, much tighter restrictions are imposed on the paint formulation than with conventional hardenable paints. The desired application, hardening, and film characteristics must all be achieved by suitable formulation of the paint itself.

This paper attempts to review some of the problems involved in the formulation of such paints and to illustrate the reasons why resins and formulations must be "tailor made" for this particular application.

Keywords

Process and methods primarily associated with drying or curing of coatings

radiation curing

Miscellaneous

formulation

La mise au point des formules de peintures durcissables par radiation

Résumé

Le durcissement de peintures par radiation offre un procédé où les revêtements sont durcis à une vitesse extrêmement rapide et où l'on peut se servir des peintures exempte de solvant. Afin de gagner ces avantages, cependant, les restrictions plus étroites s'imposent sur les formules de peintures que dans le cas des peintures durcissables par les moyen usuels. Les caractéristiques du feuil de même que celles de la facilité d'application souhaitée, et de durcissement doivent être realisées par la mise au point d'une formule convenable pour la peinture elle-même.

Cet exposé a pour but le passage en revue de certains problèmes entraînés par la mise au point des formules de telles peintures et l'indication des raisons qui exigent que les résines et les formules doivent être spécifiquement conçues pour l'usage prévu.

Die Zusammensetzung von durch Bestrahlung härtbaren Lacken

Zusammenfassung

Die Strahlenhärtung von Lacken ermöglicht ein Verfahren mit welchem Beschichtungen ungewöhnlich schnell gehärtet und lösungsmittelfreie Lacke benutzt werden können. Um von diesen Vorteilen Gebrauch machen zu können, unterliegt die Lackrezeptur viel engeren Beschränkungen, als bei Vorwendung handelsublicher, härtbarer Anstrichmaterialien. Die gewünschte Anwendbarkeit, Härtung und Filmcharakteristika müssen alle durch geeignete Zusammensetzung des Lackes als solchem erzielt werden.

In dieser Abhandlung wird versucht eine Übersicht von den beim Ausarbeiten der Rezepte für solche Lacke in Frage kommenden Problemen zu geben und klar zu machen, warum Harze und Rezepte für diese besondere Anwendungsmethode "tailor made" sein müssen.

Формуляция радиационной сушки красок

Резюме

Радиационная сушка красок является процессом при помощи которого покрытия осушиваются с чрезвычайно высокой скоростью и могут применяться краски без растворителя. Однако для приобретения этих преимуществ, налагаются значительно более суровые ограничения на формуляцию красок чем для обычных твердеющих красок. Желаемое приложение, упрочнение и характеристики пленки должны быть достигнуты путем подходящей формуляции самой краски. Статья пытается дать обозрение некоторых задач связанных с формуляцией таких покрытий и указать причины почему смолы и формуляции должны быть «точно приспособлены» для данного применения.

Introduction

One of the reasons for the slower-than-expected growth of the process for the radiation curing of paints using low energy electrons (150-500keV)[1-4] is undoubtedly to be found in the relatively sluggish development of new monomers, prepolymers, and low molecular weight resins which are amenable to this type of cure whilst being, at the same time, suitable for the numerous applications for which the process is envisaged (for example, use on a wood substrate for indoor and outdoor use, for coil coating, and for plastic substrates). In spite of the fact that the technical feasibility of the process has been accepted for at least the past ten years, European resin and paint manufacturers have been slow to realise that, if the process is to become commercially established, new prepolymers must be developed which are "tailor made" for the desired application.

Although a radiation curable paint consists, like a conventional paint, of a resin and a solvent, the range of coatings suitable for radiation curing is limited by the nature of ensuing chemical reactions. In principle, a radiation curable paint includes a resin containing polymerisable double bonds dissolved in a reactive solvent which is a vinyl monomer. The average molecular weight of the resin usually lies between 500 and 5,000. The curing of these systems involves a copolymerisation reaction between the vinyl monomer and the unsaturated sites in the resin. The fully cured coating consists of a three-dimensional network, the monomer forming bridges between the prepolymer molecules. The copolymerisation proceeds by a radical mechanism and involves a chain reaction. For such prepolymer-monomer systems of high viscosity, extremely fast rates of polymerisation are obtained as a result of the reduced mutual termination of the growing polymer chains caused by their decreased mobility. This latter phenomenon is generally known as the "Gel effect" or "Tromsdorf effect".

The formulation of a radiation hardenable paint is extremely complex and involves not only the correct choice of resins and monomers, but also the appropriate selection of pigments, fillers and surface coating auxiliaries. As the addition of, for example, non-reactive solvents, which could act as thinners, is not possible, the desired application, hardening, and film characteristics must be achieved by suitable formulation of the paint. This paper, therefore, attempts to illuminate some of the problems involved in the formulation of such paints, and to illustrate current trends affecting the growth and development of paints for the electron curing process.

Resin systems

The majority of the early work on the subject of radiation curing was performed using unsaturated polyester-styrene systems.[5–9] The reasons for this are not difficult to imagine; firstly, unsaturated polyester systems are the largest existing class of commercially available resins suitable for electron curing, and secondly they enable a direct comparison to be made with conventionally cured finishes. On the other hand, although the potential applications for these systems are numerous, especially on wood substrates for indoor use, it is obvious that unsaturated polyester resins are not particularly suitable for outdoor application and for many of the other applications for which the electron curing process is envisaged.

As it is, basically, the resinous component which controls the main features of any electron cured film, considerable research and development has been carried out in the last few years in an attempt to enlarge the range of resins suitable for radiation curing. Apart from determining the radiation dose necessary to cure the coating, the molecular architecture of the resin must, of course, ensure that the desired film and application characteristics (such as corrosion resistance, adhesion, abrasion resistance, flexibility and surface hardness etc) are achieved. The resins currently developed for radiation curing can be classified as follows.

Unsaturated prepolymers

(a) with double bonds situated along the main chain

The prepolymers included in this class of resins are those which contain double bonds arranged in a specific manner in or along the main polymer chain. Typical examples are unsaturated polyesters, diallylphthalate prepolymers and modified acrylic resins.

A considerable range of commercial unsaturated polyester resins is available for electron curing. These resins, despite their cheapness, have not become widely established for the electron curing process due to their high radiation dose requirement, the difficulties of completely overcoming oxygen inhibition on the surface of thin films, and the limited degree of latitude in determining the film characteristics by the design of the resin. The use of unsaturated polyester resins in filler coats, however, remains a practical possibility. In addition, the use of special air drying systems presents interesting possibilities and will be discussed later in this paper. Full details of experimental studies using unsaturated polyester-styrene systems under practical conditions have been described in an earlier publication.[10]

More recently, details have been published of classes of diallylphthalate prepolymers[11,12] suitable for electron curing. These are linear, low molecular weight, internally cyclised structures containing unreacted allylic groups spaced at regular intervals along the chain. The structure of the diallylorthophthalate prepolymer is believed to be that shown in Fig. 1.

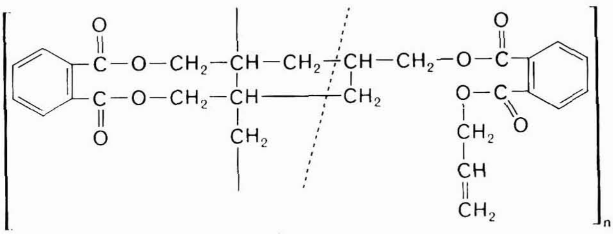

Fig. 1. Possible structure of diallylorthophthalate prepolymer

Mixtures of these commercially available diallylphthalate (that is, derived from diallyl*ortho*phthalate and diallyl*iso*phthalate) prepolymers in other olefinically reactive monomers can be cured at low radiation doses. The curing of these mixtures involves a copolymerisation reaction between the residual allylic groups and the monomer.

The commercial thermosetting allylic resins exhibit excellent physical and electrical properties which are maintained even after prolonged exposure to severe environmental conditions. Apart from their exceptional insulation characteristics, these resins are noted, in particular, for their high temperature stability and resistance to moisture and to aqueous and organic chemical media. Full details of experimental studies involving diallylphthalate prepolymer-monomer mixtures have been described in a previous paper.[13]

The potential methods for the preparation of a considerable number of other resins containing unsaturated vinyl groups spaced at regular intervals along the polymer chain are innumerable. In such a synthesis, condensation, ring-opening, and addition polymerisation reactions can all be involved. The molecular weight, degree and type of unsaturation, and basic chemical build-up of the polymer chains are the major compositional variables which ultimately determine the hardening, film and application characteristics. It might be expected, for instance, that a high degree of unsaturation and a high molecular weight would increase the efficiency of gelation, thus leading to a lower hardening dose. On the other hand, if the frequency of unsaturation is too high, steric influences might impede the reaction in the gel phase, and high molecular weight resins might produce solutions which are too viscous and which prohibit the use of normal application methods. Thus, a delicate balance exists between the molecular weight, structure, and degree of unsaturation of the resins. A typical example of a specially prepared prepolymer which belongs to this class of resins is an unsaturated acrylic prepolymer[14] (Fig. 2).

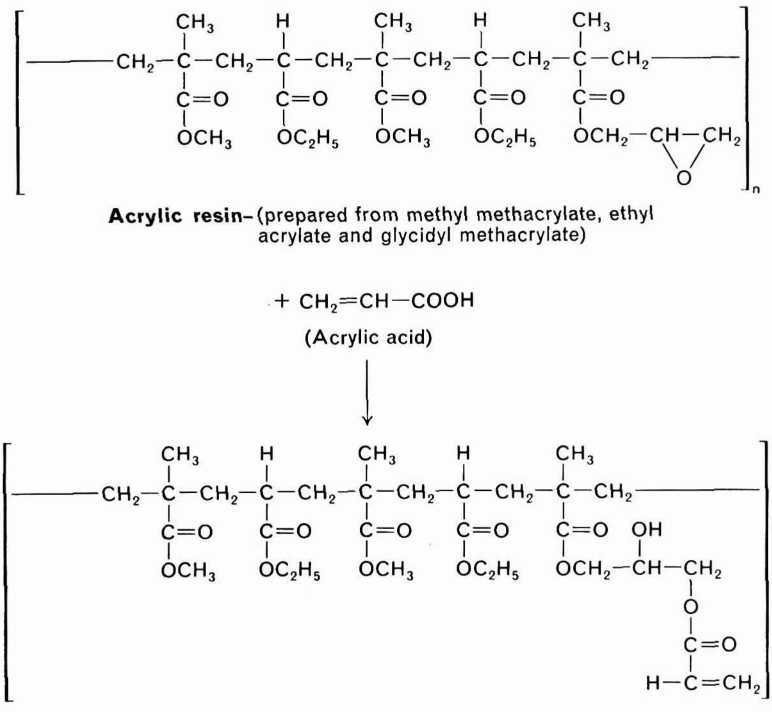

Fig. 2. Preparation of unsaturated acrylic copolymer

In the first instance, an epoxy functional, saturated, acrylic resin is prepared by the copolymerisation of various acrylic monomers and glycidyl methacrylate using conventional solution polymerisation techniques. The epoxy functional, acrylic polymer so obtained is then further reacted with acrylic or methacrylic acid to form an unsaturated hydroxy ester; that is the unsaturation is introduced into the acrylic copolymer by means of a conventional epoxy-acid ring opening reaction.

(b) With double bonds situated at the end of the polymer chains

The majority of resins reported in patent literature can be classified under this group of prepolymers. Examples representative of this class include acrylic modified siloxanes,[15] silicone modified polyesters,[15] acrylic acid adducts of diglycidyl ethers and esters,[16] divinyl adducts of n-heterocyclic compounds,[17,18] and acrylic modified polyurethanes.[19] The same criteria regarding molecular weight, concentration of double bonds, and build-up of the polymer backbone apply to these resins as do apply to those having double bonds along the main chain. The preparation of three of these resins is illustrated below.

Divinyl and tetravinyl adducts of diepoxides.[20] A typical commercial diglycidyl ether resin, prepared from the condensation of Bisphenol A and epichlorohydrin, is reacted with acrylic or methacrylic acid to give a divinyl adduct of the diepoxy compound (Fig. 3). The free hydroxy groups, formed in the preparation of the diadduct, can then be further reacted with an unsaturated acyl chloride (methacrylyl chloride) to obtain the tetravinyl adduct. The reactivity of such resins is extremely high, the resins themselves being hardened at low radiation doses (2 to 3 Mrads).

Unsaturated resins based on n-heterocyclic compounds.[17,18] Recently, a new series of unsaturated resins based on n-heterocyclic compounds has been developed. These resins, which exhibit improved chemical, mechanical and electrical properties, can be prepared by two basically different processes. The first involves the reaction of polyglycidyl derivatives of n-heterocyclic compounds with acrylic or methacrylic acid.[17] The polyglycidyl derivatives concerned are prepared by the reaction of an epihalogenohydrin or β-methyl epihalogenohydrin with a five- or six-membered n-heterocyclic compound. Thus, for instance, 1-glycidyl-3 (β-glycidyloxy-n-propyl) -5,5-dimethylhydantoin is prepared by the reaction of 3-(2′-hydroxy-n-propyl)-5-5-dimethylhydantoin and epichlorohydrin. The product so obtained can then be further reacted with methacrylic acid to give a resin having the formula shown in Fig. 4.

The second process involves the esterification of hydroxy-

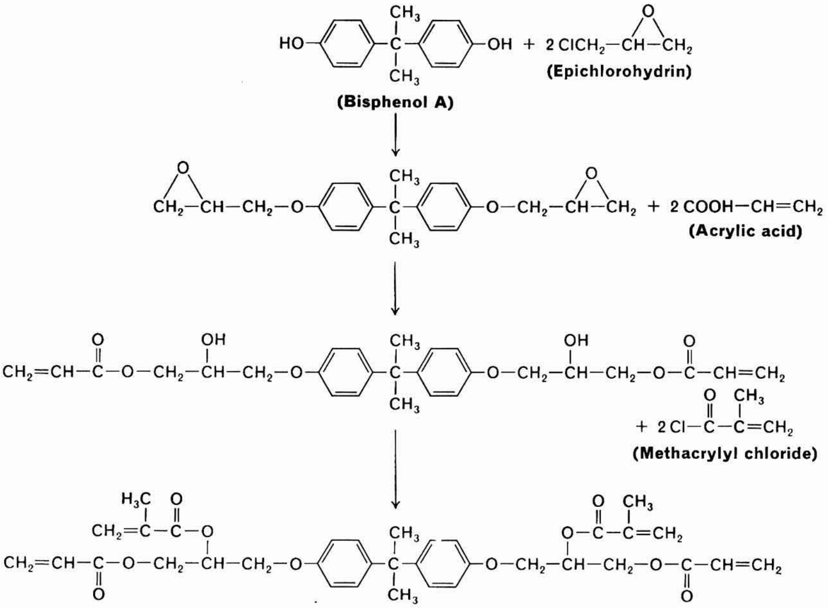

Fig. 3. Preparation of divinyl and tetravinyl adducts of diepoxides

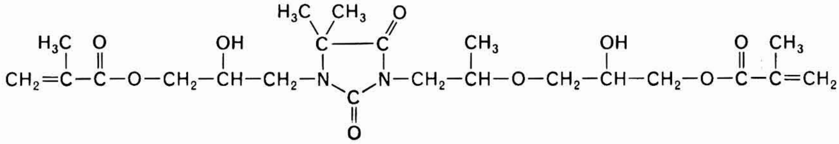

Fig. 4. An unsaturated resin which exhibits improved chemical, mechanical and electrical properties

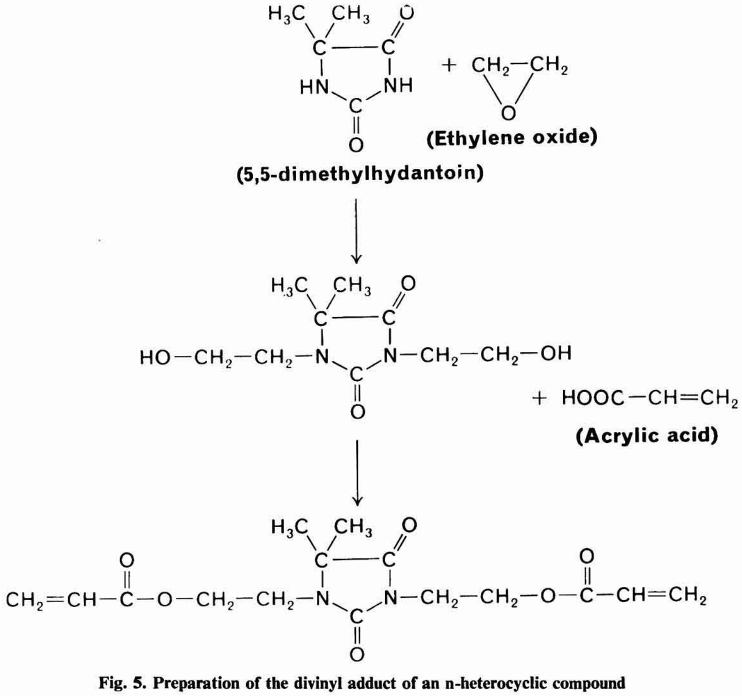

Fig. 5. Preparation of the divinyl adduct of an n-heterocyclic compound

alkyl-substituted n-heterocyclic compounds with acrylic or methacrylic acid.[18] The dihydroxy compounds concerned are prepared by the reaction of alkene oxides, such as ethylene oxide or propylene oxide, with n-heterocyclic compounds such as 5-substituted hydantoins. For example, 5,5-dimethylhydantoin is first reacted with ethylene oxide to give 1,3-bis (β-hydroxyethyl) 5,5-dimethylhydantoin (Fig. 5). The resulting product is then further reacted with acrylic acid to produce a resin which contains no secondary hydroxy groups. The resins so produced are characterised by their low viscosity, and the coatings obtained with these resins exhibit, in particular, an extremely good chemical resistance.

Divinyl adducts of polyurethane resins.[19] Isocyano-acrylic resins can be prepared by reacting an isocyanate terminated urethane prepolymer with a suitable hydroxy-substituted acrylate such as β-hydroxy ethyl methacrylate; that is, by utilisation of the hydroxy-isocyanate group addition reaction (Fig. 6). The isocyanate terminated urethane is prepared by the reaction of a suitable diisocyanate with a polyol.

As can be seen from the foregoing examples, the variations in the preparation of these resins are innumerable. A vast number of resins can be designed by simply using commercially available reactive monomers: for example, by reacting glycidyl functional monomers (such as glycidyl acrylate) with carboxyl groups; monomers containing a carboxyl group or an anhydride group (for instance, methacrylic or acrylic acid) with pendant epoxy groups; hydroxy

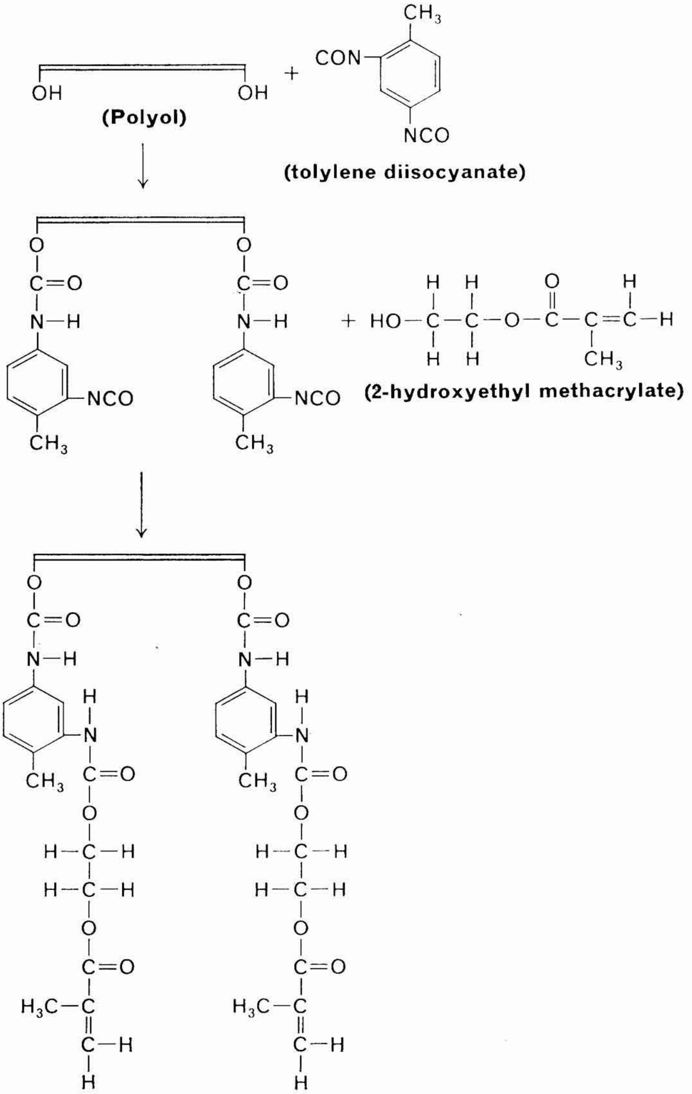

Fig. 6. Preparation of the divinyl adduct of a polyurethane resin

functional monomers (such as hydroxy propyl methacrylate) with pendant isocyanate or oxirane groups; and monomers containing an amido group (such as acrylamide or methacrylamide), again with epoxy groups.

Saturated prepolymers

It is possible to produce partially crosslinked coatings by the use of saturated prepolymers dissolved in vinyl monomers. These coatings can be produced in several ways.

One method is by use of monomer combinations containing at least a proportion of bi- or tri-functional monomers. In this case, the saturated resin is not chemically bound into the crosslinked network. The crosslinking occurs exclusively between the monomers which must be correspondingly selected for this purpose. These systems are normally, therefore, only up to approximately 50 per cent crosslinked. The degree of crosslinking cannot exceed the concentration of the monomers in the mixture. A typical example of such a system is a thermoplastic acrylic resin dissolved in a mixture of acrylic monomers, a proportion of which (5 to 10 per cent) is a bifunctional acrylate or methacrylate.

Partially crosslinked coatings can be produced, as well, by the use of polyacrylates, or copolymers, containing a polyacrylate component dissolved in vinyl monomers, an essential element of which is normally an acrylate monomer. Apart from the normal polymerisation reactions involving the vinyl monomers, partial crosslinking of the acrylate components occurs through chain transfer processes with the polymer (or monomer) to yield branched structures which are subsequently tied together by radical combination processes. Moreover, the addition of chain regulators can, in this case, increase the degree of crosslinking. An example of such a coating system is a resin mixture consisting of polymethyl acrylate, or a copolymer of methyl acrylate, dissolved in methyl acrylate monomer.[21]

Finally, recent studies have shown that mixtures of chlorinated prepolymers with various monomers can be hardened at low or medium radiation doses, and a crosslinked network can be formed.[22] Chlorinated resins which are suitable for radiation-induced crosslinking reactions in solution include polyvinyl chloride and its copolymers, chlorinated rubber, chlorinated polypropylene and chlorinated polyethylene.

In these three systems, where the polymer is in solution (or swollen) with the monomers, the prepolymer enters into the crosslinked network. The detailed mechanism of crosslinking, in particular the contribution from each of the particular reactions involved, is, at present, not clear. Initially, the radiation produces three main types of free radicals, (a) polymeric radicals formed by loss of hydrogen or chlorine atoms from the chlorinated polymer, (b) the atoms ejected, and (c) monomer radicals. It is known that, although the original resin contains no unsaturation, conjugated double bonds can be introduced into the polymer by exposure to ionising radiation with subsequent liberation of hydrogen chloride. The growing polymer chain (from the monomer) may, therefore, react directly with free radicals produced on the polymer (these polymer radicals also initiate monomer polymerisation), or with the unsaturated double bond formed in the prepolymer by the first chlorine abstraction or "molecular process", or alternatively with the conjugated double bonds formed by the second dechlorination step. The second dechlorination step may occur with or without additional activation by radiation as the chlorine in the α-position to the double bond is very labile. In addition, there may be a minor contribution to the overall crosslinked network from the crosslinking of the prepolymer itself, which could result from intermolecular dechlorination or from interaction of the polymeric radicals with neighbouring double bonds. With the use of bi- or polyfunctional monomers the degree of crosslinking is further enhanced by the random growth of a polymer chain through one of the pendant double bonds. The initial grafting and polymerisation processes need only involve one of the double bonds in the monomer to form a polymer chain containing pendant double bonds.

Monomers

The correct choice and concentration of monomer for any radiation curable paint is of extreme importance as the monomer can influence the characteristics of the coating in many ways:

(a) The monomer is the reactive crosslinking partner for the resin and thus determines, in a similar manner to the resin itself, the radiation dose required to harden the coating. In general, the acrylic acid esters are to be preferred, rather than the methacrylic acid esters and allylic monomers, which have no practical function in coatings curable at room temperature.

(b) The monomer acts as the solvent for the paint and must, therefore, be used to control the desired viscosity of the formulation.

(c) The surface of the coating is directly controlled by the monomer. The majority of monomers are relatively volatile and their use can lead to a disturbed surface. As with conventional systems, a percentage of a high boiling point monomer, such as an acrylic acid ester of the higher alcohols, can be added to the monomer to overcome these film blemishes.

Evaporation of the monomer is critical as the curing mechanism is very sensitive to monomer concentration; the use of extremely volatile monomers may necessitate the use of a monomer recovery system which can be very costly.

Apart from the choice of monomer, the concentration of the monomer is extremely important. For any particular resin, an optimum resin-monomer ratio exists with respect to the required hardening dose, degree of crosslinking and film characteristics. In general, too high a concentration of monomer can produce a lower gel fraction due to a decrease in viscosity, an increased rate of bimolecular termination (preferential homopolymerisation of the monomer), and a higher radiation dose requirement. When too little monomer is present, the resin alone predominates in the mode of crosslinking, and this too results in a lowering of the overall gel fraction. Gel efficiency is at its maximum when the relatively immobile macro-radicals are bridged by mobile monomer molecules in a free radical copolymerisation chain reaction. The crosslinking mechanisms involved are complex, however, and depend to a great extent on the molecular weight, degree of unsaturation, and design of the resin. The above-mentioned comments should, therefore, only be taken as an initial guide to this far-reaching problem. The necessary concentration of monomer for any particular resin must in every case be evaluated under practical conditions.

The following factors must, therefore, be taken into consideration when selecting a monomer for any radiation hardenable paint: solubility and viscosity of the resin-monomer system, boiling point and volatility of the monomer, copolymerisation characteristics, functionality of the monomers (that is, its effect on the degree of crosslinking), desired film characteristics, and price.

A considerable number of unsaturated monomers are currently produced commercially. One of the cheapest and most attractive, from the point of view of its high rate of radiation polymerisation, is vinyl acetate. This monomer, however, can be practically discarded due to its low boiling point and volatility and because coatings containing vinyl acetate have low weatherability and water resistance. The acrylic and methacrylic acid esters have, in comparison, a lower rate of radiation polymerisation, but can be employed to influence film characteristics in a similar way to that used in the synthesis of conventional acrylic copolymers. In this respect, the flexing action of butyl acrylate or 2-ethyl hexyl acrylate is worth noting. On the other hand, despite the advantage of their having higher boiling points, the esters of the higher alcohols are less reactive than those of the lower alcohols. Styrene, virtually the cheapest monomer available for any radiation curable paint, exhibits good copolymerisation characteristics with many resins and other monomers. In this case, however, due to the extremely high radiation doses required to cure systems containing this monomer, styrene must, for most practical purposes, be disregarded. The use of the high boiling bi-functional monomers such as 1,4 butane diol dimethacrylate and triethylene glycol dimethacrylate produces coatings with good flow characteristics and as a result of their bi-functional character they enhance the degree of crosslinking. These monomers are, however, extremely costly, and in most instances, due to their price, can only be tolerated as additives in small quantities.

Formulation

For the optimisation of radiation curable paints, not only the correct choice of resin and monomer must be taken into consideration but also the selection and concentration of suitable pigments, fillers, and coating auxiliaries, such as levelling and anti-bubble agents.

In general terms, the pigmentation of a radiation curable paint presents few problems. Inorganic pigments and fillers (titanium dioxide (rutile), barium sulphate, calcite, magnesium silicate etc) do not influence the hardening of such paints and do not normally produce any marked discoloration. Moreover, any slight colour changes observed are found to be reversible for a period of several days following the irradiation. The use of organic pigments can, on the other hand, produce a marked discoloration of the films, and these pigments may, in addition, act as inhibitors in the curing process. The use of pigments can lead to a reduction in the storage stability of paints, and organic pigments reduce the stability to a much greater extent than do inorganic pigments.

The effective flatting of radiation curable paints is difficult to achieve. The majority of conventional flatting agents have little effect in reducing the surface gloss of such paints, except when the agent is present in a high concentration. This problem can be solved only in conjunction with all the other formulation considerations; that is, choice and concentration of monomer and resin, and the most effective combination of flatting agents must be evaluated under representative conditions of use.

Radiation hardenable paints are prone, like conventional curable systems, to surface blemishes and defects (crater formation, bubbling, orange peel etc). For these systems, however, when there is only a relatively short time between coating application and hardening of the paint (normally under 0.5 min), it cannot be assumed that defects can be eliminated simply by the use of surface coating auxiliaries. In general, conventional additives, such as levelling agents and anti-bubble agents, are less effective when used in conjunction with the faster curing radiation systems than with conventional paints. The surface defects must, therefore, be avoided by correct formulation of the paint, and by careful manufacture of the resins and paints themselves. It is worth mentioning, however, that some conventional levelling agents, such as silicone oils and derivatives of cellulose acetate, have been found to be effective in improving flowout characteristics; but this is the exception rather than the rule.

Surface inhibition

The majority of radiation curable coatings do not provide a mar-proof or scratch-resistant surface when the irradiation is performed in the presence of air. This is because of the preferential interaction of the free radicals produced with oxygen rather than with unsaturated carbon-carbon double bonds, thus reducing the effective crosslinking on the surface of the films.

In recent years, cure inhibition of conventionally cured unsaturated polyester systems has been overcome by the use of chemically modified polyester resins. These systems are, in general, rather expensive, and usually rely on the addition of small amounts of cobalt driers. For instance, the incorporation of allyl ether groups in the polyester molecule itself, or the addition of compounds containing such groups to polyester-monomer systems, reduces the air inhibition effect significantly. It is assumed that the cobalt additive reacts in a similar manner to that found in conventional curing by accelerating the autoxidative polymerisation of the air drying groups. The initial autoxidation involves the formation of hydroperoxides at the activated α-methylene group adjacent to the double bond. This is followed by dissociation of the unstable hydroperoxides, and further polymerisation proceeds by means of a free radical mechanism. Cobalt compounds, or other suitable metal driers such as vanadium and manganese, can clearly increase the rate of polymerisation or crosslinking by promoting hydroperoxide decomposition, but it is believed, in addition, that the metal salts act as oxygen carriers, and that this makes oxygen available in a suitable physical state for homogeneous reaction at the reactive sites. Such polyester systems, although they generally produce excellent surface characteristics, have not become established in practice, partly due to the high radiation doses necessary for cure, and partly because of the difficulties encountered when producing these materials, and because of their cost. Recently, the use of nitro-containing compounds[23] and polyisocyanates[24] has been reported as an effective method for the reduction of the surface inhibition effect in radiation curable systems.

Most of the other methods used conventionally to avoid oxygen inhibition on the surface of the film are impracticable in the case of the electron curing of paints. The addition of skin-forming waxes (where the wax is exuded to the surface of the film due to the wax's becoming insoluble as the polymerisable system begins to crosslink) cannot be contemplated due to the extremely rapid rates of reaction encountered in radiation curing. There is insufficient time for the wax to diffuse to the surface. Alternative methods using these additives, however, are either a short preheat or a process involving the prior gelation of the coating by exposure to ultra-violet light.[25] Physical shielding, by simply covering the coating with a foil such as Mylar film, is, of course, impractical on an industrial scale. Moreover, the removal of the uncured surface by sanding or polishing, or even a solvent wash, increases the overall cost of the process.

Although the extent of surface inhibition can be reduced, and in some cases practically eliminated, by irradiating at high radiation intensities,[10] the only feasible method for obtaining a mar-free and scratch-resistant surface with the majority of radiation hardenable resin systems is to perform the irradiation under virtually oxygen-free conditions. The irradiation can be quite simply performed in a nitrogen gas atmosphere (from gas cylinders or from liquid nitrogen), or in an inert gas atmosphere (obtained by incomplete combustion of desulfurised town gas). The level to which the oxygen content must be reduced depends on the formulation of the paint, and, in consequence, on the resin system itself. In practically every case, however, the oxygen level must be maintained below 1,000 ppm. The economics of the system will, of course, play an important role in determining the choice of atmosphere.

Conclusions

Since two of the major advantages of the process for the radiation curing of paints are higher production speeds and the use of solvent-free paints, much greater restrictions are imposed on the formulation of radiation curable paints than on conventional curing paint systems. Apart from the requirement that the coating must cure with a low radiation dosage, the coating must be of suitable viscosity to enable its application by conventional techniques or by newly developed coating methods, and the films obtained must meet the minimum specification for the desired application. In addition, the paint itself must be offered at an acceptable price for a large volume market. As all these requirements must be met by suitable formulation of the paint itself, the degree of latitude regarding choice and concentration of resin, monomer, pigment, and so forth is extremely limited. As a result, resins and formulations must be "tailor made" for any particular application.

The past few years have seen the development of a considerable number of new monomers, prepolymers and low molecular weight resins. Moreover, there is an increasing awareness of the other technological problems associated with the electron curing of paints; problems such as the development of new engineering techniques to handle the new chemical systems (that is, new types of application equipment and transport mechanisms) and the design of plant to overcome oxygen inhibition. It is, therefore, the responsibility of both the paint chemist and the design engineer to co-ordinate the necessary and varied disciplines involved, to ensure that the electron curing of paints fulfils its promise to revolutionise the coatings industry.

Acknowledgments

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Next month's issue

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

The behaviour of acrylic paints for electrodeposition during the course of neutralisation and determination of the degree of neutralisation *by V. Novak*

Anti-mildew coatings. Parts I and II *by O. Pauli*

Chemical preservatives for coatings and realistic procedure for evaluating their effectiveness *by L. A. Weinert and W. W. Vanderstraeten*

Some aspects of the preservation of microbiological attack on emulsion paint systems *by G. Carter*

Incidence of microbial contamination of emulsion paint during the manufacturing process *by W. G. Miller*

Reviews

Organic polymer chemistry

By K. J. Saunders

London: Chapman & Hall Ltd., 1973, pp. ix + 473. Price £6.00

This book gives a concise account of the organic chemistry of the commercially important polymers. Although mainly intended for students of polymer science, it is also useful to those who seek initial basic information in a new field. The depth to which each subject is studied is carefully chosen to correspond to that at which fairly certain knowledge stops and speculation begins, thereby avoiding the more controversial aspects. The physico-chemical side is not dealt with, and this keeps the work to a reasonable size. Sections on the surface coatings resins are too brief to be of value to the paint technologist, who will derive most benefit from the book from its broader aspects. At £6.00, it is worth its place on the shelf of any paint laboratory where there are young technologists.

L. A. O'NEILL

Epoxy powder coatings. Bibliographies in paint technology

By R. H. Chandler

R. H. Chandler Ltd., pp. 53. Price £5.00 ($15.00)

This is a concise account of the articles, lectures and patents, issued during the past decade, in the prolific field of powder coatings. It is interesting to read the speculative comments of the introductory chapter, which includes market surveys of the depth of penetration into European industry. Following sections deal with epoxy resins, a comprehensive survey of curing agents, pigments and extenders, additives and pretreatment. Powder coating production methods are reported in a series of discussions by equipment manufacturers, and the account is completed with a reference to particle size considerations.

If the reader needs to be further confused, there are more than two hundred references, and one can only compliment the author for his diligence in abstracting this formidable collection of literature.

The bibliography is essential for all of the experts in this new technology, if only to verify that their own contributions have been faithfully recorded.

A beginner should be cautioned that these various accounts do not entirely reflect the true "state of the art", since there is much that has been left unsaid. Nevertheless, this is a worthy addition to the library shelf.

S. T. HARRIS

Chatfield's European Directory of Paints and Allied Products

By Dr C. J. Chatfield and Dr H. W. Chatfield (Editors)

The Chatfield Applied Research Laboratories pp. 331. Price £3.50 + 40p packing and postage

The emphasis in this directory is on the sources of supply of particular paints and allied products in Europe. The primary object is to help buyers, users and those who produce specifications to find sources of supply of particular products in their own country and elsewhere in Europe. It does not cover the suppliers of raw material to paint and other manufacturers.

Products are listed alphabetically according to their type and purpose. An account of the general properties and purpose of each product is given. This is followed by lists of manufacturers in the various European countries; code numbers are used to identify the manufacturers. The number of manufacturers quoted varies from one (sometimes none) for a particular product in a given country to, for example, sixty-six for "fire retardant coatings" in Great Britain. Some three hundred products are listed.

Manufacturers are listed numerically according to code number and they total 2,734. The only criticism is that where a given product has a large number of suppliers, it is necessary to decode a large number of codes to find a manufacturer in, say, a particular locality.

An index of trade names and brand names amounting to over 1,100 is given, but it is not claimed to be exhaustive. Finally, a general index is provided in English, French and German. The introductions to each section and the product titles are similarly trilingual.

The volume is well produced and appears to be reasonably free from errors. It will obviously be of great use to those for whom it is intended.

S. R. FINN

Information Received

Bakelite resins for adhesives

BXL's Thermosetting Division has published a broadsheet giving details of the various types and uses of Bakelite resins for adhesives.

Berger Paints to market powder coatings

Ault & Wiborg and Berger Paints, two leading companies marketing thermosetting powder coatings for industrial use in Britain, have announced changes in their continental licence arrangements.

For the past five years, Ault & Wiborg have held the licence to manufacture and import "Teodur" powders from Wagemakers' Lakfabrieken of Breda, Holland. However, it was amicably agreed that, because Wagemakers' had become a member of the Hoechst Group (which includes Berger), this marketing arrangement should terminate, and the "Teodur" range should be manufactured and marketed in the UK by Berger Paints Limited. Ault & Wiborg will continue to manufacture "Rockhard" powder coatings at their Birmingham factory.

Cathodic protection

The Paint Research Association has recently completed a bibliography on "Paints and Cathodic Protection." The bibliography, with references from 1960 onwards, includes full abstracts. Copies, price £5.00, are available from The Librarian, The Paint Research Association, Waldegrave Road, Teddington, Middlesex TW11 8LD.

Campbell Syntac agreement

An agreement has been reached between Akzo Coatings BV, of Holland, and Burmah Industrial Products Ltd., for close co-operation between the subsidiary companies Syntac BV and Campbell Technical Waxes Ltd., with the object of jointly increasing the prospects for both companies.

Degussa increases pentaerythritol production

Degussa, of Frankfurt am Main (Federal Republic of Germany), has decided to increase pentaerythritol production at its Bruchhausen works to 30,000 tons per year at a cost of 12 million DM.

Du Pont begins polyvinyl alcohol production at La Porte

The Du Pont Company has announced "start-up" of its new polyvinyl alcohol and vinyl acetate monomer plant at La Porte, Taxas. The plant, which has an annual capacity in excess of 100 million pounds, is the largest single-line polyvinyl alcohol unit in the world. The ethylene-based vinyl acetate monomer facility has a capacity of 350 million pounds per annum.

First British powder coating manufacturer

Vanguard Powder Coatings Limited, the first British company to be formed specifically to manufacture powder coatings for industrial finishing, has recently commenced full-scale production on the Teesside Industrial Estate at Thornaby-on-Tees.

A range of high quality powders will be marketed as "Vanclad" epoxy powders. The Vanclad range consists of high-gloss, satin, matt, metallic bronze, aluminium and textured finishes. Fourteen colour standards are being produced; special colours can be manufactured by arrangement with the company. The powders are of the "fast-cure" type, and can be applied by electrostatic spray, in an electrostatic fluidised bed, or in a cloud chamber.

ICI redevelopment at Slough

A new eleven million litres capacity decorative paints plant, incorporating bulk materials handling, is to be built by ICI Paints division at Slough on a site to be cleared by demolition. The £2.25 million project is scheduled for completion in late 1975.

Monsanto increases resin production

Monsanto has increased production capacity for amino coating resins by fifty per cent at its plant at Springfield, Massachusetts. This plant produces the company's "Resimene" melamine and urea resins.

Winstones Ltd., join Felix Bottcher

Winstones Rollers Limited, of Harefield, Middlesex, manufacturers of elastomer industrial and printing roller coverings, and Felix Bottcher of Cologne, have signed an agreement to include Winstones as a member of the Felix Bottcher Group of companies. Felix Bottcher is probably the largest manufacturer of industrial and printing rollers in the world, with an international network of agencies in over eighty countries.

New Products

Additive for viscosity control from International Colloids

International Colloids Limited have announced a "cold-stir" dispersion additive for the control of flow and viscosity in paint and varnish media. Known as "Viscaloid," it is based upon hydrogenated castor oil, and is compatible with most synthetic resins. This product is expected to be valuable for use in tin-foil coating processes in particular.

Korrodur

Compounding Ingredients Limited has introduced a new rust passivator called "Korrodur." By the addition of between three and five per cent of Korrodur into a synthetic resin anti-corrosion primer, it is possible to coat a rusty surface which has not been completely cleaned. Korrodur, a liquid product with a thirty-two per cent solids content and pH value below 3, should be mixed with the anti-corrosion primer.

Organo-silicon polymers from natural silicates

A room-temperature process for converting certain polysilicate minerals into novel organosilicon polymers, with molecular weights ranging from 1,000 to 20,000, has been developed by the Paint Research Association. The process involves the removal of inorganic cations and their replacement by triorganylsilyl capping groups. Such derived polymers are water-white in colour, and vary from viscous liquids to resinous solids.

The new polymers differ structurally from the well-known silicone oils and resins, but it is anticipated that their manufacture will be economically more attractive than conventional techniques now used for the total synthesis of normal organosilicons.

Patent applications on the process have been filed.

New latex paint from Williamson Ltd.

A new range of latex paints for interior use, marketed under the name "Abbewell," has been introduced by T and R Williamson Ltd., the Ripon-based paint manufacturers.

This water-based paint incorporates a film permeability, allowing recently-plastered walls to hydrate, and is particularly suitable, therefore, for the decoration of new buildings.

New wood primers from Carsons and Hadfields

Carson Paripan Ltd., and Hadfields (Merton) Ltd., have replaced their range of lead-based wood primers with four new products (pink and white "interior" and "exterior" wood primers) which not only fall in line with the Paintmakers' Association's recommendations of less than one per cent lead in the dry paint, but also conform to the one half per cent lead level stipulated in the Toy Safety Regulations.

Parcolene 85

A new organic post-treatment process for electropaint has been released by Pyrene Chemical Services Limited. The new treatment, known as "Parcolene 85," overcomes the effluent problems associated with conventional chromate post-treatments. Metal salts have been replaced by complete organic compounds, which give the desired improvement in corrosion resistance, but which are biodegradable. No treatment of effluent is necessary other than, in some cases, pH adjustment.

Ultra-violet curing

Scientists working for Polychrome Corporation, Yonkers, NY, have developed materials known as Uvimer TM and Flexomer TM, which, after exposure to ultra-violet light, undergo a chemical reaction allowing them to cure on almost any surface in only a few seconds with no emission of solvent into the atmosphere.

Bristol

Gravure cylinder processing

The 193rd ordinary meeting was held on Friday 26 January 1973 at the Royal Hotel, Bristol. Mr B. I. Stewart presented a paper entitled "Gravure cylinder processing and its relationship to ink manufacture."

The speaker began by outlining the gravure printing process and how it differed from other methods of printing. He went on to describe the preparation of a gravure cylinder, and how this was influenced by the specification of the ink, such as colour separation, balancing and engraving. It was important that a good working relationship be established between the ink maker and the cylinder manufacturer.

This most interesting talk was well received and a lively discussion followed, which was opened by Mr I. S. Cox.

A vote of thanks was proposed by Mr F. Ruddick and was warmly received by the twenty-three Members and guests present.

Dispersion techniques

At a meeting on 23 February 1973 at Cardiff, Mr I. Berg, of Berger Paints, presented a paper entitled "Modern dispersion techniques."

The object of a dispersion process was to obtain a stable base. Mr Berg described how stability is a function of pigment concentration, degree of dispersion, non-volatiles and viscosity. He went on to tabulate suggested starting formulations to give stable bases, in relation to the oil absorption of the pigment and to the shear rate of the mixer. Ideally, a dispersion process should be completed with a base that is sufficiently stable. However, as the initial milling formula should be as highly pigmented as possible, a reduction of particle size should be effected during milling.

The principles of dispersion were similar for all types of plant, but the construction could impose contraints, although, since dispersion was a mixing process and most efficient at laminar flow, all dispersion equipment could be regarded as mixers. The principles and relative performance of various types of plant were discussed in detail.

Specific problems could occur when milling several pigments, but co-milling was technically preferable to mixing methods. On the subject of surfactants, Mr Berg commented that although these could be effective in the early stages, they could become flocculants.

Mr Berg's wide knowledge of his subject and entertaining presentation were well received, and his many controversial comments led to a lively discussion, opened by Mr J. R. Taylor.

A vote of thanks was proposed by Mr L. J. Brooke and was warmly supported by the fifteen Members and guests present.

"The customer is always right"

On Friday 30 March 1973, at the Royal Hotel, Bristol, Mr P. L. Gollop introduced the programme for the evening, which was something of an innovation in the activities of the section, and took the form of an informal debate on the topic "The customer is always right."

Proposing the motion, Mr D. S. Newton, of British Steel Corporation, pointed out that most of us provide goods and services, and also use goods and services, so that our view varies according to the position we occupy.

The supplier must recognise that the customer is always right but not necessarily correct, and that the customer must be wooed by the supplier who should satisfy his whims and fancies.

Opposing the motion, Mr T. Jones, of Berger Paints, said that it is in the nature of business that what is right for the customer is not necessarily right for the supplier. Business is a compromise, and matters of conflict should be kept in the background.

The lighthearted approach of the principal speakers set the tone of the debate, and there followed a most lively and entertaining discussion, which ranged over many aspects of the subject.

A vote of thanks to Mr Newton and Mr Jones was proposed by Mr P. L. Gollop, and this was warmly supported by the sixteen Members present.

R.F.N.

Hull

Are emulsion paints good enough?

Mr J. Cruden, of Harlow Chemical Company, gave a lecture with the above title at the Queens Hotel, Hull on Monday 5 February. Mr F. D. Robinson was in the chair and twenty-one Members and ten visitors were present.

Mr Cruden began by discussing the adhesion and exterior durability of emulsion polymers. The adhesion of these polymers on surfaces such as wood and old gloss paint was becoming more relevant with the swing towards lower pvc formulations and the lecturer surveyed the use of nitrogen containing, adhesion promoting monomers in emulsion formulation. Appropriate groupings could be introduced "in situ," and Mr Cruden referred to the reaction between polymerised carboxyl groups (or colloidal ones, particularly if carboxyl functional) and ethylene imine. American emulsions formulated on these principles were well known, and the lecturer suggested that similar improvements would be introduced into British-made products within the next year.

Exterior durability of emulsion binders was controlled largely by achieving a balance between the scission and crosslinking reactions which proceed under the influence of ultra-violet radiation. Polymers based on vinyl acetate, methyl methacrylate, and ethyl acrylate underwent degradation, whilst those formulated on the higher acrylates, styrene or vinyl chloride underwent crosslinking reactions with an increase in molecular weight in the initial period of exposure, although they might degrade in later life.

Certain defects of emulsion paints, for example, staining, marring, blocking and solvent sensitivity, were associated with thermoplastic nature of the paint. Mr Cruden discussed various methods for rendering the paint film non-thermoplastic by the incorporation of suitable water- or alkali-soluble polymers which, in addition, can contribute to film build, dispersion and levelling. Maleinised 1:2 polybutadiene, and copolymers of maleic or fumaric acid with polyethylene oxide were mentioned. The latter polymers were partially air-drying in the absence of drier metals, but remained rather sensitive to water. The use of drying oil as a source of free radicals to polymerise vinyl monomers was discussed, as was the introduction of vinyl unsaturation into polymer molecules by reacting allyl chloride with ionised carboxyl groups in the presence of copper. These allyl groups were capable of polymerisation reactions within the film with maleic or fumaric acid copolymers.

Following a discussion period, in which Mr Cruden dealt very ably with a number of interesting questions, a vote of thanks was given by Mr B. J. Howells.

J.A.H.

Manchester

The following lectures were held at the Manchester Literary and Philosophical Society.

Synthetic stoving finishes

On Wednesday 14 February 1973 Mr D. Pountain, of WPM Paint Division, gave a most interesting lecture to a receptive audience of twenty-three Members and fourteen visitors. He described the conditions required for curing various types of thermosetting resins, and the properties to be expected from their cured films. Modern methods of application were illustrated, together with examples of end usage. Mr Pountain wound up by giving his audience a glimpse into his impression of the future for stoving finishes.

At the prompting of various questioners, Mr Pountain elaborated on various aspects of his lecture during the discussion period, and very ably dealt with the questions.

A vote of thanks by Mr H. Wilbey was well received.

Pigment dispersion

At a meeting on Wednesday 14 March 1973, Mr G. R. Robson, of ICI Organics Division, presented a paper to an audience of twenty-four Members and forty-four visitors. The size of the gathering denotes the interest stimulated by this subject, and the audience were well repaid by a lucid exposition of the principles governing dispersion and its effect on such paint properties as gloss, shade, strength, opacity, fastness and resistance to flocculation.

A lively discussion period followed the lecture, and this was very ably summed up by Dr W. Carr in proposing a vote of thanks, which was well received.

A.McW.

Midlands

Purchasing

The 161st meeting was held at the Birmingham Chamber of Commerce on Friday 19 January 1973 with the Section Chairman, Mr A. S. Gay, in the chair. This was the annual dinner meeting and began with an excellent meal in a pleasant atmosphere. The meeting was attended by sixty-nine Members and guests.

The speaker for the evening was Mr D. Brocklehurst, purchasing director of the BJN group, who gave an illuminating and entertaining talk on purchasing for the paint industry. This subject was treated by the determination of cost/benefit analysis, emphasising the contribution to increased profitability by a professional approach to purchasing. Value indices could be ascribed to the factors applying to a given raw material evaluation. For the simple case of a solvent, these could be only an index for price, for quality and for delivery (an analysis of twelve months supply, with regard to each factor, providing quantitative information). For more complicated situations, indices could be ascribed for stock rationalisation, product improvement, innovation or supplier dependence. For any given type of product, a weighting must be given to each factor, and then these indices could form the basis for a management decision with regard to supply.

Mr Brocklehurst emphasised that purchasing should be integrated with marketing, technical and manufacturing divisions when taking decisions with regard to the future policy of a company. A number of examples where modern purchasing methods were to a company's advantage were explicitly enumerated. Material rationalisation was imperative to reduce stock holdings and to prevent over-complication of formulations. The opinion was expressed that there is a tendency in the paint industry for numbers of products and materials used to be proportional to the number of chemists employed. Management ability was required to make rationalisation happen. To illustrate the point that cost reduction was not of sole importance, price support for a small company supplying a vital material was cited as a valid technique for ensuring supply.

The principles of the purchasing function were summarised as:

1. Be profit orientated rather than cost obsessed.
2. Analyse and quantify by indices the true values of alternative sources.
3. Classify raw materials.
4. Impose discipline on technical and marketing functions.
5. Standardise and rationalise.
6. Research the market of supply.

After a lively discussion and a sincere vote of thanks to Mr Brocklehurst, the chairman closed the meeting.

R.J.K.

Trent Valley Branch

The origin and extraction of natural colours and minerals

On Thursday 8 March, Mr E. Hare, of Via Gellia Colour Company Limited, gave a lecture on the origin and extraction of natural colours and minerals. This meeting was held at the British Rail School of Transport, Derby, and was attended by twenty-two Members and guests under the chairmanship of Mr J. R. Bourne.

Recent archaeological discoveries had indicated that, at a certain time in the past, the surface of the earth had broken up into "plates," each approximately 40 miles thick. These were subject to movement which in turn created new surfaces, such as volcanic rocks and ridges, besides inducing earthquake conditions.

The time scale mentioned was:

	Hundreds of millions of years ago
Earth formed	46
Oldest known rocks	39
Continents massed as "pangea"	22
"Pangea" breaks up	18
Himalayas formed	5
Alps formed	3
Carboniferous rocks formed	2
First flowering plants	1

The following mechanisms of change were then outlined by Mr Hare:

1. Carbonated water dissolves iron from rock, and subsequently precipitates it as oxide or hydroxide under suitable conditions.
2. Oxides are left as residuals in their original beds when other minerals are leached from around them.
3. Decomposition or oxidising of beds rich in iron (FeS_2) takes place. Basic igneous rocks are more readily attacked than acidicones.
4. In coal measures or on boggy ground, iron hydroxides are precipitated from solution by decayed organic matter.
5. Direct precipitation can be caused by algea or bacteria.
6. Heat from igneous sources can change crystal structure (limestone to marble; dolomite to calcite and olivine).
7. Gases from igneous sources can decompose agglomerates (by carbon dioxide—felspar to china clay).
8. Lamellar formation of minerals is created by pressure.
9. Shale, or slate, is changed by heat and magmatic fluids to mica.
10. Magmatic iron-rich fluids injected with bodies of limestone create iron oxide and/or carbonate; the calcium is discharged in solution.
11. Coalification of tropical timber, and decoalification by subsequent weathering occurs.

As far as earth colours were concerned, the Middle East was particularly rich in materials such as umbers, siennas, and oxides. The undermentioned is a summary of the places where the main deposits are found in the world.

Umber	Cyprus
Siennas	Italy
Pyrites	Cyprus, Spain and Sweden
Micaceous iron oxide	Austria, Germany, Norway, France and Spain
Barytes	Spain, China, Greece, Ireland and UK
China clay and gypsum	UK
Talc and mica	France, China and India
Diatomaceous earth	USA
Calcium minerals	UK
Haematite	Spain, Iran, UK, India and China
Limonte	France, South Africa and USA
Magnetite	Sweden

As far as barytes is concerned, the world production (expressed in units of one thousand metric tonnes per annum) is:

USA	1,000
USSR	400
West Germany	400
Sardinia	200
UK	20

Mr Hare's lecture was abundantly illustrated by an excellent series of slides, a section of which dealt very thoroughly with the techniques used for the mining and processing of iron oxide.

In addition, a film was shown depicting the mining of yellow ochre in South Africa. All phases of the process were illustrated, and a remarkable feature was that no mechanical shovels or diggers were used, excavation being carried out entirely by hand.

Mr J. Foot proposed a vote of thanks for a most absorbing and well presented lecture.

D.F.G.

Steel in fashion

The AGM was held on Thursday 5 April, at the British Rail School of Transport, Derby. This was followed by a talk by Mrs Colleran, of the British Steel Corporation, on "Steel in fashion."

Under the chairmanship of Mr J. R. Bourne, an audience of 30 Members and guests listened to a very interesting lecture covering all aspects of the use of steel in a wide variety of both household and personal articles. The lecture was supplemented with a film illustrating the many features discussed by Mrs Colleran.

A vote of thanks was proposed by Mr J. A. Burns for a most interesting and intriguing talk. The evening was completed with a buffet supper held at the Cross Keys, Turnditch.

D.F.G.

Vinyl resins for surface coatings

On Thursday 8 February 1973, twenty-one Members and guests, under the chairmanship of Mr J. R. Bourne, attended the British Rail School of Transport, Derby to hear a lecture on "Vinyl resins for surface coatings" from Mr D. J. Silsby, of Bakelite Xylonite Limited.

This lecture was given previously to the Southern Branch of the London Section, and was reported in the Journal (*JOCCA*, 1972, **56**, 260).

Mr Silsby's lecture was well illustrated with projected slides, and a very active question and answer period followed at the end of his talk. A vote of thanks for a most interesting and informative evening was proposed by Mr D. Bishop.

D.F.G.

Scottish

Eastern Branch

Modern analytical techniques

The fourth meeting of the session was held in the Carlton Hotel, Edinburgh on Wednesday 24 January 1973, when Mr P. S. Nisbet, of Croda Polymers' Ink division, Flemings of Edinburgh, gave a talk on the application of physical methods of analysis in the surface coatings industry.

Mr Nisbet began with a definitive description of the various divisions of analysis, followed by a review of the applications of techniques such as infra-red, ultra-violet, nuclear-magnetic and electron spin resonance spectroscopy, X-ray, electron and neutron diffraction, and the newer techniques of Mossbauer and Auger spectroscopy. Each technique had a specific range of application in research and industry, and, although a certain amount of overlap occured, no two techniques did exactly the same job.

A discussion followed on the theory and application of various chromatographic techniques. Mr Nisbet explained the difference between adsorption and partition methods, and stressed the importance of both stationary phase and carrier solvent with reference to paper and thin-layer chromatography. Some excellent separations were displayed, illustrating the use of ascending, descending, radial, circular and two-way chromatography, with and without the use of spray reagents. The relative merits of paper and thin-layer were discussed and the conclusion was reached that, whilst paper chromatography was the cheaper and simpler technique, thin-layer chromatography was the more versatile of the two due to the large number of stationary phases available.

Mr Nisbet explained the effect of carrier gas pressure, temperature and stationary phase in gas-liquid partition chromatography, and the use of temperature programming was displayed by means of chromatograms of aliphatic distillates.

During a question time, Mr Nisbet expressed his opinion that difficult separations were best carried out on thin layer plates by using streaks of solution, rather than spots, in conjunction with the "wedge" technique. This was exemplified by a chromatogram of a universal indicator solution showing clear separation of nine components.

P.S.N.

Chrome pigments

The fifth meeting of the session was held in the Carlton Hotel, Edinburgh on Wednesday 21 February 1973. The speaker was Dr R. Pascoe, of ICI Ltd, who lectured on "Chrome pigments up to date."

In his talk, Dr Pascoe described the development of chrome pigments from the natural lead chromate mineral, crocoisite, to the sophisticated surface-treated types available today.

P.S.N.

Film night

The sixth meeting of the session, held in the Carlton Hotel, Edinburgh, on 21 March 1973, comprised the AGM of the branch followed by a film evening.

Two films of general interest were shown; the first, "Colour" from the ICI film library, and the second, "The River must Live" from the Shell Film Library.

P.S.N.

Thames Valley

Decorating metal containers

A most interesting lecture was given by Mr A. D. Lott, of The Metal Box Co., at a meeting on 22 March, at The Beech Hotel, Beaconsfield, on "Recent developments in the printing and decorating of metal containers." Mr Tatton was in the chair.

Mr Lott pointed out the wide variety of metal containers which are now used in packing such things as processed foods, beverages, oil, paints, cosmetics, and so forth. Practically all the packaging was decorated on the outside, which entailed the use of paint.

For many years improvements had been made in the materials and equipment for this, and recently there had been an acceleration in the technical developments, some specific to metal decorating, others referring to transfer or adaptations of paper and board printing.

Most cans were produced using tinplate made by an electrolytic process, which left a thin invisible film of oxide to minimise tarnishing. It was then coated with a thin coating of dioctyle sebacate. Other methods mentioned were tin free steel (mostly from Japan), pliant steel (known as backplate), aluminium, and rigid seamless tubes and aerosol containers.

Metal decorating consisted essentially of two processes, roller coating and printing. The print, which might vary from one to five or six colours, could be applied to plain steel, or over a size coat or a pigmented coating. The decoration could be registered in relation to either the sheet itself or the decoration already on the sheet, according to the process used.

Roller coating was extensively used. A metered quantity of material was applied to the sheets by a large diameter roller. Sometimes the coating was applied to the whole sheet, but in some cases a stencil had to be cut into the application roller. To ensure satisfactory performance, materials had to be applied within fairly close film-weight and viscosity limits.

The sheets were then transported into a conveyor oven in an almost vertical position by a metal wicket which passed through the oven. The ovens were often divided into zones to allow different temperatures to be obtained enabling the desired temperature to be achieved as quickly as possible. The maximum temperature was about 400°F, whilst the printing and varnishing line maximum was about 350°F. The minimum temperature was rarely below 250°F. The printing line oven could be as short as 30ft, but up to 100ft on roller coating lines. The sheets then passed through a cooling zone to reduce thermo-plasticity and after-tack.

Materials used in roller coating were based mainly on phenolics, epoxy phenolics, epoxy esters and amines, alkyds and vinyls. More recently oil-free polyester systems and acrylics had been used, but they still lacked satisfactory tooling properties. Organosols were a fairly recent introduction, and were now being used as internal lacquers on "easy-open" can ends and on closures.

In an attempt to reduce pollution due to solvent emission from ovens, two approaches were the development of water based materials and of powder coatings.

Mr Lott mentioned various process developments for lithography, such as dry offset, where the rheological properties for uniform solids differ from those required to give sharp halftones and minimal spreading. However, it was possible to find a combination of plastic viscosity and yield value to satisfy both requirements.

Driography was similar to a lithographic plate but required no dampening because the non-image area was covered with silicone elastomer. The advantages were that it was a cheaper process than offset plates, and gave a good quality print. Its limitation was that the surface can be easily scratched, but as it was in its early stages of development, no doubt these difficulties would be overcome.

Container printing was carried out on special purpose machines by dry offset, usually using four colours, but sometimes five. In tube printing, the colours were all applied at the same time. However, by careful control over the rheological properties of the inks, and film thickness of printing, some multi-colour halftones could be achieved. The upper limit for intermittent-motion machines was probably 200 to 250 sheets per minute, whereas continuous-motion machines ran from 300 to as high as 800 per minute.

Possibly the most exciting development in the last few years was ultra-violet curing inks. These were being used for printing both paper and board in sheet form and in web, and, from the point of view of pollution, they restricted solvent emission. A limiting factor was that they needed new printing ovens. Technically, varnishes, which must be based on low viscosity vehicles, were proving more difficult to develop than inks. The high cost of ultra-violet curing materials was another deterrent, because, at present, these cost eighty per cent more than conventional offset inks.

Much still remained to be done, but the author hoped that the prospects were widening, and there will be some interesting problems facing engineers, surface coatings chemists and ink makers in the years to come.

Mr Lott had several interesting slides to illustrate his talk.

Thirty-five Members attended, and the vote of thanks was given by Mr W. Arnot. The meeting was followed by a chicken-and-chip supper.

D.F.

AGM

The Annual General Meeting was held on Thursday 12 April at 7.00 p.m., at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks. The chairman, Mr Tatton, conducted the meeting.

New officers and committee members were elected, and included a new chairman elect and Council Member, Mr Inshaw, who has served the section very well over the last few years.

An apology for absence was received from Mr Claringbold, of the Customs and Excise Service, who was to address the meeting; his colleague, Mr Dorling, took his place at very short notice, and gave a very interesting address.

The AGM closed at 7.30 p.m. with the Members and their wives sitting down to a buffet supper.

After supper, Mr Dorling began his talk about some of the strange customs, and customers, dealt with by the Excise Branch. He gave a brief discourse on the history of how the branch began, and how many of the words used initially by them were now used by everyone.

Many women were now in the Service, and one of their main duties was to search "suspects" (female, of course). On one occasion, however, when a woman was requested to search a suspicious female, she was shocked to find that this was, in fact, a man trying to evade the Customs. Many other amusing incidents were recalled, but the speaker assured everyone that most of the professional smugglers were eventually caught and punished.

Mr Bray, after explaining an incident which happened to him whilst coming through Customs, asked whose responsibility it was to reload vehicles which were stopped and searched, Mr Dorling replied that this lay with the passenger (this apparently applies even to caravans and other domiciles which are emptied to be searched). He quoted one case when the Customs Officer was not satisfied, even when the car was emptied, and eventually had a hole drilled in the chassis, which led to the car being virtually cut in half, when thousands of watches were discovered. Confiscated drinks were poured down the drain, but other contraband was sold at the retail price.

Many questions were asked about how the officers could distinguish smugglers and their hiding places, especially in the case of drugs coming into the country in ships. The speaker said that each individual officer had his own approach, but that the method was not divulged.

The meeting then closed after a vote of thanks by Mr M. Heath, followed by a hearty round of applause from the Members and their wives.

D.F.

West Riding

Microbiology and the paint industry

A meeting was held on Tuesday 13 March at the Griffin Hotel, Leeds. Mr W. R. Springle, of the Paint Research Association, presented a paper on microbiology as it affects the paint industry.

Mr Springle discussed the problem of bacterial spoilage of liquid, water-based products, such as emulsions and emulsion paints, on storage. The problems which can arise, and the causes were discussed in some detail. The "in can" biocides were normally used to prevent these effects occurring.

The lecturer then turned to the subject of attack of the dried paint film due to mould, algal or lichen growths. In this case, environment was critical and such growths were normally encountered under damp and usually warm conditions. Generally, the problem was aesthetic, but where the substrate was metal, metabolic products could be involved in corrosion. Improved ventilation would often help overcome this type of problem, but the incorporation of a film biocide into the paint was the most widely used alternative. Mr Springle then described the method evolved by the Paint Research Association for the evaluation of paints for fungicidal effectiveness.

The problem of marine fouling was considered finally, before the speaker's going on to discuss briefly the types of compounds being used to provide biocidal protection in all these areas. The technique developed by the Paint Research Association for screening such chemicals was then outlined.

Mr Springle's talk was well illustrated with colour slides, and the number of questions indicated the high degree of interest raised.

Mr T. Apperley thanked the lecturer on behalf of those present for a most interesting and well presented talk.

R.A.C.

Functional extenders in emulsion paints

A meeting was held on Tuesday 13 February at the Griffin Hotel, Leeds. Mr S. E. Maskery, of Joseph Crosfield and Sons Limited, presented a lecture with the title "Functional extenders in emulsion paints."

Mr Maskery explained that the extenders to which he referred were synthetic silica and silicates. Unlike other extenders, such as whiting, dolomite, clay and talc, the synthetic silicates contributed to film opacity. They also contributed to whiteness; helped to impart some "structure"; had a buffering action which stabilised the pH of the paint during storage, and thus minimised viscosity fluctuations; reduced the settling of pigments and extenders; and could reduce the tendency of emulsion paint films to soil.

Synthetic sodium aluminium silicates were produced by the reaction of sodium silicate and aluminium sulfate in the presence of a flocculating agent such as brine. The calcium silicates were produced in a similar fashion using calcium chloride as the metal salt, whilst the precipitated silicas were produced by the reaction of sodium silicate and sulfuric acid under controlled conditions of pH.

At the beginning of the precipitation step very small discrete particles were formed, having a diameter of 20 to 30 nanometres. These quickly formed much larger secondary particles with an average size in the order of 5 to 6.5 microns. During packing and storage, dry agglomerates of these secondary particles were formed, and these could be up to 3,000 microns in diameter. During the dispersion processes used in paint manufacture, the dry agglomerates were reduced to the secondary particles.

Addition of the silicate extender should take place after the pigment and conventioned extenders had been dispersed. This was because the silicate extenders increased the viscosity and pseudoplastic nature of the pigment dispersion, and this could reduce the efficiency of dispersion. To offset the increased viscosity which would be imparted to the finished paint, it was sometimes necessary to reformulate by changing the cellulose thickener present in the paint to a grade with less thickening power.

Because of their porous structure, the silicate extenders had a high water demand, which had the effect of reducing the amount of "free" water in the paint. It was this "free" water which allowed the paint to be applied to the substrate, and helped to give it sufficient wet edge time. If too much fine silicate was included in a paint formulation, these properties could be affected adversely. It had, therefore, become usual practice to incorporate between two and six per cent in general-purpose paints, and in this way applicational properties were maintained.

Mr Maskery discussed typical formulations for two types of emulsion paint formulated above and below the critical pigment volume concentration (CPVC). In paints formulated below the CPVC it was advisable to replace a proportion of both the titanium dioxide and conventional extender by an equivalent volume of fine silicate extender. A saving in the raw material cost could normally be achieved. A similar approach could be adopted, and end result achieved, with paints formulated above the CPVC which contained sufficient titanium dioxide to give a high level of paint hiding power and film whiteness. In the case of paints formulated with a very low titanium dioxide level, it was impractical to reduce the titanium dioxide content, because wet film opacity became inadequate. In this case, the silicate extender could be used to improve whiteness.

Two proposals had been made to explain the mechanism by which silicate extenders operated. The first theory was that the extender dispersed as small particles, about 0.3 microns in diameter, and that these particles acted as spacers for the titanium dioxide particles. This prevented the pigment particles from crowding together, which would limit their maximum optical effect.

The other explanation was that the secondary particles of silicate were not substantially dispersed in the paint, and the porous structure of the particle was maintained in the paint film. The voids, or air spaces, within the particle were too small for resin particles to enter, and hence they set up an increased difference in the index of refraction at the interfaces, so that increased opacity was developed in the paint film.

Mrs Driver asked if absorption of atmospheric moisture during storage was a problem. Mr Meskery said that it was not, because their structure differed from those of silica gels. Asked by Mr M. Smith if opacity could be improved by producing a more porous material, Mr Maskery replied that this was a possibility but one must consider that the balance of properties and applicational properties in particular could suffer as a result. In response to another question, he said that one might anticipate these materials having a matting effect if used in silk finish emulsions. However, he had no personal experience to form any definite conclusion, and it was believed that, in practice, they have been examined by some customers, and appeared to have worked.

Mr M. Smith proposed a vote of thanks to the lecturer for a very comprehensive presentation of the subject of silicate extenders.

R.A.C.

Obituary

Dr Herman Walther Talen (1900-1973)

Ordinary Member OCCA from 1946
Vice-President OCCA 1965-1967

An appreciation by Dr S. H. Bell (President 1965-67)

Dr Talen was widely known among OCCA Members at home and abroad as an outstanding scientist and technologist, an able lecturer and participant in technical discussions. His international status was apparent at various conferences and meetings in different countries, much enhanced by his linguistic ability. Those who knew him personally will remember him too, for his courtesy, kindliness, and firmness of purpose—in short, as an outstanding personality.

He was proud of his OCCA Membership and especially of his Vice-Presidency, the first of only two among our Members in Continental Europe.

Dr Talen's university studies began in Groningen and were completed in Leiden, where in 1927 he obtained his doctor's degree in Natural Sciences (organic chemistry). After a period in rubber research, he joined the paint industry in 1931 as chief chemist at Wagemakers and Sons, Breda, leaving in 1948 to direct the paint section of the Central Institute for Testing Materials at Rijswijk near Delft. This soon became the Paint Research Institute of the state research organisation (TNO) with a laboratory for marine paint studies at the naval seaport of Den Helder; and, in various ways (including collaboration with the Netherlands Association of Paint Manufacturers leading to the formation of the Association for Paint Research), the collective work on paint and its uses continuously expanded under his supervision.

He remained Director of the Institute until his retirement in 1965, when he was honoured by the award of Officer in the Order of Orange-Nassau.

In the 1950s he stimulated the formation of a group concerned with marine protection under the Organisation for Economic Co-operation and Development (OECD) and became its Chairman in 1959. Other international activities included standards work for painting of railway stock and so forth under the International Union of Railway Administration (IUIC). He was a familiar figure at conferences of the paint testing committees of the International Standards Organisation (ISO), and at the biennial assemblies of FATIPEC, where he was closely involved as a member of the scientific and technical committee of which he was Chairman from 1964 until 1966. He was nominated an honorary Member of FATIPEC in 1968.

Among the numerous occasions when I saw Dr Talen in action in international affairs, some of the happiest recollections come from meetings in London of the Organic Coatings Section of the Applied Chemistry Division of the International Union of Pure and Applied Chemistry; not least, the associated social occasions at the house of Dr L. A. Jordan, who had much to do with the founding of the Section in 1951. This confirmed not only his strength in promoting contacts between the technologists of many countries, but his capacity for enjoyment and for stimulating enjoyment in others—an important lubricant of more serious contacts.

He toured extensively in Europe and USA. He was a member of numerous societies including, besides OCCA, the American Chemical Society, the Swiss Association of Paint Chemists and the paints and pigments group of the German Chemical Society. He was also a member of the editorial board of the Dutch paint journal "Verfkroniek."

His activities continued after his retirement through lectures, articles for the technical press and consultancies. In maintaining his many personal contacts, as well as continuing to survey the technical field, he remained a regular visitor to the OCCA Technical Exhibitions.

Much more could be said of his successful deployment of his technical energies, but in writing this appreciation my mind returns again and again to pleasant personal recollections.

I stayed with him and his charming wife, Mary Talen-Sauter, at their home in The Hague many times, and toured with them the length and breadth of their beloved Netherlands. It was a delight after a day's travelling to relax over drinks before dinner, talking over the day's events, and moving on to other subjects. With his technical and scientific background, his familiarity with the social and economic history of his own and surrounding countries, and his knowledge of music (he was an orchestral violinist), and with his wife's erudition as a philologist and a classical scholar, widely versed in the arts and an expert on Norman architecture, there were numerous subjects which could be happily discussed (or at least on which I could become informed). For me, they necessarily used their fluent English, but conversation could have been in any of several languages.

Many others experienced his hospitality and enjoyed his company. They and numerous OCCA members share my own sense of loss; but there are many others who did not know him who have also benefited extensively from the life and work of a very considerable man.

S. H. Bell

Report of Council Meeting

A meeting of the Council was held at the Great Northern Hotel, London N1, on 15 February 1973 when twenty-six members of Council were present. The President, Mr A. W. Blenkinsop, took the chair. This was the first Council meeting to be held at the Great Northern Hotel and the first held since the Association vacated the offices at Wax Chandlers' Hall, Gresham Street, London EC2.

Members first stood in silence in tribute to the memory of an Honorary Member of the Association, Dr H. A. Gardner, whose death occurred at the age of 90 in the USA at the end of January. (An obituary notice appeared in the April issue of this *Journal.*)

The seriousness of the situation arising from the necessity to leave Wax Chandlers' after fourteen years was fully considered by Council. Whilst no one had wished to move the headquarters of the Association, since it was fully realised that this would undoubtedly result in a loss of staff, nevertheless the Council felt that Members would expect them to do so in view of the very great proposed increase in rent at the end of the lease. A large number of premises had been inspected in many areas surrounding London but none appeared suitable other than a self-contained small office building in Sudbury (Wembley, Middlesex).

Once the decision had been made to move to Sudbury, it became apparent that the Director & Secretary would be faced with the problem of recruiting and training a completely new staff during a time which was one of the busiest for the Association; that is, just before the twenty-fifth Exhibition and the Eastbourne Conference, the change of the *Journal* to the new A4 size (with the attendant problem of finding a new system for despatching it) and the preparation of the Annual Reports and Accounts. Nevertheless, the move was made in the week before Christmas 1972, and Members were informed of the new address immediately after Christmas in the notice of the Annual General Meeting.

Very considerable difficulty was encountered in the recruiting of suitable staff, and the situation had not been resolved by the date of the Council meeting which had had to be postponed from January. The President felt that Council should be aware of the trying circumstances during which the Director & Secretary had continued to administer the affairs of the Association, and it was unanimously agreed to record a vote of thanks to him.

The Annual Report of the Council for 1972 was adopted. The agenda for the Annual General Meeting was considered, and nominations for the vacancies among the Vice Presidents agreed.

Reports were received on the progress

made on the Eastbourne Conference and the twenty-fifth Exhibition, including the consideration of future arrangements for the Exhibition. Council had before them a report prepared by the President's Advisory Committee, and it was further reported that, on the occasion of the Silver Jubilee Exhibition, a reception would be held by the Exhibition Committee for exhibitors at the 1973 and previous exhibitions to discuss future arrangements. Eight members of Council would be in attendance.

This was the second successive meeting in accordance with the Articles at which the proposal to increase Membership subscription in 1974 was put to the meeting and carried, on this occasion by 23 votes in favour to 1 against, with 2 abstentions. Details of the proposed subscriptions will therefore be placed on the agenda for the Annual General Meeting, and it was further agreed that an explanatory note to Members should be added.

It was agreed to raise the subscription to the *Journal* received from overseas libraries and companies from £10.00 to £12.00 per annum.

In accordance with the Articles, Council resolved that Members whose subscriptions had not been received by the end of March should not receive the April and subsequent issues until payment had been received.

The Honorary Editor reported on the change of style of the *Journal* to the A4 format and informed Council that sales of the bound reprints of the 1972 Student Reviews which formed Part VII of the Paint Technology Manuals ("Works Practice") had proceeded well, after the publication earlier in the year. Some concern was felt about the delay in producing further editions of Parts IV and V, particularly since stocks of the second editions of Parts I and II were now exhausted.

It was reported that three applications had been received for the Jordan Award, and that the Committee concerned was actively considering these, with the intention of making the Award at the Annual General Meeting.

On the optional Professional Grade for Ordinary Members, it was reported that successful applications now represented 14 per cent of the Ordinary Membership at home and abroad, which was felt to be satisfactory after less than eighteen months.

Under Section Reports, the Midlands Chairman, Mr A. S. Gay, stated that the Section was hoping to replace the Midlands Paint Students' Association, whose activities had ceased, with a Student Group.

Since this was the last meeting of Council for some Section Chairmen, the President took the opportunity to thank them for their support during their terms of office.

There being no other business, the President thanked all Members for their attendance and declared the meeting closed at 4.20 p.m.

London Section

Papers from the Symposium "Automotive and other industrial finishing. What is the future?"

A bound volume containing the papers presented at the joint symposium held by the Organic Finishing Group of the Institute of Metal Finishing and the London Section of the Oil and Colour Chemists' Association are now available from the Association's offices at £5.00 (USA $13) each, post free.

The number of copies still available is very small, and orders will be dealt with in strict order of receipt. The full list of papers is given with an advertisement/order-form on page xii of this issue.

Newcastle Section

Symposium on protective paints

to be held on Tuesday 3 July 1973
at the Newcastle upon Tyne Polytechnic,
Ellison Place, Newcastle upon Tyne
NE1 8ST

A one-day Conference is being arranged as a joint venture under the sponsorship of the Oil and Colour Chemists' Association, the Corrosion and Protection Association (CAPA), and the Institution of Corrosion Technology (ICorrT). Five papers will be presented:

The mechanism of the protective action of paints

J. E. O. Mayne, University of Cambridge.

Practical technology in structural steel protection,

E. A. Watson, Berger Chemicals.

Preparation of surfaces prior to painting,

R. H. Wallington, Paint Research Association.

Painting of structural steel with reference to chemical plant,

A. F. Hall, ICI Ltd.

Marine corrosion and painting with particular reference to off-shore structures,

D. Atherton, Sigma Coatings Ltd.

The first two papers, to be given in the morning session, will deal with the basic science and technology of protective paints, whilst the three papers to be presented in the afternoon session will examine practical aspects of painting for protective action against corrosion, dealing with surface preparation methods, and the performance of paint systems in aggressive industrial and marine environments. Adequate time has been allowed for discussion; no formal records of the meeting will be taken, so it is hoped that such discussions will be lively and informative to the mutual benefit of participants.

Early registration is recommended since accommodation will necessarily be limited. Abstracts of the papers will be sent to participants upon their registering. Applications should include the sender's name, affiliation, and the address to which correspondence should be sent (preferably, including a telephone number). The fee is £6.00 for Members of OCCA, CAPA or ICorrT. Cheques should be made payable to Dr K. N. Stafford, crossed/endorsed "Protective paints symposium", and should be sent to Dr Stafford at the Newcastle upon Tyne Polytechnic, Department of Materials Science, Ellison Building, Ellison Place, Newcastle upon Tyne NE1 8ST.

News of

Members

Mr L. A. Silver, an Ordinary Member attached to the West Riding Section, has been elected to the Council for the Paintmakers' Association at its annual general meeting.

In addition, the following Members were elected:

Mr D. N. Hughes, an Associate Member attached to the Midland Section, is now the north-west England representative.

Mr A. W. Bunting, an Ordinary Member attached to the Midland Section and a Fellow in the Professional Grade, has been elected chairman of the Yorkshire and north-west England Section of the Paintmakers' Association.

Dr B. S. Gidvani, an Ordinary Member attached to the London Section, has been elected chairman of the London and Home Counties Section of the Paintmakers' Association.

Mr R. H. White, an Ordinary Member attached to the Manchester Section, has joined Synthetic Resins Limited as a senior technologist in the technical service department of its surface coatings division.

Mr I. M. McDonald, an Ordinary Member attached to the London Section, has joined Fishburn Printing Ink Company as a salesman in the north-east of England. He will be based in Leeds.

Mr P. J. Holloway, an Ordinary Member attached to the General Overseas Section, has recently been promoted to Group Leader, Rotogravure and Flexographic Inks, California Ink Division, Tenneco Chemicals Inc.

News of Members—*Cont.*

Mr P. Owens, a Registered Student, has been awarded the Bronze Medal of the City and Guilds of London Institute of Paint Makers certificate award for 1972. Mr Owens has been a trainee manager with the Silver Paint and Lacquer Company. At a reception given by the Chairman of that company and future President of the Association, Mr L. Silver, the principal of Harrogate College of Further Education, Mr P. F. Drake, said this was the first time that one of its students had gained the Bronze Medal.

Since receiving the award, Mr Owens has been promoted to Manager, of the Silver Paint and Lacquer Company's new factory at Morley.

R. D. G. Robinson, tutor at Harrogate College of Further Education, presenting Paul Owens with the Bronze Medal. In the centre is Mr L. Silver, Chairman of the Silver Paint and Lacquer Company and President Designate of OCCA.

Forthcoming Events

June

Tuesday-Saturday 19-23 June

OCCA Conference: *Towards 2000* at the Grand Hotel, Eastbourne, Sussex, England.

Friday 22 June

AGM of the Association at the Grand Hotel, Eastbourne, at 2.15 p.m.

July

Tuesday 3 July

Newcastle Section: Symposium on protective paints, to be held at the Newcastle upon Tyne Polytechnic in conjunction with CAPA and ICorrT.

OCCA–25

This year's Exhibition was a great success; within the first hour of opening, visitors from twenty-five countries had signed the Overseas Visitors Book, and some companies reported that their stocks of handout literature were used up before the end of the first day.

A review of the Exhibition, including many photographs and reports of exhibits, will appear in the next issue of the Journal.

Register of Members

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

Ordinary Members

ADEFARATI, FRANCIS BABASOLA, BSc, Berger Paints (Nig) Ltd., PMB 1052, Ikeja Industrial Estate, Lagos State, Nigeria. *(General Overseas)*

BAILEY, BRYAN RAYMOND, Lewis & Everitt (Pty) Ltd., PO Box 785, Durban. *(South Africa)*

BLUNDELL, ROBERT JOHN NELSON, BSc, "Maryvale", 60 The Common, Parbold, Lancashire WN8 7EA. *(Manchester)*

CUMMINGS, ROBERT ALLAN, 57 Meadow Road, Kingswood, Watford, Hertfordshire. *(Thames Valley)*

DAWIDOWICZ, JERZY ANTONI, PO Box 43116, Pekay Chemicals (Pty) Ltd., Industria, Transvaal, South Africa. *(South Africa)*

MARTIN, JOHN FRANCIS, BSc, 471 Richardson Road, Mount Roskill, Auckland, New Zealand. *(Auckland)*

MASKILL-SMITH, GORDON, MSc, Building Research Association, 41 Vivian Street, PO Box 9375, Wellington, New Zealand. *(Wellington)*

NAGELL, PETER A. G., 2000 Hamburg 52, Wilhelmstrasse 24. *(General Overseas)*

NIXON, MICHAEL, 29 Cowan Road, Edinburgh EH11 1RL. *(Scottish)*

PICKARD, CAREY JOHN, c/o The Marley Co. (NZ) Ltd., PO Box 58, Manurewa, Auckland, New Zealand. *(Auckland)*

SLACK, HAROLD, LRIC, 1 Lichfield Avenue, Hartshead, Ashton-under-Lyne, Lancashire. *(Manchester)*

SOAN, RICHARD ERIC, 5 Nevada Avenue, Paruranga, Auckland, New Zealand. *(Auckland)*

VAN NIMWEGEN, JACOB, 13 Da Cama Street, Welgemoed, Belleville, Cape Town, Republic of South Africa. *(South Africa)*

VOW WINTERFELDT, DOMINIK, Dorney Cottage, Collins Wood Road, Farnham Common, Buckinghamshire. *(London)*

WRIGHT, IAN LEONARD, BSc, 104 Astley Avenue, New Lynn, Auckland, New Zealand. *(Auckland)*

Associate Members

BACHMANN, GUSTAV ERICH JAKOB, Hoechst (NZ) Ltd., CPO Box 67, Auckland, New Zealand. *(Auckland)*

COOMBES, ROY MERVYN, 16 Kingdom Street, Newmarket, Auckland, New Zealand. *(Auckland)*

KEYTER, PHILIP, c/o Bayer Chemdyes (Pty) Ltd. PO Box 1366, Johannesburg, South Africa. *(South Africa)*

Registered Students

DUPLESSIS, CORNELIUS, 11 General Prinsloostr, Meyerton, South Africa. *(South Africa)*


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CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of 50p per line. Advertisements for Situations Wanted are charged at 12½p per line. A box number is charged at 5p. They should be sent to the Director & Secretary, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF

SITUATIONS VACANT

Department of the Environment
Princes Risborough Laboratory

PAINT TECHNOLOGIST

■ Develop and assess building paints and varnishes particularly on wood and wood-based panel products ■ Plan and execute projects ■ Assist in advisory work.

☐ Degree/HNC in Chemistry/C&G Final Certificate in Paint Technology ☐ 5 years' post-qualifying experience ☐ Thorough knowledge and experience of paint industry preferably in investigation of defects and performance of paint ☐ Appointment as Higher Scientific Officer (£1946-£2515) ☐ Ref SA/13/HA ☐ Closing date 22 June 1973. ☐ Application forms from the Secretary, Princes Risborough Laboratory, Princes Risborough, Aylesbury, Bucks HP17 9PX.

Science group
CIVIL SERVICE

RESEARCH CHEMIST

A very progressive company of medium size requires a Chemist to tackle problems. The position will be highly paid from the beginning, with generous working conditions and a non-contributory superannuation scheme. The research facilities are excellent in an ultra-modern factory. The successful candidate will have complete freedom to work independently and will not be frustrated by established practice, as to obtain new ideas is the main reason for offering this job. Candidates who can prove by reference to have a really successful background with special experience in paints, lacquers, printing inks etc, are invited to submit their applications to Box No. 367.

COLOURIST

Due to increased demand for ABS and expansion of its thermoplastics range, Uniroyal Limited requires a Colourist for its Chemical Division at Bromsgrove, Worcestershire. His duties will include assisting in the provision of a colour service to the Sales and Production Departments and to satisfy the demands of the customer in all areas involving Kralastic ABS, and problem solving as it arises with established and prospective clients in the UK or Europe.

The successful candidate will be in his mid-twenties and have at least three years' experience in the colouring of thermoplastics or possibly paints.

Salary will be negotiable with the usual large company benefits. Reasonable relocation expenses will be considered where necessary.

UNIROYAL

Please write with full career details to: T. F. McMahon, Personnel Manager, Uniroyal Limited, Chemical Division, PO Box 12, Bromsgrove, Worcestershire.

Prominent printing ink company in Barcelona needs, for a progressive management team, a

PRINTING INK CHEMIST

Applicants should have a university education, outstanding talent for the investigation of and experience in various graphical processes, and a good knowledge of Spanish.

Curriculum vitae in detail and pretensions to:

FICIS,
Apartado 871,
Barcelona.

CLASSIFIED ADVERTISEMENTS

SITUATIONS VACANT

CHEMIST/TECHNOLOGIST DECORATIVE PAINTS

Research and Development Department

Applications are invited from Chemists and Technologists in the Paint Industry for a vacancy in Applications Research and Technical Service Section of the Research and Development Department at Stallingborough on South Humberside. The successful applicant will probably be aged 25-35 years possessing a University degree or appropriate technological qualification and have at least five years' experience in the decorative side of the Paint Industry.

The Applications Research and Technical Service Departments are concerned with the use of the products manufactured by the Organics and Pigments Division in all types of Aqueous and Non-Aqueous Surface Coatings, the problems associated with formulation variables and fundamental studies of pigment behaviour.

The Company operates a non-contributory pension scheme and generous re-location expenses where appropriate.

Applications, in writing, giving details of qualifications and experience should be addressed to:

The Manager, Personnel Services

LAPORTE

**LAPORTE
INDUSTRIES
LIMITED**

Organics and Pigments Division,
P.O. Box 26, Grimsby, Lincs. DN37 8DP.

SENIOR INK TECHNICIAN

A Senior Technician with experience of litho and letterpress inks is required to head the Ink Section of our Customer Service and Applications Laboratory (Surface Coatings Resins Division). This is a senior position offering opportunities for progress within the company, which is part of Unilever Ltd. The successful applicant will be over 25 years of age, with at least 5 years' experience in the ink industry.

Application forms may be obtained by writing to:

**The Company Personnel Manager,
SYNTHETIC RESINS LTD.,
Edwards Lane,
Speke, Liverpool L24 9HR,**

or by telephoning the Personnel Department on 051-486 3922.

NOVADEL LIMITED

COLOUR MATCHER

Novadel Limited, manufacturers of a wide range of additives for the Plastics Industry, invite applications from experienced COLOUR MATCHERS for the vacancy in their Gillingham Laboratory.

Applicants may well have gained their experience in the Printing Ink Industry though this is only a guide. The work involves the matching and formulation of pigment pastes dispersed in polyester resin.

The salary will be negotiable according to age and experience.

Excellent canteen and Social Club facilities are available on the Site and the Company will be prepared to make some contribution towards removal expenses.

Applications in the first instance to:

THE PERSONNEL OFFICER,
NOVADEL LIMITED,
PIER ROAD,
GILLINGHAM,
KENT ME7 IRL

PIGMENT CHEMISTS and PROCESS SUPERVISORS required in USA

SUN CHEMICAL CORPORATION, who now control the largest sale of organic pigments in USA, require staff for their organic pigment plants in Cincinnati and Staten Island.

Experienced technologists from any part of Europe are invited to apply within the following categories:

(a) Pigment Chemists with 5 to 10 years' proven research experience for work in Sun's research department, with emphasis on synthesis. As Sun market a complete range of organic pigments, the applicant is likely to work in any field, which his experience dictates.

(b) Process Supervisors with knowledge of, and practised in, planning and controlling the work of plant operatives and supervising organic pigment production.

Reply in the first place to Sun's European Representative, J. G. Evans, Fieldhead, St. John's Park, Menston, Ilkley, Yorkshire LS29 6ES.

Candidates can expect an attractive salary and rewarding future.

SITUATIONS WANTED

CHEMIST, manager, ARIC, FIMF, FTSC, 35 years' experience in surface coatings industry, seeks position as Senior Chemist, Thames Valley or West London areas preferred. Write to Box No. 368.

Automotive and other industrial finishing What is the future?

A bound volume containing the papers presented at the joint Symposium held by the Organic Finishing Group of the Institute of Metal Finishing and the London Section of the Oil and Colour Chemists' Association is now available from the Association's offices at £5.00 (USA $13) each, post free.

The number of copies available is less than one hundred, and orders will be dealt with in strict order of receipt. Please use the form at the foot of this page.

The contents of the book are as follows:

REQUIREMENTS OF THE USERS

Towards greater consistency in paint finishing and motor manufacturers' requirements. *I. G. F. Walker*

Finishing in production of white goods (domestic appliances). *A. J. Ellis*

THE SUBSTRATE

The influence of cold rolled steel surfaces on paint performance. *E. Bronder and Dr D. Funke*

The finishing of reinforced plastic bodies. *A. Adams*

Self skinning PU foam for safety in construction of cars. *E. Boigk*

***Low profile polyester.** *I. Pratt*

PRETREATMENT

Metal pretreatment—meeting the technical, environmental and economic challenge of the seventies. *D. B. Freeman and D. James*

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APPLICATION

Future thinking in spray methods and technology. *I. Muirhead*

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The high speed automatic painting of car bodies with automotive colour change. *M. Burcez and K. Williams*

History of the electrostatic process—economies and relation to modern environmental needs. *P. J. Mounce*

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To: Oil and Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex, England HA0 2SF

Please send me............copies of the papers presented at the Symposium entitled "Automotive and other Industrial Finishing—What is the Future?" I enclose a remittance for.................. (each copy £5.00/USA $13.00)

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