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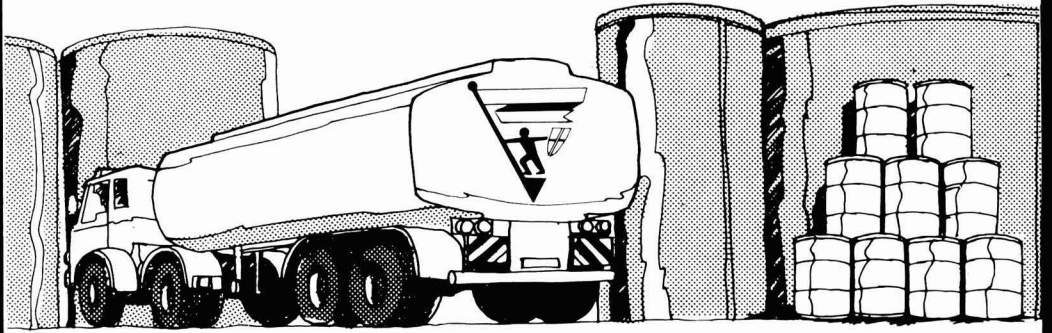
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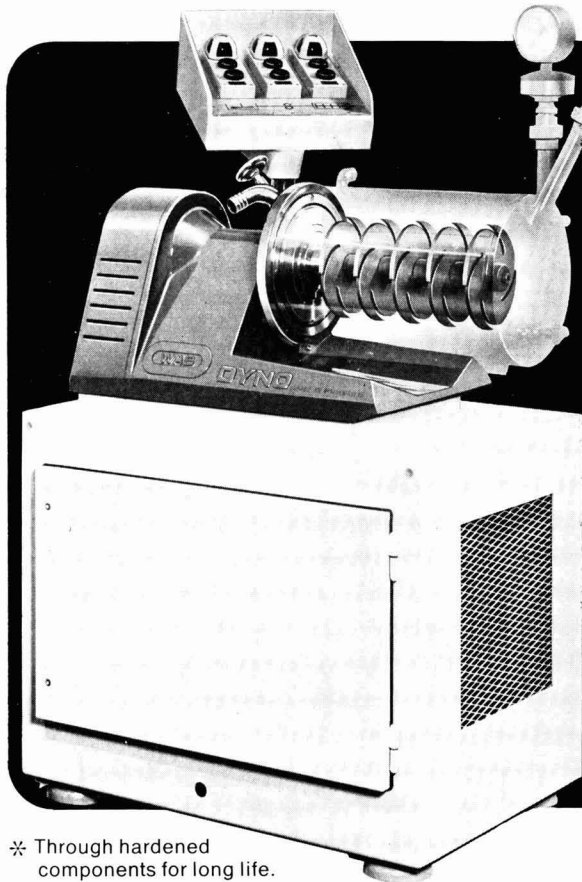
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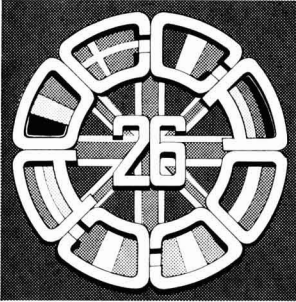
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The motif for OCCA-26 used the flags of the enlarged EEC converging on the British flag to symbolise the welcome extended to visitors from overseas to the Exhibitions for more than 25 years. (1974)



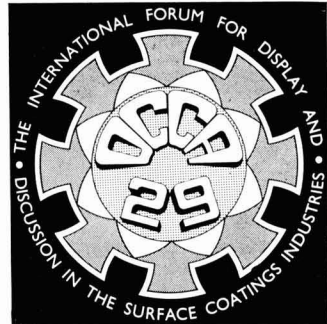
The 1974 theme continued at OCCA-27 by showing the world-wide interest aroused by the Association's annual Exhibitions in London which attract visitors from all parts of the globe.



aspect of this unique annual focal point for the surface coatings industries, which in 1977 attracted visitors from 50 countries.

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Transactions and Communications

Save your paint, your money and your substrate*

By T. R. Bullet and A. F. Sherwood

Paint Research Association, Teddington, Middlesex TW11 8LD

Summary

Some major considerations of the effective and economical protection of substrates have been reviewed. Little has been said about the development of new paints or new painting methods because it is felt that the primary need, at present, is to improve the way that paint is used rather than the material. Nevertheless, there is a case for improving the tolerance of paint to the conditions of misuse, even at the expense of some diminution of maximum performance under ideal conditions.

It is concluded that the most pressing need is for an understanding of the basic science of the degradation of substrates and protective coating technology by those responsible for design and production of painted articles, from toys to houses and bridges and for better control of preparation and painting processes, including inspection at all stages. In this way, not only will the preservation of substrate materials be enhanced, but there will be less wastage of paint, of effort and of money in the process.

Keywords

Types and classes of structures or surfaces to be coated

metal
steel
wood
masonry
timber

Processes and methods primarily associated with:

surface preparation before coating

surface preparation

application of coatings and allied products

maintenance painting

service or utility

corrosion

Properties, characteristics, and conditions primarily associated with:

dried or cured films

weather resistance

durability

Miscellaneous terms

cost

Comment faire une économie en votre peinture et en votre argent et préserver vos subjectiles en même temps

Résumé

On a passé en revue certaines importantes considérations sur la protection à la fois efficace et économique des subjectiles. On n'a pas traité en détail l'évolution de nouvelles peintures ou de nouvelles méthodes de peinture, parce qu'on croit qu'à présent, le besoin principal est d'améliorer la manière dans laquelle les peintures sont utilisées, plutôt que les caractéristiques qu'elles possèdent. Néanmoins, on peut prétendre que la tolérance des peintures aux conditions d'abus doit être améliorée, même au prix de quelque diminution du rendement maximal sous les conditions idéales.

On conclut que le besoin le plus urgent, de la part de ceux qui sont responsable pour le dessin et la production des objets peints, depuis les jouets jusqu'aux maisons et ponts, et pour l'amélioration des méthodes de préparation du subjectile, et de peinture, y compris le contrôle à chaque étape des travaux. De cette manière, on effectuera une amélioration non seulement dans le niveau de préservation des subjectiles, mais également il y aura moins de gaspillage de peinture, d'effort et d'argent.

Spare Deinen Lack, Dein Geld und Dein Substrat

Zusammenfassung

Einige gewichtigen Betrachtungen über den wirkungsvollen und wirtschaftlichen Schutz von Substraten wurden angestellt. Über die Entwicklung neuer Anstrichmaterialien oder neuer Anstrichmethoden wurde wenig gesagt aus der Überzeugung, dass gegenwärtig die dringendste Notwendigkeit dafür besteht, eher die Art der Anwendung von Anstrichmitteln zu verbessern, als das Material selbst. Jedoch lässt es sich rechtfertigen, die Toleranz von Anstrichmitteln für Missbrauch, selbst auf Kosten einer geringen Verminderung der maximalen Leistung unter idealen Bedingungen, zu verbessern.

Es wird gefolgert, dass am dringlichsten die Erweckung des Verständnisses der die Degradierung von Substraten und der Schutztechnologie betreffenden wissenschaftlichen Grundlagen seitens der für Entwurf und Erzeugung lackierter Artikel Verantwortlichen ist, angefangen mit Spielsachen bis zu Häusern und Brücken—und für bessere Kontrolle der Vorarbeiten und Anstrichprozesse, einschliesslich Inspektion aller Stadien. Auf diese Weise wird nicht nur das Substrat besser geschützt, sondern es wird auch in dem Anstrichprozess weniger Lack, Mühe und Geld verschwendet.

Introduction

Ref. 1

To most people "conservation" implies preservation of the environment—that which is good and aesthetically pleasing and, in particular, works of art and buildings.

A direct link between this concept of conservation and the conservation of resources theme of this OCCA Conference arises from the words of Donald Insall¹, a specialist in the care and restoration of old buildings:

"If a building is alive, it is also mortal. From the moment it takes life, its various materials each begin at their own rates to wear away and to decay.

*Paper presented at the Association's Biennial Conference held at the Grand Hotel, Eastbourne, Sussex from 16-19 June 1977.

"This constant process brings with it most of the problems of an ancient building. Unlike a plant or animal, a building cannot help itself by replacing its worn parts. True maintenance consists not only in renewing evident decay but also in preventing it, the key being an intelligent appreciation of the very distinct life-cycles of different building materials."

All constructional materials decay—for some the rate can be so high that their economic use is governed by the availability and employment of protectives which can provide a barrier between the material and the causes of decay: frequently these protectives are paints and allied compositions which, whilst fulfilling their protective function, can also provide decoration and so enhance the environment. Hence, the concern of the surface coatings industry must be to maintain a balance between the conservation of its materials and resources with the need not only to prolong the life of the substrate but also to enhance the appearance and conserve, or indeed, improve the environment in which we live and work.

These objectives are most likely to be achieved in a society dominated by economics if the choice of paint and painting processes is consistent with minimum effort and maximum economy. The greatest threat to continued successful use of paint is the financial loss occasioned by its misuse. The customer is persuaded, only too easily, that painting is not worthwhile; that it is better to overdesign the steelwork and let it corrode or to leave slabs of dull grey concrete unpainted rather than risk paint failure.

The correct use of paint involves selection of the right materials, proper preparation and painting by the best technique under properly chosen and controlled conditions. But even before that, the cost and effectiveness of painting can be prejudiced by design that has not considered painting problems or has resulted in built-in causes of deterioration. These considerations are reviewed in turn for the main building materials.

The protection of metals

Refs. 2-5

The Hoar report² published in 1971 focussed public attention on the cost of corrosion. It was estimated that the combined annual cost in the UK of metal protection and the consequential damage when protection was not achieved was £1365 millions; today it must be over £2000 millions. There are many components in the true cost, not all immediately obvious. Thus, engineers often overdesign steel structures because allowance must be made for possible weakening by corrosion. Fully reliable methods to prevent corrosion of bridge steel or to inhibit fouling and corrosion of sub-sea structures would enable steel to be conserved in both environments.

Press publicity when the Hoar report was issued concentrated on corrosion of cars, something of interest to every reader. Ironically, protection of steel in cars has been more successful and more economical than in most other fields of use, mainly because with mass production in a factory processes can be controlled closely at a low cost per article. Again with articles under the public eye there is a rapid feedback of any performance defects to the designers and plant engineers. Protection of a car body is a continuously monitored experiment with interfirm competition ensuring that only the most economical treatments survive. There remain problems of attack by de-icing salt and of eventual perforation due to entrapment of water and salts within partly closed structures but, generally, the performance over ten years or more of 3 mm of steel protected by perhaps 70 μm of paint is remarkable.

The less publicised problems of protecting larger steel structures and industrial plants are usually further from the best economic solutions. Rising labour costs and, perhaps even more, the rising administrative costs of organising maintenance work have prompted a move towards processes designed for a longer life to first maintenance. Specific examples of this trend include the treatments applied in the last decade to some major bridges, such as the Severn Bridge. Here steel was grit blasted, metal sprayed and painted with as many as six coats of paint. The total cost of protection, including inspection control, has in some instances been half the cost of the steel itself. In the North Sea where protection against corrosion is vital and conditions for maintenance work almost impossible, such cost levels could be justified but for most land-based structures they can not. It is not surprising that metal sprayers are now advocating the use of sealers only on sprayed metal, and paint manufacturers are promoting barrier type paint coatings rather than combinations of sprayed metal and paint. In the cases cited, fashion may have swung to treatments too complex and too expensive to be the most economical in use, but every structure presents the designer with a problem of choice. How far should he go in increasing initial costs in the hope of keeping down subsequent maintenance costs? The answer will vary, with factors such as the acceptability of some degree of breakdown, the ease of access for maintenance and any costs for loss of use during maintenance. Another often unknown factor is the reliability of the various protective systems offered. A supplier may be able to show an example of a structure that has been well protected for ten years by his system, but if two others have failed prematurely it will be difficult to know what confidence to put on an expectation of long life. Whilst so many adverse factors, such as poor surface preparation, ineffective supervision, unsuitable weather or unexpected delays, can ruin a well designed protective scheme, prediction of life to first maintenance will always be hazardous. Better planning of operations and closer control by properly trained staff are needed to reduce this uncertainty. As will be argued further, this suggests that wherever possible processes should be carried through in the shop, where conditions can and should be controlled, rather than on site.

But before the selection of the best protective system is considered there is much that can be done to simplify the problem. Bad design often accelerates a great deal of corrosion. The classic problems of dissimilar metal connections, such as the conjunction of copper and steel that occurred when ships were first copper-bottomed to inhibit fouling³ are now rare, but corrosion cells still result from contacts between stainless steel and mild steel or, especially, from patches of mill scale left on partially descaled steel. Destructive differences in potential can also result where there is a marked difference in oxygen availability, for example on a steel column partially immersed in soil or bedded in concrete. An elementary knowledge of corrosion theory should prompt a designer to avoid these situations or to specify the precautions that must be taken to avoid trouble, such as the introduction of insulating plastics between dissimilar metals or the provision of extra coatings around steel footings.

No corrosion cell will function in the absence of an electrolyte and in most situations this means water plus dissolved salts. Possibly the greatest contribution the designer can make to conservation is to remove water traps and to design details so that rain will wash away salts rather than concentrate them in pockets. Careful study of any corroded structure will usually indicate where small changes in design or construction would have eliminated trouble. Even a small detail, such as a conical rather than a flat top on a nut, can make an important improvement. Design details become

particularly important when corrosive salt solutions are known to be present. For example, on a highway bridge the surface water, possibly contaminated with de-icing salt, must be channelled away from underlying steel and the design should take into account possible leakage through expansion joints or any cracks that are likely to develop in the road surface.

The use of alternative materials of construction that are less susceptible to attack has, of course, been considered. Recently some engineers, despairing of the increasing cost of protection of steel, have been considering that so-called "weathering steels", the low alloy steels, such as Cor-Ten which, whilst retaining most of the desirable mechanical properties of the simple carbon steels, develop a protective rust patina in clean atmospheres and, it was hoped would behave satisfactorily without painting. Unfortunately, corrosion is not fully inhibited in severe marine or industrial atmospheres. Whether the cost of maintenance by paint on these low alloy steels will be significantly less than on mild steel remains to be decided, although the Paint R.A. has tests in hand for the Transport and Road Research Laboratory. In the absence of severe sulfate or chloride pollution, zinc metal coatings protect steel for long periods. On structures, such as electrical transmission towers in rural or clean urban areas, galvanising, which will often last for the designed life of the structure, is probably the most economic protection, although its initial grey colour, often turning in patches to a dark rust, may not be aesthetically pleasing. Sprayed zinc or aluminium behave similarly. In more severe conditions these non-ferrous metal coatings can fail rapidly, especially if pools of salt solution are trapped on their surfaces. This led to the development of duplex systems of metal coating plus paint advocated by van Eijnsbergen⁴, for example. These combinations can be very effective if the paint is carefully chosen (particularly for zinc)⁵ and if it is applied before any soluble salts have collected on the metal surface. However, the occasional failures due to bad choice of materials or poor control of operations and the high cost of duplex systems have diminished much of the enthusiasm for this approach that was evident a few years ago.

Protection by paint alone can still be the most economical approach but paint is also likely to fail if it is not applied to clean scale free steel. It is a waste of money and materials to apply a complex paint system to structural steel that has not been blast cleaned or pickled, or to light gauge steel that has not had a chemical cleaning or conversion treatment. The idea that deficiencies in preparation can be masked by putting on more coats of paint may survive until the work is paid for but can be very expensive in the final outcome.

Use of alternative materials

One way to minimise loss through corrosion or material degradation is to use materials less susceptible to attack. Thus old fashioned cast iron rain water pipes have largely been replaced in new buildings by rigid polyvinyl chloride pipes which are very much easier to maintain or to replace. Fabrication costs, particularly for plastics with load bearing capabilities, limit economical replacement of metals but durable plastic coatings on metals can be an important element in conservation. These range from laminated sheets, through organosol and plastisol coatings, to powder coatings. All the processes form an overlap between the paint and plastics industries, it being often almost an historical accident that determines which industry claims a process. These coatings may be rather more expensive than the average conventionally applied paint, but there can be a big performance gain resulting from uniform application under

controlled conditions. With some materials, such as the fluoropolymers, the level of durability achieved by a single 20 μ m coat of the best coatings compares favourably with that of ten times the thickness of many site applied paints.

Protection of timber

Refs. 6, 7

A high proportion of hardwoods, particularly those of tropical origin, may be employed unprotected in external situations without serious loss of integrity though with a possible deterioration of appearance. For these woods, surface coatings and treatments are largely intended for the maintenance of appearance. However, for the softwoods, an important and versatile building material, continued economic external use is entirely dependent upon effective protective systems. Over the years a wide range of clear and pigmented systems have been used with varying success, although in the post-war period difficulties have been reported more frequently.

Apart from the deleterious effects of the environment to which all external constructional materials are exposed, it must be appreciated that wood is susceptible to other destructive agencies. Wood is unique in being the only major building material directly derived from a once living organism; in fact, wood is a corpse for which nature provides abundant biological undertakers.

The greatest dangers to the integrity of wood results from contact with water—not only do changes in water content result in dimensional changes, leading ultimately to distortion and cracking, but also excessive contact with water produces conditions very conducive to biological attack.

The most durable portion of the timber is the heartwood, from the centre zones of the tree no longer involved in nutrient transfer processes. This is surrounded in trunk and branch by sapwood, rich in nutrients involved in the growth process. The residues of these nutrients in the converted timber are largely responsible for the susceptibility of sapwood to decay. At one time the heartwood would be employed in external situations and the sapwood reserved for non-critical applications. However, with the rapidly rising costs of timber it became necessary to maximise the yield of timber and hence sapwood has been extensively used in higher risk situations, and has been largely responsible for the increased incidence of decay in joinery, particularly in the period prior to the mid 1960s.

Aggravating the effects of this use of less durable timber have been changes in joinery design and construction methods brought about by mass production techniques. It could be argued that the joint construction now used allows more ready access of water to end grain and, particularly, end grain within the joint, where paints can not penetrate. Mass production methods for joinery have also resulted in the use of primers tailored to the requirements of production rather than durability⁶.

Paint, which traditionally has been employed to protect joinery, can provide a good barrier to water entry but, where water has entered at such a point as a defective joint, it can be equally effective in retarding escape of the water⁷ giving conditions where the wood rots beneath an apparently sound paint film.

A further line of defence can be obtained by subjecting the timber to various preservative treatments containing such

active agents as pentachlorophenol or tributyltin oxide, as are called for by certain local authority Building Regulations and NHBC requirements. Except under conditions of gross overload, these treatments appear either neutral or benign to paint systems, though any major changes in preservative formulation should be monitored by extensive overpainting trials.

It must be appreciated that the object of the preservative treatments is to provide defence against biological attack on the timber—they do not act as water barriers (though the so called water repellent grades may reduce the rate of water entry) and hence water can still be taken up by treated wood resulting in dimensional change and/or disruption of the paint system.

As has been discussed elsewhere⁶ the non-homogeneous structure of timber results in non-uniform dimensional changes which may subject the paint system to large and differential stresses. The high degree of film flexibility required to withstand these stresses is often found to be lacking in the rapid drying shop primers required for joinery mass production techniques. The performance of these primers is enhanced when used over timber pretreated with a resin containing preservative and this combination may be acceptable under BS 5358:1976.

Although the requirements for paint/preservative systems for external joinery have been fairly well defined, in practice, many instances occur where these systems achieve only a fraction of their potential life. This is particularly so on new properties, with all too often the failure being accepted complacently with the owner having been "brain-washed" that this is normal with modern paints. Apart from the bad publicity for the surface coatings industry, these failures and consequent maintenance operations represent both economic loss and squandering of resources.

Many failures originate in defective design and workmanship or bad building practices. A frequent design factor arises from a failure to appreciate fully the immense capability for damage possessed by water. Externally features designed to be eye-catching are incorporated into a building without sufficient consideration of possible deleterious effects which may occur, for example, by their effects on rain run off. In one building, vertical lines of strongly projecting windows channelled rain run-off in sharp lines on to a varnished wood fascia to the extreme detriment of the finish. Doors and windows frequently are fitted flush with the building surface and not inset, and so are exposed to excessive rain run off with the risk of both failure of the paint system and rapid deterioration of the joinery.

The source of water which appears to be much overlooked is condensation. The large areas of glazing and glass in-fill frequently incorporated into modern structures present extensive cold surfaces on which condensation may form and run down to settle on frame members, which seldom appear to have been shaped to shed the water and hence it enters the framings through defective joints or broken back putty.

Equally, joinery design and construction features will affect the overall performance of the painted joinery. Frame members should be of suitable cross section for the frame size and type, otherwise joint straining whip can occur in use. All members should be shaped so as to shed water rapidly and preferably all edges radiused. In addition, all joints should be cut true and be tight filling. One design feature which has been responsible for serious paint failure and joinery decay

has been the planted cill. This results in an extensive joint in an extremely high risk position.

Building practices can also result in premature failures. Poor site storage so that the shop primer is in a deteriorated or heavily soiled condition before application of the finish system is a frequent culprit, as are the activities of building operatives who apparently have never heard of a level and have installed joinery with a backwards tilt of 10–15°. A further practice which is to be greatly deprecated is the apparently growing use of a two-coat paint system (that is, a single coat of site applied finish directly over the shop primer) no doubts to reduce "first costs", though any savings could soon be lost in excessive maintenance costs.

Clear finishes for external timber have long been the source of difficulties, with varnishes frequently failing after two to three years. Maintenance after this type of finish has failed can be expensive, as any surface deterioration of the timber must be removed as it would be obvious beneath the new system. To overcome this a water repellent preservative stain for cladding was developed by the US Forest Products Laboratory under the name of the "Madison Treatment". From this has evolved a whole series of coating systems, not only for cladding but also for joinery use, with many of them claimed to be semi-transparent and hence revealing the grain structure of the timber.

The main claims for these systems are that by forming relatively thin coatings they allow ready escape of moisture which has entered the timber and that they are simple and inexpensive to maintain. Maintenance is claimed to consist of no more than wiping the old surface down and applying a further coat and, hence, to be much less costly than the maintenance of a paint system. At present, although there is some controversy, maintenance periods as short as three years have been suggested.

Though the concept of this type of protective system is of great interest, it has caused problems by placing in the hands of architects and designers systems which consist largely of dark colours. When used in the proper context there is no doubt that these can have great aesthetic appeal although the consequences of the extensive use of dark colours on timber exposed to full sun appear to have been largely overlooked. In the summer of 1976 many instances were reported of premature failure and even of severe damage to the timber through the excessive heating of dark coloured finishes.

A discussion of failures of painted joinery can result in a rather gloomy picture being presented, but it must be appreciated that it is a very one-sided picture—in practice for every failure there are many instances of satisfactory performance. An examination of the failures leads to identification of the weak points in the painting process, so that steps can be taken to avoid them. It must be further appreciated that painting cannot be considered in isolation. For a satisfactory performance to be obtained from painted joinery, consideration must cover all the other design and construction stages—if paint is used to make up for defects in other stages, disappointment accompanied by large maintenance costs and squandering of resources are probable.

Protection of masonry

Ref. 8

Although masonry is normally considered an inherently durable material, it is frequently painted for a variety of

reasons. Probably the most usual is aesthetic—paints carefully chosen for colour and texture do much to improve the environment, as has been demonstrated by the amazing transformations of whole streets under the various Civic Trust and other similar schemes. The greatest areas of painted "masonry" (in its widest sense) though are internal, where emulsion and other low sheen paints, accompanied now by the silk finishes, have taken a very large section of the wall covering market. Not the least of their advantages is the ease and rapidity of renovation and change of decorative scheme. Externally, the effects of painting on the dreary concrete boxes, now so much in favour with the construction industry, can be dramatic.

Paint systems are also frequently used in making good defects, such as surface erosion of renderings or dash finishes, reducing water uptake or penetration and in rendering surfaces more readily cleaned. Under this last heading should be included finishes formulated to allow ready removal of graffiti.

As for wood, a large proportion of masonry painting operations present no special difficulties and the results are satisfactory. Occasionally, though, a failure occurs, which if situated externally proclaims itself for all to see and is more noted than other successes which may be adjacent. The large areas which can be involved in such a failure may represent both large economic loss and significant wastage of materials.

The Building Research Establishment lists five principal reasons for masonry paint failure*:

- (1) *Moisture*—The original constructional water, water gaining access through defects in the structure or water produced by condensation.
- (2) *Salts and alkali*—Present in the material of construction or gaining access, for example from rising damp, by deposition as salt spray or occasionally from operations within the building.
- (3) *Unsuitable surfaces*—Plaster, rendering or concrete too fresh, friable or contaminated; weathered or deteriorated surfaces or paintwork.
- (4) *Unsuitable conditions*—Very high or low temperatures and humidities during application can seriously affect most paints. Dust and dirt produce a "bitty" finish.
- (5) *Wrong choice of paint*—For a particular type of material, existing decoration, or climate. The occasions when the paint itself is not of its normal quality are few, but some paints are less tolerant than others of adverse factors.

From the records of consultancy and trouble shooting enquiries undertaken by the Paint R.A., the third failure reason appears the most prevalent though it should be retitled "Failure to appreciate the condition of the surface". In a significant proportion of cases, painting or repainting appeared to have been undertaken without adequate appraisal of the surface condition. On new work, paint has been applied over surfaces weak with laitance or contaminated with mold or lichen growth, either not recognised or inadequately removed. In repaint operations the deterioration of the existing paintwork has frequently been underestimated resulting in rapid failure.

Greater care in the survey in conjunction with good surface preparation can significantly reduce these failures with

corresponding better utilisation of finance, labour and materials.

General considerations

New shop or site work

Almost all operations can be controlled more closely and carried out more economically under good factory conditions than on a building or construction site. But merely transferring an operation to a factory does not ensure good results. Recent consultancy work by Paint R.A. staff has shown how often, in a factory, painting operations can be the least esteemed task, pushed into the poorest buildings and given to the least experienced workers. There are many premises where better housekeeping, a minimal expenditure on air conditioning and better application equipment and a little training of operators would immeasurably improve the quality of painting and, in most cases, result in very substantial reduction in paint usage, or rather wastage. Fragmentation of processes amongst a succession of subcontractors is another source of difficulties and unsatisfactory performance. Thus, parts may be fabricated in one factory, galvanised or sherardised in a second and painted in a third, with all the additional handling that could be avoided in one properly organised installation. Many of the problems appear to stem from a lack of education of production engineers in the basics of protection technology, a defect common often to the training of architects and, to a lesser degree, structural engineers. The suppliers of paints and pretreatment materials might also do more to educate users and thus to correct the deficiencies that arise. Possibly, representatives have become too much professional salesmen, rather than true technical service men, for the good of industry.

Nevertheless, with all the defects of some factories, preparation and painting is more at risk on site where weather is uncontrollable and painting may be seriously affected by other processes such as concrete mixing or laying or blast cleaning that are going on simultaneously. So there is a good case for factory painting, even of window frames or of heavy structural steel. If this is done, it is imperative to reduce subsequent handling damage to a minimum. Much can be done with fabric slings instead of steel chains and the use of plastic spacers and wrappings. Equally, paint needs to be chosen to minimise damage and ease subsequent touching up.

Planning of operations so that, for example, steel for the interior of a factory which needs only minimum paint protection can be delivered to a weatherproof store rather than left in mud and water is vital to materials conservation. Forethought of this kind can avoid the necessity of applying better protection than will be required in the ultimate conditions of use or paying for expensive repairs because components have deteriorated even before erection. It is equally important that someone should have clearly defined responsibility for inspecting components in the finishing shop and again after delivery to site so that defects can be recognised and corrective measures taken before serious deterioration has occurred.

Maintenance of protection

Many articles, including most so-called consumer durables, are given a single protective treatment that is intended to last for their useful life, that is, until obsolescence or mechanical failure dictates replacement. On more substantial or expensive manufactured articles such as aeroplanes, buses and passenger coaches repainting will be carried out at least once, often for

appearance rather than protection. On most fixed structures, however, maintenance for protection is a recurring need that may involve repainting ten to twenty times in all. The development of a rational maintenance policy is an important contribution to minimising cost in use for buildings and structures.

The first consideration is often whether to maintain or to replace. Neglect can soon bring a wooden window frame or a steel fire escape to a state where attempted maintenance would be a waste of money. But periodic replacement is likely to be much more costly than planned maintenance.

Arguments have continued for long on relative merits of regular maintenance on a time schedule against maintenance only when inspection shows signs of deterioration. If a labour force is continuously employed the time schedule may well be best, provided that the timing is adjusted in relation to the observed level of performance. Where an experienced and concerned inspector is available and the work will be done by contractors, there may be a case for the inspection method but it must always be remembered that once breakdown has started it can develop catastrophically, particularly if adverse weather holds up repairs.

Successful maintenance painting with maximum economy depends greatly on preparation of the old surface. The maximum value must be carried forward from the old paint without imperilling the new paint. With the traditional white lead in oil paints used on steel or stucco, it was possible to brush down and wash the surfaces and to repaint on most occasions without removing the old film. The authors have examined films built up over 100 years with fifteen or more layers in this way. Most modern paints, such as alkyds and modified alkyds, become too hard and brittle to be repainted in this simple way many times. Chipping, cracking or peeling makes removal of part or all of the paint advisable. It will be interesting to see whether over extended periods, films of the chemically more stable emulsion polymers prove more suitable for continuous recoating. Paint removal, where necessary, is a laborious and in inexperienced hands a dangerous business. Burning off can be effective, but needs considerable skill. On structures there are interesting possibilities in wet abrasive blasting which is now coming into commercial

use. Wet blasting is likely also to be the most effective means of obtaining sound paint adhesion to those old paint films, such as glossy epoxy or polyurethane finishes which, because of their extreme solvent resistance and, often, surface contamination, are very difficult to recoat with safety. On such surfaces, a light blasting treatment both cleans and slightly roughens the surface.

Planning and site control of maintenance work is as important as for initial painting and is often more difficult. Maintenance painting is often done without the benefit of a site office and resident engineers, as on a new construction site. Inspection by a clerk of works or an inspector from an outside firm may involve a long car journey and a search on each occasion over a large site to find the painting crews, factors which are not conducive to close control. Special efforts are necessary and their cost is usually justified. Unfortunately, all too often, inspection is lax and record keeping poor, so that it is possible neither to pinpoint reasons for failure nor, at a later stage, the reasons why a particular job has been so successful. Thus over the years improvement of procedures depends greatly on the experience and observation of individuals and the scientific development of optimum procedures is virtually impossible. More planned experiments under practical working conditions would be of great value towards ultimate reduction of the cost of conservation.

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Discussion at Eastbourne Conference

MR F. ARMITAGE said that one of the most important problems with clear finishes for wood was the possible degradation of the substrate by UV light passing through them. He said that this might be a more serious problem than the moisture content of the wood. He said that UV absorbers incorporated in clear coatings had been tried but did not appear to be very successful in extending the life of the coating and asked if there was any new work on this subject to report, or if there was any simple relationship between the rate of breakdown of the wood surface and the water content or the UV light on the surface.

MR SHERWOOD said that although he did not have any definite figures, there did appear to be a relationship between

the rates of breakdown due to water content and UV degradation. On the question of degradation of wood by UV, some work now being carried out at another laboratory indicated that all of the destructive wavelengths may not be UV but may be in the visible spectrum.

MR SHERWOOD pointed out that nowadays the term "clear finishes" not only included varnishes, but also the whole range of preservative wood stains which, because they formed only a very thin film on the surface of the wood, were claimed to avoid the problems of water trapped within the wood.

MR ARMITAGE said that the point in which he was interested was whether water in the wood was more important than the effect of UV on the breakdown of the substrate.

MR SHERWOOD said that the water content of the wood could be very important especially as it effected fungal growth because fungus developing beneath the paint film could break through and disrupt the film. He could not say which of the two, in general, was the more important though both could be damaging, but their relative importance varied in particular situations.

MR E. A. WATSON recalled that a few years ago there had been considerable interest in the possibilities of using the so called "breathing paints" to overcome the problems due to retained moisture in the wood. He asked the authors to comment on the increased use of inspection techniques for painting, including those of independent inspectorates. He said he was assuming, of course, that the personnel belonging to these units were fully trained.

MR BULLETT said that on the whole they welcomed the trend towards independent inspection provided, of course, the inspectors were fully trained, but he pointed out that an inspector could waste a lot of time if he insisted on too strict adherence to some unimportant details of specifications whilst forgetting the ones that really mattered; the inspector must know his technology. He said that the PRA had been approached several times recently to initiate a training scheme for the certification of inspectors. His personal view was that a certification scheme must incorporate both a training course, with an examination, and evidence of practical experience. It could best be set up jointly between a research institute, such as the PRA, and one or more of the professional institutions, such as OCCA. There had already been informal talks, but the time was certainly ripe for a formal approach.

MR SHERWOOD said that regarding breathing paints, they had done work at the PRA to examine the various claims made for such systems. By a breathing paint they had understood it to mean that the paint allowed water to escape as a vapour more readily than it took up liquid water; they had not yet found a system for which this was true, and indeed, they felt that this was thermodynamically impossible.

MR A. B. LOCK referred to the damage to timber as a result of very dark coatings being applied, especially of the preservative stain type, and asked whether the authors believed that this type of stain was more likely to result in timber damage than if the timber had been painted in the usual way with a dark coloured paint.

MR SHERWOOD said that with the availability of these dark coloured stains architects were covering large areas with them which left them open to severe damage in bright sunshine, as during the previous summer. He said that he thought similar damage would result if large areas were painted with a black paint, but that in practice people did not cover such large areas with a dark paint as they would with a wood stain.

MR BULLETT said that preservative stain treatments were not as effective in controlling the rate of water passing through them. When there was a period of hot sun following condensation, a rapid shrinkage of the surface occurred due to dehydration inducing cracking in the face of the timber. If the surface had been covered with a paint film, which would slow down the loss of water, he said that blistering would be far more likely than cracking.

MR LOCK said that the only complaints he had received during the previous summer about paint covered surfaces were a slight increase in this type of blistering, but he did

agree with Mr Sherwood that paint was not generally used over such large areas.

MR A. T. S. RUDRAM commented that Mr Sherwood had emphasised the need for a proper preparation of a surface for the paint. He pointed out that very often a thin layer of paint is expected to do marvellous things and cover up all sorts of faults and he said he would like to suggest that in badly prepared areas the paint did not fall away from the substrate, but rather the substrate fell away from the paint.

MR SHERWOOD said that he agreed to a large extent with Mr Rudram, but felt that by following this line the paint industry might become too complacent. He suggested that a balance was needed.

MR BULLETT said that he agreed that very often the cause of a failure was the poor state of the substrate, but he suggested that it was the responsibility of the paint supplying industries to ensure that customers prepared their substrates suitably. On the point of the role of management, he suggested that it was very important that all the operations during building should be planned together and the painting should be taken into the overall construction scheme. Very often, he pointed out, the painting is left until the last couple of days and regarded as a decorative process to cover up defects in other construction processes. He suggested that it was essential that the paint be considered at the design stage and planned throughout to take its proper place in the whole construction project.

DR SMITH said he thought that Dr Mondt's paper on emulsions penetrating into the substrate was particularly relevant here as this gave the paint chemist an opportunity to improve the state of the substrate before the surface was painted.

MR F. B. REDMAN suggested that paint should be sold as a complete system rather than as a liquid in a can and that the paint industry should take on the responsibility of applying the paint system rather than leaving it to a separate industry of paint applicators where unskilled labour was rife.

MR BULLETT said there were already some areas where this was being done. In developments that were much at risk due to misapplication, a number of firms when introducing a new paint system insisted on having their own application scheme and organising the whole process. He gave an example of some of the heavy textured masonry paints where guarantees had been given and in consequence the manufacturers insisted on applying the system. He said he did not think it was practical to extend this development throughout the whole paint industry, but thought that a useful compromise would be an increased use of inspectors provided, of course, they were competently trained.

MR E. A. WATSON said that he thought there were two distinct industrial market-segments to which paint was sold. In dealing with large firms there was usually someone with a sound technical background in paint, who could follow procedures associated with paint use at the design stage, such as consulting engineers and the like. This was the ideal situation. However, in small or light engineering firms the people responsible for applying the paint were normally engineers who have no background in paint application and there was frequently no way of getting into contact with them directly. He thought it was in this area where most of the problems occurred.

The possible uses of reactive microgels in paint formulation*

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Summary

Reactive microgels are crosslinked polymer particles with diameters ranging from about 5 to some 10 nm. They are usually prepared by emulsion polymerisation of monomers, which have a higher functionality than two and, therefore, act as crosslinking units. During the polymerisation reaction not all the functional groups are used. From the residual reactive groups those located at the microgel surface are available for further reactions. Reactive microgels may be used as multifunctional crosslinkers for re-

inforcing purposes. By chemical reaction new reactive groups may be introduced at the particle surface, by which microgels can also be used as components in condensation and addition reactions.

The compact globular structure enables preparation of solutions with high solid content and reasonable viscosity. By reacting the surface groups with soluble dye molecules new organic pigments with a polymer core may be obtained.

Keywords

Types and classes of coatings and allied products

latex coating

Raw materials for coatings binders (resins, etc.)

microgel

emulsion

emulsion resin

styrene resin

divinyl benzene

Processes and methods primarily associated with manufacturing or synthesis

polymerisation

emulsion polymerisation

Les applications éventuelles des microgels réactifs dans le domaine de la mise au point de formules de peintures

Résumé

Les microgels réactifs sont particules de polymères réticulés, ayant les diamètres dans la gamme depuis 5nm. à peu près jusqu'à quelque 10nm. En général, ils sont préparés par la polymérisation en émulsion de monomères d'une fonctionnalité supérieure à deux, et qui agissent d'ailleurs, en tant qu'éléments de pontage. Dans la réaction de polymérisation, tous les groupements fonctionnels ne sont pas utilisés. Parmi les groupements réactifs qui restent, ceux qui se trouvent à la surface du microgel peuvent participer en d'autres réactions. Les microgels réactifs peuvent être utilisés en tant qu'agents de pontage multifonctionnels en vue de fournir les caractéristiques de renforcement. Par les réactions chimiques,

de nouveaux groupements réactifs peuvent être introduits sur la surface particulaire et par conséquent, les microgels peuvent être utilisés en tant que constituants des réactions de condensation ou d'addition.

La structure compacte des globules rend possible la préparations des solutions d'une teneur élevée en matière sèche et d'une viscosité raisonnable. En faisant réagir les groupements superficiels avec les molécules des colorants solubles, on peut obtenir de nouveaux pigments organiques ayant le noyau polymère.

Die Einsatzmöglichkeiten reaktiver Mikrogele in Lackvorschriften

Zusammenfassung

Reaktive Mikrogele sind vernetzte Polymerteilchen mit Durchmesser von etwa 5 bis zu über 10 nm. Sie werden gewöhnlich durch Emulsionspolymerisation von Monomeren mit einer über zwei liegenden Funktionalität hergestellt, und verhalten sich daher als Vernetzungseinheiten. Nicht alle funktionellen Gruppen werden während der Polymerisationsreaktion aufgebraucht. Von den übriggebliebenen reaktiven Gruppen stehen die an der Mikrogeleoberfläche befindlichen für weitere Reaktionen zur Verfügung. Reaktive Mikrogele können als multifunktionelle Vernetzer für Zwecke der Verstärkung benutzt werden. Mittels chemischer

Reaktion können neue, reaktive Gruppen an der Teilchenoberfläche eingeführt werden, wodurch Mikrogele auch als Komponenten in Kondensations- und Additionsreaktionen verwendbar werden.

Die kompakte, kugelförmige Struktur ermöglicht Lösungen hohen Festkörpergehaltes und niedriger Viskosität herzustellen. Durch Reaktion der Oberflächengruppen mit löslichen Farbstoffmolekülen lassen sich neue organische Pigmente mit einem Polymerkern herstellen.

Introduction

Refs. 1-8

Contrary to fibres and other polymer applications, the polymer matrix of organic coatings is usually considered to have a homogeneous non-ordered structure. It is not quite accidental, however, that earliest evidence of inhomogeneous structures was obtained from crosslinked polymers^{1,2,3,4}. Subsequently, a large number of publications appeared, which showed that inhomogeneous structures are normal rather than exceptional in the so-called "amorphous poly-

mers". The author became interested in this problem when studying the structure of crosslinked polyester resins. The final conversion during the curing reaction turned out to depend on the initial polymerisation conditions. To explain this relationship, the formation of a primary network very early during the copolymerisation has been assumed, and this determines the possible extent of the reaction, as well as its resulting morphological structure. After the formation of this network, the copolymerisation proceeds at distinct centres and from there extends into the bulk of the surrounding liquid medium. Finally, a structure results consisting of more densely crosslinked domains embedded in a less

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densely crosslinked polymer matrix. The dimensions and extension of both phases depend on the composition of the polymerisable material as well as on the condition of polymerisation. Considerable, almost simultaneous, evidence for the correctness of these assumptions was provided by small angle light scattering experiments on polyester resins by Bettelheim and Gallagher¹. These results motivated the author to consider the possibilities of synthesising polymer networks having a well-defined inhomogeneous structure^{5,6,7}. In order to apply this principle to organic coatings, it was necessary to use two separate reaction steps. In the first step, prepolymers were prepared from tetra-functional monomers, such as divinylbenzene or ethylene glycol dimethacrylate. Because of their globular crosslinked structure and their submicroscopic size these prepolymers have been named "reactive microgels".

In addition to using these microgels as multifunctional crosslinking agents for the synthesis of inhomogeneously crosslinked polymers, a wide range of other applications is possible due to the presence of pendant reactive groups at their surface. They may be modified by a wide range of chemical reactions.

Reactive microgels should principally be obtained if the polymerisation of higher functional monomers is limited to local reaction domains, that is, by favouring intramolecular against intermolecular polymerisation. There are, at least, two ways of achieving this requirement: by polymerisation of higher functional monomers either in the dilute or in the emulsified state.

The dilution method is somewhat more laborious because a large amount of inert solvent has to be removed afterwards. This method has been used to polymerise ethylene glycol dimethacrylate.

Emulsion polymerisation offers some significant advantages because of the favourable ratio of reaction volume to polymer yield. Despite the fact that emulsion polymerisation is an important and widespread industrial method for the synthesis of polymers from many monomers, it was not until recently that crosslinking monomers were used in emulsion polymerisation as the only polymerising species^{6,8}.

In the following section the preparation, characterisation and possible applications of reactive microgels will be discussed.

Preparation of reactive microgels

Reactive microgels can be prepared by emulsion polymerisation of higher functional monomers, such as 1,4-divinylbenzene (1,4-DVB) or various alkylene glycol-dimethacrylates. The gel particles so obtained have diameters between about 5 and 50 nm (Fig. 1). This range of dimensions overlaps that of commercial latices at the lower end and extends down to almost molecular dimensions (Fig. 2).

The polymerisation mechanism of such higher functional monomers differs significantly from that of bifunctional vinyl or acrylic monomers. Whereas in emulsion polymerisation of styrene, the means of regulating the number and particle size by the emulsifier concentration in the polymerisation batch is well known, both the size and the size distribution of microgels from crosslinking monomers are little influenced by this parameter. Contrary to normal emulsion polymerisation, agglomeration occurs with crosslinking monomers. Depending on the emulsifier concentration and on the monomer/water

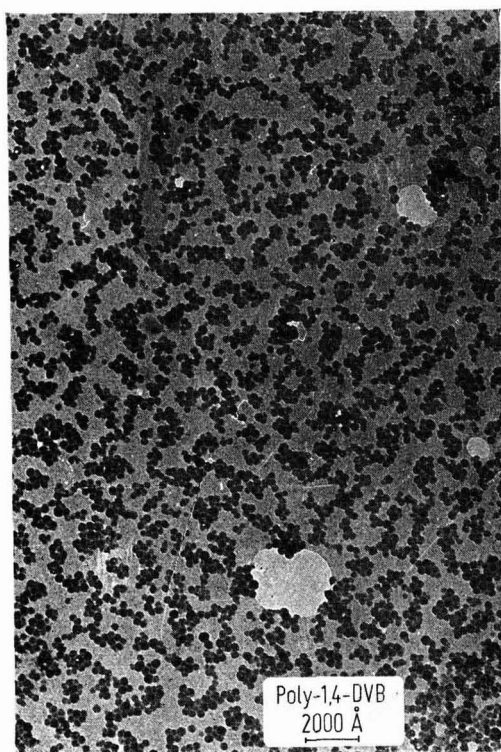


Fig. 1. Electron micrograph of microgels from 1,4-divinyl benzene

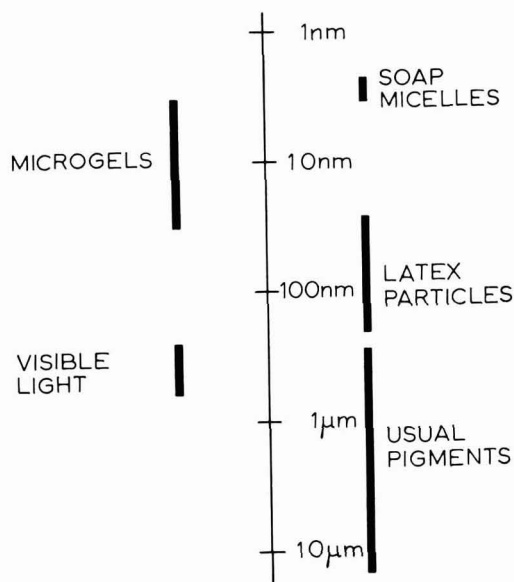


Fig. 2. Comparison of particle sizes

ratio these agglomerates may finally coagulate and coarse visible particles are formed. Even the microgels seen in Fig. 1, though having apparently a very uniform size distribution, must be considered as agglomerates of smaller primary particles which, by further addition of monomer, have finally acquired a spherical shape (Fig. 3).

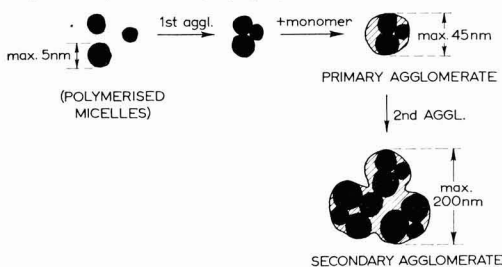


Fig. 3. Agglomeration during emulsion polymerisation of divinyl benzene

Agglomeration results from the very much higher number of micelles initiated in the emulsion polymerisation of 1,4-DVB, as compared to styrene where a deficiency of soap occurs even at an early stage of polymerisation. When microgels encounter each other in solution they may be irreversibly linked together by reaction of their pendant vinyl groups.

Characterisation of reactive microgels

The most important properties for characterising reactive microgels are their size and their number of reactive groups. The size has been determined both by soap titration and electron microscopy with good agreement.

Surface area and particle diameter

Latex particles formed during emulsion polymerisation are stabilised by adsorption of soap molecules at their surface. However, this coverage is usually not complete. If further soap is added to the reaction mixture additional soap molecules adsorb at the particle surfaces and the surface tension of the solution correspondingly decreases until a critical soap concentration is attained at which free soap micelles are formed. This point is recognisable by an abrupt transition to a constant surface tension (Fig. 4) and enables the calculation of the total amount of soap which is needed just to cover completely the surface of the particles. If the adsorption area occupied by one soap molecule is known, the total surface area of the particles may be calculated. Knowing the total amount of polymer present, the specific surface area of the particles is obtained and the mean particle diameter can be calculated, if a spherical shape is assumed.

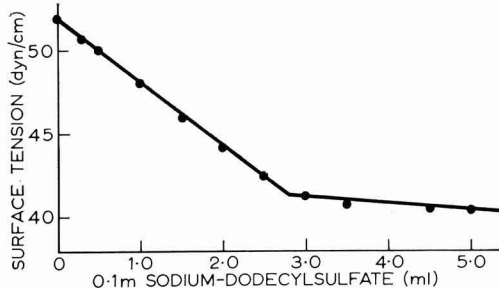


Fig. 4. Soap titration

Size and shape

By electron microscopy not only the mean particle diameter, but also a size distribution curve can be obtained (Fig. 5). Furthermore, some information is obtained on the shape of the microgel particles. Normally microgel particles are spherical as shown in Fig. 1. However, if agglomeration occurs, irregular particles shapes may be observed, depending on the time at which the sample was taken from the polymerisation batch (Fig. 6).

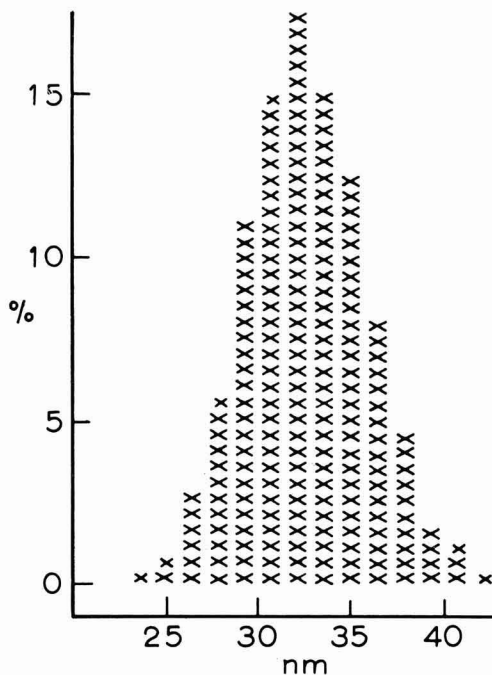


Fig. 5. Particle size distribution curve of reactive microgels from 1,4-divinyl benzene

Reactive groups

For the determination of the functional groups, infrared-spectroscopy and chemical addition reactions may be used. In the case of addition reactions, some specific peculiarities have been found. As mentioned above, microgels from DVB are highly crosslinked and non-swellable. Therefore, a quantitative determination of the number of vinyl groups depends on the rate of diffusion of the reagent molecules into the network. This can be seen from the time/conversion curves obtained by adding mercury diacetate to microgel vinyl groups (Fig. 7). At the beginning a rapid reaction takes place and the curve is practically concurrent with the ordinate. During the first thirty minutes the vinyl groups at the surface of the particles react at the same rate as those of low molecular vinyl-compounds like styrene. Then the rate of addition changes abruptly and slows down. This change in the reaction rate indicates the end of the surface reaction and the beginning of the diffusion-controlled reaction of the interior vinyl groups. After four days about 90 per cent of the vinyl groups have reacted. The residual vinyl groups are too sterically hindered to add to the reagent.

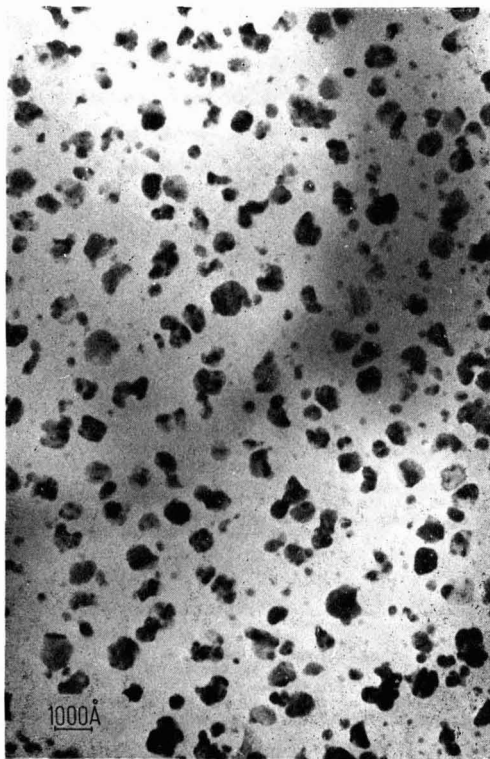


Fig. 6. Electron micrograph of secondary agglomerates

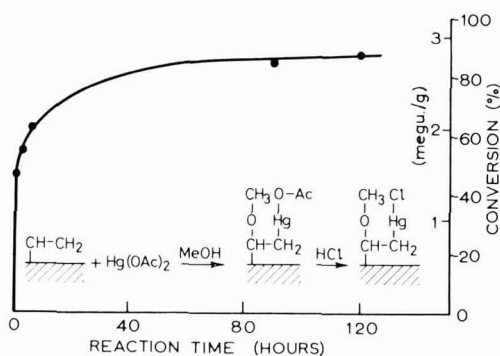


Fig. 7. Addition of mercury diacetate to a microgel batch

Potential applications of reactive microgels

Ref. 9

Viscosity behaviour

Depending on the particle size, microgels can be dissolved in monomers and solvents to give clear opalescent colloidal solutions. When rigid non-swella-ble microgels, such as those from DVB, are dissolved in benzene, toluene or styrene, solutions of very low viscosity are obtained up to concentra-

tions of about 40 per cent weight. A comparison with the viscosity of a polystyrene solution illustrates this difference very markedly (Fig. 8). Obviously the rheological behaviour of these rigid particles is similar to that of solid spheres which obey the Einstein viscosity law. Therefore reactive microgels may be used for formulation of high solid systems.

Polymer:	mol.-wt.	solvent	temp.	$[\eta]$ (ml/g)
Microgels	100.000	benzene	25 C	10
Polystyrene	100.000	benzene	25 C	50

Fig. 8. Viscosity behaviour of microgels from 1,4-divinyl benzene compared with that of polystyrene

Optical effects of microgels in graft copolymers

If the refractive index of the microgel differs sufficiently from that of the polymer matrix and if the particle size is sufficiently large, films having a tarnished white appearance may be obtained similar to that given by the addition of micronised silica.

Polymer networks with microgels as multifunctional cross-linkers

In the classical theory of crosslinking polymerisation reactions, the crosslinks are assumed to be uniformly distributed throughout the network. During the last fifteen years, however, considerable experimental evidence has been provided, which shows that such an ideal network structure is exceptional rather than normal. For various reasons in most polymer networks densely crosslinked domains are embedded within a less densely crosslinked polymer matrix.

By copolymerising reactive microgels with normal bifunctional monomers, polymer networks may be obtained, which have a well-defined inhomogeneous structure (Fig. 9).

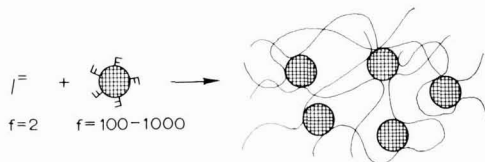


Fig. 9. Crosslinking by reactive microgels

The efficiency of crosslinking may be estimated by the amount of extractable polymer molecules, which have not been linked to the network. It can be seen in Fig. 10 that the crosslinking efficiency of DVB microgels in polystyrene varies both with the concentration and the size of the microgels.

It is reasonable to assume that the reactive groups may be located at the surface, as well as within the microgel particles. In order to find out which of these groups actually react during co-polymerisation with styrene, the concentration of the vinyl groups at the particle surface is plotted against the amount of insoluble polystyrene.

Fig. 11 shows that at a constant weight fraction of DVB-microgels, the crosslinking efficiency depends linearly on the volume concentration of reactive groups at the particle surface. This relationship implies that essentially only those vinyl groups participate in copolymerisation which are located

at the particle surface. Obviously, the rigid, highly crosslinked and non-swellable structure of these particles prevents styrene from diffusing into them and copolymerising with pendant vinyl groups still present there.

polystyrene chains is tightly connected with the particle surface thus shifting the mechanically weakest region to somewhat outside into the surrounding polystyrene matrix.

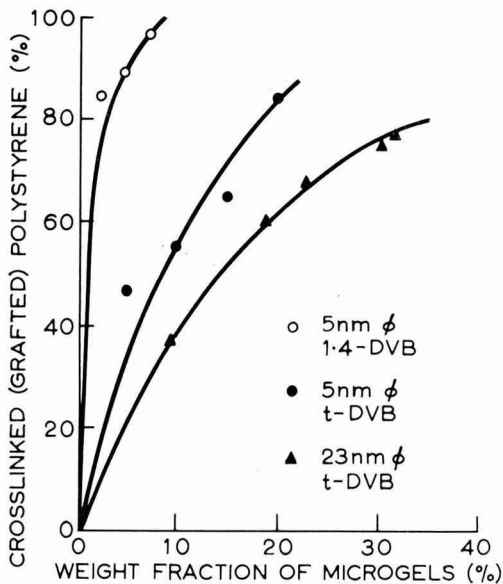


Fig. 10. Influence of particle size and concentration on crosslinking efficiency (t-DVB = technical divinyl benzene)

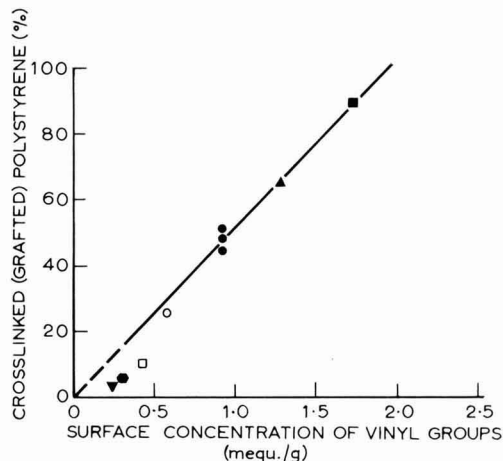


Fig. 11. Copolymerisation of 5% (weight) microgels with styrene, influence of surface concentration of vinyl groups on crosslinking efficiency

An ultra-microtome section of such a crosslinked graft-copolymer shows that the microgel particles remained well dispersed within the polystyrene matrix (Fig. 12). Moreover the fractured surface of these polymer networks indicates (Fig. 13) that the front of the fracture does not coincide with the surface of the original particles, but is somewhat distant from it. It must be concluded, therefore, that a shell of grafted

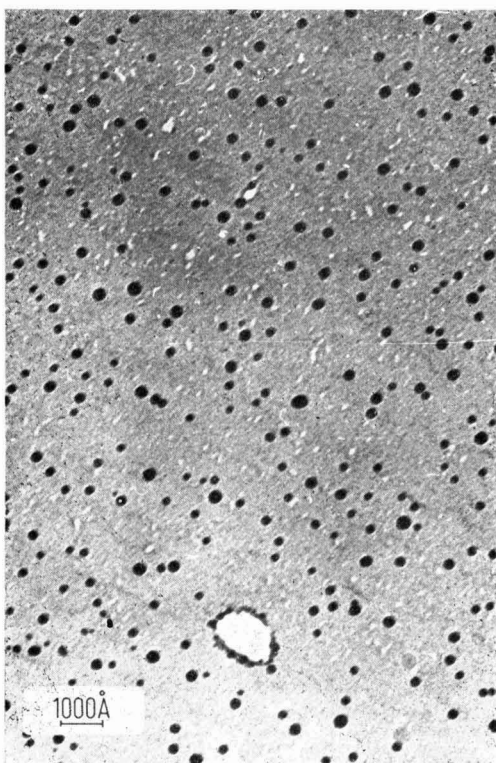


Fig. 12. Ultra-microtome section of microgel dispersed in polystyrene

From the diameters of the microgel particles shown in Fig. 12 and of the polystyrene shells visible in Fig. 13 it is estimated that an increase of the particle size of approximately 30 nm due to grafting of styrene occurs. This agrees well with an independent analytical determination which resulted in an increase of 35 nm. Similar results were obtained by incorporating reactive microgels in unsaturated polyester resins. After hydrolytic degradation the insoluble fraction of copolymer-grafted microgel was isolated. It increased with the weight fraction of microgels present and approached 100 per cent when approximately 40 per cent by weight of microgels as used (Fig. 14).

Less densely crosslinked, swellable microgels may be prepared from ethylene glycol dimethacrylate. If such reactive microgels are copolymerised with styrene, the formation of inter-particle as well as additional intra-particle network chains is possible. The relative contribution of each to the network structure depends on the microgel concentration used.

At a low microgel concentration an interpenetrating network is formed within the microgel particles and polystyrene chains are grafted to the surface. With increasing microgel concentration the distance between adjacent particles becomes smaller and smaller until a critical concentration is reached at which the particles are in contact with



Fig. 13. Fractographic view of microgel-crosslinked polystyrene

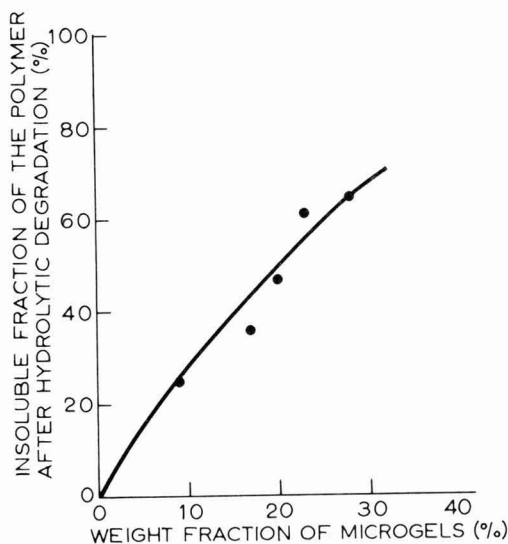


Fig. 14. Influence of microgel concentration on copolymer grafting in curing polyester resins (microgels: 23nm O , technical grade DVB)

each other. At this point it is no longer possible to distinguish between inter- and intra-particle network chains. The transition between the two structures can be seen by a change of the slope when the mean molecular weight of the network chains is plotted against the formally calculated, spatial distance between reactive groups of the microgel fraction. This is equivalent to the reverse microgel concentration (Fig. 15)⁹. By taking advantage of these parameters, the synthesis of a wide variety of well defined inhomogeneous polymer networks having different structures and properties becomes possible.

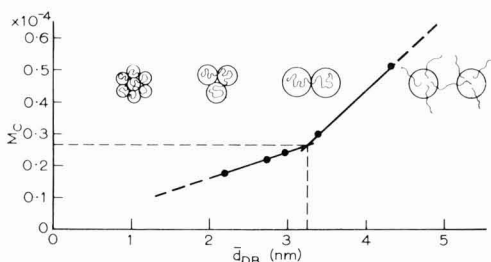


Fig. 15. Dependence of the mean network chain length, M_c, L , from the formal spatial distance between neighbouring unsaturated groups of the microgel

Chemically modified microgels

The only reactive groups which microgels carry after their synthesis are pendant vinyl or acrylic groups. Naturally, their further use is limited largely to copolymerisation with other unsaturated monomers. However, by some chemical reactions the original functional groups may be modified to enable the use of microgels as reactive prepolymer components in polyaddition and polycondensation reactions (Fig. 16). By hydroboration of the original vinyl groups with diborane and subsequent oxidation of the boron-organic intermediate, hydroxyl groups are formed on the microgels. By the reaction of perbenzoic acid with the vinyl groups of microgels, epoxide groups may be introduced.

CHEMICAL MODIFICATION OF REACTIVE MICROGELS FROM 1,4-DVB

R=	REAGENT
	$\text{B}_2\text{H}_6/\text{H}_2\text{O}_2$
	PERBENZOIC ACID
$-\text{COOH}$	$\text{O}_3/\text{H}_2\text{O}_2$
$-\text{CHBr}-\text{CH}_3$	HBr

Fig. 16. Chemical modification of reactive microgels from 1,4-DBV

Another modification enables the application of reactive microgels as a new type of polymeric support. Ozonisation of the vinyl groups and the subsequent oxidation with peracid yields carboxyl modified microgels. The polycarboxylic microgels thus obtained may be used to crosslink in film formation of high solid polyester systems. The acid groups also can easily be transformed into reactive acyl-groups. By their use amides or other nucleophilic groups can be attached to the microgels. This modification opens interesting applications for bio-chemical purposes.

Pigments with polymer cores

In organic coatings a good hiding power is frequently one of the basic requirements. This requirement prohibits the use of organic dyes which are widely used in textile colouring. A very common method of obtaining wear- and wash resistant colouration of textiles is to use reactive dyes which become firmly bound to the fibre. Despite this excellent light stability and leaching resistance, for the reason given above they have very little use in paints.

Recently it has been shown that dyes may be fixed to reactive microgels as a support. By this means new types of organic pigment have been synthesised, which consist of an inert core and a shell of surface-bound dye molecules. As an intermediate, microgels modified with hydrogen bromide have been used. Bromine atoms in the α -position to the phenylene unit may be substituted by aniline-type basic dyes. By this modification, microgels in various colours have been obtained (Fig. 17).

DYE-MODIFIED MICROGELS:

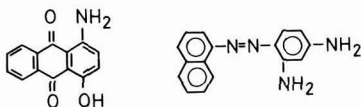
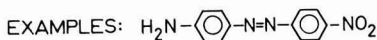
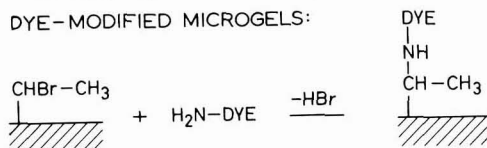


Fig. 17. Dye-modified microgels

Conclusions

Although the formation of microgels has claimed some interest in paint field for many years, it was considered as a peculiarity or a defect rather than as a potential route to useful new paint constituents. In cases where evidence for their existence was provided or, at least, their presence was assumed, very little direct information was available concerning their structure, size and interaction with the surrounding film matrix. The synthesis of reactive microgels from monomers of higher functionality yields well-defined pre-polymers. These microgels may act as multifunctional crosslinking centres in polymerisation reactions, or may be further modified by chemical reaction. The reactive microgels so obtained open some interesting prospects on various possible applications in paint films as reinforcing fillers, the formulation of high solids paints and coloured pigments with a crosslinked polymer core.

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Discussion at Eastbourne Conference

DR G. D. PARFITT said that from his experience he found the electron micrographs of the microgels very interesting because of the evidence they provided of chain formation. He said he was not sure whether this was a peculiarity of this particular electron micrograph but he found this to be very common in flocculation of small carbon particles in hydrocarbon media because of polarisation effects at the surface of the particle.

PROF. FUNKE said that in his slide the particles appear to be on the point of flocculating and this was probably an effect of the method of preparation of the samples for electron microscopy. He said if more precautions had been taken,

such as the exclusion of oxygen, then the particles would remain dispersed, at least in solution.

DR PARFITT asked whether good agreement had been found between the results obtained with the electron microscope and theory when characterising the gels by their surface area and particle size in predicting the critical micelle concentration after which the adsorption became constant.

PROF. FUNKE said that in such a case they had found good agreement between the two, but he would not like to predict that this would be so in all cases. He said the titration method they had used was open to some criticism, and to cover this they had also tried to characterise the microgels by adsorption studies.

DR L. A. O'NEILL asked if the microgels were completely soluble in solvents, such as benzene, and if they were not, how the molecular weight of 100,000 in the viscosity/molecular weight relationship had been obtained. He also asked how stable the microgels were, commenting that with reactive pendant groups present he thought they would be fairly unstable on storage.

PROF. FUNKE said that it was necessary to take some precautions to avoid the microgels reacting, even in a solid state. It was necessary to store the microgels at low temperatures or to keep them in solutions in the absence of oxygen. Regarding the solubility, with the very small microgels the solutions obtained were clear, but with larger particles in the range of 30 to 50 nm, colloidal solutions are obtained with characteristic bluish green or yellowish colours. Prof. Funke said that the measurement of the molecular weight was made using a light scattering technique.

DR L. VALENTINE asked how the rheological characteristics of the microgels varied, particularly in relation to the concentration. He asked to what maximum concentration they could be prepared and for details of their high shear-rate viscosity characteristics.

PROF. FUNKE said that to measure the intrinsic viscosity he had used very dilute samples, but that they had also measured the viscosity of solutions containing up to 20 per cent by weight of microgels and compared them with solutions of polystyrene. Although he could not give any specific figures he felt that a 20 per cent solution of microgels did not significantly affect the viscosity of the solvent. High shear characteristics of reactive microgel solutions had not yet been studied.

DR VALENTINE said that he was more interested in the properties at the preparation stage and would like to know at what sort of maximum concentration it was possible to work and what were the rheological characteristics.

PROF. FUNKE said that by using an emulsion polymerisation technique when preparing the microgels they had used similar reaction conditions to those used in the polymerisation of polystyrene, and it was possible to prepare the microgels in the same amount as when styrene is polymerised under similar conditions. They had used the same emulsifier and the same monomer/water relationship and they had not encountered rheological problems during preparation.

MR F. ARMITAGE said he would be interested to hear what Prof. Funke thought about the possibility of using these materials in a system for radiation curing, and whether he thought that the presence of these particular particles would enhance the performance of films cured in this way as opposed to more conventional types of binder.

PROF. FUNKE said they had not studied this question in the laboratory, but he thought it would be possible to use microgels in radiation curing. He thought that when using radiation curing a very definite homogeneous structure resulted as compared with that obtained for crosslinking reactions initiated by peroxides, and so he thought the reactive microgels, when cured by radiation would have a very well defined structure and result in microgel particles connected by chains between them, and no cross linking taking place between chains.

A study of the effects of thiol modification of saturated alkyd resins on their ease of cure with aminoplasts*

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Summary

Saturated alkyd resins have been prepared using mercapto-acids as modifiers. The thiol groups thus introduced can be reacted with aminoplasts. Model compound experiments have shown that the thiol/aminoplast reaction is much faster than the corresponding alcohol/aminoplast reaction and results in the formation of a thioether linkage.

Two types of modified alkyds have been made: those soluble in organic solvents and those which could be solubilised in water as their amine salts. The modifying agents were mercaptoacetic

acid, 3-mercaptopropionic acid and mercaptosuccinic acid. Thiol levels in the modified products ranged from 0.33 to 1.28 mol kg⁻¹. All give acceptable properties on curing with aminoplasts, and all cure more rapidly or at lower temperatures than their unmodified counterparts. Differences between the mercapto-acids, as modifiers, are relatively small, but on balance mercaptoacetic acid is preferred. Some practical limitations of the modified products—which are still under investigation—have been encountered.

Keywords

Types and classes of coatings and allied products
stoving finish

Raw materials: binders (resins, etc.)

alkyd resin
amino resin
thio resin

Properties, characteristics and conditions primarily associated with:

coatings during application
curing rate

dried or cured films
chemical resistance

Une étude de l'influence qu'exerce la modification par les groupements thioliques des résines alkydes saturées sur leur aptitude à être durcies par les aminoplastes.

Résumé

On a préparé des résines alkydes saturées en se servant des mercaptoacides comme modifiants. On saurait faire réagir les groupements thioliques ci-introduits avec les aminoplastes. Au moyen des expériences entraînant l'emploi des composés-types, on a démontré que la réaction thiol/aminoplaste est plus rapide que la pareille réaction alcool/aminoplaste, et qu'elle aboutit à la formation d'une liaison thioétherique.

On a préparé deux types d'alkydes modifiées: celles solubles aux solvants organiques, et celles dont leurs sels aminiques sont solubles à l'eau. Les agents modifiants étaient les acides mercapto-

acétique, 3-mercaptopropionique et mercaptosuccinique. Dans les résines modifiées la teneur en groupement thiolique se varie à partir de 0,33 à 1,28 mol kg⁻¹. Toutes les résines mettent en évidence les caractéristiques satisfaisantes lors de leur durcissement par les aminoplastes, et toutes sont durcies plus rapidement ou à des températures plus basses que leurs homologues non modifiés. Les différences qui existent entre les mercaptoacides, en tant que modifiants, sont relativement peu importantes, mais en fin de compte on préfère l'acide mercaptoacétique. On a rencontré certains inconvénients dans la pratique des résines modifiées qui restent encore sous investigation.

Eine Untersuchung der Auswirkungen von Thiomodifikationen gesättigter Alkydharze auf die Leichtigkeit ihrer Härtung mit Aminoplasten

Zusammenfassung:

Unter Benutzung von Merkaptoaciden als Modifikatoren wurden Präparate von gesättigten Alkydharzen angefertigt. Die auf diese Weise eingeführten Thioalkoholgruppen können mit Aminoplasten reagieren. Experimente mit Modellverbindungen zeigten, dass die Thiol/Aminoplast Reaktion viel schneller als die entsprechende Alkohol/Aminoplast Reaktion vor sich geht und die Bildung einer Thioätherbindung ergibt.

Zwei Typen modifizierter Alkyde wurden hergestellt: solche, die in organischen Lösungsmitteln löslich sind und solche, die als deren Aminosalze wasserlöslich gemacht werden konnten. Die

Agenzien für die Modifikation waren Merkaptoessigsäure, 3-Mercaptopropionsäure und Merkaptobernsteinsäure. Die Thiolgehalte der modifizierten Produkte lagen zwischen 0,33 bis 1,28 mol kg⁻¹. Nach Härtung mit Aminoplasten besitzen all diese akzeptierbare Eigenschaften und alle härten schneller oder bei niedrigeren Temperaturen, als ihre nichtmodifizierten Vergleichsverbindungen. Die Merkaptoaciden zeigen nur verhältnismässig geringe Unterschiede als Modifikatoren, Merkaptoessigsäure wird jedoch vorgezogen. Grenzen in der praktischen Verwendung der modifizierten Produkte, welche sich noch im Untersuchungsstadium befinden, wurden beobachtet.

Introduction

Refs. 1-5

The thiol group (-SH) offers many attractive synthetic possibilities, because of the comparatively facile and efficient reactions it will undergo by various mechanisms. Polythiols, *i.e.* compounds bearing two or more thiol groups per molecule, are thus quite easy to convert into polymeric structures which are crosslinked. This can be accomplished by

means of a second polyfunctional component with which the thiol groups will react (for example, polyunsaturated compounds or polyepoxides) or reagents can be used (for example, lead dioxide) which will cause the thiol groups to become oxidised to form disulfide crosslinks.

Thiol-terminated polymers have been known for fifty years^{1,2}. They became the basis for a type of mastic, which is still widely used. Other uses of varying importance include

*Paper presented at the Association's Biennial Conference held at the Grand Hotel, Eastbourne, Sussex from 16-19 June 1977.

curing agents for epoxy resins³, UV-curable wire enamels⁴ and textile treatment—particularly wool shrinkproofing⁵.

In the present work certain polythiols have been investigated as components of potentially fast-curing industrial coating resins. The resins have been prepared in such a way as to give molecular structures akin to those of conventional saturated alkyd resins, but modified to contain thiol groups. These polythiols are termed "thiol-modified saturated alkyd resins". Their ability to cure with aminoplasts has been examined, in the hope that such systems would need lower temperatures or shorter times of cure compared to analogous coatings based upon unmodified alkyds. This is considered to be a worthwhile objective which could lead to substantial energy savings.

Conventional saturated alkyd resins are low molecular weight, highly branched polyesters with terminal hydroxyl and carboxyl groups. The hydroxyl groups predominate, and it is their reaction with aminoplasts to form ether linkages which is the principle means of crosslinking. This can be represented as follows:



where $\sim\sim\sim$ represents an alkyd residue and R can be H or CH_3 in methylated aminoplasts, and H or C_4H_9 in butylated aminoplasts. The curing of films of alkyd/aminoplast blends is normally accomplished by heating.

Fast or low-temperature curing systems are also well established, but frequently cannot be used because of pot life restrictions or side effects arising from the use of strong acid catalysts.

New alkyd resins based on the chemistry now described could provide an extra dimension in the formulation of fast curing systems. It is in this context that the present report on the effects of thiol modification on the rate of cure of saturated alkyd is presented.

Experimental methods

Refs. 6-8

Materials used

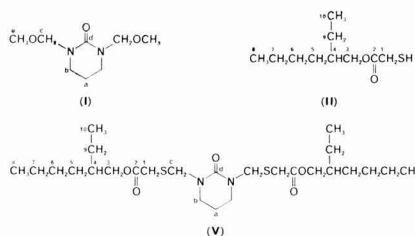
Model compounds. Tetrahydro-1,3-bis(methoxymethyl)-2(1*H*)-pyrimidinone (I) was prepared using a method described by Petersen and Reuther⁶, with minor modifications. Properties: b_{3-5} 134.6°C, m.p.t. 47-50°C (lit.⁶ 48-50°C), analysis ($\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3$): found (calculated) C 50.81 (51.05), H 8.43 (8.57), N 14.63 (14.88), O 25.77 (25.50). Purity (>99 per cent) was confirmed by GLC, and structure by ^{13}C NMR using authentic tetrahydro-3,5-bis(methoxymethyl)-4*H*-

1,3,5-oxadiazine-4—one for comparison. Signal assignments for (I) are given in Table 1.

Table 1
 ^{13}C NMR chemical shifts (ppm) for model compounds (I) and (II) and their reaction product (V).

Carbon*	Compound	
	(I)	(II)
a	21.7	21.5
b	44.4	44.6
c	78.3	51.0
d	155.3	155.1
e	54.7	—
1	—	26.0
2	—	170.8
3	—	67.2
4	—	38.8
5	—	30.3
6	—	28.9
7	—	22.9
8	—	14.0
9	—	23.6
10	—	11.0

*Carbon atoms are identified in the following structural formulae



2-Ethylhexyl mercaptoacetate (II) was obtained commercially, washed with NaHCO_3 solution, then repeatedly with distilled water and finally distilled. Properties: $b_{1,5}$ 100°C, thiol value 4.98 mol/kg (calcd. 4.90), analysis ($\text{C}_{10}\text{H}_{20}\text{O}_2\text{S}$): found (calcd.) C 58.93 (58.79), H 9.92 (9.87), O 15.64 (15.66), S 15.53 (15.70). Purity (GLC) >99 per cent. ^{13}C NMR data is given in Table 1.

n-Butyl glycolate (III) was prepared by refluxing *n*-butanol (2.5 mol), 66 per cent aq. glycolic acid (0.5 mol) and *p*-toluenesulfonic acid (0.005 mol) with 150 ml toluene, water being removed via a separator. After 4 hours the reaction mixture was cooled, washed with aq. KHCO_3 , dried over Na_2SO_4 , filtered and distilled. Properties: $b_{2,5}$ 64°C, n_D^{20} 1.4245, saponification value 7.61 mol/kg (calcd. 7.58), hydroxyl value 7.61 mol/kg (calcd. 7.58), analysis ($\text{C}_6\text{H}_{12}\text{O}_3$): found (calcd.) C 54.54 (54.53), H 9.11 (9.15). Purity (GLC) >98 per cent. Structure confirmed by ^{13}C NMR (Table 2).

Table 2
 ^{13}C NMR chemical shifts (ppm) for *n*-butyl glycolate (III) and related compounds

Compound	Chemical shift					
	1	2	3	4	5	6
$\text{HOCH}_2^1\text{COOH}^2$	60.2	174.8				
$\text{HSCH}_2^1\text{COOH}^2$	26.2	172.0				
$\text{HOCH}_2^1\text{COOCH}_2^3\text{CH}_2^4\text{CH}_2^5\text{CH}_3^6$ (III)	59.9	172.7	63.7	30.5	18.7	13.6
$\text{HSCH}_2^1\text{COOCH}_2^3\text{CH}_2^4\text{CH}_2^5\text{CH}_3^6$	25.8	170.7	64.6	30.4	18.8	13.6

Reagents. Laboratory or analytical reagent grade chemicals were used in all analyses and tests except the gelation tests using *N,N,N',N'*-tetra-*n*-butyl thiuram disulfide (TBUT). This is a rubber accelerator obtained from Robinson Bros. Ltd as Robac TBUT.

Alkyd resins (starting materials). Pentaerythritol (m.pt 263-265°C) was from B.D.H. Ltd and said to contain only traces of dipentaerythritol. Cardura "E", the glycidyl ester of C₉-C₁₁ branched chain fatty acids, was from Shell Chemicals Ltd. Mercapto-acids were from Robinson Bros. Ltd: mercaptoacetic and 3-mercaptopropionic acids >95 per cent pure (thiol value), mercaptosuccinic acid (m.pt 153-154°C) >97 per cent pure (thiol value). Coconut oil fatty acids were "white distilled" grade from Victor Wolf Ltd; acid value 4.82 mol/kg, iodine value 8 cg I₂/g. Other polyols, acids, anhydrides and solvents were from commercial sources and used as received.

Proprietary alkyd and aminoplast resins. A short oil saturated alkyd resin with composition close to that of the experimental products (S. series) was chosen for purposes of comparison. This resin is designated S.8 and its composition (calculated from the literature) and properties are given in Table 3.

Table 3
Composition and properties of "solvent-soluble" alkyd resins (S series)

Alkyd resin	Composition ^a (mol)							Properties		
	PA	COFA	GLYC	PE	MAA	3MPA	MSA	Viscosity ^b Pa s	Acid value ^c mol/kg	Thiol value ^c mol/kg
S.1	1.00	0.44	0.90	0.04	—	—	—	0.52	0.42	—
S.2	1.00	0.44	0.84	0.08	—	—	—	1.39	0.46	—
S.3	1.00	0.44	0.79	0.16	0.16	—	—	0.54	0.38	0.35
S.4	1.00	0.44	0.63	0.32	0.32	—	—	0.64	0.49	0.75
S.5	1.00	0.44	0.48	0.48	0.48	—	—	1.82	0.40	1.01
S.6	1.00	0.44	0.48	0.48	—	0.48	—	0.20	0.47	1.28
S.7	1.00	0.84	2.00	—	—	—	0.91	3.94	0.56	1.18
S.8	1.00	0.48	0.92	—	—	—	—	0.98	0.13	—

^aPA = phthalic anhydride, COFA = coconut oil fatty acids, GLYC = glycerol
PE = pentaerythritol, MAA = mercaptoacetic acid, 3MPA = 3-mercaptopropionic acid
MSA = mercaptosuccinic acid.

^b50% xylene solutions.

^cExpressed on 100 per cent resin.

A highly methylated melamine-formaldehyde (MF) resin was used. It has a low molecular weight (about 70 per cent monomeric with respect to melamine, determined by GPC) and is >97 per cent non-volatile. The M:F:CH₃ ratio is approximately 1:6:4. It is infinitely dilutable with water. This resin is designated A.1 for present purposes.

A general purpose *n*-butylated MF resin was also used. It is a 60 per cent solution, in *n*-butanol, of viscosity 0.9-1.7 Pa s. 5g tolerate 25-40ml of white spirit or >100ml of industrial ethanol. This resin is designated A.2.

Model compound experiments

Two series of experiments were carried out:

(a) reactions between the model compounds without solvent or catalyst, the mixtures being heated in an oil bath at

120°C for varying periods, in sealed glass tubes under nitrogen,

(b) reactions in toluene (*ca.* 6 per cent solutions) with benzoic acid as catalyst, the mixtures being stirred and held thermostatically at 100 ± 1°C and sampled at intervals. In both cases, 1:2 molar ratios of (I) to (II) or (III) were taken. Samples required for later analysis were kept at -80°C.

Gel permeation chromatography (GPC). Samples were diluted to 5 per cent with *N,N*-dimethyl formamide (DMF) and 100 μ l portions analysed on a column packed with Fractogel OR 2000 (a lightly crosslinked polyvinyl acetate supplied by E. Merck of Darmstadt) with DMF as eluant (0.5 ml/min, 20°C) and a differential refractometer detector.

Gas-liquid chromatography (GLC). Toluene solutions of model compounds, containing eicosane or octadecane as internal standard, were analysed using a Varian AEROGRAPH 1860-4 gas chromatograph with flame ionisation detector and electronic integration. Column packing was 3 per cent Dextril on AW DCMS Chromosorb W (100-120) for reaction mixtures (I) and (II) and 10 per cent Dextril on the same

support for (I) and (III). Programmed column temperatures were: 100-160°C at 8°C/min, 160-320°C at 20°C/min and then isothermal at 320°C.

Thiol value. Reaction mixtures of (I) and (II) in toluene were analysed for thiol content at frequent intervals. Each sample (2-5g) was weighed into a mixture of isopropanol (150ml) and water (15ml) and immediately titrated with aqueous 0.05N iodine in potassium iodide solution, until a faint permanent yellow end point was obtained.

¹³C nuclear magnetic resonance (NMR). 30 per cent solutions of the compounds were prepared in DMSO containing 20 per cent v/v DMSO-d₆ (for field frequency stabilisation) and tetramethyl silane (reference). Spectra were recorded on a Varian CFT-20 spectrometer operating at 20 MHz and a spectral width of 4000Hz (200ppm).

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Methods of preparation of alkyd resins

S. Series. The compositions are given in Table 3. The products (except for the proprietary alkyd S.8) were made as follows:

Polyols, acids, phthalic anhydride and 10 per cent of their weight of xylene, were melted under nitrogen in a 1 litre flange flask fitted with an anchor stirrer, water separator and reflux condenser, and heated with an electric mantle. The reaction mixture was heated gradually to 175–180°C, allowing water to collect in the separator. When the acid value had fallen to approximately 0.5 mol/kg, heating was discontinued and the resin was cooled, diluted to 50 per cent solids with xylene, and filtered.

W. Series. These resins were made by a three-stage process published by Amoco Chemicals⁷. The composition of each stage is given in Table 6. Using apparatus as described for the *S. series*, the initial charge was heated under nitrogen to 180°C and held until the epoxy value had fallen below 0.018 mol/kg. The reaction mixture was then cooled to 130°C and the second stage addition made together with xylene to assist water separation. The reaction mixture was heated gradually to 230°C, allowing water to separate, and held until the acid value had fallen to 0.4 mol/kg. After cooling to 170°C, the remaining anhydride was added and the reaction mixture heated to 180°C to a final acid value of 0.70–0.85 mol/kg. Xylene was then removed under vacuum and the resin cooled and diluted to 70 per cent solids with 2-*n*-butoxyethanol and filtered.

Methods of testing alkyd resin solutions

Acid value. A sample containing approximately 0.001 mol of acid was accurately weighed and dissolved in 100 ml of 2-ethoxyethanol. 10 ml 2.5 per cent potassium chloride solution were added and the solution titrated with 0.1N sodium hydroxide (aq.) using a pH meter and taking the end point as the point of inflexion of the pH *v.* ml of titrant curve (approx. pH 9). Acid value = titre \times 0.1/W mol/kg, where W = sample weight in grammes.

Epoxy value. A sample containing approximately 0.001 mol of epoxy was accurately weighed and dissolved in 25 ml glacial acetic acid. 2.5g tetraethylammonium bromide and 2 drops of Crystal Violet indicator were added and the mixture stirred until clear. The solution was titrated with 0.1N perchloric acid to an apple green end point. The procedure was repeated in the absence of a sample to obtain a blank. Epoxy content = 0.1 (titre-blank)/W mol/kg where W = sample weight in grammes.

Thiol value. A sample containing approximately 0.001 mol of thiol was dissolved in 150 ml peroxide-free 2-*n*-butoxyethanol and 25 ml distilled water added. The solution was titrated with 0.1N iodine solution to a faint permanent yellow end point. Thiol value = titre \times 0.1/W mol/kg, where W = sample weight in grammes.

Viscosity. Brookfield Model LVT, 25°C.

Solids content. 1g samples stoved 30 minutes at 150°C.

Gelation tests. Some of the thiol-containing resins were tested for their ability to gel, using two distinct methods.

- (1) Gelation with tetrabutyl thiuram disulfide (TBUT). 5.00g resin were thoroughly mixed with 0.52g TBUT

and allowed to stand at 30 \pm 2°C. The condition of the mixture was observed at intervals.

- (2) Gelation with dimethyl sulfoxide (DMSO). 5.00g resin were mixed thoroughly with 0.20g DMSO in a glass tube, which was then placed in an oil bath at 140°C. The condition of the mixture was observed at 5 minute intervals.

Preparation of paints

S. Series alkyd/aminoplasts. The following formulations (a) and (b) were prepared by dispersing the pigment in the alkyd resin and adding the aminoplast and solvents after dispersion.

	(a)	(b)
Alkyd resin (S.1 to S.8), 50 per cent solution	64.30	55.96
Aminoplast (A.1 (methylated MF) (A.2 (butylated MF))	8.04 —	— 19.98
TiO ₂ (RHD4—Tioxide Int. Ltd.)	27.66	24.06
Xylene: <i>n</i> -butanol 2:1 by weight as required to reduce viscosity to 0.5–1.0 Pa s		
Pigment: binder ratio	0.69:1	0.60:1
Alkyd: MF ratio	80:20	70:30
Solids of paint	60–65%	60–65%

W. Series alkyd/aminoplasts. Formulation (c) was prepared as follows:

	(c)
Alkyd resin (W.1 to W.4), 70% solution	34.18
Aminoplast A.1 (methylated MF)	4.20
Fluorochemical additive (FC 430—3M's Ltd.)	0.03
TiO ₂ (RCR6—Tioxide Int. Ltd.)	16.73

The above mixture was milled on a 3-roll mill at 1.03 MPa and then the following added:

N,N—Diethylaminoethanol	2.19
De-ionised water	41.13
Pigment: binder ratio	0.6:1
Alkyd: MF ratio	85:15
COOH: NR ₃ ratio	1:1
Solids of paint	45%

Methods of evaluating cured films

Curing speed of clear films of alkyd/aminoplast blends. Mixtures were unpigmented versions of the paint formulations. 50 μ m thick films on tinplate were stoved for periods varying between 5 minutes and 1 hour (occasionally longer) at 90–200°C. The state of cure was assessed by rubbing the films with cotton wool soaked in xylene or acetone (10 to-and-fro rubs). The coating was rated as cured when the solvent did not significantly soften the film.

Assessment of pigmented coating. 50 μ m thick films were applied using a wire-wound application bar. After stoving, coated panels were conditioned at 21°C and 65 per cent relative humidity before testing.

Hardness: Persoz method (ISO.1522—1973 E) on glass plates.

Gloss. ASTM D523 at 60° angle relative to the appropriate unmodified alkyd resins S.1 or W.1 as 100 per cent standards.

Mandel bend test: BS 3900 Part E1 using the type 1 apparatus; films on 0.25 mm tinplate.

Adhesion: Epprecht Twist-o-meter method⁸, using films on chromate treated aluminium.

Erichsen cupping test: ISO.1520—1974 E using films on chromate treated 0.7 mm soft aluminium.

Staining tests: Tomato ketchup, brown sauce, lipstick and brown boot polish were applied to portions of white pigmented coatings and left for 48 hours. The panels were then scrubbed clean with soapy water. The boot polish needed removal with methyl ethyl ketone. Any residual staining marks were noted.

Exterior durability: Coated panels exposed at an inclination of 45°, facing South. Assessed monthly for chalking, discolouration and blistering.

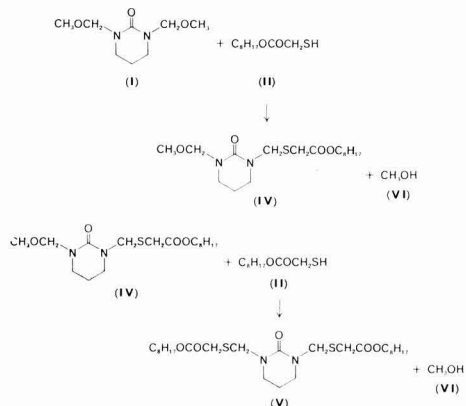
Results

Ref. 9

Model compound experiments

(a) Uncatalysed, no solvent

Fig. 1 shows the results of GPC analysis of reaction mixtures of (I) and (II) heated for varying periods of time at 120°C. The analyses show the gradual formation of three products of reaction, (IV), (V) and (VI), followed by the disappearance of one of these, (IV).



The roman numerals indicating the above compounds are shown in Fig. 1 assigned to the appropriate peaks. Methanol, having a refractive index less than the eluant (DMF) appears as a "negative" peak. Fig. 1 (f) shows that the reaction goes nearly to completion. Only a small amount of slightly higher molecular weight material in the region of 40 counts can be seen. The product (V), after vacuum treatment to remove methanol, was examined by ¹³C NMR. With the help of known substances, all signals were accounted for and assigned unequivocally to the carbon atoms of (V) as shown in Table 1.

Fig. 2 shows the GPC traces of the reaction between (I) and *n*-butyl glycolate (III) under the same conditions as the above thiol reaction. It is evident that only a slight degree of reaction occurs. The experiment was repeated in an open tube placed in an oil bath at 120°C, in order to allow methanol which might be inhibiting the reaction, to escape. The

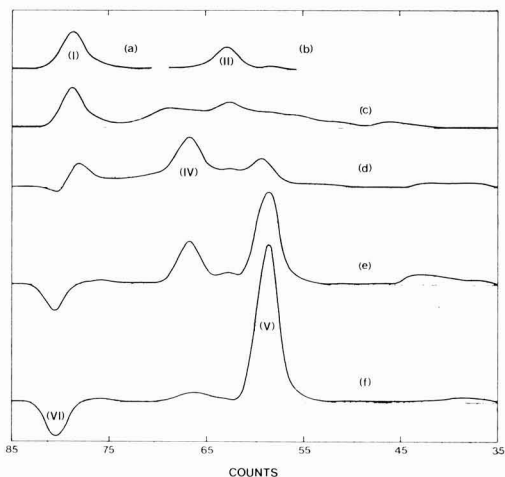


Fig. 1. GPC: (a) model aminoplast (I), (b) model thiol compound (II); (c)–(f) 1 mol (I) + 2 mol (II) reacted, (c) 5 min. at 40°C, (d) 2 min. at 120°C, (e) 5 min. at 120°C, (f) 30 min. at 120°C

resulting GPC trace was identical to that obtained in the sealed tube (Fig. 2 (c)). This experiment shows clearly that the alcohol reaction is much slower and less efficient than the corresponding thiol compound reaction. This result is in accordance with expectations, since thiols are well known to be much more powerful nucleophiles than alcohols.

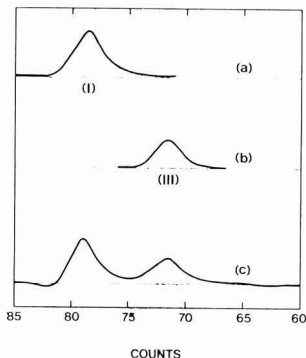


Fig. 2. GPC: (a) model aminoplast (I), (b) model hydroxyl compound (III); (c) 1 mol (I) + 2 mol (III) reacted 30 min. at 120°C

(b) Catalysed, toluene solvent

Fig. 3 shows the effect of benzoic acid on the extent of the reaction between (I) and (II) after 1 hour at 100°C. In subsequent experiments the benzoic acid concentration was maintained at 0.07 mol/kg, both to give convenient reaction times, and also because at this level the thiol:acid molar ratio was approximately the same as that in the fastest curing experimental alkyl resin S.5 (Tables 3 and 7).

The variation of degree of reaction with time for thiol (II) and alcohol (III) reactions with the model aminoplast (I) is shown in Fig. 4. The curve obtained for the thiol reaction, measured iodometrically, is in fair agreement with the corresponding GLC determinations and both show that over 80 per cent reaction is obtained after 2 hours at 100°C. An induction period of 10 to 15 minutes is evident. This phenomenon has been previously reported by Petersen in

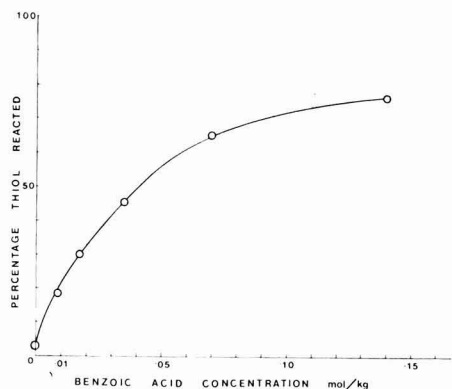


Fig. 3. Catalytic effect of benzoic acid on reaction between model aminoplast (I) and model thiol compound (II), (0.2M in toluene), after 60 min. at 100°C

analogous studies⁹. The GLC traces (not reproduced here) also showed the appearance and disappearance of the monothioether (IV) and the formation of the bis-thioether (V) in a manner very similar to that observed in the GPC study (Fig. 1). Fig. 4 also shows the reaction of (I) with the alcohol (III), determined by GLC. Less than 10 per cent reaction occurs after 2 hours.

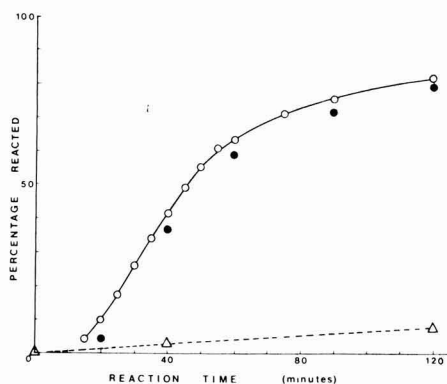


Fig. 4. Model compounds (0.2M in toluene) reacted at 100°C. O and solid line = (I) + (II), based on thiol titration of residual (II). ● = (I) + (III), based on GLC determination of residual (II). △ and dotted line = (I) + (III), based on GLC determination of residual (III).

This result shows very clearly that, under acid-catalysed conditions, the alcohol (III) again reacts much less readily than the thiol (II) with the aminoplast model compound (I).

Modified alkyd resins

Two series of alkyd resins have been studied, those which are soluble only in organic solvents, designated S series, and those which, as their amine salts, are soluble in water, designated W series.

Table 3 shows the composition and properties of the S series. The formulation principle employed with S.3 to S.6 was to replace part of the glycerol in an unmodified alkyd by an equimolar mixture of mercapto-acid and pentaerythritol. With mercaptoacetic acid, this procedure gave modified products of higher acid value and/or viscosity than the unmodified products. Hence the control alkyds had to be re-formulated with some pentaerythritol in order to give products which could be used for a fair comparison.

Calculation shows that the thiol values recorded in Table 3 are in some cases rather less than expected. This data is summarised in Table 4, where measured sulfur contents are shown in comparison with values calculated from starting materials and from thiol determinations. These results suggest that very little sulfur is lost to the system under the conditions of preparation of the resins.

The fact that thiol modification with mercaptoacetic acid gave higher viscosities and lower thiol values (78 per cent) than expected suggests that a degree of reaction of the thiol groups may be occurring, e.g. esterification, forming bridging

$$\begin{array}{c} \text{O} \\ || \\ \text{—S—C—} \end{array}$$

linkages in the resin. In the case of S.6, where 3-mercaptopropionic acid is used, the retention of thiol value is higher (92 per cent) and the resin viscosity is relatively low, so presumably much less reaction of thiol groups has occurred. However, the number of results available is not considered sufficient to prove that this difference in behaviour is significant.

The formulation of S.7, which contains mercaptosuccinic acid, necessarily differs in several respects from the S.1 to S.6 series, on account of the two carboxylic acid groups in the modifying mercapto-acid. In this case also, the thiol value is lower than expected (77 per cent), presumably through side reactions such as esterification.

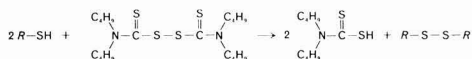
Several tests were made of the ability of the modified alkyds to gel, and the results are shown in Table 5. These tests were carried out for two reasons. Firstly, to demonstrate that the resins are polyfunctional with respect to thiol. All

Table 4
Sulfur contents of alkyd resins (S series) modified with various mercapto-acids

Alkyd resin (modifying acid)	Thiol value mol/kg	% S (by analysis)	% S (calculated from starting materials)	% S (calculated from thiol value)	Thiol S as % of total S (analysed)
S.5 (mercaptoacetic)	1.01	4.12	4.27	3.23	78.4
S.6 (3-mercaptopropionic)	1.28	4.44	4.19	4.10	92.3
S.7 (mercaptosuccinic)	1.18	4.88	5.01	3.78	77.5

of the modified products in the S series could in fact be gelled. Secondly, the tests show that the gelation time is directly associated with the level of modification. Tests such as these could conceivably be of value in characterising products for control purposes to ensure consistency of performance from batch to batch. The reactions believed to be taking place in these tests are shown below. The case of R—SH representing a particular —SH group on an alkyd residue R— is depicted.

TBUT gelation



DMSO gelation



Table 5
Gelation testing of thiol-modified S series alkyd resins

Alkyd	Thiol value mol/kg	TBUT gel time	DMSO gel time
S.3	0.35	>20 hr	40 min.
S.4	0.75	4.5 min.	20 min.
S.5	1.01	3.5 min.	10 min.

The composition and properties of the W series of alkyd resins are summarised in Table 6. The formulation principle observed here is the replacement of neopentyl glycol in the control resin W.1 by successively increasing equimolar amounts of mercaptoacetic acid and glycerol. In this series the thiol values obtained on the final products W.2–W.4 are in the region of 65 per cent of their expected values, but viscosities are not significantly different from the control resin W.1. The explanation here may be that some of the thiol groups are reacting with the trimellitic anhydride in the last stage of the reaction, thus forming only pendant groups on the resin molecule, which would not cause the viscosity to increase.

Curing speed

In this study the curing speed, or rate of cure, has been based on the measurement of the solvent resistance of clear films of alkyd/aminoplast blends after stoving for various periods of time. Using this method, consistent comparative results were conveniently obtained. It is realised, however, that the curing conditions required to achieve a high degree of solvent resistance are not necessarily those which would be best for a practically useful coating.

The results obtained with the S series of alkyds are given in Table 7. The results show:

Table 6
Composition and properties of "water-soluble" alkyd resins (W series)

Alkyd resin	Composition (mol)							Properties			
	Initial charge ^a			Second stage additions ^b				Final stage addn. TMA	Viscosity ^c Pa s	Acid value ^d mol/kg	Thiol value ^d mol/kg
	AD	CE	IPA	NPG	MAA	GLYC	TMA				
W.1	0.40	1.00	1.20	1.00	—	—	0.17	0.17	6.9	0.69	—
W.2	0.40	1.00	1.20	0.67	0.33	0.33	0.17	0.17	6.7	0.78	0.33
W.3	0.40	1.00	1.20	0.45	0.50	0.50	0.17	0.17	9.9	0.78	0.53
W.4	0.40	1.00	1.20	0.20	0.75	0.75	—	0.34	3.6	0.86	0.73

^a AD = adipic acid, CE = Cardura "E", IPA = isophthalic acid (*i.e.* 1,3-benzene dicarboxylic acid).

^b NPG = neopentyl glycol (*i.e.* 2-hydroxymethyl-2-methylpropan-1-ol), MAA = mercaptoacetic acid, GLYC = glycerol, TMA = trimellitic anhydride (*i.e.* 1,2,4-benzene tricarboxylic acid cyclic 1,2-anhydride).

^c 70 per cent in 2-*n*-butoxyethanol.

^d Expressed on 100 per cent resin.

Table 7
Curing speed, at various temperatures, of clear films of S series alkyd/aminoplast blends, measured by solvent resistance

Alkyd ^a / aminoplast ^b	Weight ratio ^c	Cure time (minutes) to resist xylene rub							Cure time (minutes) to resist acetone rub						
		75°C	90°C	110°C	130°C	150°C	175°C	200°C	90°C	110°C	130°C	150°C	175°C	200°C	
S.1/A.1	80/20							>60							
S.1/A.2	70/30							>60							>60
S.2/A.1	80/20							>60							>60
S.2/A.2	70/30							>60							>60
S.3/A.1	80/20					>60	10	5							
S.3/A.2	70/30	>250	45	10	10	10	5	5			>60	10	5		
S.4/A.1	80/20		>60	45	20	10	5	5							
S.4/A.2	70/30	>250	45	10	10	5	5	5			>60	60	20	10	5
S.5/A.1	80/20		60	45	20	10	5	5							
S.5/A.2	70/30	150	30	10	10	5	5	5			60	30	20	5	
S.6/A.1	80/20		>60	45	20	20	10	5							
S.6/A.2	70/30	>250	45	20	10	5	5	5			60	30	10	10	5
S.7/A.1	80/20		>60	30	20	10	5	5							
S.7/A.2	70/30	>250	45	10	10	10	5	5			>60	45	20	10	5
S.8/A.1	80/20							>60							>60
S.8/A.2	70/30							>60							>60

^aAlkyds described in Table 3. ^bAminoplast A.1 is a methylated MF resin. Aminoplast A.2 is a butylated MF resin.

^cWeight ratios based on non-volatile contents of resins.

- (1) All the modified alkyds (S.3–S.7) cured much more rapidly at any given temperature than the control unmodified alkyds (S.1, S.2 and S.8).
- (2) Alkyd resin blends with the butylated MF resin (A.2) cured more rapidly than blends with the methylated MF resin (A.1).
- (3) The rate of cure depended on the level of thiol present. Thus the rate in order of decreasing mercaptoacetic acid modification was S.5 > S.4 > S.3.
- (4) The type of thiol used was evidently not a major factor affecting cure speed, but mercaptoacetic acid (S.5) appeared slightly more effective than 3-mercaptopropionic acid (S.6) which in turn appeared slightly more effective than mercaptosuccinic acid (S.7). However, differences in viscosity and resin composition, which clearly will influence apparent cure speed, should be taken into account when assessing these results. Thus S.7 has the highest viscosity in the S series, but a rather different composition to S.5 and S.6, so that no firm conclusion can be drawn in this case. S.6 on the other hand has the lowest viscosity in the S series, and might, therefore, be equally fast or faster than a mercaptoacetic-modified product of equal viscosity. Such differences, however, are small compared with those between modified and unmodified alkyds.

Curing speed was also monitored by measurements of the hardness of films (S series/A.2) after curing for various

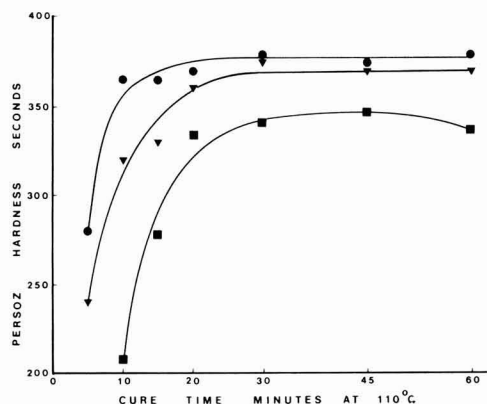


Fig. 5. Hardness of clear films of S series alkyd/aminoplast A.2 after curing at 110°C. ■ = S.1 (unmodified); ▼ = S.3 (thiol-modified); ● = S.5 (thiol-modified).

periods of time at 110°C. The results are shown graphically in Fig. 5. It can be seen that the two modified resins S.3 and S.5 hardened more rapidly than the unmodified resin S.1. Furthermore, the hardness obtained with S.3 and S.5 levelled out at a significantly higher level than that of S.1. Stoving S.1 for 120 minutes at 110°C even lowered the hardness to 275 seconds, thus confirming the trend shown on the graph at 60 minutes.

In the case of the W series (Table 8), the results show;

- (1) A definite but much less pronounced difference between modified and unmodified alkyds in favour of the modified products.
- (2) The rate of cure again depended on the level of thiol present. Thus the rate, in order of decreasing mercaptoacetic acid modification, was W.4 > W.3 > W.2 > W.1 (unmodified).

Table 8
Curing speed, at various temperatures, of clear films of W series alkyd/aminoplast A.1 85/15 blends, measured by solvent resistance.

Alkyd ^a / aminoplast ^b	Cure time (minutes) to resist xylene rub			Cure time (minutes) to resist acetone rub		
	115°C	130°C	150°C	115°C	130°C	150°C
W.1/A.1	>60	30		>60	50	
W.2/A.1	>60	50	10	>60	>60	30
W.3/A.1	60	20	5	>60	40	15
W.4/A.1	30	20	5	>60	40	10

^aAlkyds described in Table 6.

^bAminoplast A.1 is a methylated MF resin.

Properties of pigmented films

S series. The results of evaluating paint films of the S series alkyd/aminoplast blends are given in Tables 9 and 10. Cure schedules were chosen which were expected to be adequate, based on the known cure speeds. However, the results are not necessarily the best which could be obtained.

All the modified S series alkyd/aminoplast A.1 systems (Table 9) were given much shorter cure times at 175°C (15 or 30 minutes) than the unmodified systems (90 minutes). The modified systems gave results generally comparable to those of the unmodified systems, but the more highly modified products S.5, S.6 and S.7 were somewhat less flexible at equal (S.6) or less (S.5 and S.7) hardness.

Table 9
Properties of pigmented films of S series alkyd/aminoplast A.1 80/20 blends

Alkyd ^a / aminoplast ^b	Cure schedule	Properties					Relative gloss
		Persoz hardness s	Mandel bend test mm	Erichsen cupping test mm	Reverse impact 1.5 mm		
S.1/A.1	90' @ 175°C	255	1.5	4.7	Pass	100	
S.2/A.1	90' @ 175°C	280	1.5	5.0	Pass	88	
S.3/A.1	30' @ 175°C	245	1.5	5.0	Pass	86	
S.4/A.1	15' @ 175°C	244	1.5	5.2	Pass	>100	
S.5/A.1	15' @ 175°C	242	3	3.5	Fail	97	
S.6/A.1	30' @ 175°C	264	3	4.5	Fail	110	
S.7/A.1	15' @ 175°C	204	3	3.4	Fail	105	
S.8/A.1	90' @ 175°C	257	1.5	5.0	Pass	75	

^aAlkyds described in Table 3.

^bAminoplast A.1 is a methylated MF resin.

Table 10
Properties of pigmented films of S series alkyd/aminoplast A.2 70/30 blends

Alkyd ^a / aminoplast ^b	Cure schedule	Properties				
		Persoz hardness s	Mandrel bend test mm	Erichsen cupping test mm	Adhesion to aluminium M Pa	Relative gloss
S.1/A.2	60' @ 200°C	250	6	2.5	60	100
S.2/A.2	60' @ 200°C	302	9	3.0	65	99
S.3/A.2	12' @ 150°C	231	6	4.5	68	99
S.4/A.2	12' @ 150°C	263	9	2.5	70	100
S.5/A.2	8' @ 150°C	295	9	2.5	68	102
S.6/A.2	12' @ 150°C	245	6	2.9	64	100
S.7/A.2	12' @ 150°C	220	7.5	2.3	67	99
S.8/A.2	60' @ 200°C	246	3	4.0	65	85

^aAlkyds described in Table 3.

^bAminoplast A.2 is a butylated MF resin.

In the S alkyd/A.2 systems (Table 10) the modified alkyd systems were cured at 150°C for 8 or 12 minutes compared with 200°C for 60 minutes for the unmodified alkyd systems. Again the properties of the two groups were broadly similar, differences being less than in the S alkyd/A.1 series. This may be a consequence of the more comparable degree of cure arising from the choice of cure schedules for the modified and unmodified products in the case of the S alkyd/A.2 series.

The stain resistance of all resins in the S series was satisfactory (cure conditions shown in Table 10) except in the case of the brown boot polish stain. In this case all the modified resins S.3 to S.7 were satisfactory (no stain) but the three unmodified resins stained; S.1 and S.2 moderately, S.8 slightly.

W series. The results of testing paint films of the W series alkyd/A.1 blends are given in Table 11. The control alkyd system (W.1) was cured at 180°C for 60 minutes, whereas the three modified systems (W.2, W.3 and W.4) were cured at 135°C for 50 minutes. This series of tests showed that the difference between the modified and unmodified products was very slight. The modified products were, however, marginally less flexible although they showed an interesting trend towards increasing hardness with increasing degree of thiol modification.

Paint films cured as shown in Table 11 were exposed to weathering with the following results:

W.1 (unmodified)	Unchanged after 18 months.
W.2 (modified)	Very slightly chalking after 18 months.
W.3 (modified)	Unchanged after 18 months.
W.4 (modified)	Unchanged after 12 months (test continuing).

None of the panels showed any tendency towards yellowing.

Discussion

Refs. 9-13

The model compound studies reported here were carried out in order to provide a firm basis for interpreting the fast-curing behaviour of the thiol-modified alkyd resins. It is interesting to note that a related series of reactions was carried out by Petersen⁹ in which *n*-dodecane thiol was reacted with a variety of textile aminoplasts in order to compare their reactivities. In the present experiments the authors used an aminoplast model compound (I) and compared the reactivity of a thiol (II) and an alcohol (III) towards this aminoplast. This compound (I) is, in fact, included among the many aminoplast substances which Petersen reacted with *n*-dodecane thiol. The thiol-modified alkyd resins of the present study are, however, mercapto-acid esters, and of the ones studied, mercaptoacetates, have been shown to be particularly effective. A mercaptoacetate has, therefore, been chosen as the model compound thiol (II);

Table 11
Properties of pigmented films of W series alkyd/aminoplast A.1 85/15 blends

Alkyd ^a / aminoplast ^b	Cure schedule	Properties					
		Persoz hardness s	Mandrel (1.5 mm bend)	Erichsen cupping test mm	Reverse impact mm	Adhesion to aluminium M Pa	Relative gloss
W.1/A.1	60' @ 180°C	200	Pass	9	4.5	35	100
W.2/A.1	50' @ 135°C	205	Pass	6.5	4	40	104
W.3/A.1	50' @ 135°C	220	Pass	8	4	40	105
W.4/A.1	50' @ 135°C	230	Pass	6	4	40	105

^aAlkyds described in Table 6.

^bAminoplast A.1 is a methylated MF resin.

the model hydroxyl compound (III) is a closely related oxygen analogue.

The results of the model compound studies show conclusively that the mercaptoacetate thiol group is far more reactive than the corresponding hydroxyl group. The reaction conditions in these studies necessarily differ from those which would prevail in a practical coating, but the two series of experiments (a) and (b) give essentially the same results under widely varying conditions *viz.* (a) uncatalysed, no solvent, 120°C, sealed tube (b) catalysed, toluene solutions, 100°C, open to atmosphere. The concentrations in series (a) were 3.3 and 4.4 mol/kg (thiol and hydroxyl respectively) and in series (b) 0.2 mol/kg. The most significant difference between the conditions in the model compound experiments and a practical coating concerns the relative ease of elimination of the reaction product methanol (IV). In series (a) the reactants were generally in sealed tubes, but when the reaction between (I) and (III) was repeated using an open tube, the result was exactly the same *i.e.* still only a small degree of reaction. In series (b) the reaction between (I) and (III) proceeded only to the extent of about 10 per cent, hence the level of methanol formed was still only very low. It was also independently established that the majority of the methanol escaped from the reaction system under the conditions of the (b) series of experiments. It is reasonable to conclude, therefore, that coating systems with mercaptoacetate groups would crosslink considerably more rapidly than corresponding systems with hydroxyl groups.

The ¹³C NMR examination of the model compound reaction product (V) (Table I), shows conclusively that the crosslinking structure is:



The methylated model compound aminoplast was the only one studied, although in practice many commercially used aminoplasts are based on *n*- or *iso*-butanol and also contain substantial amounts of *N*-methylol groups. However, it is assumed that these would react with the thiol groups in an analogous manner, with the elimination of butanol or water instead of methanol.

It is worth noting that conventional saturated alkyd resins frequently have hydroxyl values in the region of 1.5–2 mol/kg. This would now appear to be considerably more than is actually required for crosslinking. Such levels are, however, dictated as much by the need to obtain short process times and to reduce gelation tendencies as to provide adequate crosslinking sites. Thus the unmodified S series products described in the present study have hydroxyl values of this order of magnitude (1.75 mol/kg, calculated). The modified products were, of course, also formulated in this way in order to minimise differences between modified and unmodified products. Thus S.5, in addition to a thiol value of 1.01 mol/kg, also has a calculated hydroxyl value of 1.25 mol/kg.

If one simply takes a control alkyd, such as S.1, and reacts this with mercaptoacetic acid for example, the mixture either gels or cannot be processed to the same acid value/viscosity range as the unmodified product. There might be advantages in completely re-formulating thiol-modified alkyds to minimise the hydroxyl content, but such an exercise is outside the scope of the present study.

The thiol values needed to provide adequate crosslinking in modified alkyds are much lower than the hydroxyl

values of unmodified products. Thus reasonable results are obtained at a thiol value of 0.75 mol/kg (S.4 Tables 3 and 7) or even 0.35 mol/kg (S.3). This suggests that the modified products are not only more rapid but also more efficient in their crosslinking reactions. This may mean that a lower proportion of aminoplast would be needed compared to the requirement for a conventional system, and that aminoplast self-crosslinking reactions would be diminished. This could lead to a better balance of physical properties in a manner related to that described by Koral and Petropoulos¹⁰ for hexamethoxymethyl melamine/alkyd reactions. However, these aspects of the modified products have not yet been examined.

It may be mentioned that unsaturated alkyds resins can also be modified, with mercaptoacetic acid for example. There are, however, difficulties in obtaining stable products either during processing or storage. A further modification possibility concerns the use of 2-mercaptoethanol. Alkyd resins modified with this compound can be prepared, but thiol yields are lower than expected and the products are generally less attractive than mercapto-acid modified alkyds. Of the three mercapto-acids examined, mercaptoacetic appears to be the most promising from the point of view of cost and performance. However, all three types of resin are quite practicable and could be capable of being developed on an industrial scale.

Many other polythiols could be used as co-reactants for aminoplasts. Varied types have been claimed for treating cellulosic textiles, in conjunction with aminoplasts^{11,12}. Smith *et al.* have also described the use of amino-thiol-terminated polypropylene sulfides with aminoplasts as coating resins¹³.

The advantages of the mercaptoacetate modified alkyds are their ease of preparation, reasonable odour and flexibility of formulation, giving coatings of good properties which cure much more rapidly than unmodified products.

In further evaluations of the modified products, three disadvantages have been encountered:

- (1) Inadequate storage stability of the S series/aminoplast blends. Results have been variable and not all the factors are yet understood. The W series alkyd/aminoplast A.1 blends, however, are stable longer than 6 months at room temperature.
- (2) The W series of products cause discolouration when applied to bare steel. This would preclude their application as 1-coat white or pale-coloured finishes.
- (3) The W series of products do not provide satisfactory electrodeposition coatings, the films becoming ruptured at very low voltages.

These limitations are mentioned here for the sake of completeness and further work on these problems is intended.*

Conclusions

1. Saturated alkyd resins containing reactive thiol groups can be readily prepared by formulating with mercapto-acids.

*Thus some promising results have recently been obtained using high solids thiol-modified alkyd resins. These show faster cure than standard products, and appear to have adequate stability. High solids systems are of great importance as a means of reducing unnecessary use of organic solvents.

2. In conjunction with aminoplasts, these modified alkyd resins can be cured through the formation of thioether

\times NCH₂SCH linkages.

3. The reaction is acid-catalysed.

4. Under comparable conditions, the reaction is much faster than the corresponding reaction of conventional, saturated alkyds.

5. Fast cures are obtainable with alkyds having thiol contents well below the hydroxyl contents of conventional resins. This suggests that the thiol/aminoplast reaction is much more efficient than the corresponding hydroxyl reaction.

6. Alkyd resins modified with thiol groups offer encouraging prospects for the saving of energy and the improvement of productivity.

7. Thiol modification of water-soluble and high solids alkyds can provide products which are not only faster curing, but also offer substantial savings in the use of organic solvents.

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Discussion at Eastbourne Conference

MR E. L. FARROW said a very interesting development had been described, and he would be interested to have information about the detergent resistance of the films obtained by thiol modification and also about their colour and colour retention. He pointed out that a large proportion of industrial coatings were to produce white articles and he asked if the lecturers could indicate how these resins perform in the domestic appliance field.

MR MOSS said that the colour of the products in a solvent based system was initially comparable with the standard products on the market and that no subsequent changes in colour upon ageing were evident. He said that detergent tests had not yet been made on the system, as they were still working upon other problems, such as can stability, but he thought that stain resistance was a fairly good indication of the overall resistance of the paint and this has, in fact, been improved by using this system.

MR A. THORNHILL commented that when considering alkyds, the standard curing schedule used would be around 30 mins at 120°C as opposed to 60 mins at 175°C which had been quoted in the paper. He also asked if the lecturers could supply more information on the comparison of the physical properties of the thiol modified alkyd resins when compared to ordinary alkyd/melamine or alkyd/UF resins. He asked if any suitable applications for them could be suggested and if they were commercially available. He suggested that the potential ability to reduce the stoving schedule was a significant advance.

MR MOSS said that when choosing the cure schedules they had chosen the tests of resistance to MEK as a standard in order to achieve a comparable degree of crosslinking with the control alkyds. He appreciated that it was not a cure schedule that would be used in practice. Referring to the graph of Persoz hardness given in the paper, he pointed out that the figures were taken at 110°C thus giving a better comparison of the properties. Mr Moss said that the modified products gave a slightly harder film than the control alkyds; the stain resistance was improved and the flexibility was reduced slightly, but not enough to give rise to any serious problems. He said that the products were not yet commercially available as they were still working on some problems concerning the stability of the systems.

MR F. ARMITAGE asked how the cost would compare with standard products.

MR MOSS replied that the cost factor would be comparable with that of a normal modified alkyd.

MR A. G. HOLT asked how the authors thought this particular development compared in respect of cost savings with other research going on with the same objective. He had in mind powder coatings and water-based and high solid systems.

MR MOSS said that he thought this was another contributory development in this field. He said they had developed water-based systems with a thiol modification in the same way that they had developed solvent based systems and that high solids coatings should also be possible. They were trying to

bring together all aspects of energy and solvent saving into one set of products.

MR K. H. ARBUCKLE, commenting on the relative lack of stability of the system, suggested that this might to some extent be due to the particularly high acid value levels that were being used; up to three times the conventional amount.

MR MASSY said that he agreed and that they had shown that the stability of the resins improved if they were reacted to a lower acid value and, in fact, they were looking at such products at that time. In the experiment they had reviewed the maximum acid levels quoted for the commercial products available, but in fact one of the control alkyds that they were using actually had an acid value of one quarter of the maximum value specified. Mr Massy commented that it would be interesting to know what degree of package stability was

expected. In conventional systems, he said a shelf life of at least six months is required and this could be achieved using certain classes of thiol modified alkyds but that with the "S" series described in this paper there were still a few problems in this respect.

MR P. JEFFERY said that in his experience when thiol groups were introduced into compounds it usually caused an objectionable smell. He asked if this occurred with these particular resins.

MR MOSS said that some odour was produced but from the work they had done in the laboratory, he would not rate the odour as any more objectionable than the smell of xylene which was also present. He said that the amount of odour depended on the degree of reaction of thiol into the alkyd resin; if it is completely reacted the smell would be low.

Labelling of dangerous substances and preparations in the EEC*

By R. W. Kay

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Summary

The EEC has issued a number of directives on the classification, packaging and labelling of dangerous substances and preparations and this process is continuing. These directives have two main aims, the removal of barriers to trade within the Community, and the protection of any user of these products, whether a worker or a member of the public.

Keywords

Specifications, standards and regulations
labelling laws and regulations

La désignation de substances et préparations dangereuses dans la CEE

Résumé

La CEE a promulgué une série de directives sur la classification, le conditionnement et la désignation de substances et préparations dangereuses, et elle continue cette opération. Ces directives ont deux buts principaux, l'enlèvement des obstacles commerciaux dans la Communauté, et aussi la protection de tout usager de ces produits qu'il soit ouvrier ou membre du public.

Dans le Royaume Uni, les décrets pour mettre en vigueur la direc-

tiive in the United Kingdom, regulations to implement the substances directive will have been brought into force in early 1977 and regulations for solvents will follow at a later date. Another directive which concerns paints, varnishes, adhesives, printing inks and related products is still under discussion in Brussels. It is the intention of the EEC that this series of directives will eventually cover a much wider range of preparations, for example pesticides and household products.

Kennzeichnung gefährlicher Güter und diesbezügliche Vorarbeiten der EWG

Zusammenfassung:

Die EWG gab eine Anzahl von Direktiven für die Klassifizierung, Verpackung und Kennzeichnung gefährlicher Substanzen heraus; diese Vorarbeiten gehen weiter. Die zwei Hauptziele dieser Direktiven sind die Entfernung von Barrieren, die den Handel innerhalb der Gemeinschaft behindern, sowie der Schutz von wer immer diese Produkte anwendet, sei er Arbeiter oder Mitglied der Allgemeinheit.

Im United Kingdom dürften Bestimmungen zur Inkraftsetzung der Direktive für Substanzen anfangs 1977 in Kraft treten; die für Lösungsmittel werden später folgen. Eine andere Direktive bezüglich Anstrichfarben, Lacke, Klebstoffe, Druckfarben und verwandte Produkte wird noch in Brüssel besprochen. Die EWG hat die Absicht, mit dieser Serie von Direktiven schliesslich eine viel grössere Reihe von Erzeugnissen zu erfassen, a.B Pestizide und Haushaltprodukte

Introduction

Work on the labelling of dangerous substances falls into two interrelated, but somewhat different groups: labelling for transport purposes and labelling to warn the user of a product. As yet, it has not proved possible to produce a simple label which is suitable for both purposes. For purposes of transport, international systems have been developed, based on United Nations recommendations, and these labels have a danger symbol within a coloured diamond. Diamond-shaped labels are also being used for the transport of dangerous goods within the United Kingdom. The classification of dangerous goods in transport is linked closely with the type of packaging, storage *etc* which is allowed.

The Factory Inspectorate (now part of the Health and Safety Executive) has always had a considerable interest in the classification of dangerous substances, although there are few requirements for labelling in the Factories Act. With the introduction of the Health and Safety at Work Act, manufacturers and suppliers are required to provide adequate information for the safe use of substances at work and an adequate label can be regarded as going some way towards meeting this obligation.

Prior to our entry into the EEC, the main work of the Factory Inspectorate in the field of user labelling took place in the Council of Europe, where a set of recommended standards for the labelling of about 750 substances has been produced. The position has changed with our entry into the Common Market and the labelling directives of the Community will be implemented gradually by the United Kingdom. Requirements for a package to carry the names of dangerous substances, danger symbols and warning phrases are in accord with the increased demands from workers' representatives and consumer protection bodies for more explicit information about the risks involved with a product.

There already exists in the United Kingdom a number of excellent labelling systems which have been developed by individual firms and industrial associations although these will be replaced in time by the EEC requirements. The labels recommended by the Chemical Industries Association are a good example.

EEC directives

Article 100 of the Treaty of Rome states that "The Council shall issue directives for the approximation of such provisions

*Paper presented at the Association's Biennial Conference held at the Grand Hotel, Eastbourne, Sussex from 16-19 June 1977.

laid down by law, regulation or administrative action in Member States as directly affecting the establishment or functioning of the Common Market." This Article is aimed at removing barriers to trade between the Member States, and the directives on the labelling and classification of dangerous substances and preparations are regarded as removing such barriers. Directives are Community instruments binding upon each Member State as to the result to be achieved, whilst leaving to national authorities the choice of form and methods. In the United Kingdom the directives will probably be implemented by regulations under the appropriate enabling powers.

The Health and Safety Executive is the government department concerned with three EEC labelling directives. The first of these, the Classification, Packaging and Labelling of Dangerous Substances can be regarded as the parent directive in the field and the second, on Dangerous Preparations (Solvents), concerns the labelling of solvent mixtures. Both of these directives were finalised by the EEC before our entry, although we were consulted on amendments to the Dangerous Substances Directive, and the Solvents Directive in 1972. The third directive on paints, varnishes, printing inks, artists colours, adhesives *etc* is under discussion in Brussels at present. During our work on the preparation of any directive, we have the fullest consultation with industry, trade unions, consumers' associations and other government departments.

The present position within the EEC with regard to the Substances and Solvents Directives is that only Germany, France and Belgium have introduced laws for their implementation. The three new Member States, Ireland, Denmark and the United Kingdom, were originally allowed until mid-1976 to implement these directives, but this date has been put back because of the late completion of amendments in Brussels.

Dangerous substances directive

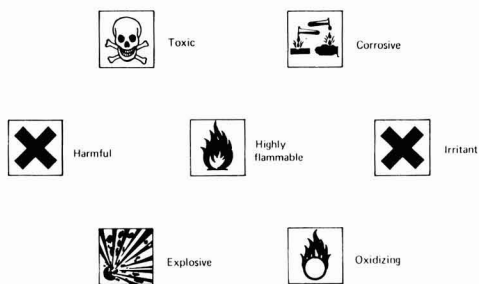
The Dangerous Substances Directive is based almost entirely on the original work of the Council of Europe, published in the so-called Yellow Book, Dangerous Chemical Substances and Proposals concerning their Labelling. The Yellow Book is concerned with chemical elements and their compounds as they occur naturally or in manufacture. Some 750 substances will appear in the 4th edition of the Yellow Book and also in the latest amendment of the Substances Directive.

There are five basic parts to the EEC label:

1. Name of the substance (IUPAC or common name)
2. Origin
3. Danger symbol(s)
4. Risk phrases
5. Safety phrases.

In the directive, the substances have been divided into defined classes and each class in turn is related to a danger symbol (Fig. 1). In order to limit the number of symbols to two on any label, one symbol is taken from the explosive, oxidising, highly flammable group and one from the toxic, corrosive, harmful, irritant group. These symbols were originally proposed by the International Labour Organisation, ILO, Chemical Industries Committee and then taken up by the Council of Europe and EEC. They are shown on an orange/yellow background and each symbol should occupy 1/10th of the area of the label.

Indication of General Nature of Risk



The above symbols shall be in black on an orange-yellow background

Fig. 1. Some classes of dangerous substances and their hazard symbol

The effect of the danger symbols is reinforced by the so-called R and S (risk and safety) phrases, which give warning of the dangers of the substance in the package and advice on how to combat that danger. These phrases are found in the Annexes of the directive and only R phrases are compulsory at present, but this position will soon be changed and S phrases will also be mandatory. When all the components are put together, the result is shown in the label for aniline (Fig 2). This contains two risk and three safety phrases and the number has been limited deliberately in order to achieve a simple label with maximum effect.

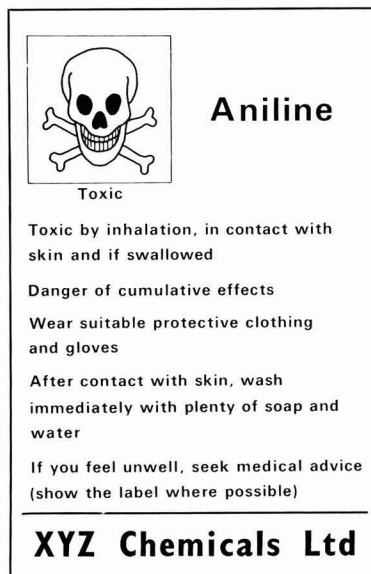


Fig. 2. A typical label

There are other requirements in the directive, for example, that labels must have certain minimum sizes, and to allow labels to either be stuck to or printed on the package. Member States may require the label to be in their national language and this is an obvious requirement, otherwise the labels would lose their effect. Where packages must carry a transport label,

the directive allows certain derogations to prevent the use of two sets of symbols. In the case of a single package, the transport label can be used together with the requirements for the name, origin and risk phrases from the directive. For an outer package which contains inner packages, the outer package should be labelled with the transport label and the inner packages in accordance with the directive.

One of the problems which faces any labeller is how to place adequate information on a small container. Any safety effect is lost if too much small print is crammed into a tiny label. The directive allows simpler warning labels to be placed on containers less than 125 mls and it is hoped that a balance has been achieved between the demands of safety and space.

Although there are requirements in the directive for the packaging of dangerous substances, these are couched in such general terms that they only reflect the normal practices of industry.

Solvents directive

The Directive for the Classification, Packaging and Labelling of Dangerous Preparations (Solvents) is an off-shoot of the Dangerous Substances Directive and deals with methods of assessing the toxicity of solvent mixtures. The classification scheme was developed by Professor Sampaolo of Rome. Some 64 solvents are named in the directive and the two main classes, toxic and harmful, have been further divided into sub-classes which are derived from a detailed and complex toxicological study. Each sub-class is given two numerical indices and the overall toxicity/harmfulness of any solvent mixture can be obtained by substituting the appropriate index in an additivity formula of the type Σ (percentage \times index). $\geq X$. Although this is a somewhat empirical approach, the results appear to be consistent with experience. Any solvent mixture which contains benzene, for example, would be classed as toxic at a benzene content of more than 1 per cent and harmful from 0.2–1 per cent.

If a calculation has shown that a solvent mixture requires a toxic or harmful symbol, the name of any toxic ingredients

must be shown on the label together with the names of any harmful ingredients at certain specified levels. The manufacturer is also required to supply not more than four relevant risk phrases, and the relevant safety phrases should accompany the package. Other general requirements of this directive are similar to the requirements of the Substances Directive.

Draft paints, varnishes, printing inks, adhesives, artists colours etc. directive

The draft Paints etc. Directive will follow basically the lines of the other directives. Classification of individual substances will be as in the Dangerous Substances Directive and, for solvents, the provisions of the Solvents Directive will apply, calculating the percentage weight of each solvent from the total weight of the paint. During the discussions on this directive in the Working Group in Brussels, it was decided that there was no general additivity principle which could be applied to give an assessment of the overall risk of these products, and it was found necessary to try to establish a concentration at which each individual constituent would make the preparation toxic, harmful, corrosive etc.

There are still outstanding problems in this directive which relate to the quantity of information which should be required on the label. These problems are particularly acute for countries with large export markets and, where the exact destination of a product cannot be predicted, some labels may have to be printed in the six official languages of the Community.

Conclusion

The EEC is committed in its programme to a gradual extension of its labelling directives, although the field of dangerous preparations is so vast that this work will take many years. The existing directives will also have to be updated to include dangerous substances which are new to the market or have previously been overlooked. Once these labels have appeared in the United Kingdom, it may be that experience in use will suggest refinements which can be included in the future.

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Discussion at Eastbourne Conference

MR A. B. LOCK asked if Mr Kay thought there was a conflict between the implementation of the EEC labelling regulations and the Health & Safety at Work Act in so far as that for a paint manufacturer, adherence to the regulations would not be sufficient to protect him in law against the Health & Safety at Work Act. In particular, new knowledge, especially on existing substances not hitherto considered hazardous, indicating that they might now be hazardous would not come within the EEC regulations, but the manufacturer would be obliged to notify users of its presence or put it on the labels under the Health & Safety at Work Act. He wondered if there was any way of combining the two requirements.

MR KAY said that one of the problems with the Health & Safety at Work Act is that it is an enabling act and that some of the sections cover a very broad area, in particular

Section 6 of the Act which refers to duties of manufacturers and suppliers of substances. This section has caused problems for both industry and the Health and Safety Executive. Section 6 can be satisfied by means of a warning label which is supplemented by a data sheet giving information about the dangers when using the substance and suggestions for first aid treatment. He pointed out that the information in the EEC labelling system was by no means comprehensive. Clearly where there is an EEC label the manufacturer who uses it will be complying with the labelling regulations, but the problem arises when there is no standard label and the manufacturer does not know whether to use the EEC standard danger symbols.

Mr Kay said he thought the problems would be alleviated when the proposed 6th amendment became law and definite criteria were given to the manufacturer to cover labelling. The major problem at the moment regarding these proposals was to define the scope of the notification of information

about new substances. The original proposals, when costed for Britain, had worked out at about £250 000 per substance, but the more recent estimates were reduced to about £30 000, so it appeared that the trend was for a more simple notification system. Proposals for a scheme under the Health and Safety at Work Act are based on a similar approach. Clearly, there would be a need of a large run-in period for the scheme and the Health & Safety Executive were in close liaison with manufacturers to see how they were getting on and what could be done to help them.

MR D. HOWE pointed out that the 6th amendment was part of the dangerous substances labelling directive, and yet to most people this suggested control of use. He asked Mr Kay if he was satisfied that notification would be used only for labelling or whether this notification system effectively would be used to control the use of new chemicals. He suggested that the notification of new chemicals should not come under a labelling directive but under a separate control of use directive.

MR KAY said that the proposed notification scheme had been included in the dangerous substances labelling directive

and, in fact, the French had suggested that the manufacturer should propose how the use of his substance should be controlled in order that Brussels could use this information to control its use. This was an extremely contentious point and had split the members of the Community down the middle. At present, the UK and several other countries believe that there should be no control of use in the labelling directive and that suggestions for control of use should not be part of the notification scheme, whilst other member states feel that this directive is the correct place to insert requirements for control of use so that when a new substance is notified, conditions for its use are laid down at the same time. He said that the UK is at the moment trying to separate these two functions, preferring that the legislation upon the control of use should be carried out by the individual countries. In the cases of extremely dangerous substances, control throughout the EEC could be achieved by means of the existing control of use directive which at present contains PCB's and vinyl chloride (in aerosols).

Mr Kay said he was not sure what the outcome of the current conflicts would be.

Next month's issue

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

Atmospheric corrosion testing of metallised, metallised and painted, and painted steel by *S. Haagenrud*

Ultraviolet light curing: some benefits and recent advances by *M. A. Parrish*

Analysis of the constant-rate period of ink drying by *H. Hardisty*

Determination of solubility parameters of polymers by a group contribution technique by *H. Ahmad and M. Yaseen*

Correspondence

Recent developments in antifoulings

Sir,

Contributions to *JOCCA* are usually informative, but only rarely controversial. All the more welcome and stimulating, therefore, is Dr Christie's paper in the September edition. In his conclusions he attacks the over-selling of a number of products readily identifiable "to the initiated" (by means of quotation from their own publicity), and his scepticism will be widely shared. However, he makes considerable claims for another product or principle (which shall, of course, be nameless!), amongst which is the statement that "Test plates attached to a ship's underwater hull conclusively demonstrated the correlation between progressive surface smoothing and decreased drag, as measured in a hydrodynamic flume".

This is a considerable claim, which, if verified, would completely revolutionise the art of antifouling. But Dr

Sir,

To put Mr Milne's implied criticism into context I must also refer to my paper where the difficulty of establishing the relationship between surface smoothing and ship performance is clearly stated. As Mr Milne would be one of the first to acknowledge, it is important to be able to establish this relationship in the practical situation and as mentioned, this is currently being followed on several ships. The plate tests formed an early part of the overall approach to demonstrate the power of the self-polishing principle.

In answer to the criticism of "attacking the competition"

Christie cites no source of evidence for this claim. Why not, since he is so hard on the claims of others? Elsewhere he quotes a dozen sources for his information, and since two of them are himself and two of them are myself, I have no quarrel as to their quality or authority, but he cannot, himself, expect the privilege of attacking the competition in your columns without giving us the opportunity to test the quality of his own sources. The article, after all, purports to review "recent developments in antifoulings". How can he review something which is not yet established fact?

Yours faithfully,

A. MILNE

*Camrex (Holdings) Ltd,
Research & Development Division,
Camrex House,
PO Box 34,
Sunderland.*

26 September 1977

unfairly, I would point out that a preprint of the paper was available to all those present at Eastbourne.

Yours faithfully,

A. O. CHRISTIE

*International Marine Coatings,
R & D Laboratory,
Stoneygate Lane,
Felling,
Gateshead,
Tyne & Wear,
NE10 0JY*

11 October 1977

Professional grade

At a meeting of the Professional Grade Committee held on 12 October the following admissions were approved. The Sections to which the members are attached are shown in parenthesis.

Fellow

Davidson, John Dixon Wilson (*Scottish*)

Transferred from Associates to Fellows

Beachen, John Frederick (*Auckland*)
Wood, George (*London*)

Ernst, Joel (*London*)

Associates

Jenkins, Brian Gordon Allan (*Auckland*)
Nelson, John George (*Auckland*)
Peng, William Yeo Kok (*General Overseas—Singapore*)
Durant, Leslie Arthur William (*London*)
Braund, Valerie Mavis (*Bristol*)
Bose, Sunil Kumar (*London*)
Semple, James William (*London*)
Awan, Mumraiz Khan (*General Overseas—Kuwait*)

Section Proceedings

Natal

Conservatism in the paint industry

A meeting of the Natal Section was held on Wednesday 29 June at the Ocean Terminal Restaurant, Durban, when 20 members and guests were present to hear a lecture entitled "Conservatism in the paint industry" by Mr G. Carr of Industrial Oil Processors.

Mr Carr noted that, whilst it was the function of the paint manufacturers to supply the paint trade, this was not all it should do. The development of new products was of vital importance to the manufacturers and raw material suppliers alike. It appeared that the paint trade had no idea of where it was going, but just followed the old ways blindly. One text-

book, Watmin's, had been used through 14 editions dating from 1736 to 1900.

It was noted that as early as A.D. 1100, Theophilus had been making varnishes with linseed oil and gum. It was shown that many discoveries had been made in the chemical industry that were only used by the paint manufacturers many years later. In 1804—white lead, 1835—vinyl chloride, 1839—styrene from gum, yet this fact was not even mentioned in Mattiello of 1941-46. 1910—casein powders, 1912—acrylic resins, 1914-20—styrene butadiene discovered looking for a rubber substitute. It was not actively used in the paint industry for how many years? 1920—vinyl chloride/vinyl acetate copolymers, 1921—glyptal alkyds discovered while looking for

mica substitutes, 1933—titanium dioxide by the chloride process. These discoveries had been made, but it took years before they made their appearance in paint manufacture. The driers field had shown terrific changes, and it was noted that at least three times in the last 15 years Zirco had been heralded as the answer to all problems.

It appeared that there were still three separate groups; supplier, manufacturer and user, and the lecturer suggested that the time had come for them to work together for their mutual benefit.

The vote of thanks was proposed by Mr J. Gush.

Information Received

ECC go International

The sales and marketing companies Clay Division of the English China Clays Group have become one corporate group and have changed their name to ECC International. The two main reasons given for the change are that the companies' exports to more than 60 countries now account for 80 per cent of the UK china clay production, and the markets for the Division's products have become more international as more of the customers themselves operate on an international basis.

In addition, the division also has production units in Australia, North America and continental Europe, and last year £80 million of the divisional turnover was generated outside the UK.

Of the division's total production, no less than 80 per cent is sold to the paper industry, as a filler or coating pigment, and at the moment, a new product called Superfill is being developed which can be used in high proportions in printing paper to reduce the amount of pulp required and thus conserve the rapidly diminishing forests.

Organic pigments complex

The Sun Chemical Corporation has announced that work has begun on the new 240 acre site in Michigan, USA, for what is expected to be the world's largest complex solely for the production of organic pigments.

The initial part of the \$30m complex is scheduled for completion by the end of 1978 and will manufacture diarylide yellow pigments, at present produced at a plant in Rosebank, New York, which will be able to double its production of azo red pigments once the new plant is in operation.

Subsequent developments at the complex will be for the manufacture of quinacridone, phthalo blue, phthalo green and pigment intermediates, and the complex is expected to be completed within five years.

Colour concentrates agents

Phillips Petroleum Co. UK Ltd have been appointed sales agents in the UK for the American Thermoplastic Corporation, a subsidiary of the Phillips Petroleum Company.

ATC manufacture a range of high-quality colour and speciality concentrates, which are supplied in pellet form and are blended with thermoplastics using standard screw-type processing equipment.

New solvents plant

A new hydrocarbon solvents plant is to be built at the Shell oil refinery at Stanlow, Ellesmere Port. The new facilities, costing £6 million, are scheduled for completion in 1980, will replace the existing plant, and will be run by Shell UK Oil, whilst the products will be marketed by Shell Chemicals UK Ltd.

Cabot purchase "Tribaloy"

The Cabot Corporation of America has purchased from Du Pont the patent rights, trade marks and technology for the manufacture and sale of "Tribaloy" compositions worldwide. These compositions are a family of proprietary nickel-base and cobalt-base alloys which offer good wear-resistance and are used for coating moving parts subject to high wear.

UK marketing organisation

The entire equity of Bush Beach & Segner Bayley Ltd has been acquired by Degussa, Frankfurt am Main, and from October the new firm, Degussa Ltd, will take on the full marketing of the company's products in the UK. Bush Beach & Segner Bayley were formerly acting as agents for Degussa in the UK.

Overseas marketing for Mastermix

During the past year, Mastermix has reconstructed its overseas marketing by appointing agents in most European countries to handle its range of dispersing, mixing and milling machines for the surface coatings industry.

The aim has been to establish a more direct technical contact with customers entailing extensive overseas travel of sales staff and technicians. During this programme, the company has largely used its own Twin Comanche aircraft which has enabled the reaction time to requests to be reduced.

New products

Plastigen P

BASF have available Plastigen P, an aqueous solution of a polymer which can be used for viscosity modification and lubrication in paper and board coating colours. The product is also claimed to enhance the rheological properties of coating colours.

Also available is Propiofan 661D approx. 50 per cent, a fine particle size, low viscosity, aqueous dispersion of a vinyl propionate/acrylic ester copolymer with good pigment binding capacity. The films produced are flexible and have good weather and soap resistance, and are recommended for weather resistant exterior paints and highly filled interior paints.

New water borne coatings

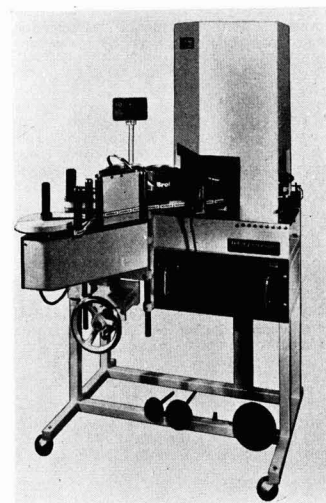
The Donald Macpherson Group's Industrial Division has recently developed a revolutionary weldable water borne primer which does not burn to any great extent and thus results in the minimum damage to the paint film when pre-constructed sections are welded together. This has the advantage of reducing the amount of repainting necessary, and thus the risk of corrosion, and also of improving the working environment during welding.

New resins

Esso Chimie, an Essochem Europe Inc. affiliate, have begun production of Escorez 1304 and Escorez 1315 resins at their plant near Le Havre, France. These resins, previously imported from the US, are used as tackifiers in many adhesive coating applications.

Paint tin labelling

Pals Precision Applicators Ltd have available a new range of labelling machines suitable for labelling paint cans where a standard label is required with the colour code inserted after filling. These range from a semi-automatic label dispenser, which applies a label to a can presented by hand, to the Can-A-Ply, a fully automatic machine which can be used for pre-labelling or for "in line" use with filling machines.



The Can-A-Ply fully automatic labelling machine

New hammer mills

Glen Creston Ltd have announced the introduction of a new series of hammer mills with output from 25 kg/hr to 2000 kg/hr, capable of reducing fist-size chunks to about 100 microns. A booklet has been produced describing the new series.

Versatile surfactant

Air Products and Chemicals Inc. has introduced a new and versatile addition to the Surfynol surfactant product line, called Surfynol SE, a nonionic, highly water dispersible surfactant which can act as an effective wetting agent, non-foamer and viscosity stabiliser.

Stable at emulsion concentrations of 75 per cent in water, Surfynol SE is easily mixed and has applications in water-based paints, inks, dye processing, paper coatings and aqueous lubricants.

Level measuring instruments

Foster Cambridge, a member of the George Kent Group, has introduced its new Series 80 range of level control instrumentation, which has applications in controlling the levels of liquids, slurries or powders in tanks.

The new range has been standardised and the components simplified, whilst still giving a wide choice of options for various situations, and because of the lack of moving parts, is robust and needs little maintenance.

Safe storage

Flametamers International Ltd have added 'Arrestoflame' multi-purpose stores to their ranges of storage and dispensing containers for inflammable substances. These are pre-fabricated modular constructions and can be supplied in most sizes and forms.

Pneumatic tyred fork lift trucks

Eurostac Fork Lift Trucks Ltd have introduced two new models, EPI250 and EPI600 to the range of Eurostac trucks announced earlier this year. The new models have pneumatic tyres which enable them to mount minor obstacles, a characteristic which has been demanded by many customers.

New filler

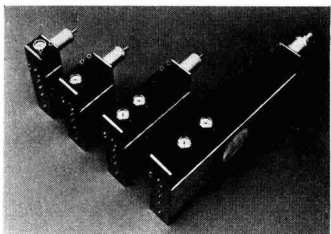
Nuemo Ltd have introduced their latest palletised container filler which is capable of filling 5 to 45 gallon containers with foaming or non-foaming liquids with fingertip control. The machine is air operated and works to ± 0.25 per cent by volume with short filling times.

Anti-vacuum valves

Porter Lancastrian are manufacturing a new range of stainless steel deadweight anti-vacuum valves which may be used on tanks where danger of corrosion by the elements or contents are high.

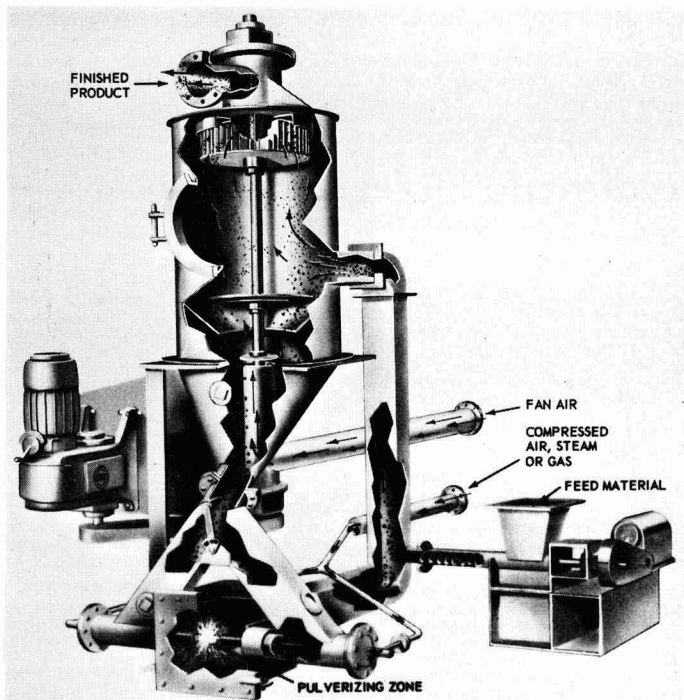
Vacuum pumps

PIAB Materials Ltd have available a new range of compressed air operated ejectors which can pull a vacuum of 85 per cent with a high air flow rate. The ejector is



The new range of ejectors for vacuum pumping

essentially a five stage amplifier with built-in valving for the automatic control of the air flow/vacuum ratio. One of the major advantages of such ejectors in vacuum holding or conveying systems is the lack of moving parts which increases reliability.



A diagrammatical representation of the new Majac air impact pulveriser from Donaldson Europe SV

Majac air impact pulveriser

Donaldson Europe SV have available a new Majac air impact pulveriser which has been designed to mill hard materials, such as quartz, to finenesses of below 15 microns. The grinding occurs in the collision of two opposed particle laden air streams, produced by air or steam driven injectors.

Specialised conventional lacquers

Paper Lacquers Ltd have announced that their range of UV lacquers has been supplemented by the introduction of a range of specialised conventional lacquers for the printing industry. These include high gloss water based lacquers for calendering, high scuff resistant matt finishes, special coatings for wallpapers and other coatings to specific requirements.

The new range will be manufactured also by Pearl Paints Ltd.

Literature, courses etc.

Preservatives, biocides and antifouling agents

This publication has recently been produced by R. H. Chandler Ltd and contains a survey of work on antifouling agents, mildewicides, fungicides and other biocides and can preservatives that have appeared in literature and patents in the last ten years.

Decorating colours

The Ceramic Colours Division of Degussa has revised its 'Recommendations on the use of decorating colours and glazes containing lead or cadmium' to incorporate the latest EEC regulations.

Diazo compounds guide

DOMMDA, the Drawing Office Material Manufacturers and Dealers Association, have published a 'Guide to good practice for the safe handling of diazo compounds.'

European aerosols on par with US

Metal Box Ltd, a major European producer of aerosol cans, has announced that the production of aerosols in Europe has now increased to almost the level of the US figure, and with consumption per capita still lower in Europe, they state that the prospects for the future of this expanding market are good. A special booklet has been produced by Metal Box graphically describing the current trends.

Analytical instruments survey

Perkin-Elmer Ltd have available a new booklet giving a complete survey of their most advanced analytical instruments, together with a review of the major techniques used in analysis.

Interference filter booklet

OCLI Europe, the marketing and sales division of Optical Coating Laboratories Ltd, have published a 50-page booklet listing the stock interference filters available for the visible range of the spectrum.

Technical bulletin

The National Gallery has launched a new technical bulletin which describes recent work and research of the Scientific and Conservation departments at the Gallery, to aid the spread of the information which these departments come across.

OCCA

60th Anniversary



Celebrations

As members will be aware, the Association celebrates the 60th Anniversary of its foundation in May 1918, and it is felt that members would like some details of the proposed celebrations which will take place on 11 and 12 May 1978.

The actual date of the foundation of the Association was 16 May 1918, but it has been decided that the Thursday and Friday are more appropriate times to hold the celebrations.

The May 1978 issue of the Journal will contain an article by Dr S. H. Bell, OBE (President 1965-67) on main Association events since the 50th Anniversary in May 1968. Already many companies have reserved advertising space in this important issue in order to congratulate the Association on this achievement, and others wishing to do so can obtain full details from the Assistant Editor at the Association's offices at the address on the contents page.

Commemorative Lecture and Dinner



John Methven

The Commemorative Foundation Lecture (instituted in 1963 in memory of the late H. A. Carwood, Esq., the first Honorary Secretary of the Association) will be given

in the Court Room at the Painters' Hall, Little Trinity Lane, London EC4, on the evening of Thursday 11 May by John Methven, Director General of the Confederation of British Industry. Admittance to the Lecture will be by ticket only and will be followed by a short reception. Dinner will be taken in the Dining Hall of the Painter Stainers' Company at 8.00 p.m. Informal dress will be worn.

Tickets for the Lecture and Dinner will be available from the Association's offices at a cost of £12.00 plus VAT, and members will be sent an application form giving details in due course. The price of the ticket also includes the reception between the Lecture and Dinner, wines with the meal, and port or brandy after the meal. Past Presidents, Past Honorary Officers of the Association and Honorary Members will be invited as guests of the Association.

Commemorative Dinner Dance

The Association's Dinner Dance will be held at the Savoy Hotel, London WC2, on the evening of Friday 12 May, and Presidents of other societies, together with their ladies, will be invited to attend. Tickets, price £15.00 plus VAT will be available from the Association's offices, and members will again be sent full details.

Non-members who wish to receive application forms should write to the Director & Secretary at the Association's offices as soon as possible, particularly if they wish to make up parties (up to 12 per table) for the Dinner Dance.

On 23 June an inaugural meeting was held at the Ambassador Hotel, Salisbury, with 21 members present to hear Mr D. Pienaar, Vice-President of the South African Division, give a lecture entitled "Weights and Measures". (See October JOCCA, p426 for photograph).

On 21 July a meeting was held at the Ambassador Hotel, Salisbury, when 23 members were present to hear Mr J. Ebdon give a lecture entitled "The prevention of corrosion by means of surface coatings".

The third meeting was held on 25 August at the same venue when 27 were present to hear Mr L. V. Diedericks of Dulux Paints give a lecture on "The composition of paints".

On 8 September, the fourth meeting of the proposed branch was held when 29 members were present to hear Mr I. Lancaster, National Chemical Products, Transvaal, deliver a lecture entitled "Solvents".

Manchester Section

OCCA Golf Tournament

Wednesday 7 September, Stockport Golf Club, Cheshire, was the neutral venue for this Stableford competition, with the West Riding Section providing the main opposition to the Manchester contingent. 57 members and visitors were present to enjoy the good weather and variable golf.



Mr J. Mitchell presenting Mr J. R. Hastie with the Golf Tournament prize

Transvaal Section

Rhodesian Branch

The following four meetings of the proposed Rhodesian Branch of the Transvaal Section have been held:

The L. H. Silver Cup and replica, Manchester Section Golden Jubilee Trophy and Chairman's Tankard were won by Mr J. R. (Ian) Hastie of the Manchester Section with 37 points. The Chairman, Mr J. Mitchell, presented the 43 donated prizes, and the leading visitor was Mr R. H. Kershaw. An excellent meal was enjoyed by all, especially the Red Rose victors.

F.B.W.



OCCA-30 Exhibition

Alexandra Palace, London. 18-21 April 1978

The continuous dialogue

in the

surface coating industries

The Exhibition, which is known as the international forum for technical display and discussion in the surface coatings industries, is the most important annual event of its kind in the industries and it offers an unparalleled opportunity for a continuous dialogue on technical advances and problems between suppliers and manufacturers in an informal atmosphere.

Many young technologists and scientists who visited the earlier Exhibitions have now risen to high positions within their organisations and the advantage to exhibitors of keeping in constant contact with their counterparts in the manufacturing industries needs hardly to be stressed.

In recent years the Exhibitions have been visited annually by representatives from 50 countries and bringing all these interested parties together at a regular meeting is in itself invaluable when exhibitors consider the cost in time and travel which would be entailed in making personal contact with these visitors each year.

Information in foreign languages

As in previous years, the Association will be circulating information leaflets in six languages, which will contain application forms for those wishing to purchase copies of the *Official Guide* and season admission tickets before the Exhibition.

Official Guide

This unique publication contains descriptions of all companies and their exhibits at the Exhibition and is issued to each Member of the Association at home and abroad together with season admission tickets. As in 1977, several Sections will be organising coach parties to visit the Exhibition and any Members interested should contact their local Section Hon. Secretary. (Full Section Committee lists for 1978 were published in the August issue of the *Journal*.) It is also hoped that several parties will be organised from overseas to visit the Exhibition.

Advertising facilities

Advertising space is available in this important publication to both exhibitors and other organisations which are not able to show at the 1978 Exhibition. The *Official Guide* will be published early in 1978 so that visitors can obtain copies and plan the itinerary for their visits. Clearly, the *Official Guide* is a publication that will constantly be referred to both before and after the Exhibition and consequently any company wishing to advertise in the *Guide* should

book space as soon as possible. Details of the advertising rates are available from Mr D. M. Sanders (Assistant Editor) at the

address on the contents page. As in previous years the *Official Guide* and season admission tickets will be available several

★ ★ ★ ★ ★ ★ ★ ★

WELCOME, JAPAN!

★ ★ ★ ★ ★ ★ ★ ★

For many years one of the largest markets for company and library subscriptions to the Association's monthly *Journal* has been Japan, and a pleasing feature in recent months has been the increase in the number of requests to publish in Japanese papers which have originally been printed in *JOCCA*. Now, in 1978, direct exhibits from Japan will be displayed at OCCA-30, together with exhibits from organisations in **Belgium, Canada, France, East Germany, West Germany, Holland, Hungary, Italy, Poland, Spain, Switzerland, UK and USA.**

A full list of exhibitors will be published in the January issue of the *Journal* following the Exhibition Committee meeting to allocate the space and the notification of stand areas to exhibitors.

Exhibitors are now sending in details for their editorial entries in the *Official Guide* and, following the successful innovation for OCCA-29, they will also be submitting news items and photographs of latest developments for publication in the *Journal* in the months leading up to the Preview issue (April 1978).

weeks in advance of the Exhibition (pre-payment only) from the Association's offices but they will also be available for purchase at the entrance to the Exhibition Hall. A charge is made for both the Official Guide and the season admission tickets to the Exhibition. The policy was introduced several years ago to deter casual visitors who otherwise collected large quantities of technical literature from exhibitors stands; the policy has been welcomed by exhibitors and has in no way acted as a deterrent to bona fide visitors to the Exhibition.



London Transport

Heathrow Central Terminal

London Transport have announced that the extension of the Piccadilly Underground line to the new Heathrow Central Terminal at Heathrow Airport will be opened in December this year.

The first stage of the project was completed with the opening of the Hatton Cross station on the outskirts of the airport in July 1975. Work on the Heathrow Central Terminal was begun in April 1971 and has cost about £27 million, but upon opening it will provide a direct link for visitors arriving at the airport to travel into the centre of London.

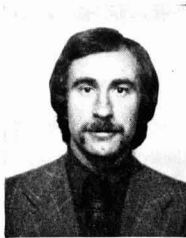
The advantage to overseas visitors travelling to OCCA-30 is enormous, as it now greatly simplifies the journey, both to hotels in central London where they may be staying, and to the Exhibition. Visitors arriving at Heathrow Airport will now be able to board a Piccadilly Line train at the airport building itself which will take them directly to Turnpike Lane Station, from where the Association will be running a free bus shuttle service to and from the Exhibition. The journey from central London to Turnpike Lane station takes approximately 18 minutes.

The Piccadilly Line is being equipped with new trains in readiness for the opening of Heathrow Central. Many of the new trains are already in service, and are similar in appearance to the latest "silver" tube trains, but have a different size and layout which give more space for passengers with luggage. This makes the new enlarged Piccadilly Line one of the most reliable and comfortable forms of transport in London.

All OCCA Exhibitions have been held in London, which affords excellent travel and hotel facilities for visitors from both overseas and the United Kingdom. In pursuance of the theme of the Exhibition —**The continuous dialogue**— it is felt that Exhibitors will like to know that the Exhibition Committee has also reserved Alexandra Palace for April 1979 and will hold its annual Exhibitions there subsequently in April each year.

It will also be appreciated that for exhibitors and visitors staying in London, the capital city offers the finest variety of entertainments for the evenings after the Exhibition.

News of Members



Mr G. J. Dawson

Mr G. J. Dawson, an Ordinary Member of the Manchester Section, has taken an appointment at Kronos Titanium Pigments Ltd after finishing his thesis for a Master of Science degree at Newcastle University on flame retardants.

Mr A. C. W. Jones, an Ordinary Member attached to the London Section, has retired from his position as technical director at Burrell Colours after 49 years in the chemical industry and 44 years with Burrell. Mr Jones will remain with Burrell Colours in a consultative role.

Dr E. Inman, an Ordinary Member attached to the London Section, has taken over the position vacated by Mr Jones, having moved from Ciba-Geigy earlier this year.

Dr C. Midcalf, an Ordinary Member attached to the Manchester Section, has been appointed chief chemist with responsibility for research and development for the company, and Mr L. J. Williamson, also a member of the Manchester Section, has been appointed to the post of chief analyst, responsible for a new central analytical function based at the Stockport laboratory.

Mr A. G. Ogilvie, an Ordinary Member attached to the London Section, has taken up the position of technical liaison executive for the London-based technical staff of Burrell Colours.

Bristol Section

Annual Dinner Dance

The Annual Dinner Dance of the Bristol Section was held on Friday 1 April 1977 at the Mayfair Suite of the New Bristol Centre, which has been the home of this event for many years. The Section was very happy to greet as its formal guests Mr Brian Addenbrooke, President of the Birmingham Paint, Varnish and Lacquer Club, and Mrs Addenbrooke, Mr Ray King, Chairman of the Midlands Section, and Mrs King, Mr John Tooke-Kirby, Chairman of the London Section, and Mrs Tooke-Kirby, Mr Robert Hamblin, Director & Secretary, and Mr W. J. McWaters.

In welcoming the guests, Mr L. Brooke, Chairman of the Section, said how much the Section relies on the support given to this event by the business houses, and expressed pleasure that thanks to this support the attendance this year had reached a record figure of over 190. He complimented Mr A. Lageu, Social Secretary, for all his efforts and arrangements, and wished everyone present an enjoyable evening.

Responding on behalf of the guests, Mr Addenbrooke spoke with warmth of the close links which exist between the Birmingham PVL Club and the Bristol Section of OCCA, which are sustained through joint functions during the year.

The dancing went with a swing and during the interval a prize draw was held at which the presentations were made by Mrs Brooke.



Top Table Guests at the Bristol Section Dinner Dance (from left to right): Mr R. H. Hamblin, Director & Secretary, Mrs Tooke-Kirby, Mr J. Tooke-Kirby, Chairman, London Section, Mr B. Addenbrooke, President, Birmingham PVL Club, Mrs Addenbrooke, Mr L. J. Brooke, Chairman, Bristol Section, Mrs Brooke, Mr R. J. King, Chairman, Midlands Section, Mrs King and Mr W. J. McWaters

Register of Members

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

Ordinary Members

DHANOON, TAHSIN, BSc, 13/2/23 Harithiah, Baghdad, Iraq.
(*General Overseas*)
FAIRLIE, JOHN, BSc, 23 Ballocome Drive, Plains, Airdrie, Lanarkshire ML6 7NB.
(*Scottish*)
FARLA, ALBERT EDWARD, Roinks Nigeria Ltd. PO Box 937, Lagos, Nigeria.
(*General Overseas*)
GOODWIN, PETER CHARLES, BSc, 36 Abbey Walk, Heath and Reach, Leighton Buzzard, Beds.
(*Thames Valley*)
HARRISON, RICHARD WILLIAM, LRIC, 3 Boswell House, Felcourt Drive, Bradford BD4 0PH.
(*West Riding*)
JEFFS, DAVID, 24 Whieldon Road, Holmbush, St. Austell, Cornwall.
(*Bristol*)

LANE, KIM, BSc, Dulux NZ Ltd, 526 Ellerslie, Panmure Highway, Mt. Wellington 6, New Zealand.
(*Auckland*)
MANDAGI, WILLY, BSc, GRIC, PT Danapaints, Jl Pemuda-Pulogadung, PO Box 93/Jng, Jakarta, Indonesia.
(*General Overseas*)
VAIDYANATHAN, L. G., BSc, Myul Chemicals (P) Ltd, 17-A Industrial Suburb, Tumkur Road, Bangalore 22, India.
(*General Overseas*)
Associate Member
DOWNING, JOHN, 55 Glendown Avenue, Templeogue, Dublin 12.
(*Irish*)
Registered Student
MASON, STEPHEN, 41 Frankburn Road, Streetly, Sutton Coldfield, West Midlands B74 3QH.
(*Midlands*)

Forthcoming Events

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

November

Tuesday 1 November

West Riding Section: "Wood preservatives" by Dr G. Hall of TRADA at the Mansion Hotel, Roundhay Park, Leeds 8 at 7.30 p.m.

Thursday 3 November

Newcastle Section: "External pipe line coatings" by Mr D. Grey, Gas Board at St. Mary's College, University of Durham, Elvet Hill Road, Durham.

Friday 4 November

Irish Section: Annual Dinner Dance, Clarence Hotel, Dublin 2, at 8.30 p.m.

Monday 7 November

Hull Section: "Defoamers" by Mr R. W. Harrison of Diamond Shamrock (UK) Ltd, at the George Hotel, Land of Green Ginger, Hull at 6.30 p.m.

Tuesday 8 November

Scottish Section: "Dispersion—the key factor in pigment theory", by Dr W. Carr. Joint meeting with Society of Dyers and Colourists at the North British Hotel, Glasgow, at 7.30 p.m.

Thursday 10 November

Midlands Section—Trent Valley Branch: "Production control" by Mr D. J. Murray of Crown Decorative Products at the Crest Hotel, Pastures Hill, Littleover, Derby, at 7.00 p.m.

Thames Valley Section: "Infologistics for individuals (How to cope with the information explosion)" by Dr D. Moody of OCCAM, at the Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks at 6.30 for 7.00 p.m.

Friday 11 November

Manchester Section: "Theory versus practice in vacuum, pressure and centrifugal filtration" by Dr A. Rushton, UMIST, at the Manchester Literary and Philosophical Society, Manchester at 6.30 p.m.

Wednesday 16 November

London Section: "The influence of solar radiation on paint films". Day meeting in association with Thames Polytechnic, Woolwich at 10.00 a.m.

Ontario Section: "New approaches to the development of properties in paint films" by Prof. Schreiber of University-Polytechnic of Montreal at the Skyline Hotel, Toronto, at 6.00 p.m.

Thursday 17 November

Manchester Section: Student lecture "Epoxydised resins for anticorrosive coatings" by Mr A. McKay, Ciba-Geigy Plastics & Additives Co. at the Manchester Literary and Philosophical Society, Manchester at 4.30 p.m.

Wednesday 23 November

Scottish Section—Eastern Branch: "Pigment dispersion techniques—chipping" by Messrs P. J. Holland and D. Bradshaw of Foscolour Ltd, at the Alfton Hotel, 6 Grosvenor Crescent, Edinburgh 12, at 7.30 p.m.

Friday 25 November

Bristol Section: "Film for packaging" by Dr C. R. Oswin of British Cellophane Ltd at the Royal Hotel, Bristol at 7.15 p.m.

Midlands Section: Student lecture "Further education for surface coatings technicians" by Mr D. Clements at the Calthorpe Suite, County Ground, Edgbaston, Birmingham at 6.30 p.m.

West Riding Section: Dinner Dance at the Crown Hotel, Harrogate.

December

Thursday 1 December

Newcastle Section: "Some aspects of the marketing of paint" by Mr G. Campbell, Crown Decorative Products, at St Mary's College, University of Durham, Elvet Hill Road, Durham.

Monday 5 December

Hull Section: "Subjective comparisons—what does influence you?" by Dr W. E.

Craker, Laporte Industries Ltd, at the George Hotel, Land of Green Ginger, Hull, at 6.30 p.m.

Manchester Section: Lecture—Joint Institute of Printing/OCCA Manchester Section meeting—details to be announced.

Tuesday 6 December

West Riding Section: "Printing ink systems for textile colouration by sublimation and diffusion transfer methods" by Mr F. D. Hough, Coates Bros. Inks Ltd, at the Mansion Hotel, Roundhay Park, Leeds 8, at 7.30 p.m.

Thursday 8 December

Scottish Section: "Chemical waste disposal" by J. Smith, Re Chemicals International Ltd, at the Bellahouston Hotel, Glasgow, at 6.00 p.m.

Thames Valley Section: "Steel blasting—recent developments" by Mr T. W. Kelsall, KUE Engineering Ltd, at the Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks, at 6.30 for 7.00 p.m.

Friday 9 December

Irish Section: "Up to date position of EEC legislation on dangerous substances/preparations" by Mr F. Shaughnessy, Department of Labour, at the Clarence Hotel, Dublin 2, at 8.00 p.m.

Wednesday 14 December

Ontario Section: Ladies' evening. "Colour in fashion" by Miss P. Buchanan, T. Eaton Co. Ltd, at the Skyline Hotel, Toronto, at 6.00 p.m.

Scottish Section—Eastern Branch: "Hot stamping foils and gold leaf" by Mr B. J. Sitch, George M. Whiley Ltd, at the Alfton Hotel, 6 Grosvenor Crescent, Edinburgh 12, at 7.30 p.m.

1978

January

Wednesday 18 January

Ontario Section: "Anticorrosive functional pigments" by Dr P. Marr, Reed Ltd, at the Skyline Hotel, Toronto, at 6.00 p.m.

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New DPP plant, Pernis, Netherlands.
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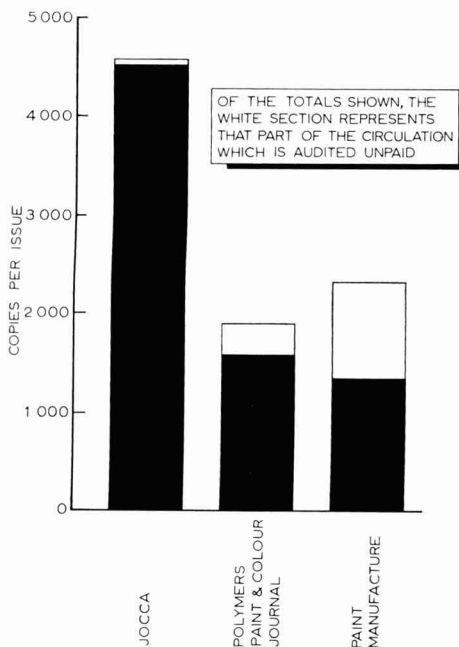
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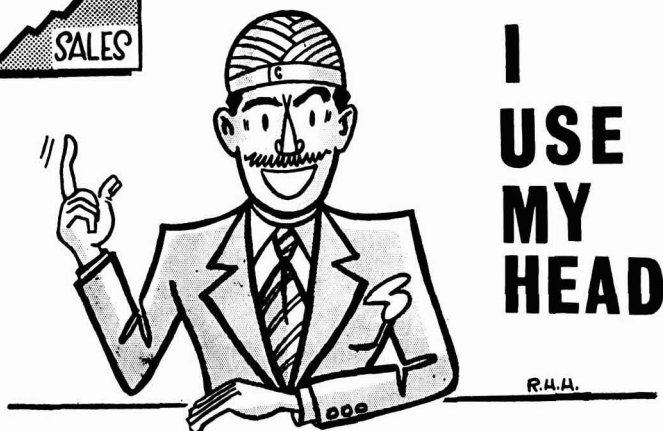
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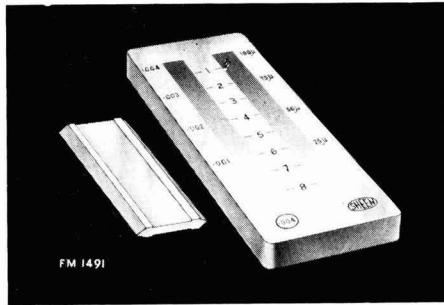
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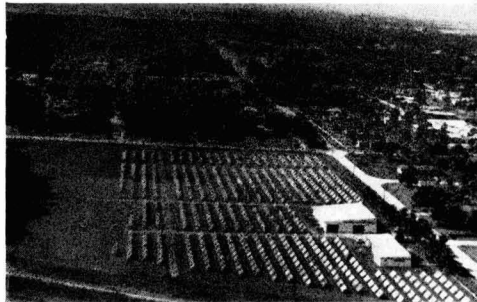
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