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OIL &
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OCCA-34 REVIEW
A NEW CONCEPT

***WINNER OF THE 1980 ABC REED INTERNATIONAL AWARD

†A new development in water-based can coatings
C. G. Demmer and N. S. Moss

Lower temperature curing blocked isocyanate for use in powder coatings
P. McBride

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†This paper formed the basis of 3 lectures at OCCA-34

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Editorial correspondence should be addressed to the Hon. Editor, *JOCCA*, Oil and Colour Chemists' Association at the address below.

General correspondence should be addressed to:

R. H. Hamblin, MA, FCIS,
Director & Secretary,
Oil and Colour Chemists' Association
at the address below.

Tel: 01-908 1086
Telex: 922670 (OCCA G)
Telegrams: OCCA Wembley

Assistant Editor: D. N. Buddles, BSc

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Transactions and Communications

A new development in water-based can coatings*

By C. G. Demmer and N. S. Moss

Epoxy Products Business Centre, Plastics Division, Ciba-Geigy Plastics and Additives Co., Duxford, Cambridge CB2 4QA, England

Summary

Demands for conservation and reduced solvent emission have led to increased interest in water-based systems for the internal lining of both food and beverage cans. The exacting requirements for these coatings are described. A number of the synthetic routes that have been devised to prepare water-dilutable can coating resins are reviewed. The chemistry and technology of a novel resin system that has been developed recently to meet these requirements is highlighted. Evaluation results for coatings based on this resin system are presented to show that suitable formulations can be developed to fulfil the major requirements for both beverage and food can linings.

Keywords

Types and classes of coatings and allied products

can coating
water base paint

Properties, characteristics and conditions primarily associated with

raw materials for coatings and allied products

water dispersible

Raw materials for coatings

raw materials used in manufacture or synthesis of ingredients for coatings

amino acid
phenol

Un nouveau développement en revêtements à base acqueuse pour boîtes à conserves

Résumé

Les exigences pour la conservation et la réduction de dégagement de dissolvant ont conduit à un intérêt toujours plus grand dans des systèmes à base acqueuse pour le revêtement intérieur de boîtes à conserves destinés aux aliments et aux boissons. Les exigences précises pour ces revêtements sont décrites. Une série d'itinéraires synthétiques qui ont été imaginés pour préparer des résines solubles à l'eau pour revêtements boîtes à conserve sont examinés. La chimie et la technolgie d'un système de résine original qui a été développé récemment pour satisfaire à ces exigences sont particulièrement soulignées. Des résultats d'évaluation de revêtements basés sur ce système sont présentés dans le but de montrer que des formulations appropriées peuvent être développées pour satisfaire aux exigences les plus importantes pour les revêtements de boîtes à conserves tant pour les aliments que pour les boissons.

Eine Neuentwicklung auf dem Gebiete der wasserverdünnbaren Doseninnenschutzlacke

Zusammenfassung

Die Forderungen des Umweltschutzes und Bestrebungen zur Verminderung der Lösemittelemissionen haben ein wachsendes Interesse an wasserverdünnbaren Systemen für den Innenschutz von Konserven- und Getränkedosen hervorgerufen. Die kritischen Anforderungen an diese Lacke werden beschriben. Ein Überblick von synthetischen Methoden zur Herstellung wasserverdünnbarer Doseninnenschutzlacke wird gegeben. Die chemie und Technologie eines neuen Harzsystems, das kürzlich zur Befriedigung dieser Anforderungen entwickelt worden ist, werden vorgestellt. Prüfungsergebnisse für Lacke, die auf diesem System aufgebaut sind, werden angeführt. Es wird gezeigt, dass man geeignete Formulierungen entwickeln kann, die die Hauptanforderungen an den Innenschutz von Getränke- und auch Konservendosen erfüllen.

1. Introduction

Coatings for the interior of metal containers for food and beverage, and also collapsible tubes have until recently been based on polymer solutions at relatively low concentrations in organic solvents. The solvent in the coatings acts only as a carrier to convert the resins into a form suitable for application to the substrate. It adds unnecessarily to the applied cost of the coating and also poses risks of flammability and toxicity.

Of the existing solvent-based coatings for this market,

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*This paper formed the basis of three lectures delivered at the OCCA-34 Exhibition, 27-29 April 1982.

epoxy resins, derived from Bisphenol A, form an important part of the resin requirements. They are used in combination with aminoplast or phenolic crosslinkers for:

- Internal lacquers for 2-piece beer and beverage cans.
- 2-piece can ends.
- 3-piece can ends and bodies for beverage and food.

Epoxy-urea formaldehyde resin combinations give rapid cure, good product resistance, especially to alcohols and carbonated beverages, and may also give a lower applied cost than epoxy-phenolic resin combinations. Formulations of this type would therefore be most widely used for coating beer and beverage cans both of 2- and 3-piece construction, and could be applied by spray or rollercoating.

Epoxy-phenolic resin combinations give resistance to product processing, sulfur staining and good flexibility. Coatings of this type are most commonly applied by rollercoating to metal used for fabricating 3-piece can bodies and ends for the food packaging industry.

With the advent of the Los Angeles County Rule 66 in the 1960s restricting the emission of volatile organic solvents, and more recently with the EPA regulations governing the volatile organic content of coating solvents, the change toward various alternative technologies had become significant in the USA by the late 1970s. Legislation in the UK has been less restrictive on organic solvent emission, but recently there has been increasing pressure both on this issue and in other areas such as the reduction of fire risks, the reduction of energy costs and the need to reduce raw material costs, particularly of an item which ultimately forms no part of the finished coating.

To meet these requirements several new technologies have been considered (these are in addition to physical techniques such as solvent absorption and recovery systems and exhaust gas burners on ovens):

- High solids coatings

  Whilst some increase in solids content of existing systems can be made, e.g. from 35-40 per cent to 50-55 per cent, without major sacrifice of properties, the problems of increasing to 70 per cent solids are considerable. Can stability and application properties become a problem and the volatility of the lower molecular weight polymers used becomes significant.

- Powder coatings

  Powder coatings are used on cans for coating of side seams and have been considered for the complete coating. Problem areas are film thickness, which is normally much too high and therefore costly, cure speed and suitability of the systems for foodstuff contact.

- Aqueous powder suspensions

  This development of powder coatings enables lower film thicknesses to be applied, but for foodstuff contact the choice of binder systems is limited and the technology is still at a very early stage.

- Ultraviolet curable systems

  Only for use on can exteriors since they are not currently approved for foodstuff contact.

- Water-dilutable/soluble systems

  These materials are the main subject of this paper, in particular some of the research and development activities and recently patented technology of Ciba-Geigy.

2. Requirements for water-dilutable can coatings

The following performance profiles were compiled in consultation with the manufacturers of can coatings:

2.1 For 2- and 3-piece food cans

- Dry film thickness 2-5 μm when applied by rollercoating or spraying.
- At application viscosity the solids content should ideally be 35-40 per cent for rollercoating or 25 per cent for spray coating.
- Cure in 8-10 minutes at 200°C or less (1-2 minutes at 215°C for spray coatings).
- Good adhesion to tinplate and tin-free steel.
- Wedge bend test 80 per cent +.
- Resistance to sterilisation at 120°C for 90 minutes.
- Resistance to 5 per cent acetic acid at 98°C for 3-6 hours.
- Must impart no flavour to can contents.
- Must prevent sulfur staining of tinplate.

2.2 For beer and beverage cans

- Dry film thickness 2-5 μm when applied by rollercoating or spraying.
- At application viscosity the solids content should ideally be *ca.* 35 per cent when applied by rollercoating for 3-piece cans, and *ca.* 25 per cent when spray applied to 2-piece cans.
- Cure for 1 minute at a peak metal temperature (PMT) of 215°C.
- Good adhesion to tinplate, tin-free steel and aluminium.
- Pale in colour.
- Wedge bend test 80 per cent +.
- Resistance to boiling water for 1 hour.
- Resistance to beer pasteurisation at 80°C for 30 minutes.
- Resistance to carbonated beverages.
- Freedom from tainting of can contents (flavour test).
- Resistance to dilute acids at 98°C for 1 hour.

2.3 General

- Storage stability for basic components – minimum 12 months.
- Storage stability for complete coating – 3-6 months.
- Must conform with current regulations such as the US Food and Drug Administration Regulations 21 CFR 175.300 (relating to food contact applications including alcoholic beverage use).
- Must contain the minimum possible level of organic

coupling solvent. To conform with US environmental regulations this must be not more than 20 per cent by volume of organic solvents.

- Applied cost must not exceed that of a conventional solvent-based coating for the same application.

One of the most difficult of these requirements to meet is conformity with FDA regulations. The list of approved or safe ingredients for use in coatings has been built up over many years around solvent-based systems and is, therefore, very restrictive on the type of chemistry which can be utilised. Whilst the FDA regulations are not a legal requirement in the UK, the can industry prefers to conform to the regulations as a basic standard of suitability for foodstuff contact.

The use of water as a solvent itself introduces several problems. Although the requirement is for a resin which is water-dilutable for application, after curing the resin must be completely insoluble to provide a protective coating. Thus the hydrophilic groups that are introduced to confer water-dilutability have to be carefully selected so that their hydrophilicity does not diminish the resistance properties of the cured coating and to ensure that they are not leached out of the cured coating. To meet the stability requirements listed above, the system has to remain unaffected by the aqueous environment for a considerable time. This has proved another exacting challenge and many of the systems initially studied have been ruled out by their poor hydrolytic stability.

The chemical routes available for the production of novel water-dilutable can coatings are further restricted by the need to keep cost as low as possible so as not to off-set completely any cost savings arising from reduction of solvent content.

3. Review of existing technology

Refs, 1-18

The aim of this section of the paper is to discuss some of the chemistry that has been put forward as a means of preparing water-dilutable can coatings and to examine the effect of the constraints described above on these proposals.

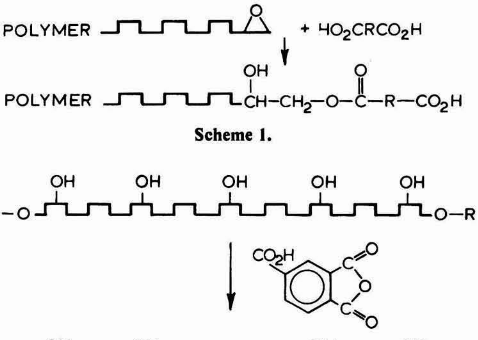
Because the list of possible options is so large, for the sake of the present paper the intention is to review only the more important methods that have been proposed for producing water-dilutable derivatives of epoxy resins for use in can coating systems.

The epoxy resins conventionally used for solvent-based can coatings are produced by the reaction of bisphenol A with epichlorohydrin and are of the general structure shown in Figure 1.

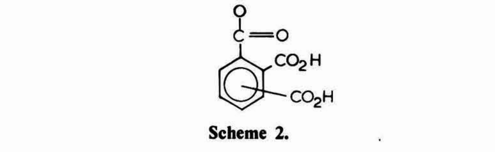
Average values of n are typically 8-20 in the resins used for can coating applications. Reaction with aminoplasts or phenolic resins is mainly via the hydroxyl groups on the polymer backbone; the cure is not dependent on the presence of epoxy groups. Resins of this type are normally applied as solutions containing 60-75 per cent organic solvents.

The aim of most (though by no means all) of the synthetic routes that have been suggested is the introduction into the polymer of a carboxyl group, which can be neutralised with a volatile amine to confer water-dilutability. If the solubilising group is attached via reaction of the epoxy groups, the secondary hydroxyl groups along the backbone of the polymer are available for the cure reaction with aminoplasts or phenolic resins, as described above for solvent-borne epoxy resins.

One of the simplest methods of introducing a carboxyl group into an epoxy polymer is to react the epoxy groups with a dibasic acid as illustrated in Scheme 1. An alternative method that can be applied to any hydroxyl-containing polymer is the reaction of a 1,2-carboxylic anhydride with an appropriate fraction of hydroxyl groups (sufficient hydroxyls should be retained to permit crosslinking). This chemistry is shown in Scheme 2. Solid epoxy resins capped by reaction with monohydric phenols or monocarboxylic acids have been used as suitable starting polyols[1]. However, using an unmodified solid epoxy resin, esterification of the hydroxyl groups can also be achieved whilst retaining a substantial amount of the epoxy groups[2]. Water-solubility can easily be obtained by these methods, but the ester linkages are susceptible to hydrolysis[3] – with the result that water-solubility cannot be retained for a sufficiently long time.



Scheme 1.



Scheme 2.

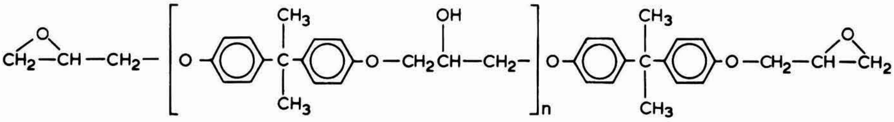
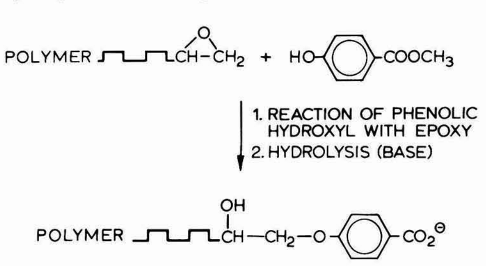


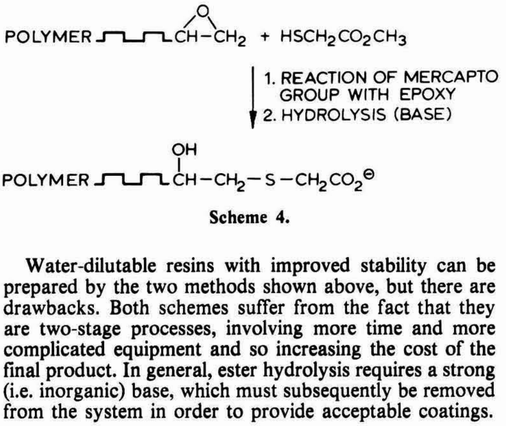
Figure 1. Idealised structure for a Bisphenol A epoxy resin

In order to introduce carboxyl groups linked to the backbone resin by non-hydrolysable bonds, several two-step processes have been tried as illustrated in schemes 3 and 4. For example, reaction of the phenolic hydroxyl of the methyl ester of p-hydroxybenzoic acid with an epoxy provides a non-hydrolysable, bond and subsequent hydrolysis of the methyl ester produces the carboxyl group, which can be neutralised to obtain water-dilutability[4].

Alternatively the mercapto-group of methyl thioglycolate can be reacted with an epoxy group-containing polymer, again providing the non-hydrolysable link. The water-solubilising carboxylate ion is generated by hydrolysis of the methyl ester[5].



Scheme 3.

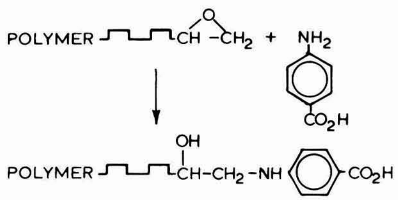


Scheme 4.

Water-dilutable resins with improved stability can be prepared by the two methods shown above, but there are drawbacks. Both schemes suffer from the fact that they are two-stage processes, involving more time and more complicated equipment and so increasing the cost of the final product. In general, ester hydrolysis requires a strong (i.e. inorganic) base, which must subsequently be removed from the system in order to provide acceptable coatings.

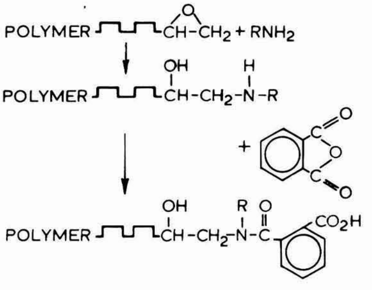
An interesting development has been the reaction of p-aminobenzoic acid with epoxy groups, which is seemingly unique. Competition between the amino and carboxyl groups for the available epoxy groups would be expected, as is found with other amino acids. However, reaction occurs almost exclusively at the amino group. This reaction has been used as a method of preparing non-hydrolysable carboxyl functional resins (see Scheme 5) which are neutralised to obtain water-dispersibility[6].

Stable aqueous systems are obtained which show good application properties and which can be cured to produce tough, resistant coatings. The main drawbacks to this route are the high price of p-aminobenzoic acid and the rather slow reaction of p-aminobenzoic acid with epoxy resins[7]. It is claimed that under specific conditions amino acids other than p-aminobenzoic acid can be reacted with epoxies to prepare carboxyl group-containing resins[7].



Scheme 5.

Amide linkages have also been exploited as a means of attaching a carboxyl group to a resin via a non-hydrolysable link. In the case of epoxy resins, the epoxy group is first reacted with a primary amine or ammonia and then the amine-tipped polymer is reacted with an anhydride, as depicted in Scheme[8] 6. Water-dilutable compositions based on these products show rather poor resistance properties[9].



Scheme 6.

As well as these modifications to epoxy resins, efforts have also been directed towards utilising acrylic resin technology in the production of water-dilutable can-coating resins. It was soon recognised that initial attempts to use acrylics as the sole resin would not lead to a satisfactory balance of properties in the product[10].

Instead, acrylic-epoxy coating compositions were explored. The epoxy resin is combined with a carboxyl-containing acrylic copolymer which is neutralised with a volatile amine[11]. Aqueous coating compositions of these adducts have exhibited poor storage stability and are said to have poor resistance to water when cured, because the adducts are susceptible to hydrolysis[12,13]. More recently it has been claimed that, if the epoxy resin is reacted with the carboxyl-containing acrylic under specific conditions, instability is no longer a problem and cured coatings show good resistance to boiling water[12].

An alternative approach to producing a stable system is to react an epoxy resin with a mixture of unsaturated monomers under conditions which favour the formation of graft copolymer – usually a high concentration of initiator such as benzoyl peroxide is used[13]. The grafting obtained is said to be predominantly via hydrogen abstraction along the epoxy backbone rather than via carboxyl-epoxy esterification. This latter reaction can be avoided completely by first capping the epoxy resin and then reacting with unsaturated monomers[14]. The final composition comprises a mixture of (1) acrylic grafted to epoxy, (2) ungrafted acrylic and (3) unmodified epoxy (Figure 2)[10]. Provided that sufficient grafting is achieved, the water-dilutable resins produced show good resistance to boiling water when cured with a suitable crosslinker.

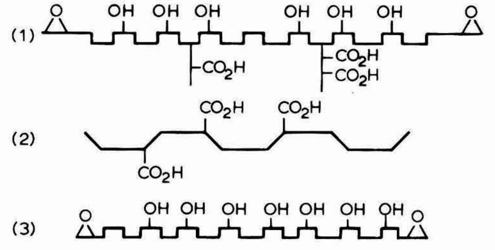


Figure 2. Mixture of components in epoxy/acrylic graft systems

The patent literature abounds with methods of preparing water-dilutable cationic resins for use in electrodeposition, but so far cationic systems have had little impact on the can-coating sector. One of the major reasons for this is probably the lack of amines already approved by FDA. Although there are a number of amines in the FDA list, only a restricted number appear in the relevant subsection. Also, cationic systems have only a limited storage stability when combined with the crosslinker. Acids are used to neutralise the cationic resins, which means that to achieve water-dispersibility the pH is slightly below pH 7 and under these conditions co-reactants such as UF and MF resins will slowly polymerise – increasing the viscosity of the dispersion. However, by careful formulation cationic systems can be obtained which have reasonable storage stability before cure and chemical resistance properties after cure[15], though not quite up to the standard of solvent-based epoxy systems.

The methods described so far have relied on the introduction of ionisable groups into the polymer and depend upon a neutralising agent to achieve water-dilutability. Other lines of investigation that have been pursued are the use of external emulsifiers and the introduction of hydrophilic groups into the epoxy resin to produce dispersions which can be directly diluted with water.

In fact a spectrum of resin systems is possible ranging from very hydrophilic epoxy resins, which are readily diluted and form dispersions with extremely small particle size, to unmodified high molecular weight epoxy resins requiring a surfactant to achieve water-dilutability and having a larger, but nevertheless still very small, particle size (0.1-1.0 µm)[16].

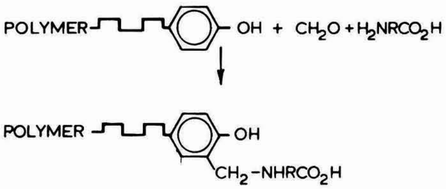
The hydrophilicity of the modified epoxy resin can be varied by altering the proportion of the hydrophilic moiety built into the backbone[17]. Coating solutions containing these hydrophilic epoxies have excellent handling properties, but the films produced are lacking in chemical resistance. On the other hand, high molecular weight epoxies needing external surfactants[18] possess exceptional chemical resistance, but the application properties are less than satisfactory. A reasonable compromise can be achieved with a combination of a hydrophilic epoxy resin and an emulsified unmodified epoxy resin[16].

Clearly there has been significant progress in the development of water-dilutable can coatings, but there is still considerable scope for improvements to be made to achieve satisfactory systems, i.e. water-dilutable resins conforming to the FDA regulations which at the same time match the outstanding application and resistance properties characteristic of solvent-borne epoxy systems.

4. New development

Refs, 19-22

The chemistry of the Mannich reaction has been the subject of substantial research since it was first studied by Mannich[19] in 1912, and this has led in turn to numerous industrial applications[20]. Amino acids are one group of compounds that readily undergo the Mannich reaction and yet they have received little attention[21]. The present report is concerned with the discovery that the Mannich reaction of an amino acid and a phenolic-OH containing polymer, as shown in Scheme 7, can be utilised to prepare some very interesting water-dilutable resins[22].



Scheme 7.

There are several advantageous features of this system. The carboxyl group is linked to the resin via non-hydrolysable bonds, so good hydrolytic stability would be anticipated. The Mannich reaction of amino acids with phenolic-OH containing polymers is rapid and several simple amino acids are readily available at commercially acceptable prices. Provided that the basic phenolic containing polymer is carefully selected, systems in conformance with the FDA Food Additive Regulations can be formulated. Coating systems on this basis have been found to give very low levels of extractives, e.g. 8 per cent alcohol extractives as described in FDA section 175.300 *ca.* 0.01 mg/sq inch. Suitable basic resins can be obtained by the modification of an epoxy resin with a multifunctional phenolic material. The secondary hydroxyl groups in the epoxy backbone are then available for crosslinking reactions. The molecular weight of the water-dilutable resin can be varied within wide limits according to the molecular weight of the epoxy resin used, and the Mannich reaction with amino acids allows considerable scope for varying the acid value of the resin. By these means it is possible to produce a spectrum of water-dilutable resins from the completely soluble to those with borderline solubility which resemble emulsions in appearance and properties.

From these a polymer variant has been selected for general evaluation. The properties and coating performance of the selected polymer version (SPV) are detailed below together with some information on the effect of composition changes.

A wide variety of co-reactant resins can be used to cure these new anionic resins. Water-soluble aminoplasts, e.g. methylated melamine formaldehyde and methylated urea formaldehyde resins, and water-dispersible phenolic resins are commercially available and are readily incorporated with the new resins. Also, non-water-dispersible resins, such as butylated benzoguanamine formaldehyde and butylated phenolic resins, can be formulated into water-dilutable coatings, the new anionic resin performing as a dispersant for the insoluble resin.

5. Evaluation of selected polymer version (SPV)

5.1 Typical properties

- Organic solvent content – *ca.* 40.2 per cent as butoxyethanol.
- Volatile amine content – *ca.* 3.0 per cent.
- Polymer content – *ca.* 56.0 per cent.
- Viscosity at 25°C – 50-100 Pa s typically.
- Gardner colour – *ca.* 5 units.
- Acid value of polymer solids – *ca.* 50 mg KOH/g.
- Hydroxyl equivalent weight of backbone polymer – *ca.* 320.

The anionic polymer has been evaluated with a wide variety of crosslinking agents both for food can and beer and beverage can applications.

5.2 Application and curing

All systems have been tested over electrolytic tinplate and aluminium. Diluted lacquers were applied by draw down bar at the application solids applicable to the end-use to give dry film thicknesses of 2-4 µm (film weight 2.5-5 mg/sq inch). Coated panels were cured in a forced air oven for either 3 minutes at 215°C (simulating 1 minute 215°C PMT) or 5, 12 and 20 minutes at 200°C.

5.3 Testing methods

- MEK rub test

  Number of double rubs with a cloth soaked in methyl ethyl ketone to produce obvious effect on the coating.

- Wedge bend test

  The coated panel is bent over a 6 mm mandrel and then deformed by impact to give a wedge tapering from 6 mm to zero over a 10 cm length. It is then immersed in copper sulfate solution and the percentage of the length unaffected is determined.

- Resistance to boiling water and 5 per cent citric acid

  The panels are immersed for 60 minutes in test liquids at 100°C and assessed for adhesion (crosshatch), blistering and film discolouration.

  Results for all resistance tests are rated for both adhesion and film integrity on a 0-5 scale, where 0 is the best result. In the tables, results are expressed as 0/0 = adhesion/film integrity.

- Beer pasteurisation

  The panels are immersed for 30 minutes in commercial lager beer at 80°C and checked for adhesion (crosshatch) and blistering or discolouration of the coating. Ratings are expressed as for those of boiling water resistance.

- Sterilisation resistance

  Panels are "pressure cooked" for 1 hour at 120°C to simulate food processing. This test has also been used for screening in beer and beverage applications. Ratings are expressed as for boiling water resistance.

- Acetic acid resistance

  The panels are immersed for 3 to 6 hours in a 5 per cent solution of acetic acid at 98°C. Assessment and ratings as for boiling water resistance.

- Acetic/tartaric acid resistance

  The panels are immersed for 4 hours in a solution of 5 per cent acetic acid and 2 per cent tartaric acid at 98°C. Assessment and ratings as for boiling water resistance.

5.4 Results

- Evaluation for beer and beverage applications

Table 1 illustrates the effect of variation of type and quantity of amino resin crosslinker on the performance in beer and beverage application testing. The evaluation programme has shown that it is not necessary to use a water-soluble aminoplast since conventional butylated solvent-based aminoplasts of the type normally used in coatings for this application can also be introduced into the water-dilutable polymer system. Such blends are equally stable, the disadvantage of the butylated compared to the water-dilutable methylated resins being that butylated aminoplasts are normally sold as solutions of *ca.* 60 per cent in organic solvent. However, there are now a limited number of 100 per cent solids butylated resins available from sources in the USA. The resins A, B and C in Table 1 are all commercially available highly methoxymethylated melamine resins.

It can be seen from Table 1 that the use of urea formaldehyde resin results in generally better resistance to boiling water and dilute acids. The use of benzoguanamine formaldehyde resins is also possible, and although giving reduced resistance to the MEK rub test at equivalent addition levels to MF resin, can give improvements particularly in adhesion in tests involving the more aggressive acids.

The molecular weight of the backbone polymer is critical in the formulation of systems for beer and beverage applications. The choice of molecular weight was influenced by several factors. Very high molecular weight polymers require low application solids contents and/or higher contents of water-miscible organic solvents.

Table 2 illustrates some of the effects of varying the amino acid and molecular weight of the backbone polymer on the performance of cured coatings.

The polymers referred to in Table 2 were therefore prepared from backbone polymers of "low" and "medium" molecular weights. They were solubilised with amino acids A, B and C. So far as possible, identical reaction conditions were employed. The results in Table 2 show that polymers of medium molecular weight yielded coatings with much better resistance to beer, boiling water and sterilisation. This molecular weight corresponds to the selected polymer version. It can also be seen from Table 2 that polymers of medium molecular weight yield coatings with much greater flexibility in the wedge bend test. The choice of amino acid also has a pronounced effect on coating properties, amino acid C being superior particularly in resistance tests. Amino acid C is used in the selected polymer version.

- Evaluation for food can applications

To achieve the required properties for food can applications, in particular the resistance to sterilisation and to dilute acetic acid, phenolic resin curing agents have been evaluated with the selected polymer version.

Table 1

Testing of selected polymer version for beer and beverage applications

Co-reactant	Solids ratio SPV/ co-reactant	Cure temp/time at PMT	MEK rub resistance	Wedge bend test % pass	Beer pasteur-isation test	Boiling 5% citric acid resistance	Boiling water resistance
None		215°C/1 min	3	86		0/4	
Methylated Melamine Formaldehyde Resin (A)	94:6	215°C/1 min	19	88	0/0	0/1	0/1
„ (A)	89:11		34	88	0/0	0/1	0/1
„ (A)	80:20		>50	90	0/0	0/2	0/1
„ (B)	80:20		>50	88	0/0		0/0
„ (C)	80:20		>50	90	0/0	1/2	0/0
Methylated Urea Formaldehyde Resin	94:6	215°C/1 min	6	90	0/0	0/2	0/1
„	80:20		>50	88	0/0	0/1	0/0
Methylated Benzoguanamine Formaldehyde Resin	94:6	215°C/1 min	4	88	0/0	0/3	0/1
„	89:11		16	88	0/0	0/1	0/0
„	50:50		48		0/0	0/1	0/0
Butylated Urea Formaldehyde Resin	94:6	215°C/1 min	6	90		0/3	0/1
„	89:11		20	90	0/0	0/0	0/0
„	80:20		47	87	0/0	0/0	0/0
„	67:33		>50	80	0/0	0/0	0/0

Table 2

Effect of amino acid type and backbone molecular weight

Backbone polymer molecular weight	Amino acid	Ratio of polymer/ MF	Cure temp/time PMT	MEK rub resistance	Wedge bend test % pass	Beer pasteurisation test (1 hour)	Boiling water resistance (1 hour)	Sterilisation resistance 120°C/1 hour
Low	A	75:25	215°C/1 min	>50	70	4/0	3/5	4/5
Low	B	75:25		>50	77	4/0	44/1	4/2
Low	C	75:25		>50	87	2/0	2/1	4/2
Low	B	80:20		>50	75	4/0	4/2	4/2
Medium	B	80:20		>50	90	3/0	3/0	4/2
Medium	C	80:20		>50	92	0/0	0/0	1/1

It has been established that the type of phenolic resin used is of particular importance and that both water-soluble and solvent-soluble phenolic resins can be incorporated into the system with the anionic resin acting as the dispersant for the insoluble co-reactants. Relatively high levels of co-reactant can be incorporated in this way. The viscosity/solids relationship is dependent on the solubility of the co-reactant used, higher solids contents being possible with insoluble co-reactants.

Table 3 illustrates the effect of variation of the type and level of phenolic resin co-reactant.

In Table 3 the phenolic resins are coded as follows:

(A) Conventional butylated bisphenol A formaldehyde resin (supplied as a solution in butanol).

(B) Un-etherified resole from a substituted phenol (supplied as a solid and used as a butanol solution).

(C) Un-etherified resole from a substituted phenol (supplied as a solid and used as a butanol solution).

(D) Proprietary phenolic resin emulsion.

(E) Proprietary phenolic resin emulsion.

(F) Water-soluble phenolic resole (non-ionic).

(G) Experimental water-soluble bisphenol A resole.

The results in Table 3 show that when combined with suitable phenolic resins (A and F), coatings can be obtained which fulfil the resistance requirements for food can applications. The use of pre-emulsified phenolic resins D and E was detrimental to the resistance properties of the cured coatings.

Stability testing

Data have been accumulated during the development programme which indicate that the stability of products prepared from Mannich reactions with amino acids is satisfactory.

The selected polymer version described above has been stored at 23°C for 12 months with only a 10 per cent increase in viscosity. Dilutability is not affected by long term storage. When formulated with a water-soluble methylated melamine formaldehyde resin and diluted to application solids, an increase in viscosity of 5 per cent was observed over a 12 month period. Cure tests after 12 months storage on the formulation described above gave performance results similar to those obtained initially.

Table 3

Effect of variation of phenolic resin level and type (tests on tinplate unless specified)

Phenolic resin	Ratio of SPV/PF (solids)	Cure temp/time at PMT	MEK rub resistance	Wedge bend test % pass	Sterilisation test (tinplate)	Boiling 5% acetic acid (3 hours)	Boiling 5% acetic acid (6 hours)	Sterilisation test (aluminium)	Acetic/tartaric acid test (4 hours)
A	75:25	200°C/12 min	>100	85	0/0	1/0	1/1	0/0	0/2
A	67:33	200°C/12 min	>100	80	0/0	0/0	0/1	0/0	0/1
A	67:33	200°C/20 min	>100	80	0/0	0/0	0/1	0/0	0/1
B	75:25	200°C/12 min	70	80	0/1	5/4	5/4		
B	60:40	200°C/12 min	>100	83	0/1	0/3	1/3		
C	67:33	200°C/12 min	21	90	0/0	1/4	2/5		
D	75:25	200°C/12 min	47	82	4/5	1/3	4/5		
E	75:25	200°C/12 min	12	77	0/5	1/5	2/5		
F	90:10	200°C/12 min	5	88	0/2	3/5	5/5		
F	75:25	200°C/12 min	7	85	0/0	0/1	0/1		
F	67:33	200°C/12 min	11	85	0/0	0/0	0/1		
F	90:10	200°C/ 5 min	3	80	0/2	5/5	5/5		
F	75:25	200°C/ 5 min	3	85	0/1	0/2	2/2		
F	67:33	200°C/ 5 min	7	84	0/1	1/2	4/2		
G	75:25	200°C/12 min	13	87	0/1	0/5	0/5		

The stability of other formulations will vary with the co-reactant used. The results of shorter term stability tests with water-insoluble aminoplasts and phenolic resins also appear to be satisfactory.

6. Conclusions

Water-dilutable polymers are currently regarded as having considerable potential for producing environmentally acceptable can coatings. As a result of intensive work in this field, many synthetic routes have been devised. They have had varying degrees of success. The aim has been to produce water-dilutable systems matching the excellent application and resistance properties characteristic of conventional solvent-based coatings, and conforming with the requirements of the FDA.

A promising new route to water-dilutable coatings involves the Mannich reaction of amino acids with resins containing phenolic-OH groups. Using this route it is possible to prepare resins which, when formulated with suitable co-reactant resins, fulfil the major requirements for beverage and food can linings. No problems are envisaged with routine high volume manufacture of these products.

Acknowledgment

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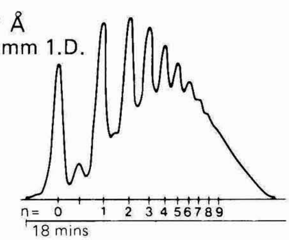
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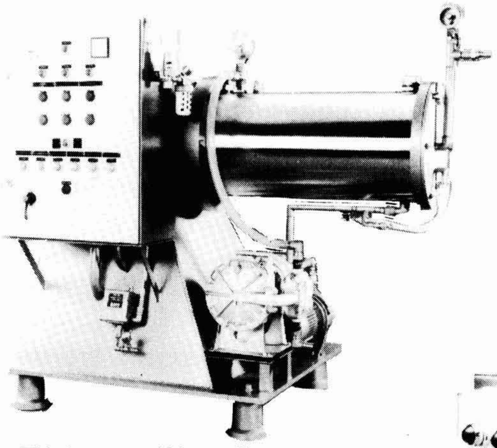

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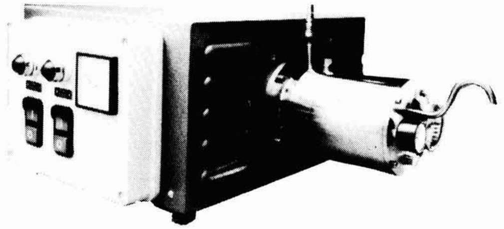

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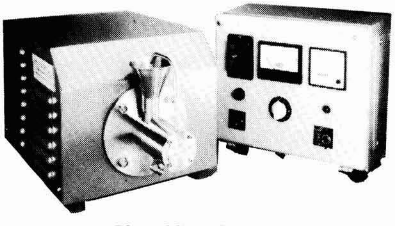

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Lower temperature curing blocked isocyanate for use in powder coatings

By P. McBride

Eastman Kodak Ltd, Eastman Research Laboratory, Acornfield Road, Kirkby, Liverpool L33 7UF, England

Summary

The development is described of a blocked isocyanate which may be used in conjunction with a hydroxylated polyester resin to provide a system which will cure at lower temperatures than is necessary with the usual polyester resins.

The system is intended for use with powder coatings applied by electrostatic spraying.

Keywords

Properties, characteristics and conditions primarily associated with

coatings during application

curing temperature

Raw materials for coatings

binders (resins, etc.)

polyester resin

raw materials used in manufacture or synthesis of ingredients for coatings

isocyanate adduct

Types and classes of coatings and allied products

powder coating
stoving finish

Processes and methods primarily associated with

manufacturing or synthesis

block polymerisation

application of coatings and allied products

electrostatic coating

Un isocyanate bloqué durcissable à température moins élevée, et destiné à être utilisé en revêtements en poudre

Résumé

On décrit la mise au point d'un isocyanate bloqué que l'on peut utiliser en combinaison avec une résine polyester hydroxylée afin de créer un système durcissable à température moins élevée que celle exigée par les résines polyesters classiques.

Le système est destiné à être utilisé en revêtements en poudre pour application par pistolage électrostatique.

Ein blockiertes Isozyanat für Pulverbeschichtungen, das bei niedrigerer Temperatur gehärtet wird

Zusammenfassung

Die Entwicklung eines blockierten Isozyanats wird beschrieben, dea mit einem hydroxylierten Polyesterharz angewandt werden kann, um ein System anzuliefern, der bei niedrigerer Temperatur als der notwendiger im Falle der gewöhnlichen Polyesterharze gehärtet werden kann.

Das System ist zur Anwendung mit der eletrostatischen Spritzpulverbeschichtungen bestimmt.

Increasing awareness of the problems of environmental pollution, coupled with the severe increase in raw material and energy prices – witnessed over the last decade – has resulted in the coatings industry developing new types of coating systems. These systems have been designed to minimise pollution and/or energy usage. One of the most promising of the new systems is powder coating. This represents the ultimate in non-polluting compositions in that it consists of 100 per cent solids in the form of a finely divided powder.

The technique of powder coating is, by now, well known. The powder is electrically charged during spray application and the substrate to be coated is earthed (Figure 1). Thus the charged powder is attracted to the earthed substrate and covers it. The coated substrate then undergoes stoving in the normal manner; the powder melts, flows out and a smooth continuous finish results. From a pollution standpoint, the advantages of powders over conventional solvent-based coatings are:

(i) No polluting solvent is involved

and

(ii) Expensive loss of raw material via venting to the atmosphere is minimised

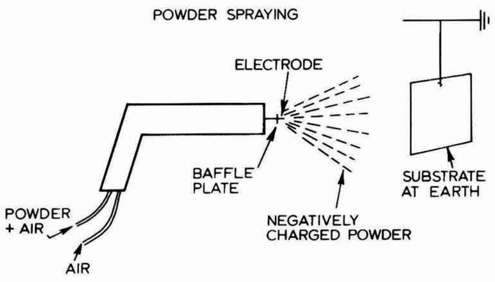


Figure 1. The powder coating process

Hydroxylated polyester resins are widely used in powder coatings and because of Eastman's position as a major supplier of glycols and diesters for use in such polymers, we at Eastman Research Laboratory, Kodak Ltd, Kirkby, have been particularly interested in promoting these systems. However, powder coatings based on hydroxyl-functional polyesters generally demand higher stoving temperatures than those required for conventional liquid coatings e.g. 180°C/15 minutes for powder compared to 135°C/25 minutes for conventional liquid coatings. We see that while powders minimise the pollution problems, there is still a need from an energy viewpoint for a polyester-based powder coating which cures at a lower temperature than is currently required. The present work was carried out in response to this need.

It is important to appreciate at the outset that a number of conflicting requirements of powder coatings actually limits the extent to which cure temperature can be reduced. For example, it is vital that the finely divided powder remains in a free flowing state even after extended storage. Any cold flow which results in agglomeration of the powder would render the coating unusable. To avoid cold flow, the base resin used in the powder should have a glass transition temperature (T_g)$\geqslant$ 60°C. Such a resin will generally have a softening range of 90-100°C. How this restricts the minimum achievable cure temperature becomes apparent when one considers the technique used to mix the powder ingredients. The ingredients are melt compounded in what is essentially a high shear extruder. This ensures the intimate and uniform dispersion of all ingredients, which is necessary to achieve good coating properties. A resin with a softening range of 90-100°C will need to be melt mixed at 100-110°C. In order to avoid any premature crosslinking during melt compounding, it is essential that the cure reaction does not take place at the mix temperature. Indeed, to be fail-safe, cure should not commence until some 20°C above this temperature. Furthermore, to achieve good flow out of the coating on fusion, it is desirable that there be a suitable induction period between melting of the resin and the increase in viscosity of the melt due to onset of cure. Bearing these factors in mind, we conclude that, with current polyester resins, a temperature of 140-150°C would represent the minimum achievable cure temperature consistent with the foregoing requirements.

Awareness of the foregoing restrictions enables us to more clearly define our ultimate objective. Namely, to devise a cure reaction for hydroxyl-functional polyesters which complies with the following property profile:

(i) Effect cure at temperatures of 140-160°C in $\leqslant$30 minutes.

(ii) Emit no volatiles during cure.

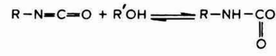
(iii) Impart good physical properties to the finished coating.

(iv) Permit all coating ingredients to be melt mixed without any pre-cure occurring.

(v) Allow sufficient flow of the molten coating during fusion to give a high gloss finish with good appearance.

(vi) Allow stable storage of the powder coating.

A crosslinking reaction which theoretically meets requirements (i) and (ii) is that between hydroxyl and isocyanate groups (Figure 2).

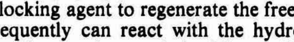


$$R{-}N{=}C{=}O + R'OH \rightleftharpoons R{-}NH{-}\underset{O}{\underset{\|}{C}}OR'$$

Figure 2. Reaction between isocyanate and hydroxyl

This is an addition reaction involving no elimination products. One problem, however, from our point of view is that it can take place at temperatures as low as 90°C in 30 minutes.

Therefore, in order to satisfy items (iv), (v) and (vi) of the profile it is necessary to "block" or "mask" the isocyanate group in a manner which will render it inactive at temperatures $\leqslant$140°C but allow its regeneration above 140°C. Isocyanates can be blocked by reaction with a number of active hydrogen compounds (Figure 3).

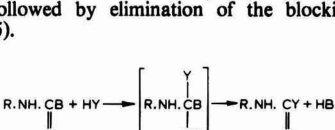


$$R{-}N{=}C{=}O + HB \rightleftharpoons R{-}NH{-}\underset{O}{\underset{\|}{C}}B$$

Figure 3. Blocking of isocyanate with active hydrogen compounds

The reaction is reversible and at elevated temperatures tends to proceed from right to left. Two mechanisms have been proposed for the reverse or "unblocking" reaction.

Mechanism (a) proposes elimination of the active hydrogen blocking agent to regenerate the free isocyanate, which subsequently can react with the hydroxyl groups on, for example, a polymer chain (Figure 4).

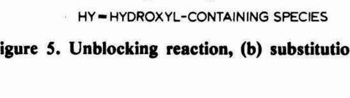


$$R.NH.\underset{O}{\underset{\|}{C}}B \rightleftharpoons R.N{=}C{=}O + HB$$

$$R.N{=}C{=}O + HY \longrightarrow R.NH.\underset{O}{\underset{\|}{C}}Y$$

Figure 4. Unblocking reaction, (a) elimination – addition

Mechanism (b) suggests that an intermediate adduct is formed between the blocked isocyanate and the hydroxyl group, followed by elimination of the blocking agent (Figure 5).



$$R.NH.\underset{O}{\underset{\|}{C}}B + HY \longrightarrow \left[R.NH.\overset{Y}{\underset{OH}{C}}B\right] \longrightarrow R.NH.\underset{O}{\underset{\|}{C}}Y + HB$$

Figure 5. Unblocking reaction, (b) substitution

Table 1
Thermal dissociation of urethanes

Structure	Dissociation temperature (°C)
Alkyl-NHCOO-alkyl	250
Aryl-NHCOO-alkyl	200
Alkyl-NHCOO-aryl	180
Aryl-NHCOO-aryl	120

The rate and extent of the unblocking reaction are dependent on many variables e.g. temperature, presence of catalysts and the structure of the isocyanate and blocking agent. The effect of structure on the thermal dissociation of blocked isocyanates is shown in Table 1. This indicates that the most effective blocked isocyanate from our viewpoint would be dervied from an aromatic isocyanate and an aromatic blocking agent. However, practical considerations againmpose restrictions on our choice. It is well-known that aromatic isocyanates impart poor weather resistance to a coating and result in yellowing of the coating on outdoor exposure.

For this reason, we selected an alicyclic bis-isocyanate, 1,4-cyclohexane bis(methyl isocyanate), CHBMI for short, as our base isocyanate (Figure 6). Another reason for choosing this material was that the CHBMI was inherently less thermally volatile than the more commonly used isophorone diisocyanate.

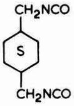


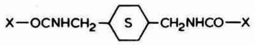
Figure 6. 1,4-cyclohexane bis(methylisocyanate) – CHBMI

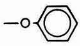
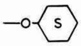
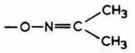
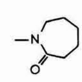
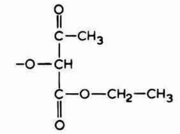
This can be seen from the thermogravimetric data shown in Figure 7. The reduced thermal volatility of the CHBMI means that it will be less susceptible to loss by evaporation from the molten coating during the fusion cycle. We also found that the CHBMI would readily react with a range of active hydrogen-containing, potential blocking agents to give adducts which were free flowing solids. Solid materials are easy to handle and are ideally suited for use in powder coatings in that, being solid, they will not lead to the sort of blocking problem encountered when liquid additives are used in powder formulations. A series of blocked adducts of CHBMI with a number of different active hydrogen compounds were synthesised. These are shown in Table 2.

Phenol, cyclohexanol, acetoxime, ε-caprolactam and ethyl acetoacetate were the blocking agents used. An investigation into the catalysed cure behaviour of these intermediates with a hydroxyl-functional polyester was then carried out.

For preliminary cure studies, a liquid hydroxylated polyester with the properties shown in Table 3 was chosen as control resin.

Table 2
Structure of CHBMI adducts

General formula


Blocking agent	X-structure	Adduct molecular weight
Phenol		376
Cyclohexanol		388
Acetoxime		334
ε-caprolactam		418
Ethylacetoacetate		448

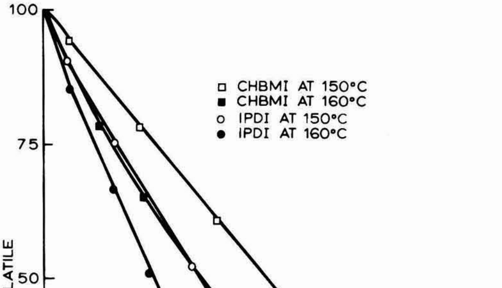


Figure 7. TGA of base isocyanates

This resin, code named UP-5-IT, is an ECPI-formulated polyester based on the proprietory Eastman glycol trimethylpentanediol (TMPD), trimethylol propane, isophthalic acid and adipic acid. It has an $\overline{Mn}$ of 1,700 and an OH number 125. A liquid polymer was chosen for the preliminary investigation because the fluid nature of the

Table 3
Hydroxylated polyester used for preliminary cure studies

Resin	Monomeric components	$\overline{Mn}$	OH No.
UP-5-IT	TMPD® glycol Tri-methylol propane Isophthalic acid Adipic acid	1700	125

polymer facilitated rapid and intimate mixing of the resin with the CHBMI adducts and catalysts under laboratory conditions. In order to achieve comparable mixing of a solid resin with the solid adducts, melt mixing would be necessary. The process requires considerable amounts of components and is both tedious and time consuming. A number of catalysts were selected for investigation on the basis of their being representative of the type of compounds recommended for the catalysis of isocyanate/hydroxyl cure. These fall into two broad categories: tertiary amine catalysts and metal cure catalysts. The mechanism of amine catalysis of the isocyanate/hydroxyl reaction is quite complex, but a simplified picture is adequate to explain the main features, Figure 8.

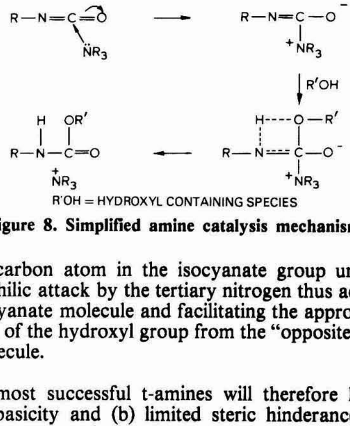


Figure 8. Simplified amine catalysis mechanism

The carbon atom in the isocyanate group undergoes nucleophilic attack by the tertiary nitrogen thus activating the isocyanate molecule and facilitating the approach and reaction of the hydroxyl group from the "opposite" side of the molecule.

The most successful t-amines will therefore have (a) strong basicity and (b) limited steric hinderance of the nitrogen atom. Typical of the t-amines investigated were 1-methyl imidazole, acridine, triethylene diamine and hexamine. A limited number of quaternary ammonium salts were also studied including hexadecyl trimethyl ammonium stearate and tetramethylammonium chloride.

The mechanism of metal catalysis of the isocyanate/hydroxyl reaction is considerably more complex than that of t-amine catalysis.

Basically the catalysis involves a co-ordination mechanism, with the metallic compound co-ordinating with the isocyanate and the hydroxyl group in such a way as to bring the reactants into more intimate contact. Infrared and NMR studies substantiate a co-ordination complex mechanism, but it is far more complex than the simplified representation in Figure 9 which is sufficient for the present purpose.

Metal catalysts chosen for our investigation included metal octoates, metal salts and organometallics such as dibutyltin diacetate and dibutyltin dilaurate.

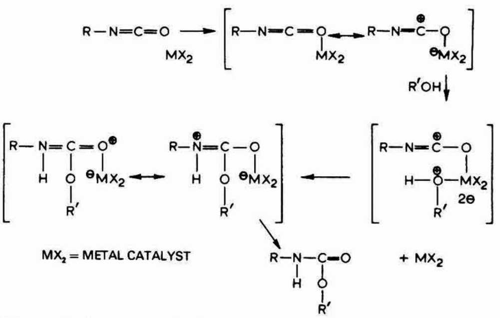


Figure 9. Isocyanate-hydroxyl reaction. Simplified mechanism of metal catalysis

Cure behaviour of the catalysed and un-catalysed mixtures was investigated using a Ferranti-Shirley Cone and Plate Melt Viscometer. This instrument monitored the increase in viscosity of the mixtures with time for different cure temperatures. We confined our investigation to the temperature range 100-160°C. A typical torque versus time plot obtained using the viscometer is shown in Figure 10. The gel time of each mixture was then determined from these torque/time graphs. This is defined as the time taken for the curing mixture to solidify and break up under the shearing action of the rotating disc of the viscometer. Gel times were then plotted against temperature.

Figure 11 presents the composite results obtained on resin/adduct mixtures cured with 2 per cent w/w of 1:1 dibutyltin diacetate and hexadecyl trimethyl ammonium stearate. This catalyst combination was found to be most effective in promoting hydroxyl-blocked isocyanate cure. From the results it can be seen that two of the five adducts viz. caprolactam- and cyclohexanol-blocked CHBMI gave

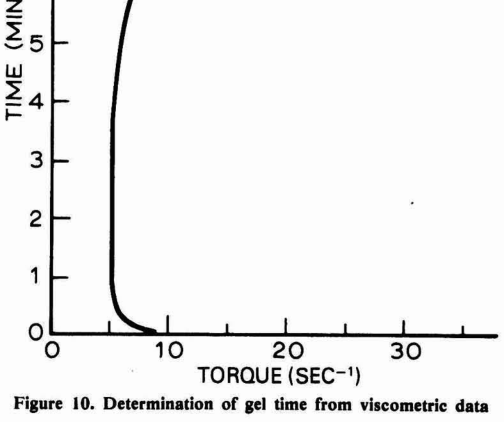


Figure 10. Determination of gel time from viscometric data

Table 4
Powder formulations containing CHBMI/DIBK

	Formulation		
	A	B	C
Polyester resin A	70		
Polyester resin B		71	
Polyester resin C			69.1
CHBMI/DIBK	21	20	21.9
10% DBTDL in resin B	10	10	10
R-TC4 pigment	50	50	50
Benzoin	1	1	1
Modaflow	1	1	1

Table 5
Resins used in powder formulations

Resin	$\overline{\text{Mn}}$*	OH No.	T_g (°C)	Melt viscosity (cps)† 160°C	191°C
A	1800	59	46	6 700	1500
B	2400	56	62	>10 000	4600
C	2700	62	56	>10 000	4900

*VPO, †Ferranti-Shirley Melt Viscometer, 563 sec^{-1} shear

no reaction with the UP-5-IT at temperatures below 150°C. The three remaining adducts, however, caused gelation of the control resin at temperatures below 150°C, the most effective being the phenol-blocked CHBMI. However, practical considerations again limit our choice. It was felt that evolution of phenol during cure would not be tolerated by an increasingly pollution-conscious industry, and no further work was carried out on the intermediate. Again, the ethyl acetoacetate-blocked CHBMI caused unacceptable yellowing during cure and was also considered unworthy of further investigation. The acetoxime-blocked CHBMI therefore appeared to be the most promising contender for a low temperature curing agent for hydroxyl-functional polyesters. Evaluation of this adduct in a polyester-based powder coating confirmed that it would effect cure at 160°C in 15 minutes to give finished coatings having very good physical properties. However, a low gloss finish was obtained. Examination showed this to be caused by micro blistering of the coating surface as a result of emitted volatile being entrapped in the cured coating. The source of these volatiles appeared to be free acetoxime blocking agent. It was thus obvious that a less volatile oxime was required, and two further adducts of CHBMI with high boiling cyclohexanone oxime and diisobutyl ketoxime (DIBK) were synthesised (Figure 12).

Heated cell infrared spectroscopy showed that the cyclohexanone oxime adduct did not un-block below 180°C, whereas the CHBMI/DIBK intermediate was active at 130-140°C. A preliminary cure investigation using the Melt Viscometer demonstrated that the DIBK adduct would readily gel a hydroxylated polyester resin at 160°C. The final stage of our evaluation, therefore, was to test the adduct in full powder coating formulations. The formulations used are shown in Table 4.

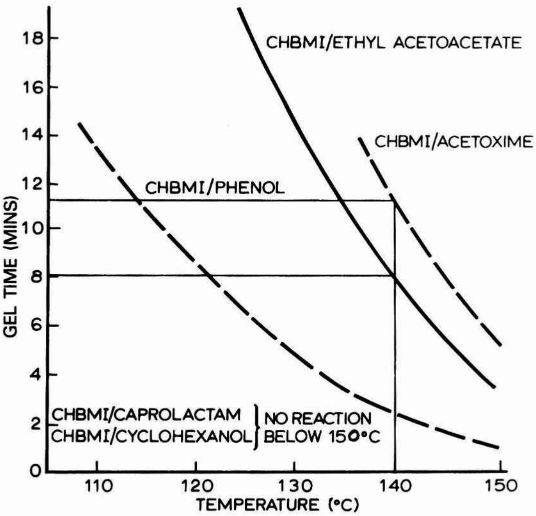


Figure 11. Effect of temperature on gel time for selected CHBMI adducts in UP-5-IT. Catalyst system: 2% w/w (on resin) of 1:1 dibutyltin diacetate/hexadecyl trimethylammonium stearate

All three formulations, A, B and C, are based on commercial polyester resins currently used in powder coatings. Dibutyltin dilaurate was used as the catalyst in these formulations. The Modaflow is a commercial flow aid and benzoin is incorporated as a release agent for evolved volatiles.

The properties of the resins used in the formulations are listed in Table 5. All are branched, hydroxyl-functional terephthalate esters. The lower molecular weight resin A, by virtue of its relatively low melt viscosity, was specifically designed to give good flow at lower fusion temperatures (e.g. 160°C). The DIBK adduct could be readily melt compounded into these formulations without any danger of pre-cure. The resulting powders were free-flowing and remained so for at least four months laboratory storage. Properties of the coatings obtained from these formulations are shown in Table 6.

It can be seen that the CHBMI/DIBK adduct gives high gloss smooth coatings with all three formulations on curing for 15 minutes at 160°C. Physical properties range from very good with resins B and C to excellent with resin A. Furthermore, the coating appearance was considered superior to the type of finish obtained with currently used commercial, blocked isocyanates. This is difficult to demonstrate without showing the finished coating as it is necessary to appreciate the low orange peel/high gloss

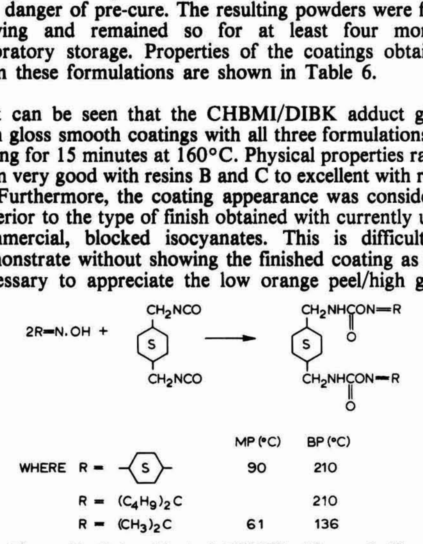


Figure 12. Oxime-blocked CHBMI of low volatility

Table 6
Coating performance of formulations containing CHBMI/DIBK after stoving for 15 minutes at 160°C

Property	Formulation		
	A	B	C
Thickness (μm)	57	53	45
20° Gloss	77	65	70
Hardness	HB	HB	F
Front/reverse impact strength (inch/lb)	>160/>160	80/15	80/40
Flexibility	excellent	very good	very good
Smoothness	excellent	excellent	excellent

finish given by the CHBMI/DIBK system. Nevertheless, I have attempted to graphically demonstrate the difference in orange peel obtained using CHBMI/DIBK and a widely used commercial blocked isocyanate in Figure 13.

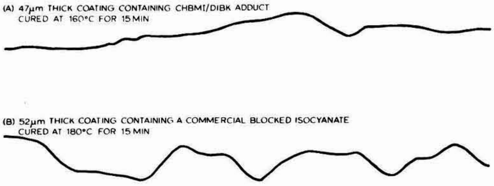


Figure 13. Surfometer traces of cured powder coatings

This shows surfometer profiles of the surface of two powder coatings of comparable coating thickness. Profile (A) was obtained from a coating containing the CHBMI/DIBK adduct which was stoved at 160°C for 15 minutes. Profile (B) is for a coating based on a commercial blocked isocyanate which was cured at 180°C for 15 minutes. It is apparent that the smoothest profile is that given by the blocked CHBMI crosslinking agent. It was also found that the CHBMI/DIBK adduct gave good properties even at stoving temperatures as low as 150°C. This is illustrated in Table 7.

Table 7
Coating performance of formulation A on stoving at 150°C

Property	Time	
	15 min	2 × 15 min
Thickness	43 μm	43 μm
Front/reverse impact (inch/lb)	24/<2	>160/>160
Pencil hardness	F	F
20° Gloss		73
Orange peel	medium	medium
Acetone resistance	break up	fully resistant

Here it can be seen that it is necessary to extend the stoving time to 30 minutes to achieve maximum physical properties and chemical resistance. Coatings stoved at 150°C/30 minutes have somewhat higher orange peel than those obtained at 160°C/15 minutes, presumably as a result of the poorer flow of the base polyester resin at the lower temperature.

Figure 14 compares the cure behaviour at 160°C of two powder formulations based on hydroxylated polyester resin. One formulation contains the CHBMI/DIBK adduct, while the second contains a commercial polyfunctional blocked isocyanate curing agent designed for use in lower temperature cure powder coatings. This is a tri-functional blocked isocyanate based on trimerised isophorone diisocyanate masked with caprolactam and it represents the current state of the art for lower temperature curing polyisocyanates. It can be seen that the commercial curing agent gives an induction time (T_2), prior to the onset of cure, of only five minutes, half that obtained with the CHBMI/DIBK adduct. Cure results in a marked increase in viscosity of the molten mix and this impedes the smooth flow out of the coating. Thus, the longer the period of low viscosity prior to cure the more chance the molten coating will have to flow out to a smooth finish. The relatively high induction time given by the blocked CHBMI intermediate is believed to be largely responsible for the high gloss smooth coatings characteristic of this crosslinker.

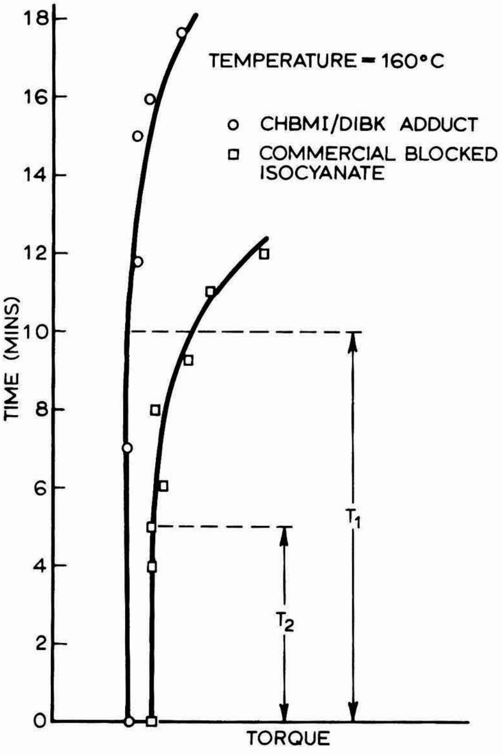


Figure 14. Torque vs. time plots for powders based on polyester resin A

To summarise, a new composition (viz. an adduct of 1,4-cyclohexane bis(methylisocyanate) and diisobutyl ketoxime) has been prepared which substantially meets the previously defined property profile for a low temperature curing agent for use in hydroxylated polyester-based powder coatings.

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Factors affecting metal marking of organic coatings*

By L. A. Simpson

BTP Tioxide Ltd, Central Laboratories, Portrack Lane, Stockton-on-Tees, Cleveland, England

Summary

The occurrence of metal marking is apparent in the coatings industry but its causes are not well known. Results in this report show that when hard pigment particles are at or close to the surface of an organic coating, they can abrade a bare metal object which is subject to a dynamic force. Abraded metal is then transferred to the organic coating which produces a characteristic "metal mark".

A test method for assessing metal marking is discussed and factors associated with the organic coating which are responsible for its abrasivity are examined. In addition, methods for decreasing metal marking are suggested.

Keywords

Properties, characteristics and conditions primarily associated with

materials in general

particle size

bulk coatings and allied products

pigment volume concentration

dried or cured films

gloss
hardness

Processes and methods primarily associated with

analysis, measurement or testing

metal marking test

manufacturing or synthesis

flocculation

French and German for Simpson Paper

Les facteurs qui exercent une influence sur le marquage des surfaces peintes par les objets métalliques

Résumé

Le phénomène du marquage des surfaces peintes par les objets métalliques est bien connu en l'idustrie de peintures, mais en grande partie on ignore les causes. Les résultats présentés dans cet exposé montrent que dans le cas où les particules de pigments durs se trouvent proche où à la surface d'une peinture, elles peuvent abraser tout objet en métal nu qui est soumis à une force dynamique quelconque. Alors il y a un transfert du métal abrasé à la surface peinte, et par conséquence le "marquage métallique" caractéristique est mis en évidence.

On discute une méthode d'essai pour apprécier l'importance du marquage métallique pour chaque peinture et l'on considère quelles sont les caractéristiques de la peinture qui sont responsables des tendances abrasives. On propose d'ailleurs des méthodes pour diminuer l'incidence de marquage métallique.

Die Faktoren, die Metallmarkierung beeinflussen

Zusammenfassung

Das Phänomen der Metallmarkierung ist bei der Lackindustrie wohl bekannt, aber die Ursache sind nicht so. Die in diesem Aufsatz dargestellten Resultate zeigen dass wenn die Teilchen harten Pigments sich in der Nähe oder an der Oberfläche einer Beschichtung befinden, können sie jedes zu einer dynamischen Kraft neigende Objekt aus nichtangestrichem Metall abreiben. Es gibt dann eine Übertragung des abgereibenen Metalls zu der Beschichtungsoberfläche und daher die charakteristische "Metallmarkeirung" sich hervorbringen.

Ein Prüfverfahren den Metallmarkierungsgrad zu bestimmen wird diskutiert, und die Beschichtungseigenschaften, die die Abreibung fördern überlegt.

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*Presented on behalf of the Association at the October 1981 Detroit Convention of the Federation of Societies for Coatings Technology, when it received the only Roon Award of 1981. Acknowledgement is made to the Federation for permission to publish the paper in this *Journal.*

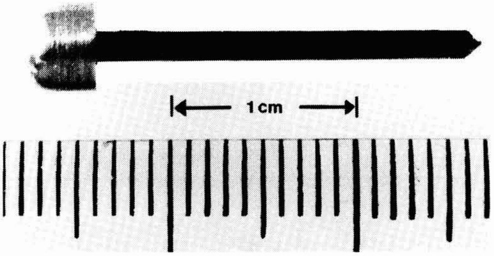

Figure 1. Stylus used for metal marking

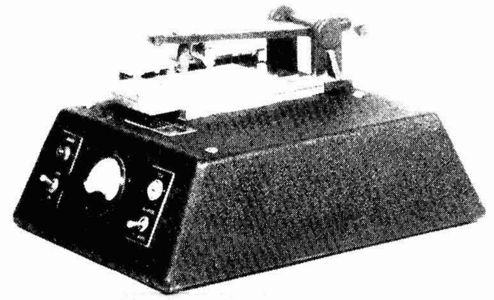

Figure 2. Apparatus used for metal marking

Introduction

Ref. 1

The ability of an organic coating to withstand streaking or marking when a metal object is dragged across the surface of the coating is referred to as metal marking or ring resistance. Examples of potential metal marking are: rubbing one's belt buckle or ring against a car as it is being washed, a child sliding a metal toy along a wall or over a piece of furniture, and a housewife dragging a metal wash basket from the top of a washing machine. Metal marking is also encountered in the coatings industry (in particular coil coating and roller coating applications) where on the production line, coated articles may come into contact with the uncoated parts of similar articles. In all of these cases the decorative appearance of the article is affected because a small amount of metal or metal oxide has been transferred to the coating due to the abrasive wear of the metal by the surface of the coating.

In essence metal marking is probably the result of hard asperities situated at the surface of the coating which indent, groove and then cut material out of the metal object. It would be expected that with harder metals there would be less indentation by the hard asperities and consequently the abrasive wear or metal marking would be decreased.

It is important that metal marking is not confused with marring since both are the consequence of the application of a dynamic mechanical force. To illustrate the difference between these two properties, consider a loaded metal stylus which traverses an organic coating. For relatively low loads, elastic deformation of the surface occurs and if the asperities at the surface of the organic coating are hard, metal marking may ensue. On increasing the load on the stylus, metal marking will increase but a stage will be reached whereby there is permanent deformation of the surface and within the area of deformation the coating will rupture. This stage of rupture is often referred to as the onset of marring. If for example a coating was extremely soft, then metal marking would not occur although marring would undoubtedly be evident (NB Occasionally other definitions for marring are used and these can be found in the literature – e.g. see Gardner/Sward[1]).

From the few examples mentioned above it is evident that metal marking is quite a common problem although it would appear from the literature that it is a problem which has not been investigated to any great extent. In addition a standard method for assessing metal marking has not been developed and accepted by the coatings industry since the subjective test of rubbing a coin or gold ring over the coating under study is still widely used. Thus a programme of work was designed to establish a test method for measuring metal marking, and to determine the factors responsible for metal marking.

Experimental

Ref. 2

A test method for assessing metal marking

From the point of view of producing a reproducible metal mark, the following two factors are important: (1) the type of metal used and its shape, and (2) the load which is applied to the metal. A metal stylus was used in this programme of work for marking and is shown in Figure 1 where a hemispherical tip which is supported by a copper coated steel rod has a diameter of approximately 4.5 mm. Tips of different composition were examined and details are discussed in the section below. A scratch resistance test machine manufactured by Research Equipment Ltd which was already in the laboratory was used for supporting the stylus. With this apparatus (Figure 2) the load applied to the metal stylus is easily varied by placing known weights above the stylus. The coatings under study were applied to glass plates (15 cm × 10 cm × 0.2 cm) to produce a 25 μm thick dry film and the glass secured to the bed of the machine by means of a clamp. The bed is essentially a sliding panel (velocity = 3.5 cm/s) driven by a constant-speed motor. Thus the procedure for marking the panel involves inserting the appropriate metal stylus into the chuck, balancing the beam using a counter load such that the stylus comes smoothly into contact with the coating, applying a known load to the stylus, and, finally, moving the coating in order that the stylus traverses one length of the coating. This procedure was repeated several times using fresh areas of film so as to ensure the reproducibility of the mark. (NB In all cases, the direction of movement of the film was the same.)

It was evident from preliminary work that the type of substrate did not generally affect the result (e.g. card, tinplate, glass and polyester film gave the same results within experimental error). However, with a substrate such as wood which has a relatively coarse surface texture, the surface roughness of the paint film was affected and metal marking was generally much greater. (NB The effect of surface texture on metal marking is discussed in the section below.) Thus for the test method it was decided to use glass as the substrate since it was readily available, optically smooth, and could be used at elevated temperatures for stoving paints.

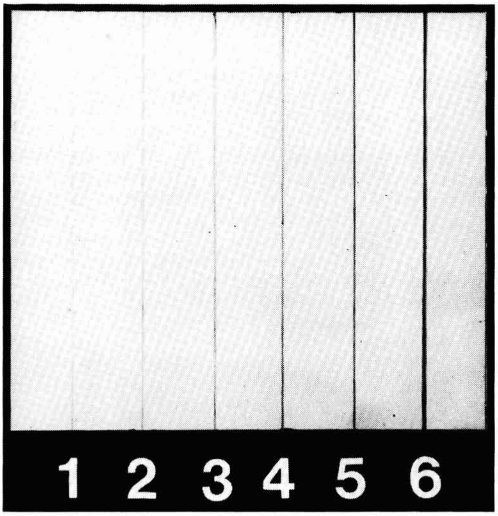

Figure 3. Reference standard used for rating metal marking

Several methods for quantifying the degree of metal marking were evaluated. For example, attempts were made to measure the amount of metal per unit length of mark deposited onto the coating. In one case simple gravimetry was employed, and another method involved the use of X-ray fluoresence spectrometry in order to detect the amount of iron (using a steel stylus) and zinc (using a zinc stylus) on the surface. With both of these methods the experimental error was sigficantly large, therefore it was decided to resort to the use of a series of standard marks (Figure 3) based upon a numerical scale of between 0 and 6, where 6 represented maximum metal marking and 0 no marking. In some cases a metal mark rating fell between two of the standard ratings (e.g. 2 and 3) and therefore an intermediate rating was given (e.g. 2+). Thus a total of 13 ratings were available using this particular standard.

When using this method for assessing metal marking it was found that the assessment of the mark should preferably be carried out in daylight, and that the test method was only applicable for white and pastel tinted coatings.

Methods used for evaluating the surface characteristics of a coating

Since metal marking is primarily a surface phenomenon it was expected that several techniques would have to be employed in order to characterise the surface of an organic coating. Thus, the following properties were studied:

Surface roughness

The surface roughness and texture of an organic coating were assessed using two techniques. Firstly, a mechanical/electrical profilemeter (i.e. Talysurf) was used, which enabled surface roughness to be quantified. In addition it was possible to obtain a graphical output on the surface profile. The parameter used to give an indication of surface roughness was the centre-line average (CLA) value, which is defined as the arithmetical average value of the departure of the surface profile above and below a reference line. It follows from this definition that a perfectly smooth surface has a CLA value of zero. Further details of this measurement are given in BS1134:Parts 1 and 2:1972.

The second technique used was microscopy, which involved the use of a Carl Zeiss Photomicroscope III and a Jeol 100CX (with scanning attachment) electron microscope. Details of specimen preparation are given in the appropriate sections.

Gloss

In order to give an indication of the degree of pigment dispersion at the surface of a coating, gloss was sometimes measured (see Simpson[2] for further details). Thus, 20°, 60° and 85° gloss values were obtained using a Byk-Mallinckrodt glossmeter (NB In all cases, the coatings (25 µm thick) were aged for at least 24 hours before gloss measurements were taken from the coatings, which were applied to glass).

Hardness

In addition to using the Mohs scale of hardness, which gives an indication of the hardness of pigment and extenders, the hardness of the coating was measured using a König pendulum hardness tester. In all cases, the coatings under study were applied to glass so that the thickness of the dry film was approximately 25 µm. After ageing for at least 24 hours, the time taken for the pendulum's amplitude to fall by half was recorded. (NB The longer the time period, the harder the film.)

Materials

In order to cover a broad spectrum of coatings, a variety of pigments, extenders and resin systems were used. Details of the grades of pigment used are given in the Appendix, whereas information on the extenders and resin systems are given in the appropriate sections below.

Results and discussion

Refs, 2-8

The effect of hardness of metal and the force between metal and coating

Since it was assumed in the introduction that metal marking is the result of abrasive wear of the metal, one would expect that increasing the hardness of the metal and decreasing the load applied to the metal would result in a decrease in metal marking. In order to confirm this supposition, four metal styli based on steel, aluminium, zinc and brass were used to mark an acrylic based emulsion paint which was only pigmented with a typical general purpose rutile grade of titanium dioxide (pigment A) at a pigment volume concentration (PVC) of 20 per cent. Various loads were applied to each metal stylus, and the subsequent marks were rated. In addition, for the aluminium stylus, the average width of each mark was measured using an optical microscope. In Table 1 the marking results are given and it can be seen that, irrespective of load, steel has marked the least, brass and zinc the most and aluminium has exhibited only slightly more marking than the steel stylus. If one considers the Mohs hardness of these metals (viz. steel = 5-8.5, aluminium = 2-2.9, brass = 3 and zinc = 2.5) the results given in Table

Table 1
The effect of stylus type and load (on the stylus) on marking an emulsion paint (20% PVC)

Stylus type	Mark rating				
	25 g load	50 g load	100 g load	200 g load	300 g load
Steel	1	2	2+	3+	3+
Aluminium	2	2+	3+	4	4+
Brass	2	3	4	5	6
Zinc	2	3	3+	5	6
Width of aluminium mark (μm)	135	210	270	285	300

6 = severe marking, 0 = no marking

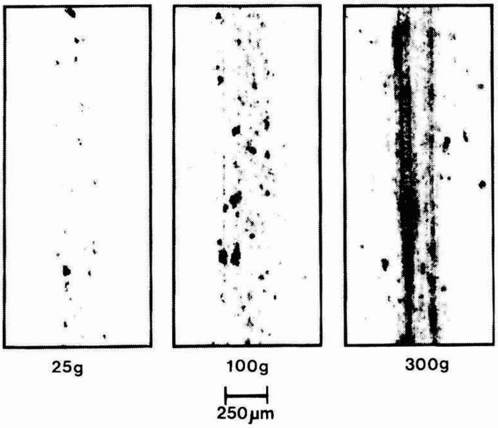

Figure 4. The amount of aluminium deposited onto an emulsion paint as a function of load

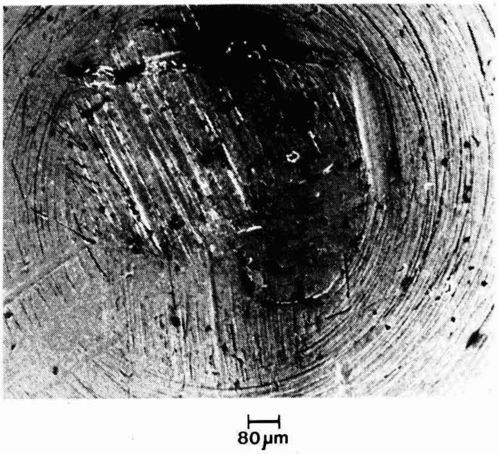

Figure 5. A scanning electron micrograph of the tip of a worn brass stylus

1 can to some extent be predicted. However, there is a slight anomaly in that the aluminium stylus was not producing the same amount of metal marking as brass or zinc, this is probably attributable to the relatively hard aluminium oxide layer which is on the surface of the aluminium stylus.

The effect of increasing the load on the metal stylus has undoubtedly caused metal marking to increase, as shown by the results in Table 1. This is because the increase in force between metal and coating has resulted in a greater penetration into the coating by the stylus which has inevitably produced a wider metal mark. Thus, the number of contacts between the metal and the irregularities at the surface of the coating which are responsible for the abrasion has increased. In order to illustrate this, the aluminium marks obtained using 25 g, 100 g and 300 g loads were examined in cross-polarised light using an optical microscope. In Figure 4, micrographs of the marks clearly show that at the low load of 25 g, the areas where metal is deposited (black areas) are relatively far apart, but on increasing the load to 100 g and 300 g, these areas have increased in size. (NB Although considerable marking occurred with the 300 g load, there was still no sign of surface rupture.)

Since the metal stylus is being abraded during the metal marking test (see Figure 5 for a scanning electron micrograph of the tip of a brass stylus which has been used several times) it is important to ensure that the stylus is changed at regular intervals in order to obtain reproducible results. This interval depends upon the conditions under which the stylus is used (e.g. the load, the type of metal and the nature of the organic coating).

Since it can be inferred from these results that as far as metal marking is concerned the type of metal stylus used and load should not affect the relative difference between coatings, the subsequent work was mainly confined to the use of steel and brass styli, and an appropriate load was selected which produced adequate metal marking.

The influence of pigment and extender

Since the organic coating is the abrasive element which is responsible for metal marking, there are several formulation variables which could contribute to this abrasivity. Basically, a coating contains two major components which could affect its abrasivity and these are pigment/extender and binder. It is the former component which will be discussed in this section.

When formulating a coating using either pigment or extender, or both, a variety of materials are available which differ in chemical composition, shape, mean particle size and hardness. One would expect the hardness of the pigment/extender to be the most important factor from the point of view of abrasion, followed by shape and mean size. In order to determine the importance of pigment/extender with regard to metal marking, emulsion paints where the pigment/extender is exposed at the surface of the coating so that it can abrade the metal were prepared. A typical rutile grade of titanium dioxide (pigment B) and several commercially available extenders were selected in order to cover a range of hardness values; these were individually incorporated into the emulsion paint system (based on an acrylic emulsion) at a PVC of 30 per cent. In Table 2 a list of the properties of the pigment/extenders are given, and it can be seen that differences in hardness are accompanied by differences in shape and mean particle size. The paints produced were drawn down onto glass and after 24 hours drying were marked with a steel stylus using 50 g and 200 g loads. In addition, the surface roughness (CLA value) of each film was measured and these results together with the metal mark ratings are given in Table 3. It is clearly evident from these results that titanium dioxide, which is the hardest of the minerals studied, exhibits the worst metal marking and the smoothest film. Thus, in this case, the metal stylus is in contact with a considerable number of hard titanium dioxide particles which are protruding above the surface of the emulsion. In contrast, talc is extremely soft and no metal marking was evident although some marring occurred. To illustrate the difference between the titanium dioxide and talc additioned coatings, the marks were examined in cross-polarised light (using a microscope) so as to highlight the areas where metal is deposited, and a Nomarski interference contrast attachment was also used in order to study the topography of the surface. In figures 6(a) and 6(b) micrographs of the titanium dioxide additioned coatings are shown, and in figures 7(a) and 7(b) micrographs of the talc coating are given. With the titanium dioxide coating metal marking is evident (Figure 6(a)), and when the coating is examined using interference contrast microscopy (Figure 6(b)) the titanium dioxide which is responsible for the abrasion can be seen as small white particles within the lines of deformation. In contrast, no metal was deposited onto the talc coating although the surface was deformed, as shown by the "stress whitening" in Figure 7(a).

The results given in Table 3 do not show a perfect correlation between hardness of pigment/extender and metal marking since the surface roughness is another factor which has to be considered when examining the interaction between metal stylus and coating. Obviously, a surface which contains relatively few but large (in height) asperities will reduce the area of contact between the metal and film and should therefore decrease the extent of the metal marking. This is illustrated in Table 3 where if hardness was the only determining factor, the micronised silica gel should have exhibited the same marking as the china clay; since this did not occur and the micronised silica gel coating was significantly rougher than the clay coating, the above proposition could explain this difference. Although with the various extenders the differences in metal marking are relatively subtle, the conclusion that titanium dioxide at the surface of a coating will increase metal marking is clearly evident.

To illustrate further the deleterious effect of titanium dioxide on metal marking, the same emulsion paint system as used above was pigmented with the same grade of titanium dioxide at a PVC of 20 per cent and used as a control coating. Several extenders (see Table 4 for properties) were then individually incorporated into this system such that the total volume concentration of pigment plus extender was 50 per cent. Coatings were prepared and marked using a 50 g loaded steel stylus and the surface roughness measured. These results, which are given in Table 5, again show that titanium dioxide at the surface of a coating increases metal marking since the inclusion of extender causes a reduction in marking. Again this is probably due to the fact that the relatively coarse extender which has increased the surface roughness of the coating has reduced the area of contact between stylus and pigment. It is only with the hard quartz extender that there was little reduction in marking. At first glance this result is a little surprising since one might expect that the incorporation of extra material similar in hardness to titanium dioxide would produce an increase in metal marking. However, this extender is extremely coarse (10 µm mean size) and presumably the area of contact is between the quartz and stylus. Consequently, the contact between titanium dioxide and the metal stylus is negligible.

Table 2

Shape, mean size and hardness of pigment and extenders

Pigment/extender	Particle shape	Mean particle size (µm)	Hardness (Mohs)
Pigment B	nodular	0.25	6-6.5
China clay (calcined)	lammellar	2.00	4.0
Talc	lammellar	3.00	1.0
Aluminium silicate	ultrafine	0.03	2-3
Micronised silica gel	nodular	2.50	3-5

Table 3

Metal marking and surface roughness of an emulsion paint based on several pigment/extenders

Pigment/extender	Mark rating 50 g steel stylus	Mark rating 200 g steel stylus	CLA (µm)
Pigment B	3+	4+	0.13
China clay (calcined)	1+	2	1.68
Talc	0	0	0.75
Aluminium silicate	0	0	2.74
Micronised silica gel	0	1	2.36

6 = severe marking, 0 = no marking

Table 4

Shape, mean size and hardness of several extenders

Extender	Particle shape	Mean particle size (µm)	Hardness (Mohs)
China clay (calcined)	lamellar	2.0	4.0
Talc	lamellar	3.0	1.0
Calcite	nodular	2.0	3.0
Quartz	nodular	10.0	7.0

Thus, the technique of reducing the area of contact between stylus and titanium dioxide is one possible method by which metal marking can be decreased. To illustrate this the following example is given:

Matt emulsion paint

An emulsion paint containing pigment B at a PVC of 30 per cent was used as a control. In order to decrease the area of contact between the metal stylus and pigment, relatively large spherical fillers were selected. Thus, glass

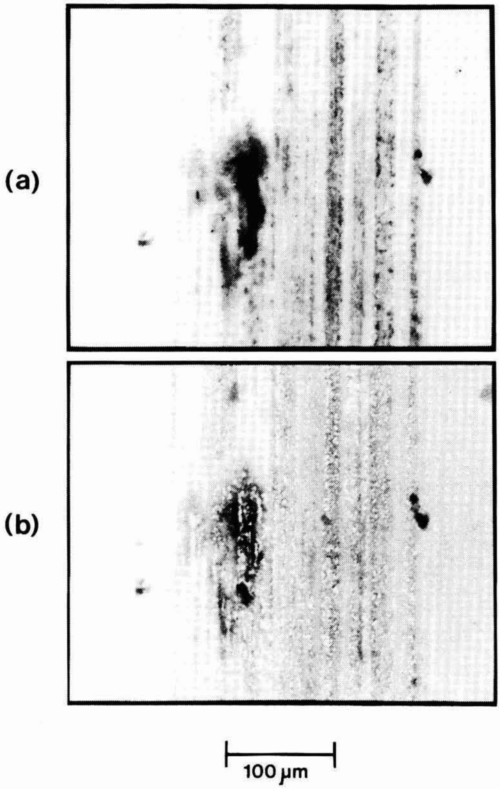

Figure 6. Optical micrographs of a marked emulsion paint containing only titanium dioxide

Table 5

Metal marking and surface roughness of an emulsion paint containing (a) only titanium dioxide (pigment B) and (b) a blend of titanium dioxide (pigment B) and an extender

Pigment/extender	Mark rating (50 g steel stylus)	CLA (µm)
Pigment B (control)	3+	0.14
Pigment B + China clay (calcined)	2	1.50
Pigment B + Talc	1+	0.62
Pigment B + Calcite	1+	0.71
Pigment B + Quartz	3	3.50

6 = severe marking, 0 = no marking

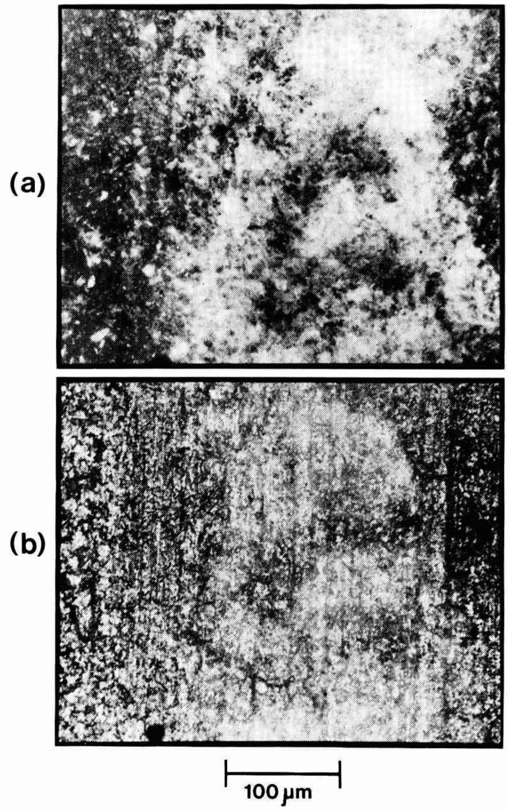

Figure 7. Optical micrographs of a marked emulsion paint containing only talc

Table 6

Metal marking, surface roughness and gloss of an emulsion paint containing different amounts of polyester beads

Coating	Mark rating		CLA (µm)	85° gloss
	50 g steel stylus	200 g steel stylus		
Control (pigment B)	4	6	0.14	41
5% beads	1	5	0.75	31
10% beads	0	2+	1.18	13
20% beads	0	2	1.84	4
30% beads	0	2	2.35	3

6 = severe marking, 0 = no marking

ballotini (10 µm mean size), a PTFE dispersion (0.3 µm mean size) and an aqueous dispersion of solid polyester resin beads (15 µm mean size) were considered. Since all three types of beads exhibited similar effects (i.e. solid polyester beads were similar in performance to the ballotini but slightly better than the PTFE dispersion), only the results of the polyester beads will be given. The beads were added to the emulsion paint to give volume

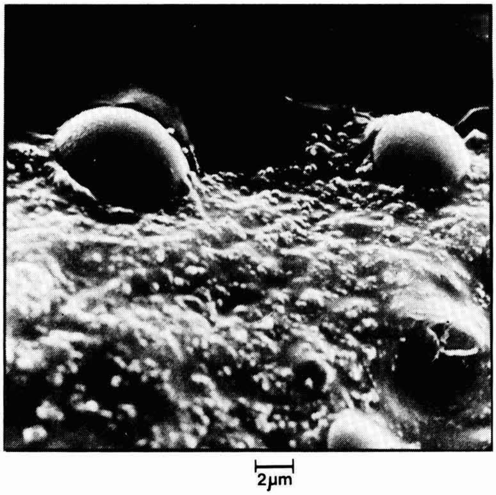

Figure 8. A scanning electron micrograph of a section of an emulsion paint containing 30% (by volume) polyester beads

concentrations of the beads in the dry film of 5, 10, 20 and 30 per cent. Surface roughness and gloss (85°) of each film were measured and the films were marked using a steel stylus (50 g and 200 g loads). In Table 6, the results show that the addition of beads, which has caused the gloss decrease due to the increase in surface roughness, has significantly diminished the extent of the metal marking. As mentioned above, this decrease in marking is due to the decreased contact between stylus and pigment and this can be easily appreciated if the surface of the coating is examined using a scanning electron microscope. For this purpose, the paint film which contained 30 per cent beads was embedded between two layers of epoxy resin and sectioned. In Figure 8, a section of the edge of the coating shows the polyester beads protruding above the film where the pigment is present. It is also interesting to note that there is no pigment on the surface of the beads. The difference in marking between the control and the bead additioned films is evident irrespective of load, although at the high load there is some marking on the beaded paints which must be due to the inherent abrasive nature of the beads. This can be seen in Figure 9 where optical micrographs of the metal mark which was on the 10 per cent beaded film (using a 200 g steel stylus) show metal deposited (black areas) on and in close proximity to the beads.

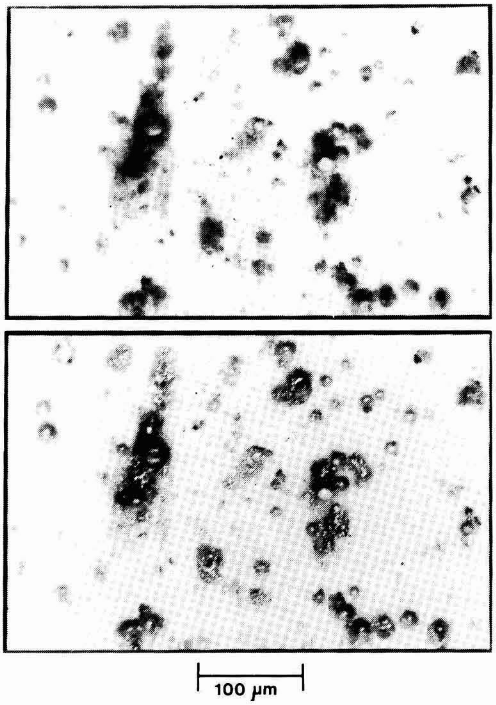

Figure 9. Optical micrographs of a marked emulsion paint containing 10% (by volume) polyester beads. The black areas indicate metal marking.

Anatase versus rutile titanium dioxide pigment

Since the anatase form of titanium dioxide is a little softer than the rutile crystal (i.e. 5-5.5 (Mohs hardness) for anatase versus 6-6.5 (Mohs hardness) for rutile), one might expect that anatase titanium dioxide would exhibit slightly less metal marking than the rutile form. It is shown in the next section that the degree of pigment dispersion in a coating plays an important part in affecting metal marking, therefore in order to compare two types of titanium dioxide it is important to ensure that the state of dispersion is the same. For this purpose, an emulsion paint (based on an acrylic emulsion) was formulated and pigmented with an uncoated grade of anatase titanium dioxide (pigment C) and an uncoated grade of rutile titanium dioxide (pigment D) such that the PVC varied from 20 to 50 per cent by 10 per cent steps. In order to give an indication of pigment dispersion, the surface roughness of each coating was measured and the coatings were marked using a 50 g loaded steel stylus. The results are given in Table 7 and it can be seen that within experimental error both rutile and anatase based coatings exhibit similar surface roughness values for the same PVC, but the anatase coating is always slightly less prone to metal marking. The results also show that as the PVC is increased the degree of metal marking is increased. Obviously, this increase in metal marking, although not large, is the result of increased contact between metal and titanium dioxide. Generally, the difference between rutile and anatase forms would probably not be very significant, as shown by these results, particularly when other variables such as pigment dispersion play an important role in affecting metal marking.

The effect of pigment dispersion

In the above section, the effect of pigment and extender on metal marking was illustrated using a "model" paint. However, this type of system would generally have no practical significance with regard to the coatings industry. Thus, in the work that follows, typical industrial finishes were selected.

It is well known that the degree of pigment dispersion in a coating can significantly affect such optical properties as gloss. For example, in a system where the pigment is flocculated, the pigment particles protrude further out from the surface of the coating, thereby resulting in a

Table 7

Metal marking and surface roughness of an emulsion paint pigmented with anatase (pigment C) and rutile (pigment D) titanium dioxide at various PVCs

% PVC	Mark rating for pigment C (50 g steel stylus)	Mark rating for pigment D (50 g steel stylus)	CLA (μm) for pigment C	CLA (μm) for pigment D
20	2	3	0.12	0.12
30	2+	3	0.16	0.14
40	3	3+	0.19	0.15
50	3	4	0.21	0.17

6 = severe marking, 0 = no marking

rougher surface which produces a decrease in gloss. From an abrasive wear point of view, if more of the abrasive element is exposed, one would expect an increase in metal marking (cf. the effect of increasing PVC on metal marking – Table 7). It is important to note that this increase in surface roughness is relatively small and must not be confused with the large increases in surface roughness which occur when extenders are used.

In order to illustrate the effect of dispersion, three coated grades of rutile titanium dioxide (i.e. pigments A, E and F) were selected which were known to exhibit differences in dispersion in an alkyd/urea formaldehyde stoving paint. The paints (pigment/binder = 1:1) were stoved on glass for 30 minutes at 120°C (recommended stoving schedule) and the following measurements were taken: (i) metal mark rating using a 200 g load on a brass stylus, (ii) surface roughness and (iii) 20° gloss. In Table 8 the results are given and it can be seen that although there are only small differences in surface roughness, they have been sufficient to affect the degree of metal marking such that the metal marking has increased with increasing surface roughness.

It is well known that the presence of an acid catalyst in an acid catalysed alkyd/urea formaldehyde stoving paint can affect the shelf life of the paint by flocculating the pigment. From the above findings it would be deduced that the degree of metal marking would also be affected. Therefore, an acid catalysed alkyd/urea formaldehyde paint containing 10 per cent para-toluenesulfonic acid based on weight of urea formaldehyde resin was formulated using pigment B at pigment/binder = 1:1. After the addition of acid, the paint was drawn down on glass and stoved for 30 minutes at 120°C. The paint was then allowed to age for 5 hours and 24 hours and after each period the paint was drawn down and stoved as above.

Table 9

Metal marking, surface roughness and gloss of an acid catalysed alkyd/urea formaldehyde paint as a function of age of paint

Age of paint (hours)	Mark rating (200 g brass stylus)	CLA (μm)	20° gloss
Fresh	3+	0.059	45
5	4	0.074	38
24	4+	0.232	4

6 = severe marking, 0 = no marking

Gloss and surface roughness measurements were carried out on the films in order to give an indication of the pigment dispersion at the surface of the coating, and metal marking was rated using a 200 g loaded brass stylus. In Table 9 the results are given and it can be seen that the effect of ageing the paint, which has resulted in pigment flocculation, has caused the metal marking to increase slightly.

A comparision between titanium dioxide pigments produced using the chloride and sulfate processes

Since it is frequently mentioned (particularly with regard to gravure printing inks) that titanium dioxide pigments manufactured using the chloride process are more abrasive than sulfate route pigments, if it were true one might expect that this difference would be reflected in metal marking resistance. In order to determine if this was the case, two chloride pigments (pigments B and G) and one sulfate grade (pigment H) were incorporated into an alkyd/urea formaldehyde and an alkyd/melamine formaldehyde paint. The paints (pigment/binder = 1:1) were stoved on glass for 30 minutes at 120°C (for the alkyd/UF system) and 150°C (for the alkyd/MF system). The paints were also overbaked for 60 minutes at 180°C (for the alkyd/UF system) and 200°C (for the alkyd/MF system). As a measure of pigment dispersion the 20° gloss of each film was recorded and each panel was marked using a 400 g loaded brass stylus.

In Table 10 it can be seen that given the same degree of pigment dispersion (i.e. gloss) there is little difference in metal marking between a chloride and a sulfate grade pigment. Thus, irrespective of the stoving schedule, pigments B and H exhibit similar gloss and metal marking. However, with pigment G the dispersion is relatively poor and therefore it is more prone to metal marking.

Table 8

Metal marking, surface roughness and gloss of an alkyd/urea formaldehyde paint pigmented with three different grades of titanium dioxide

Pigment	Mark rating (200 g brass stylus)	CLA (μm)	20° gloss
A	2+	0.027	77
E	3	0.033	72
F	5	0.038	48

6 = severe marking, 0 = no marking

Table 10

Metal marking and gloss of two alkyd stoving paints pigmented with chloride and sulfate grades of titanium dioxide

Pigment	Normal stoving schedule				Overbake stoving schedule			
	Alkyd/UF		Alkyd/MF		Alkyd/UF		Alkyd/MF	
	Mark rating (400 g brass stylus)	20° gloss	Mark rating (400 g brass stylus)	20° gloss	Mark rating (400 g brass stylus)	20° gloss	Mark rating (400 g brass stylus)	20° gloss
B	3	72	1+	77	5	51	2	73
G	3+	66	2+	72	6	25	3	54
H	3	72	1+	79	5	39	2+	68

6 = severe marking, 0 = no marking

Thus, these results (and others not mentioned in this report) would therefore suggest that given the same degree of pigment dispersion, there is no inherent difference between a chloride and a sulfate grade pigment from the point of view of surface abrasivity.

The effect of resin system

The above findings have illustrated that pigment dispersion can affect metal marking, but in order for this to be the case, the pigment must be present at the surface of the coating. For example, in Figure 10 an electron micrograph of a section of a pigmented alkyd/melamine formaldehyde paint which is known to exhibit metal marking shows the pigment protruding slightly above the surface of the resin. It is known that, depending on the resin system used, a clear resin layer can be formed at the surface of the coating (Simpson[2]) and this phenomenon is illustrated in Figure 11 where an electron micrograph of a section of an air drying polyurethane paint film is given. A clear layer is often found in air drying decorative paint systems and this is the reason why this type of system does not often exhibit metal marking, although marring is likely to occur due to the relatively soft resinous surface.

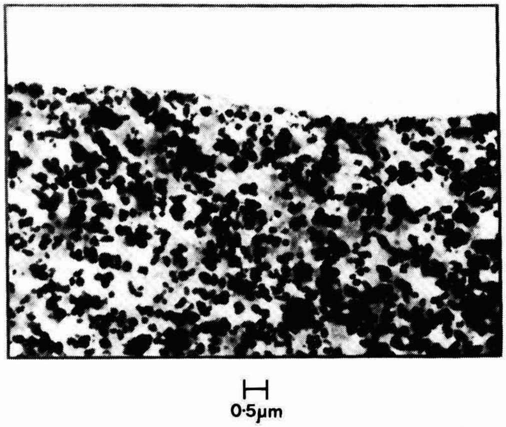

Figure 10. An electron micrograph of a section of an alkyd/melamine formaldehyde paint film

To illustrate the protective effect of depositing a thin layer of resin between the surface of a coating and the metal stylus, a thermoplastic acrylic paint was formulated using pigment B such that the pigment/binder = 0.8:1. This paint was stoved for 30 minutes at 138°C after which gloss, surface roughness and metal marking (600 g loaded brass stylus) measurements were taken. Using a K-bar applicator, a thin layer of the acrylic resin used in the paint was applied over the surface of the coating such that its dry film thickness was about 2 μm. This system was then stoved as above and the same measurements taken from the coating. It can be seen from the results which are given in Table 11 that the presence of a thin layer at the surface of the coating has decreased the metal marking and has also caused the gloss to increase.

Table 11

Metal marking, surface roughness and gloss of a thermoplastic acrylic paint

Coating	Mark rating (600 g brass stylus)	CLA (μm)	20° gloss
Thermoplastic acrylic system	2	0.021	70
Thermoplastic acrylic system plus resin at the surface	0	0.019	84

6 = severe marking, 0 = no marking

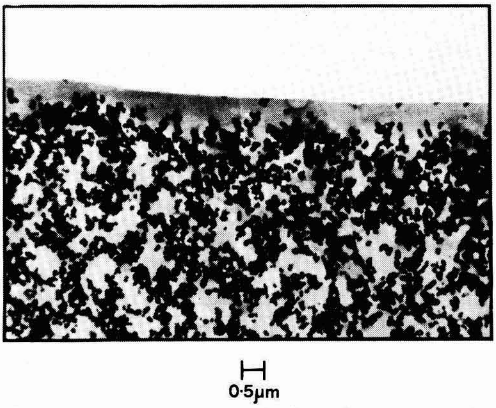

Figure 11. An electron micrograph of a section of an air drying polyurethane paint film which exhibits a clear layer

Figure 12. An electron micrograph of the surface (replica) of an acrylic water-based coating containing 0.05% catalyst

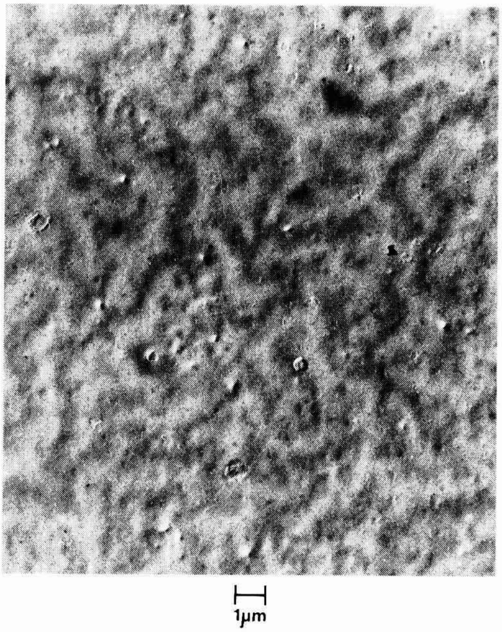

Figure 13. An electron micrograph of the surface (replica) of an acrylic water-based coating containing 0.1% catalyst

Since various factors associated with the resin can determine whether or not a clear layer is formed (Murley and Smith[3], and Simpson[2]) these factors will also influence whether or not metal marking is likely to occur. Another factor associated with the resin which can play a part in affecting metal marking is resin hardness. To illustrate this, two styrene/acrylic emulsions (E_1 and E_2) of different hardness values (i.e. Sward rocker (per cent): $E_1 = 38$ and $E_2 = 11$) were used in order to produce 20 per cent PVC emulsion paints based on pigment B. The paints were drawn down on glass and after the films had aged for 24 hours, gloss, surface roughness, metal marking (using a 30 g loaded brass stylus) and pendulum hardness measurements were carried out. The results are given in Table 12 and it can be seen that the paint based on the harder of the two emulsions (i.e. E_1) exhibited slightly more marking even though the surface roughness was slightly less than the other system. Since metal marking was also carried out on the clear emulsion films and showed no effect, illustrating that the resin does not to any great extent abrade the metal, the results in Table 12 suggest that there is a synergistic effect between emulsion and pigment. Perhaps the "exposed" pigment is partly coated by the emulsion which affects the relative hardness of the exposed pigment and therefore influences the extent of the metal marking. If this result is considered in broader terms then one could infer that the degree of cure of a crosslinked resin system could also affect metal marking. Unfortunately, variations in a curing schedule not only affect e degree of cure but also influence the extent to which pigment is present at the surface as shown by Table 10, and therefore a change in one parameter could affect several other variables which might influence metal marking.

Table 12

The effect of emulsion type/hardness on metal marking

Emulsion	Mark rating (30 g brass stylus)	Hardness (sec)	CLA (μm)	20° gloss
E_1	4+	40	0.15	38
E_2	3	19	0.21	35

6 = severe marking, 0 = no marking

To study this aspect further, a water-based acrylic coating containing pigment B (pigment/binder = 1.1:1) was formulated such that the amount of catalyst (para-toluenesulfonic acid) varied from 0.05 to 0.2 per cent on weight of paint. Paints were drawn down on glass and stoved for 5 seconds at 210°C. Metal marking was assessed using a 1,200 g loaded brass stylus, and 20° gloss measured. In addition, the surface topography of each coating was studied using an electron microscope.

With the scanning electron attachment it was evident that there was no titanium dioxide present at the surface of any of the coatings, and by using an etching technique (see Simpson[4] for details) it was clear that the levels of catalyst had not affected the state of pigment dispersion. Consequently, in order to study the surface features of the coatings in more detail, replicas were obtained and examined using a transmission electron microscope (see Kay[5] for technique). In figures 12, 13 and 14, micrographs of the surface of paints containing 0.05, 0.1 and 0.2 per cent catalyst are shown and it is evident that: (i) there is no titanium dioxide present at the surface and (ii) the surface roughness has decreased with increasing catalyst content.

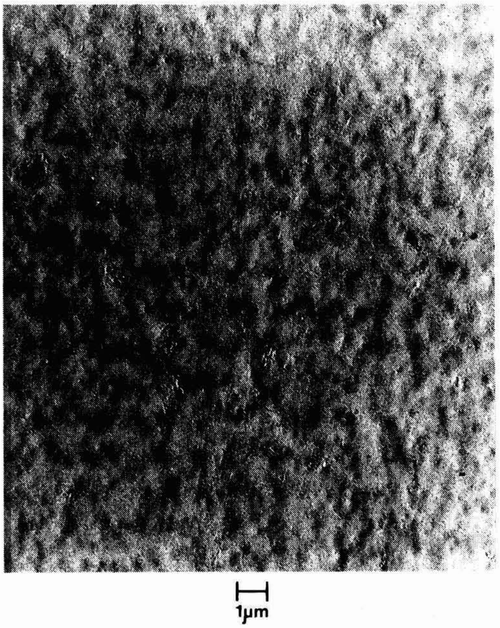

Figure 14. An electron micrograph of the surface (replica) of an acrylic water-based coating containing 0.2% catalyst

The metal mark ratings and gloss values are given in Table 13 and it can be seen that with increasing catalyst content the metal marking has decreased and the gloss increased due to a decrease in surface roughness. Thus, the addition of catalyst, the primary purpose of which was to influence the rate of cure, has also reduced the surface roughness and therefore reduced the abrasivity of the coating.

In order to determine if there was a primary factor associated with the resin system which was responsible for metal marking, five paint systems (containing pigment B) were arbitrarily selected for metal marking. In Table 14 the resin system used, pigment/binder ratio and stoving conditions are given. In addition to making these paints, the resins were also used to produce clear films (using the same stoving conditions) so that pendulum hardness values could be obtained. (NB Since it is known that the presence of titanium dioxide can to some extent affect the degree of cure of a paint system (see Akay[6] *et al.*) and therefore the hardness of the cured resin, the method of measuring the hardness of the unpigmented system was the only way by which an indication of resin hardness in the paint system could be obtained.) In Table 15, metal mark ratings (using a 400 g loaded brass stylus) and surface roughness values of the pigmented films are given together with the hardness values for the clear resin films. It can be seen from these results that the hardness of the resin does not play a major part in affecting metal marking but it is clearly evident that there is a good correlation between surface roughness and metal mark rating. This would suggest that with all the resin systems studied, the primary factor which is responsible for metal marking is presumably the extent to which the pigment exerts its presence at the surface of the paint film and this is the result of a specific interaction between pigment and resin.

Table 13

The effect of catalyst on metal marking and gloss for an acrylic water-based paint

Catalyst level (%)	Mark rating (1200 g brass stylus)	20° gloss
0.05	1+	63
0.10	1	65
0.20	+	71

6 = severe marking, 0 = no marking

Table 14

Stoving schedule, pigment/binder ratio and resin systems used in order to make various paints

Resin system	Pigment/binder ratio	Stoving schedule
Alkyd/urea formaldehyde	1:1	30 minutes at 120°C
Alkyd/melamine formaldehyde	1:1	30 minutes at 150°C
Thermosetting acrylic	1:1	30 minutes at 120°C
Thermoplastic acrylic	0.5:1	30 minutes at 138°C
Modified polyester	1.5:1	15 minutes at 150°C

Table 15

The effect of hardness of resin and surface roughness on metal marking

Resin system	Hardness of resin (sec)	Mark rating (400 g brass stylus)	CLA (μm)
Alkyd/urea formaldehyde	141	3+	0.045
Alkyd/melamine formaldehyde	87	3	0.040
Thermosetting acrylic	149	2	0.022
Thermoplastic acrylic	174	2	0.021
Modified polyester	30	3	0.040

6 = severe marking, 0 = no marking

A simple theory of metal marking

From the onset of this project it was appreciated that metal marking was an abrasive wear phenomenon since certain simple experiments confirmed that wear was occurring (e.g. metal marking was proportional to the load applied to the stylus). When two surfaces are brought together (e.g. organic coating and metal stylus) they only touch at the tips of the highest asperities. Thus, the real area of contact which is the important factor from a wear point of view is, in general, only a small part of the

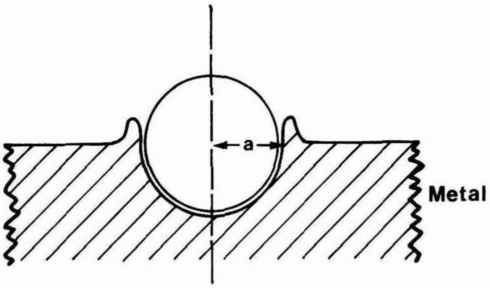

Figure 15. The indentation of a metal surface by a sphere

apparent area of contact. Since it is difficult to assess the distribution of real areas of contact between an organic coating and a metal stylus, one must consider the simple case of a spherical particle (representing a titanium dioxide crystal protruding above the surface of the organic binder) indenting a smooth metal surface (see Figure 15).

Using Hertz[7] equation, the radius "a" of the circular area of contact formed when a sphere of radius R is pressed against a flat surface under a load P can be calculated as follows:

$$a = (\frac{4}{3} \frac{K}{E} P R)^{\frac{1}{3}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where E = Young's modulus of the metal surface

and K = Constant depending on the Poisson ratios of the sphere and metal surface.

It can be seen from Equation (1) that if the load applied to the sphere increases "a" increases, and if the hardness of the metal is increased (i.e. E) "a" will decrease.

In order to calculate a value for "a" using this equation, consider a 200 g load which is applied to a steel stylus such that a 300 µm width mark is produced (e.g. see Table 1). From Talysurf profiles and energy dispersive X-ray microanalysis carried out on marked stoving paints, it would appear that points of contact between stylus and coating occur at approximately 10 µm intervals. Assuming that at these points of contact this is only one titanium dioxide particle ($R = 0.1$ µm), the load applied to this particle can be calculated (e.g. $P = 2.2 \times 10^{-4}$ kg). For a titanium dioxide/steel interface, $K \simeq 1.58$ and $E = 210 \times 10^9$ Pa. Thus, substituting these values into Equation (1) results in "a" having a value of approximately 0.1 µm. (NB This value can only be considered as approximate since accurate values were not available for calculating K.) It is therefore apparent using this value for "a" that when a 200 g load is applied to a steel stylus, titanium dioxide particles will penetrate the metal surface by about 0.1 µm. If, for example, the same paint system was flocculated, then the number of points of contact would probably be decreased. But given the same applied load, P would then increase and so would the degree of indentation.

Equation (1) illustrates the fact that spherical particles like titanium dioxide will indent a relatively hard metal surface such as steel. However, in order to simulate the process of metal marking this indented particle has now to be subjected to a dynamic force which will result in metal being ploughed and transferred to the organic coating. Archard[8] has shown that when this occurs the amount of metal removed (δV) at any one point of contact is:

$$\delta V = \gamma a^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where γ is a constant and the total wear rate (W) is given by:

$$W \propto \Sigma \frac{\delta V}{2a} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where the summation is carried out for all the individual areas constituting the total area of contact.

Thus, using equations (2) and (3) it follows that:

$$W \propto \Sigma \frac{\gamma a^2}{2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Equation (4) therefore shows that the wear rate of metal which is related to the degree of metal marking is proportional to the area of contact.

Conclusion

The work has shown that metal marking is an abrasive wear phenomenon and is significantly affected by the type of metal used and certain formulation variables appertaining to the organic coating. From the point of view of coating composition, titanium dioxide pigment is one of the most important components which is responsible for metal marking and therefore it is vital that it is as well dispersed as posible so that it does not affect to any great extent the surface roughness. Thus, there is no one grade of titanium dioxide which will inherently offer much better metal marking resistance than another since the primary factor which influences metal marking is the state of pigment dispersion at the surface of a coating (i.e. the best grade of titanium dioxide will be that which exhibits the highest gloss).

In order to reduce metal marking two techniques can be adopted. Firstly, a coarse and soft extender/filler can be incorporated into the coating in order that the contact between metal and titanium dioxide is reduced. Obviously this procedure would result in a matt finish, but it is very effective. There are various paint additives referred to as slip aids which are claimed to reduce metal marking and these basically operate using the above principle (e.g. polypropylene beads). The second technique is to select a pigment/resin system which produces a clear layer, or alternatively use a two-coat application such that the final coat is a clear lacquer. In both cases, very high gloss will be obtained and there will be negligible metal marking. Additives are available, which are often silicone based, that function in a similar way to this technique in so far as they produce a thin layer of material between the surface of the coating and the metal, thereby lubricating the surface. However, the disadvantage with this type of product is that recoatability or printing can be a problem.

Acknowledgments

The author wishes to thank the directors of BTP Tioxide Ltd for permission to publish this paper, colleagues in Central Laboratories for helpful discussions, and Mr D. Foulger for carrying out most of the experimental work.

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Appendix

Typical properties of titanium dioxide pigments used in programme

Pigment	Crystal size (μm)	Manufacturing process	Rutile or anatase	Coated or non-coated
A	0.23	sulfate	rutile	coated
B	0.22	chloride	rutile	coated
C	0.15	sulfate	anatase	non-coated
D	0.22	sulfate	rutile	non-coated
E	0.23	sulfate	rutile	coated
F	0.17	sulfate	rutile	coated
G	0.24	chloride	rutile	coated
H	0.21	sulfate	rutile	coated

J. Oil Col. Chem. Assoc., 1982, 65, 276-279

Film characteristics of linseed epoxy esters prepared from novolac-based polyepoxide resins

By A. K. Vasishtha and D. Agrawal

Department of Oil and Paint Technology, Harcourt Butler Technological Institute, Kanpur – 208002, India

Summary

Epoxy esters were prepared by reacting linseed oil fatty acids with polyepoxide resins based on phenol-formaldehyde novolac resins. Samples were prepared with polyepoxides of different epoxide equivalents and were compared with those based on bisphenol A; the films of novolac-based epoxy esters were found to have better resistance to alkali and acid. The water resistance of all the epoxy ester films was found to be good.

Keywords

Types and classes of coatings and allied products

epoxy ester coating

Properties, characteristics and conditions primarily associated with

dried or cured films

chemical resistance
water resistance

Raw materials for coatings

binders (resins, etc.)

epoxy resin

raw materials used in manufacture or synthesis of ingredients for coatings

linseed fatty oil

Les caractéristiques de feuil des esters époxydes des acides gras d'huile de lin à partir des novolaques basées sur les résines polyépoxydes

Résumé

On a préparé les esters époxydes en faisant réagir les acides gras d'huile de lin avec les résines polyépoxydes basées sur les résines novolaques formophénoliques. On a préparé des échantillons de polyépoxydes ayant de divers équivalents époxydes et l'on les a comparés avec ceux basés sur le bisphénol-A. On a trouvé que les feuils des esters époxydes basés sur les novolaques possèdent une meilleure résistance aux alcalis et aux acides. On a trouvé que la résistance à l'eau de tous les feuils des esters époxydes est bonne.

Filmeigenschaften der Leinöl-Epoxidester, die mittels auf Novolak gegründetenen Polyepoxidharze hergestellt wurden

Zusammenfassung

Epoxidester wurden bei der Reaktion zwischen Leinöl-Fettsäure und auf Phenol/Formaldehydenovolakharze gegründeten Polyepoxidharze hergestellt. Muster wurden aus verschiedenen Epoxidäquivalenze erhaltenden Polyepoxiden hergestellt und mit derjenigen auf Bisphenol-A gegründet verglichen. Es wurde gefunden dass die auf Novolak gegründeten Epoxidesterfilme bessere Alkali- und Säurebeständikeit zeigten, und dass die Wasserbeständigkeit aller Epoxidesterfilme sich gut zeigten.

Introduction

Refs, 1-5

Vasishtha and Kaushal[1] prepared polyepoxide resins based on phenol-formaldehyde novolac resins and it was reported that the heat cured films of these resins possessed better hardness than the films of epoxy resins based on bisphenol A. Cured epoxy resin films based on novolacs have been reported to have excellent resistance to solvents and saponifying agents[2,3].

The esterification of the hydroxyl groups in the epoxy resins with carboxylic acids brings significant changes in the solubility patterns and other properties of these resins. Chandra and Karamchandani[4] reacted epoxy resins with rosin acids. The resulting esters were compatible with drying oils and soluble in mineral spirits. Jaeger *et al.*[5] prepared epoxy esters with drying oil fatty acids to obtain products close to alkyd resins.

The present paper reports the film properties of epoxy esters prepared by the reaction of linseed oil fatty acids with novolac-based polyepoxide resins.

Experimental

Refs, 6, 7

Materials

Phenol

BDH, LR grade phenol was used for the preparation of novolac resins.

Formaldehyde

BDH, 37.4 per cent w/v formaldehyde solution LR grade was used for the preparation of novolac resins.

Bisphenol A

Bisphenol A obtained from Amrut Industrial Products, India was used for the preparation of epoxy resins.

Epichlorohydrin

Danpha Chemicals, LR grade epichlorohydrin was used for the preparation of epoxy resins from both novolacs and bisphenol A.

Sodium hydroxide

Sarabhai, M. Chemicals, LR grade sodium hydroxide was used in the preparation of epoxy resins.

Fatty acids

Linseed oil fatty acids prepared in the laboratory by splitting linseed oil were used for the preparation of epoxy esters.

Preparation of novolac resins

Three samples of novolac resins with different ratios of phenol to formaldehyde were prepared by placing 250 g batches of phenol and 250 ml of water in a three-necked flask. The pH was adjusted to 0.5 with sulfuric acid and the contents were heated to 80°C with constant stirring. Calculated quantities of formaldehyde were added over a period of 3-4 hours. The temperature was maintained and stirring continued for an additional half an hour, after which the water was removed under vacuum.

Preparation of epoxy resins

Novolac resins prepared as above were reacted with different proportions of epichlorohydrin at 102-105°C. Calculated quantities of 10 per cent sodium hydroxide solution were added gradually to the reactants over periods ranging from 2 to 4 hours. Heating was further continued for half an hour after which the contents were dissolved in toluene and the salts, formed during the reaction, were removed by filtration. The toluene was then removed under vacuum at 160°C. Nine samples of epoxy resins (three samples from each novolac) were thus prepared.

Three control samples of epoxy resins based on bisphenol A were also prepared in this manner.

Epoxide equivalents of each resin sample were determined by the pyridinium chloride method[6].

Preparation of epoxy esters

Epoxy esters from novolac-based epoxy resins and bisphenol A-based epoxy resins (control) were prepared by reacting these resins with linseed oil fatty acids. Calculated quantities of fatty acids were placed in a three-necked flask fitted with a stirrer, condenser, thermometer and inert gas inlet tube. The contents were heated to 100°C at which point the resin was added and this temperature was maintained for two hours. The temperature was then raised to 240°C at which the esterification of the epoxide/hydroxyl groups was expected to take place[7]. This temperature was maintained until the desired acid value was obtained. The esters were then cooled and thinned with appropriate solvent (an 80:20 mixture of white spirit and xylene).

Evaluation of film characteristics

The epoxy esters were thinned to brushable consistency and appropriate quantities of cobalt and lead naphthenate driers were added. Coatings were applied on previously prepared tin and glass panels with a brush to obtain a uniform coat. After tack-free drying, the film properties such as hardness, flexibility, and resistance to alkali, acid and water were determined by the usual procedures.

Results and discussion

Ref. 1

The details of linseed epoxy ester formulations are given in Table 1. Samples were prepared and these were divided into three groups, A, B and C, according to the epoxide equivalents of the polyepoxide resin used for the preparation of the epoxy esters; i.e., group A – samples prepared from epoxy resins having epoxide equivalents between 1148 to 1400, group B – samples prepared from epoxy resins having epoxide equivalents between 1456 to 1675, and group C – samples prepared from epoxy resins having epoxide equivalents between 1721 to 1982. For the purpose of comparison, each group contained one sample of epoxy ester prepared from epoxy resin based on bisphenol A; the other samples were prepared from those based on novolac resins. All the samples prepared were of medium oil length, ranging from 50 to 53, and all produced a clear solution in an 80:20 mixture of white spirit and xylene. Table 2 shows the performance of the prepared epoxy ester films with regard to drying time, scratch hardness and flexibility. The resistance of these films to alkali, acid and water is given in Table 3.

Drying time

All the samples required 24 hours for tack-free drying. This was mainly because of the similar oil lengths of the esters and the same level of driers used in their formulation.

Scratch hardness

Films of esters prepared from novolac-based epoxy resins possessed comparatively better scratch hardness than the films of those prepared from bisphenol A-based epoxy resins. These results are in conformity with the observations made in the case of cured films of epoxy resin[1]. The behaviour can be attributed to the relatively larger proportion of aromatic rings present in the novolac molecules. The differences, however, are less significant in these air dried films because of the presence of long chain fatty acids in the epoxy ester molecules, which results in a

Table 1
Linseed oil epoxy ester formulations

Sample code	Type of phenol used for preparation of epoxy ester	Phenol/formaldehyde mole ratio used for preparation of novolac	Molecular weight of the novolac resin (calc.)	Epoxide equivalent of the epoxy resin before esterfication	Oil length of the epoxy ester	Acid value of the epoxy ester	Clarity of the epoxy ester in 80:20 white spirit/ xylene mixture (50% solution)
A-I	bisphenol A			1208	52.5	3.4	clear
A-II	novolac	3:2	518	1148	53.0	2.3	clear
A-III	novolac	5:3	412	1250	52.5	3.2	clear
A-IV	novolac	2:1	306	1400	52.5	2.8	clear
B-I	bisphenol A			1526	51.0	4.9	clear
B-II	novolac	3:2	518	1456	52.0	2.9	clear
B-III	novolac	5:3	412	1581	51.0	3.3	clear
B-IV	novolac	2:1	306	1675	51.0	6.2	clear
C-I	bisphenol A			1721	50.5	5.3	clear
C-II	novolac	3:2	518	1753	51.0	2.6	clear
C-III	novolac	5:3	412	1878	50.5	5.3	clear
C-IV	novolac	2:1	306	1982	50.0	2.5	clear

Table 2
Drying time, scratch hardness and flexibility of the epoxy ester films

Sample code	Drying time (tack free) (h)	Scratch hardness (load in kg)	Flexibility (1/8 inch mandrel)
A-I	24	1.4	pass
A-II	24	1.6	pass
A-III	24	1.5	pass
A-IV	24	1.5	pass
B-I	24	1.3	pass
B-II	24	1.7	pass
B-III	24	1.6	pass
B-IV	24	1.5	pass
C-I	24	1.3	pass
C-II	24	1.5	pass
C-III	24	1.7	pass
C-IV	24	1.4	pass

Table 3
Alkali, acid and water resistance of epoxy ester films at ambient temperature (30°C)

Sample code	10% sodium hydroxide solution (10 days)	20% sulfuric acid solution (15 days)	Distilled water (15 days)
A-I	2	4	5
A-II	4	5	5
A-III	3	5	5
A-IV	3	4	5
B-I	2	4	5
B-II	3	5	5
B-III	2	4	5
B-IV	4	5	5
C-I	2	5	5
C-II	3	4	4
C-III	3	5	5
C-IV	4	5	5

5 = film unaffected, 4 = slight colour change and loss in gloss, 3 = slight colour change and slight wrinkling, 2 = wrinkling or blistering, 1 = flaking or part removal of film, 0 = complete removal of film

general decrease in the hardness of these films. No significant differences in film hardness were observed on account of differences in the P/F ratios used in the preparation of the novolac resins.

Flexibility

All the test samples passed the flexibility test, which was expected of the epoxy esters of medium oil length.

Alkali resistance

The alkali resistance of the novolac-based epoxy esters was slightly better than that of the epoxy esters based on bisphenol A. No definite relationship could be established between the alkali resistance and the molecular weight of novolac, or the epoxide equivalent of the epoxy resins used for the preparation of epoxy esters.

Acid resistance

All the epoxy ester films showed good acid resistance when immersed in 20 per cent sulfuric acid solution for 15 days at ambient temperature. However, some of the samples, namely A-I, A-IV, B-I, B-III and C-II, developed a slight pink colour during this period of immersion. No significant effect of the type and molecular weight of the phenol, or the epoxide equivalent of the epoxy used for the preparation of the esters was observed in relation to the acid resistance of the film.

Water resistance

The water resistance of all the epoxy ester films was found to be good. This was attributed to part of the free hydroxyl groups in the epoxy resins reacting with fatty acids to form esters. Only in one sample, C-II, was there loss in gloss.

Conclusion

In general it can be stated that novolac-based epoxy esters of linseed fatty acids have a strong potential for being used as air drying speciality finishes where mild resistance to chemicals and water is required of the coating system.

[Received 8 October 1981

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Next month's issue

The Honorary Editor has accepted the following papers for publication. They are expected to appear in the August issue:

Water-soluble epoxy vehicles *by N. Krishnamurti, M. M. Shirsalkar and M. A. Sivasamban*

Accelerated corrosion tests in the motor industry *by H. McArthur*

Studies in maleation and preparation of meleopimaric acid from gum rosin of Pinus roxburghii *by S. C. Saksena, H. Panda, Ahisanuddin, Rakhshinda*

Corrosion inhibitors – an alternative to active anticorrosive pigments? *by W. Funke (short communication)*

Corrigendum

"Aqueous gloss enamels" by A. Mercurio, K. Kronberger and J. Friel, June 1982 (*JOCCA*, 1982, **65**, 227)

The following correction was unfortunately not received in time for appropriate alterations to be made to the final published text.

The passage beginning on the last line of page 229 (which runs over on to page 230) reading: "Hoy^2 of Union Carbide has shown ... critical film forming stage." should instead read as follows:

"Hoy^2 of Union Carbide has shown quantitative correlation between amount of coalescent distributed in the polymer and subsequent efficiency in lowering the minimum film formation temperature. This suggests that re-distribution of coalescent into the polymer phase from the aqueous phase during drying has not occurred to a sufficient degree to aid coalescence during the critical film forming stage when latex particles first touch and begin to sinter. Upon further water evaporation, coalescing solvent must perforce re-distribute into the polymer phase and this will help longer film coalescence."

news

Further information on any items mentioned below may be obtained by circling the appropriate *Reader Enquiry Service* number on the form at the back of the *Journal*. Enquiries will be forwarded to the organisation concerned.

Noisy paint!

ICI Paints Division has been analysing the noise paint makes when it is subjected to stress. The analysed sounds can predict when paint is likely to crack, how strong it is and how long it will last. These "acoustic emissions" are tell tale signs of structural failure in paint polymers when they are stretched.

ICI claims to be the first paint manufacturer to study and use this technique for paint research. It has, however, been used for some years in studying metal failure in various applications.

By using these sounds, amplified many times, it is now possible to detect cracks inside the paint and on the surface long before they appear to the naked eye.

Trevor Strivens, ICI Paints Division physics group leader, research department, commented: "We can now, in some cases, considerably reduce the time needed to assess paint failure due to weathering or exposure in corrosive environments.

"Conventional methods of assessing paint failure can be costly, time consuming and not very discriminating or informative. The use of acoustic emission therefore is a great step forward. We can quickly and effectively identify problems with new formulations and test paint that has failed in certain environments."

Acoustic emissions are made by many materials when subjected to stress. For instance they have been studied in the metals used in North Sea oil rigs and on aircraft wings.

A more familiar example is the cracking sounds made by ice when someone walks on a frozen pond; these sounds result from stress caused by the person's weight which begins to form small cracks in the ice.
Reader Enquiry Service No. 31

Nynas oils distributor

A. Johnson & Co. (London) Ltd has been appointed the sole distributor in the UK and Ireland for the Nynas range of naphthenic base and process oils. The oils are commonly known as pale oils and are used in the manufacture of inks, paints, rubber and specialised chemicals.
Reader Enquiry Service No. 32

Cricket sponsorship

Home Charm Paints has announced that it is taking over the major sponsorship of Yorkshire County Cricket Club this season, following the withdrawal of support by a rival paint manufacturer.

The deal, which includes sponsorship of Yorkshire Youth Cricket as well as five major county matches, was announced by Ray Illingworth, Yorkshire's manager, at Headingley on Tuesday 4 May.

Leslie Silver, chairman of Batley-based SPL (Holdings) Ltd, who manufacture Home Charm paints, said "Negotiations with Yorkshire Cricket Club have yet to be fully completed, but if this seasons experiment fulfils our expectations, we would be looking forward to continuing our support during coming seasons."
Reader Enquiry Service No. 33

Surface coatings at South Bank

Many members of the UK coatings industry will have heard of a proposal to concentrate the teaching of polymer technology in London at the Polytechnic of North London by transferring the polymer section from the Polytechnic of the South Bank.

Initially this was to have included the well-known Borough School of Surface Coatings, but this is no longer the case. Following representations from the coatings industry and discussions with the polytechnics concerned, the Inner London Education Authority has now agreed that only plastics technology will go to North London. The teaching of surface coatings will remain at the Borough Road site of the Polytechnic of the South Bank where it has been since the inception of the polytechnic in 1892.
Reader Enquiry Service No. 34

International Paint acquisition

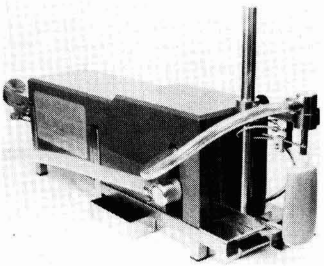
International Paint has acquired all the share capital of Litoverti Tintas Graficas SA of Sao Paulo, Brazil. Litoverti are manufacturers of packaging coatings.
Reader Enquiry Service No. 35

new products

New filling machines

The latest range of filling machines from Universal Fillers is the Posifill.

It comprises the Posifill 400 and Posifill 1000, having a range of fill from 40 cc up to just under 400 cc, and from 100 cc up to just over 1,000 cc respectively.



A Posifill unit from Universal. The volume of fill is set by turning a hand wheel at the rear of the machine

Pneumatically operated, the machines are said to be suited for operation with flammable liquids. Being designed with a slim profile they can be placed next to each other to form 2, 3 or 4 multi-head units – each one being independent of the others so that when required they can be reverted to single or twin-head units as desired.

Universal describes the horizontal design as an easily handled unit, being portable and virtually a maintenance engineer's dream – clean to strip down, supremely accessible components, simple circuitry and basic valving which does not require him to be an electronics or pneumatics expert.

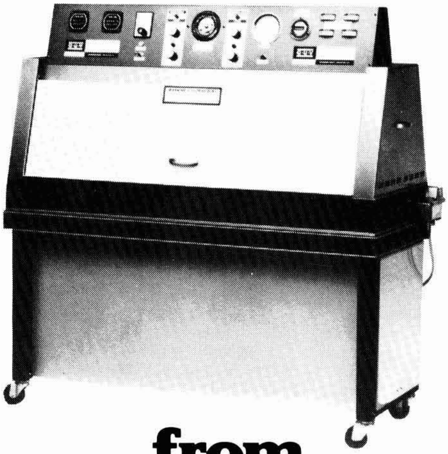
Posifills have as standard a two speed filling facility, enabling the body of the bottle to be filled at maximum speed, but when the neck is reached the speed is reduced to finish the fill cleanly with no spurting of product from the neck.
Reader Enquiry Service No. 36

Rust stabilising primers

Following the successful launch of Comma Rust Stabiliser and Primer No. 1 in both the industrial market and the DIY market (where the product is called Comma Stop Rust), a complete range of four specialised anticorrosive primers are now available from Comma Oil & Chemicals Ltd.

A major feature of the primers is that surfaces to be treated do not first require shot-blasting. All four products have been developed to meet a wide field of application and may be applied directly over firmly adherent corrosion, including the two-pack epoxy primer (No. 4). The unique pigment reacts with the rust changing it to a stable iron oxide, magnetite (Fe_3O_4), thereby preventing rust creep. None of the products contain either lead, acid or zinc.
Reader Enquiry Service No. 37

Come Rain...
...Come Shine



from Q-PANEL

Q·U·V Accelerated Weathering Tester

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- * Faster testing.
- * Sunlight simulated by fluorescent UV lamps.
- * Low running costs with minimal maintenance.
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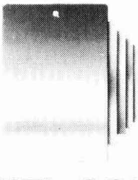
- * Universally accepted.
- * Available in Steel or Aluminium.
- * Degreased before packing for immediate use.
- * Wide range of sizes and surface finishes available ex stock.



Q-PANEL

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102 Taylorson Street, Ordsall,
Salford M5 3HA, England.
Telephone: 061-872 1152

Reader Enquiry Service No. 180

Security paint

Battelle of Washington, USA claims to have developed a paint that is virtually impossible to remove. According to the inventor Earl C. Martin, a senior research scientist in Battelle's Chemical Technology Department, "The paint can be used to help reduce theft by permanently marking small tools, office equipment, heavy equipment, unique art objects and personal property."

Dr Marilyn E. Walsh of Battelle's Human Affairs Research Center in Seattle said estimates of theft from businesses run as high as $75 billion annually and went on "Much of this loss can be attributed to the inability of firms to trace and identify their property". She added that a permanently affixed paint, such as that developed by Martin, could significantly aid businesses in theft detection and prevention.

The paint can be applied to metal, wood, plastic or rubber items. "It is extremely difficult to completely remove the paint even from a relatively smooth metal surface," Martin said. "If you get it on your hands, you just have to wait for it to wear off."

Each customer's paint is mixed with a unique combination of chemical ions. Three methods can be used to identify the paint and suspected stolen property.

The first level of identification is the paints colour. The second level of detection uses ultraviolet light. Fluorescing materials are mixed with the paint so that it will glow when placed under an ultraviolet lamp. The final and most precise level of identification uses x-ray fluorescence. It is said to take about three minutes to positively identify a unique paint.

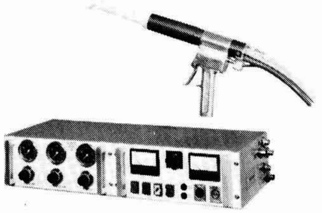
The paint can also be applied so that it is invisible. It is suggested that this could be used for protecting art objects such as paintings, vases and rugs without defacing them.

Originally developed to identify government property on the Department of Energy's Hanford site in south-central Washington State, the paint is now used at the Los Alamos National Laboratory in New Mexico and on several corporate farms near Hanford.

A Battelle sponsor is exploring commercialisation of this concept as a significant addition to industrial security.
Reader Enquiry Service No. 38

New powder coating equipment

Britain's leading manufacturer of electrostatic powder coating equipment, Volstatic Coatings Ltd, has introduced its Series 2 range of electrostatic generators and pneumatic control modules. The new range is claimed to provide the most advanced and compact powder charging systems in the world.



The Series 2 powder coating equipment from Volstatic is a modular system allowing the interchange of components. Above is shown an air ionising hand gun and a 30 kV electrostatic generator and pneumatic control module

The range includes modules for hand and automatic applications. It embraces both 80 kV high voltage equipment and 30 kV low voltage equipment for the new Volstatic low voltage air ionising technology.

The charging voltage to the spraygun is supplied through the patented Volstatic liquid filled cable, which means that no resistors are needed in the sprayguns and there is no danger of short circuit in the event of damage to gun or cable.

The pneumatic control modules incorporate regulators and pressure gauges for powder transport and for supplementary air.
Reader Enquiry Service No. 39

Kremlin launch Kontour

Kremlin Spray Painting Equipment Ltd has launched a new range of electrostatic spray equipment in the UK known as Kontour. Its design incorporates some of the latest electronic advances and has important built-in safety features which have already made the new electrostatic spray equipment readily acceptable in Europe, according to Kremlin.

A key feature of Kontour is the electronic generator incorporated in the barrel of the gun, which creates the high voltage. This generator consists of an electronic oscillator, a transformer and a cascade. Instead of the usual high voltage cable, there is a simple flexible wire leading from a power pack to supply the Kontour generator with a constant 12 volt supply. This gives a variable electrostatic force of between 0-80 kV.

Kontour is available as an air system in both manual and automatic forms, and as an airless version. A Kontour Airmix system is also available in manual and automatic forms.
Reader Enquiry Service No. 40

Digital thickness meter

Sheen Instruments, well-known in the paint industry for many years, has introduced the SS1200 digital coating thickness meter.

It has a single continuous scale ranging from 0 to 1,200 microns for measuring paint, plastics, grp, glass and other non-magnetic coatings such as zinc on iron and steel (thous also may be displayed by throwing the appropriate switch).

Sheen says it has paid particular attention to the fascia design of the SS1200, with the digital readout on the top so that it can be read at a glance while in the normal operational position of hanging at waist level from a shoulder strap. The design objective was to make the new thickness meter "easy to read, hold and carry".

Full calibration facilities are said to enable accurate measurements to be made of coatings applied to blast-cleaned steel.

The instrument is fitted with a constant pressure probe of a new design to average measurements and minimise compression of coatings. It is claimed to measure to an accuracy of ±2 per cent or ±2 microns, whichever is the greater.

As the digital display is a single scale, there is no need to recalibrate between measurements taken on a primer and subsequent coatings. Another refinement is that the last digit is rounded up or down to provide the equivalent of an additional half-digit accuracy.

Thedisplay is also fitted with a hold position which remembers the last reading. This should be useful when readings must be taken in difficult locations or poor light. The SS1200 is battery or mains operated.
Reader Enquiry Service No. 41

Paint and corrosion remover

Elcometer Instruments Limited recently reached an agreement with Nitto Kohki Europe Co. Ltd to act as agent for the Nitto range of hand held engineering tools. In particular, Elcometer Instruments intended to promote the Nitto Pneumatic Jet Chisel range and Air Chipper.

The Nitto range of Jet Chisels are designed for use in the welding industry, construction industry, casting and forging industries.

According to Elcometer the Jet chisels will be of particular interest for the removal of faulty paintwork and corrosion prior to repainting.
Reader Enquiry Service No. 42

news

Paint finishing plant

A newly developed range of industrial paint finishing plant has just been introduced by Peter Franklin Associates in conjunction with manufacturers, Lenesco Ltd.

The two companies have combined to offer the necessary design, manufacture and installation services of a complete range of spray booths, stoving ovens and other spray shop equipment.

Reader Enquiry Service No. 43

literature

Painting woodwork

The structure of wood and its effect on the application and durability of paints and preservatives are discussed in Building Research Establishment Digest 261, "Painting woodwork", which was published on 1 May 1982. Copies are available from HMSO, price 55p each (plus postage).

Notes are included on moisture content and dimensional changes, permeability, effects of sawing, planing and sanding, and external influences such as water, solar radiation, micro-organisms and the risk of decay. Preservatives are considered in relation to paint and details are given of the recommended four-coat paint system for new wood, the painting process and putty and glazing compounds.

Reader Enquiry Service No. 44

XVI FATIPEC Congress

The book of the XVI FATIPEC Congress is now available. The theme of the Congress was: "Evaluation and foresight of film properties of organic coatings by the use of modern analytical methods" 9-14 May 1982.

The book – in four volumes (1,392 pages) – contains the complete texts of the 10 plenary lectures and the 54 short lectures presented during that week.

It can be obtained at a cost of 4,500 + 200 (postage) Belgian francs by ordering from: ATIPIC, Square Marie Louise 49, B-1040 Brussels, Belgium. Prepayment is required: account No. 210-0235175 of ATIPIC, Société Générale de Banque, Agence Dilbeek, Chssée de Ninove 84, B-1710 Dilbeek, Belgium.

Reader Enquiry Service No. 45

meetings, etc.

Phosphating and metal pretreatment

A further two-day technical training course in phosphating and metal pretreatment has been announced for 20 and 21 October 1982 by Pyrene Chemical Services Ltd. Further information can be obtained from the Marketing Services Officer, Pyrene Chemical Services Ltd, Ridgeway, Iver, Bucks SL0 9JJ, Tel: 0753 651812.

Printing technology

The Yorkshire Branch of the Institute of Printing is holding a one-day seminar on "Paper, plates, inks and printability – a technology update". The seminar will be held on Friday 24 September 1982 at the University of Leeds. Further information is available from Dr J. T. Guthrie, Dept. of Colour Chemistry, University of Leeds, Tel: 0532 31751 ext. 6123.

people

Dr John P. Ferguson, until recently sales director of Instrumental Colour Systems, has joined Impex Trading Ltd of Newbury as deputy general manager.

Dr Ferguson will be responsible for developing the sales of the recently introduced low cost Tri-Color colour difference meter and also for developing the company's export marketing efforts on behalf of various British instrument manufacturers in the Pacific, Far East and Australasia.

Mr G. A. Upfill-Brown, director, International Paint plc, has been appointed the director responsible for developing the group's interests in the Far East, including the operations in Korea, Singapore and Hong Kong where he is now based.

occa news

For information on membership of OCCA, enquiries should be sent to the Association's offices, see front cover for address.

News of members

Peter Gaskell

Mr Peter Gaskell has recently been appointed by Capricorn Chemicals Ltd as southern area technical representative.

Peter has many years experience and an excellent technical background in surface coatings and adhesives, and will further strengthen Capricorn's sales team. He is well known in the paint, ink and adhesives industries due to his long association with a large UK resin supplier.

Leslie H. Silver

The congratulations of the Association are intended to Leslie H. Silver (President 1973-75) on being awarded an OBE in the Queen's Birthday Honours List for services to export.

Transvaal Section

Annual general meeting

The annual general meeting of the Transvaal Section was held on 21 April 1982 in the Wine Centre of the Stellenbosch Farmers' Winery, Johannesburg.

The formal business of the evening was supplemented by a talk on wine appreciation and a cheese and wine party.

The incoming committee for 1982/83 consists of:

Mr Gorden Munro – Chairman
Mr Eric Timm – Hon. Secretary
Mrs Helen Gaynor – Hon. Treasurer
Mr Peter Marples – Hon. Publications Secretary
Messrs Peter Gate, Clive Peddie, Eric Sharpe – Committee members

The retiring Chairman, Mr Bob Rouse, has been appointed South African Vice-President in succession to Mr Roly Eglington of Durban.

P.M.

West Riding Section

Annual general meeting

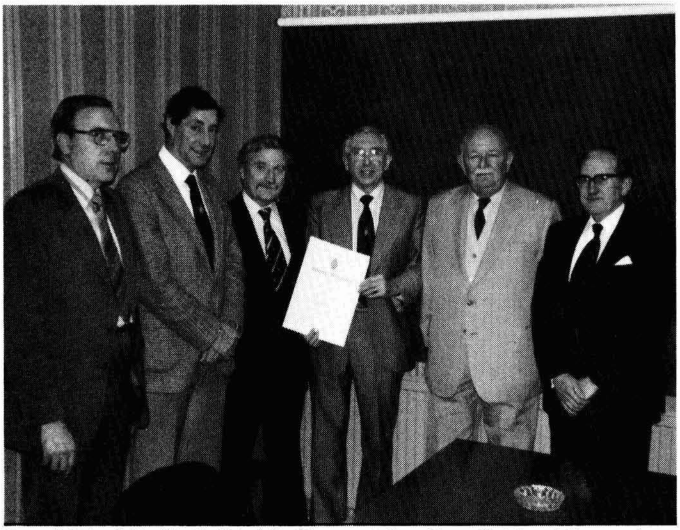
The annual general meeting of the West Riding Section was held on 6 April 1982 at the Mansion Hotel, Leeds.

During the formal part of the meeting, the Chairman, Mr R. A. C. Chappell, gave his review of the past session. Mr Chappell commented on the healthy financial state of the Section and also on the support that was received for the lecture meetings.

Following the formalities, two films were shown. The first one was a very interesting film on the historical developments of paint. This described how paint technology had evolved from the early cave dweller up to modern dry surface coatings. The second film, entitled "Chemicals from oil", gave a detailed account of the types of products that are derived from oil and also their end-uses.

The evening was rounded off with an excellent buffet supper.

D.V.M.



From left to right: Mr T. Entwistle (Representative, Cape, Natal and Transvaal sections), Mr J. R. Bourne (Hon. Secretary), Mr D. J. Morris (President), Dr F. M. Smith (Immediate Past President and Representative, Wellington Section), Mr C. Butler (Representative, Auckland Section), Mr R. H. Hamblin (Director & Secretary)

Newcastle Section

Annual ladies night

The Newcastle Section's annual ladies night was held at the Five Bridges Hotel, Gateshead on Friday 19 February 1982 and was attended by 209 people. The principal guests were the President, chairmen from Trent Valley Branch, West Riding and Thames Valley sections and their ladies, and the Director & Secretary, Mr R. H. Hamblin.

Music was provided by the George Rowell Orchestra which was much appreciated by all those attending.

H.F.

OCCA International Working Group

A meeting of the Working Group took place on 6 January 1982 at the offices of Mebon Ltd, when Dr F. M. Smith showed other members of the Group the Scroll of Honorary Membership of OCCA Australia which he had just received.

Reports of Council meetings

Wednesday 24 February 1982

A meeting of the Council took place at 2.00 p.m. on Wednesday 24 February 1982 at the Great Northern Hotel, King's Cross, London N1 9AN. The President (Mr D. J. Morris) was in the Chair and there were 26 members present.

It was reported that Mr G. Wood and Mr G. T. Flood had agreed to act as the Association's representatives on BSI Committee DOS/3/10 – Chemistry and Chemical Technology and PVC/1/13 Methods of Test for Pigments, respectively.

A report was given on progress made on the compilation of information by constituent members, sought by the International Co-ordinating Committee, on research establishments and weathering sites for the surface coatings industries. Various suggestions were made on likely sources and the Director & Secretary would follow these up, in addition to the information already received from the Paint Research Association and the European Committee of Paint, Printing Inks and Artists' Colours Manufacturers' Association.

The draft annual report of the Council for 1981 was considered and a minor correction made.

The President reported that the ballot for President Designate had resulted in Mr C. N. Finlay being appointed. Mr Finlay thanked the Council for the honour bestowed upon him.

Dr H. R. Hamburg and Mr C. Butler were nominated as Vice-Presidents. Nominations for the two remaining vacancies among the Vice-Presidents were made and the Director & Secretary would report to the next meeting if the members concerned could accept.

Since Dr H. R. Hamburg had completed six years as Hon. Treasurer, it was necessary to find a successor. The Director & Secretary reported that he had spoken to a member of Council who would consider the nomination and inform him before the next Council meeting.

Reports were received on the arrangements for the Savoy Dinner Dance and for the AGM Luncheon Lecture, with which would also be held the Council Reunion. The Director & Secretary reported that Dr Rhodes Boyson, MA, MP, Parliamentary Under Secretary for Education had accepted the invitation to speak on "The role of government in education and science".

It was resolved unanimously that any member whose current subscription was three months in arrears should not receive issues of *JOCCA* after 1 April 1982 until payment of all subscriptions due and would not be entitled to receive any issues published during the period of arrrears.

With regard to the 1982 Exhibition, Council were reminded that the date for the Savoy Dinner Dance had had to be moved because of the FATIPEC Congress and that it would take place on the middle day of the Exhibition. The suggestion made by the Director & Secretary that lectures, films, demonstrations by exhibitors as an extension of exhibition facilities should be allowed had been implemented as far as the holding of lectures was concerned and 12 such talks (which could be on commercial as well as technical themes) had so far been arranged. The Manchester Section intended to organise their usual train

occa news

party on the middle day. The importance of the Audit Bureau of Circulations Exhibition Data Form in certifying the analysis of attendance at the Exhibition was emphasised.

Discussion took place on the level of 1983 membership subscriptions and the amounts being charged by the six sections overseas for 1982 membership subscriptions. It was agreed that members would prefer small regular increases in inflationary times rather than larger increases at infrequent intervals. It was resolved (subject to a second confirmatory resolution at the next Council meeting) that the 1983 membership subscription should be £25 for Ordinary and Associate Members, £6 for Retired Members and Registered Students up to 21 years of age, and £12.50 (i.e. half the Ordinary rate) for Registered Students between the ages of 21 and 25.

On the publication field it was stated that, although papers were forthcoming for the *Journal*, there was a considerable need for writers of monographs such as the monograph on "Marine Finishes". It was hoped that any members who were able to prepare monographs on "Automotive" and "Aircraft Finishes" could be persuaded to contact the Director & Secretary as quickly as possible.

The reader enquiry service was reported to be well supported.

Details of the progress made in the arrangements for the technical sessions at the 1983 Conference at York were given.

A new working group had been set up on Technical Education by the Paintmakers Association and the Hon. Technical Education Officer and the Director & Secretary had been invited to attend. Information was received on both the courses arranged by the Ontario Section and on aspects of distance learning being considered by the Technical Training Board for the Printing Ink Industry.

On the Professional Grade, it was reported that the Professional Grade Committee had transferred two Associates to Fellowship and admitted two candidates to Associateship.

A meeting of the working group on OCCA International would take place at the Exhibition when Mr R. E. Rouse (Vice-President Designate, South African Division) and Mr R. Bettison (Vice-President, New Zealand Division) would also attend. Mr P. Birrell (Vice-President and Representative on Ontario Section) would be meeting members of the working group after the Council meeting.

Reports on section activities at home and overseas were received.

The Federation of Societies for Paint Technology would be holding their 1982 Annual Meeting in Washington on 3-5 November and their 1983 meeting in Montreal. An Association paper had been arranged for presentation at Montreal and offers for a paper at Washington would be welcome.

There being no other business, the President thanked those who would relinquish their *ex officio* places on Council at section AGMs held before the next Council meeting in April and declared the meeting closed at 4.45p.m.

Thursday 15 April 1982

A meeting of the Council took place at 2.00 p.m. on Thursday 15 April 1982 at the Great Northern Hotel, King's Cross, London N1 9AN.

The President (Mr D. J. Morris) was in the Chair and 19 members attended. The President extended a welcome to Mr A. R. van Spall who was attending Council for the first time in his capacity as Representative of the Hull Section.

It was reported that Mr B. F. Gilliam had been able to accept nomination as Hon. Treasurer of the Association and that Mr H. J. Furuhjelm and Dr T. A. Banfield would fill the two remaining vacancies among the Vice-Presidents.

In the report on the Savoy Dinner Dance arrangements, Council were pleased to learn that Mr J. Foxton (a past President of OCCA Australia) and Mrs Foxton would be able to attend the Dinner Dance as guests of the Association and that Mr Foxton would also attend the meeting of the working group on OCCA International as an observer. At the conclusion of the speeches at the Dinner, the scroll of Hon. Membership would be presented to Mr L. H. Silver (President 1973-75).

For the Council Reunion/AGM Luncheon Lecture on 16 June, five past Presidents and three past Hon. Officers had so far accepted invitations to be present.

The number of members whose 1982 subscriptions had not been received was slightly higher than in April 1981 but a further reminder would be sent later in the month. It was unanimously resolved that the names of any members whose 1982 subscriptions had not been received by 30 June should be removed from the Register.

A resolution confirming the one passed at the February Council meeting for the 1983 membership subscriptions was passed with one dissentient. A resolution confirming the 1982 membership subscriptions for the six overseas sections as resolved at the February Council meeting was also passed.

The annual accounts for 1981 and the estimates for 1982 were adopted. Various suggestions for increasing the revenue of the Association were discussed, including the possibility of incorporating additional papers of a technological nature into the *Journal* and thus increasing its appeal. It was pointed out that the *Journal* was read by a large readership (as shown on the ABC's Media Data Form) and that a large number was sold to libraries of companies and institutions so that care had to be taken to meet their requirements; the suggestion being made was for an addition to the present papers. It was hoped that members who could offer such papers would do so by contacting the Director & Secretary.

On the Exhibition it was reported that ten more stands had been allocated and that 16 talks by 13 exhibitors had been arranged. The Director & Secretary asked for volunteers to chair the lecture series and this was arranged. It was felt that this new concept was one which would have the support of visitors and exhibitors alike. The Review of the Exhibition would concentrate on new aspects of exhibiting.

The Hon. Editor commented that he and the Director & Secretary had long sought to encourage papers in the *Journal* on the subject of coatings application but these were extremely difficult to obtain; the assistance of any members of the Association for possible publications would be much appreciated.

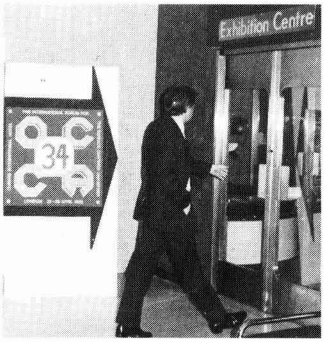
Similarly, the call for papers at the 1983 York Conference had brought in a number of offers but members who felt that they could present papers within the theme or knew of others (whether members or non-members) who could do so were urged to contact the Director & Secretary as quickly as possible. It was planned to publish the programme in the autumn.

Further information on progress towards distance learning for students was given to Council and, in this connection, the work undertaken by in-house training had to be considered as well as the training offered by institutions.

On the Professional Grade, it was reported that three Fellows and four Associates had been admitted.

Reports on section activities were received.

There being no other business the President thanked all those who would be retiring from Council at the annual general meetings of either the Association or the sections for their help and guidance during the past year and declared the meeting closed at 4.14 p.m.



OCCA-34 Review

THE INTERNATIONAL FORUM FOR DISPLAY & DISCUSSION IN THE SURFACE COATINGS INDUSTRIES

ABC
A member of the Audit Bureau of Circulations

aeo
A member of the Association of Exhibition Organisers

International attendance

The 34th Annual Exhibition of the Oil & Colour Chemists' Association (*"the international forum for display and discussion in the surface coatings industries"*) took place in London at the Cunard International Hotel, 27-29 April 1982. Included amongst the exhibits were items from 11 overseas countries and the Exhibition attracted an international **audited attendance** from 32 overseas countries. It is stressed that the Association completes the ABC's Exhibition Data Form, which allows for checks on completed registration cards by independent auditors, and analysis of acceptable cards by data processors. The **audited attendance** also once again revealed the very high level of personnel attracted to the Exhibition, since 34 per cent of those attending were of owner/director/manager status, a factor which was commented upon by exhibitors.

Audited attendance

The countries from which overseas visitors came were:

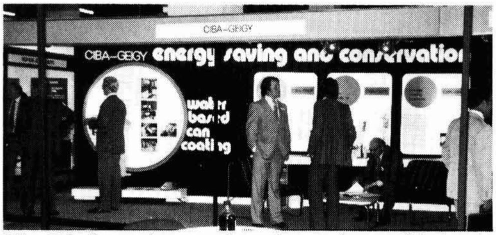
Austria
Australia
Belgium
Brazil
Canada
Cyprus
Denmark
Egypt
Eire
Finland
France
Germany
Greece
Hungary
India
Italy
Netherlands
New Zealand
Norway
Pakistan
Peru
Portugal
Romania
Spain
South Africa
Sweden
Switzerland
Thailand
Turkey
United Arab Emirates
United States
Yugoslavia

The crowd puller

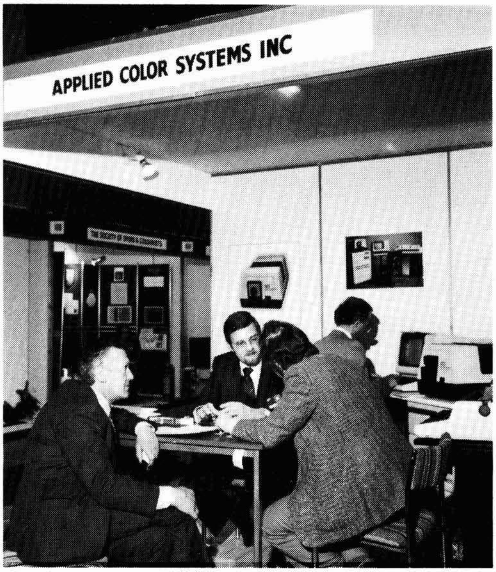
The percentage analysis of visitors by job function is as follows:

	per cent
Director/owner	16.33
Management	17.82
Section head/group leader	5.10
Chemist/physicist/technologist	19.63
Lab assistant/technician	9.34
Sales and marketing	16.01
Buyers	2.43
Administration/secretarial	4.08
Lecturer/student	1.33
Other	2.04
Item not completed	5.89
	100.00

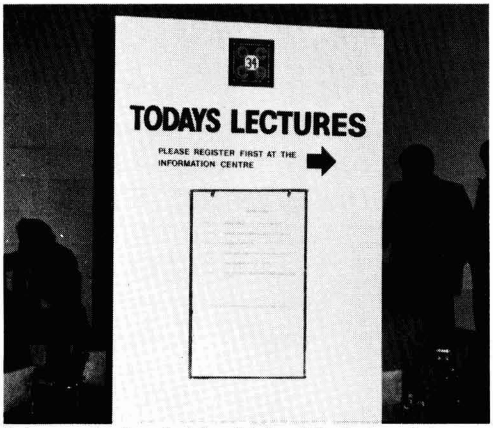
One of the overseas exhibitors at OCCA-34 – Chemolimpex of Hungary



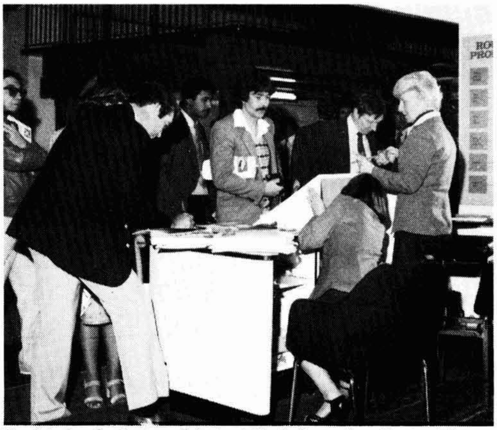
Ciba-Geigy's stand attracted much attention as did also the three lectures on "A novel resin system" given by the company. The paper on which these lectures were based is published in this issue



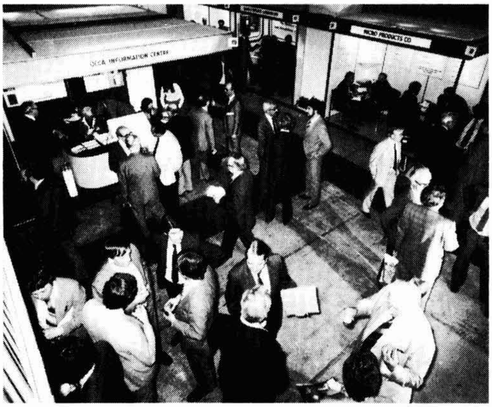
Another overseas exhibitor was Applied Color Systems Inc.



A large notice board giving details of the lectures being presented each day was situated inside the main entrance by a seating area which was much used by visitors



Registering for lecture tickets at the Information Centre. Sixteen lectures were given by thirteen exhibitors and this innovation was popular with both visitors and exhibitors



A general view of the area in front of the Information Centre. The audited attendance figures show that visitors came from 32 overseas countries

The lecture given by Silberline Ltd on "Aluminium pastes in surface coatings" attracted a good attendance and visitors were able to discuss points made afterwards at the Silberline stand

The percentage analysis of visitors by products manufacturered was:

	per cent
Paints	25.03
Coverings and coatings	6.99
Resins	9.89
Pigments and dyes	8.56
Dispersions and solvents	2.83
Inks and graphic materials	6.59
Plastics	1.57
General chemicals	12.95
Other	16.33
Item not completed	9.26
	100.00

Lectures – a new concept

At OCCA-34 an innovation, which was widely welcomed by both exhibitors and visitors, was the extension of Exhibition facilities by the provision of talks on commercial or technical themes by exhibitors in a separate lecture room. Sixteen talks were given by thirteen exhibitors over the three days and these attracted attendances as high as 70 on one occasion. One lecture was given on the three successive days of the Exhibition by an exhibitor and another exhibitor spoke on two occasions. Admission to the lectures was free of charge but those wishing to attend were asked to register for tickets at the Information Centre. It was stressed by the Director & Secretary of the Association that this series of lectures was completely different in concept from the idea of an exhibition organised in conjunction with a conference or seminar on a defined topic.

In addition to a large notice board showing the lectures which were being given on particular days, announcements were made over the public address system calling attention to these throughout the day. Exhibitors who took part in the series have notified the Association that they found this a most helpful extension of the Exhibition, in that they could draw attention by visual aids to particular aspects of their research or developments which could then be discussed in greater detail on their stands.

The thanks of the Association are due to those members who acted as chairmen for the various lectures and kept to the tight time schedule.

The lectures given were on the following subjects:

A novel resin system (Ciba-Geigy)

Prohesion testing (C & W Specialist Equipment)

Economic use of computers in the surface coatings industries (SBA Commercial Systems)

Tin chemicals for industry (International Research Institute)

Painting inspection (Institution of Corrosion Science & Technology)

Aluminium pastes in surface coatings (Silberline Ltd)

Rheology (Carri-Med)

Colour measurement (Pacific Scientific)

Metal intermediate bulk containers and powder handling system (Bernt Iversen & Son)

Direct characterisation of coatings on a substrate by PL – DMTA (Polymer Laboratories)

Sampling of powders, particle size analysis, lightfastness testing, flow microcalorimetry (Microscal)

Hazard labelling in the surface coatings industries (SBA Commercial Systems)

Biocides in paint (Durham Chemicals)

As an example of the type of lecture which was given, the following report has been received from the International Tin Research Institute on their lecture.

Tin chemicals for industry

Mr Colin J. Evans, head of development at the International Tin Research Institute in London, described the organisation and aims of the Institute, which, together with the nine Tin Information Centres located in principal tin-using regions of the world, make up the International Tin Research Council. This body is supported entirely by Indonesia, Malaysia, Nigeria, Thailand and Zaire and exists to maintain markets for tin.

Chemical research projects at the Institute which are relevant to the oil and colour industries were described. A number of ceramic pigments based on tin oxide are used commercially; these include chrome-tin pink, tin-antimony grey and tin-vanadium yellow. Structures of these pigments have been determined and attempts are being made to create new colours by doping the tin-oxide-based structures with other metal ions. Progress in research with organotin compounds was reviewed. Bis(tributyltin)oxide, TBTO, is used in over 60 commercial wood preservative formulations in the United Kingdom alone. Novel tributyltin compounds are being synthesised and tested for their effectiveness in wood preservation. One such compound, tributyltin ethanesulfonate, is water-soluble and a 2 per cent aqueous solution shows comparable effectiveness to TBTO in organic solvent. This could open up new markets for organotin wood preservatives.

Mono-organotin compounds, of the type $RSnX_3$, are being studied at the Institute in order to develop commercial outlets for these little-used compounds, which have low mammalian toxicity. Certain mono-butyltin and mono-octyltin compounds exhibit marked hydrophobic properties and their potential in waterproofing building materials and cotton textiles was described. The compounds are also used in synergistic mixture with di-organotin compounds as stabilisers for PVC, and studies are concentrating on determining the nature of this synergism.

Other research topics were touched upon and included development of new organotin compounds for use in antifouling coatings with a wide spectrum of biocidal action, rust-inhibiting primer paints for steel structures, based on hydroxystannates and stannates of calcium strontium and zinc, and the use of various hydroxystannates and metastannates as smoke suppressants in glass reinforced polyester. Environmental studies of the mode of breakdown of organotin compounds to harmless inorganic forms of tin were also described.

Services available to industry were described and included publications, a technical advisory service which is free and entirely confidential to tin users, and a technical information bureau containing a specialised file of information on tin technology. The lecture ended with the screening of a 17 minutes colour film, "Vital link", describing the Institute's development activities.

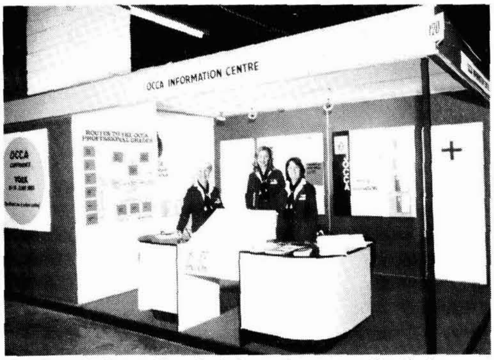
Afterwards a number of questions were posed on specific aspects of the research and these were dealt with by Dr Peter Smith, head of the Chemistry Division. One question was concerned with the possible reaction of TBTO in treated wood with carbon dioxide to form tributyltin carbonate in situ; *the reaction could not be equated directly with reaction of TBTO in the atmosphere when carbonate was only formed very slowly. Dr Smith confirmed that the Institute was also studying the stability of TBTO in treated wood. Comments were elicited on he comparative performance of mono-organotins and silicone as water repellants; in some environments, the organotin compounds might prove more stable. Interest was also shown in the work on rust-inhibiting primer paints.*

At the entrance to the hall, the Association engaged commissionaires to help with registration and to direct visitors

Visitors discussing points of detail at the Roban/Sartorius stand

The International Tin Research Institute's stand. The Institute presented one of the lectures and a summary is included in this review (see above)

The attractive layout of the Hoechst/RCL/Harco room, which as well as displaying information about products, was decorated in a manner to draw attention to the draw for the Munich Oktoberfest



The Association staff at the information centre. On display were details of JOCCA (ABC circulation, 1981, 4,178 – more than double that of any other UK journal in this field) other OCCA publications, membership and the Professional Grade, all of which aroused considerable interest

An interesting competition was held on Durham Chemical Ltd's stand. Visitors were invited to estimate the percentage of cobalt contained in a drier solution and a visitor is shown making his estimate. Nearest to the correct figure of 1.6 per cent was Mr W. Phillips of Crown Decorative Products who won a bottle of whisky

The three ladies in national costume in the Hoechst/RCL/Harco room with the drum for the special draw for visitors. The winner of a weekend for two at the Munich Oktoberfest was Mr E. J. Bassett-Cross (see below)

Alan Dodds – publicity and creative services manager of Hoechst UK Limited – is seen on the right handing Edward Bassett-Cross – general manager, Overseas Division, International Paints – his air tickets and hotel reservations for a weekend for two at the Munich Oktoberfest. Mr Bassett-Cross won this prize in the draw held by Hoechst/RCL/Harco at OCCA-34 and will be flying with his wife to Germany on 1 October for the last weekend of the Munich Beer Festival. They will stay at the luxurious Vier Jahrenzeiten Hotel (The Four Seasons) for two nights and will return on Sunday evening (see above)

The interesting layout of the Kirklees room in which visitors could also try their skill at darts

General

The Association provided seating areas which were in constant use for those wishing to talk to acquaintances and to make notes.

Visitors commented on the admirable opportunity afforded by the Exhibition's new arrangements to discuss technical and commercial problems, to raise points at lectures, to discuss them in detail afterwards and to meet colleagues in the supplying industries for informal talks.

Exhibitors reported that they had been extremely busy. For example, Sheen Instruments wrote "... has been one of their [Sheen's] most successful exhibitions ever. Firm orders worth nearly £25,000 were taken and serious enquiries potentially worth five times that figure were received. Particular interest was shown in the new Sheen range of corrosion control equipment ... as well as the new MFT Bar which was launched at OCCA ... this instrument was well received by many manufacturers and users of emulsions ..."

Pearson Panke Equipment reported that their "... first OCCA Exhibition stand proved to be highly successful with a continuous stream of visitors right up to and after the final closing time ... Stephen Panke, chairman of Pearson Panke Equipment Ltd and Bjorn Erichsen, joint managing director of Erichsen, who were both in full time attendance at the Exhibition both announced that they were extremely pleased with the quantity and quality of interest shown."

The cost effective Exhibition

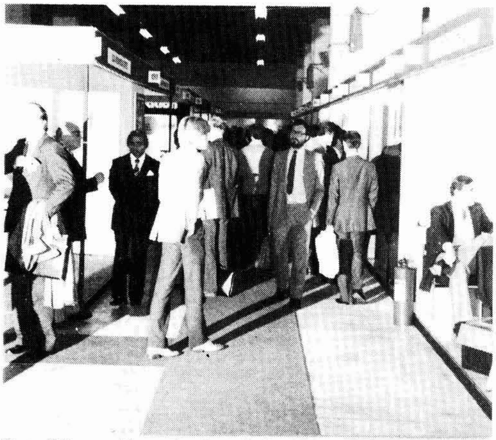
It is not intended this year to give detailed reports of all exhibits since these were covered in the *Official Guide* (and supplement) and the April Preview issue of this *Journal* but rather to show the way in which the Exhibition arrangements were successfully changed this year to meet changing circumstances within the industries. Judging by the **audited attendance** and the wide interest shown in both stands and in the extension of Exhibition facilities by the presentation of talks by exhibitors, this year the OCCA Exhibition, acknowledged as the crowd-puller, lived up to its aim of providing an international forum for **display and discussion** for the surface coatings industries.

Savoy Dinner Dance – a prestigious OCCA-sion!

On this occasion, the Association's prestigious Savoy Dinner Dance was held as the social highlight of the Exhibition on the middle day, Wednesday 28 April. At 7.00 p.m. the majority of guests were received by the President (Mr D. J. Morris) and Mrs Morris in the River Room, overlooking the Thames; the top table guests assembled meanwhile in the Parlour Room. Dinner was taken in the Lancaster Room when the company received the President and the guest of honour (Mr Norman Mischler, chairman of Hoechst UK and Berger, Jenson &

Discussions on the stand of Micro Products Co.

(Left to right) Mr D. J. Morris (President), Mrs Morris, Mrs Mischler, Mr N. Mischler (guest of honour)



One of the corridors; the Association arranged red carpet in the corridors to complement the green and yellow felt coverings to the fascias, these being the three colours of the special motif of OCCA-34, designed by the Director & Secretary

Pearson Panke Equipment Ltd showed for the first time at an OCCA Exhibition and their success is recorded in their report, part of which appears in the text above

Visitors from overseas divisions and OCCA Australia at the Savoy Dinner Dance (standing from left to right) Mr R. A. Bettison (Vice-President, New Zealand Division), Mr D. J. Morris (President), Mrs Morris, Mr R. E. Rouse (Vice-President Designate, South African Division), Mr J. Foxton (a past President of OCCA Australia), Dr F. M. Smith (Immediate Past President and Representative, Wellington Section) (seated from left to right) Mr J. R. Bourne (Hon. Secretary), Mrs Bourne, Mrs Rouse, Mrs Foxton, Mrs Smith

The President (left) making the presentation of a Scroll of Honorary Membership to Leslie Silver (President 1973-75 and currently President, Paint Research Association)

Nicholson) together with their ladies. After dinner, the President first proposed the Loyal Toast and then extended an address of welcome to the guests. These included the principal officers of many other societies, research and trade associations as follows:

Dr G. de W. Anderson (Managing Director, Paint Research Association) and Mrs Anderson

Mr D. A. Bayliss (President, Institution of Corrosion, Science & Technology) and Mrs Bayliss

Dr J. V. Butcher (President, Society of Dyers & Colourists) and Mrs Butcher

Mr R. Chester (President, Paintmakers Association)

Professor Sir Ewart Jones (President, Royal Society of Chemistry) and Lady Jones

Mr M. J. Levete (Director, Paintmakers Association) and Mrs Levete

Mr L. H. Silver (President, Paint Research Association) and Mrs Silver

Lt. Col. L. E. W. Stokes-Roberts (Master, Painter Stainers Company) and Miss Amanda Stokes-Roberts

Mr B. Watkins (Chairman-Designate, British Resin Manufacturers Association) and Mrs Watkins

Dr S. Wernick, OBE (President, Institute of Metal Finishing)

Mr G. B. Young (President, Society of British Printing Ink Manufacturers) and Mrs Young

In addition, the President extended a special welcome to the representatives of the overseas divisions of the Association: Mr R. E. Rouse (Vice-President Designate, South African Division) and Mrs Rouse and Mr R. A. Bettison (Vice-President, New Zealand Division) and to Mr J. Foxton (a past President of OCCA Australia) and Mrs Foxton. He also touched on the international aspects of the Association's activities and co-operation with similar organisations abroad. He paid a charming compliment to the ladies and thanked his wife, Marian, for her help and encouragement throughout his first year as President. He concluded his speech by asking the members of the Association to drink a toast to the guests and ladies, coupled with the name of the guest of honour, Mr Norman Mischler.

In his reply on behalf of the guests, Mr N. Mischler mentioned the very great part played by the Association in the surface coatings industries since its foundation in 1918 and wished it continued growth and prosperity. In a witty and well-received speech he related some very amusing anecdotes and concluded by asking the company to join him in a toast to the Association, coupled with the name of the President.

Following the speeches, the President presented a scroll of Honorary Membership of the Association, the highest honour which can be bestowed on a member, to Leslie Silver (President 1973-75) who, in his service to the paint industry, had achieved the unique distinction of having been elected President of all four organisations connected with the industry. The scroll reads as follows:

OIL & COLOUR CHEMISTS' ASSOCIATION

It was unanimously agreed this day by the Council of the Association to confer

HONORARY MEMBERSHIP

upon

LESLIE HOWARD SILVER

President of the Association 1973-75, having also served as Honorary Secretary and Chairman of the West Riding Section, Vice-President, Elective Council Member and Representative on Council of West Riding and Auckland Sections, in recognition not only of his outstanding service to this Association but also to mark the unique distinction of having been elected as President of three other organisations serving the surface coatings industries: the Paint Research Association, the Paint Industries Club and the Paintmakers Association of Great Britain Limited and to express the admiration of the members for the way in which he has at all times discharged his duties and upheld the prestige of this Association.

D. J. Morris *President*

J. R. Bourne *Honorary Secretary*

R. H. Hamblin *Director & Secretary*

2 December 1981

Mr Silver thanked the President for the honour bestowed upon him and stated that he had derived the greatest pleasure from his term of office as President of the Association.

The President, the guest of honour and their ladies then withdrew and later rejoined the company for dancing to the Ted Hetherington Orchestra until 1 a.m., with a break at 11 p.m. for a mystifying demonstration of magic by Alan Shaxon and Anne, followed by the traditional tea and pastries. The function concluded at 1.00 a.m. with the singing of Auld Lang Syne, followed by the National Anthem.

It was generally agreed that the holding of the Dinner Dance during the Exhibition had enabled exhibitors to entertain their customers at a very special *OCCA*-sion and that the evening had been most successful.

DYNAMIC MECHANICAL THERMAL ANALYSER

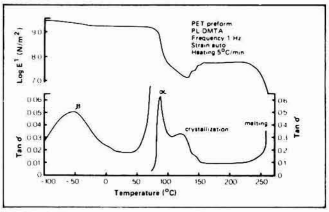
No other single technique can so rapidly provide such detailed structural information on polymeric materials

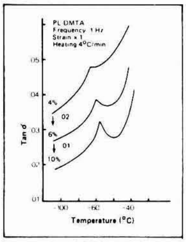
Assessment of the damping factor (tan δ) and dynamic storage modulus (E′ or G′) detects essentially all motional and structural transitions in polymeric materials as they occur during a wide temperature sweep.

APPLICATIONS

- **Engineering Design Data**
- **Crystalline Polymers**
- **Polymer Blends**
- **Polymeric Glasses**
- **Rubbers**
- **Fibres and Films**
- **Activation Energies**
- **Composites**
- **Coatings**
- **Liquids, Waxes, Bitumens, etc.**

Frequencies	.033, .1, .33, 1.0, 3.0, 10, 30 and 90 Hz Selected by push button or remotely
Modulus Range	Young's 10^5 N/m^2 – 10^{11} N/m^2 Rigidity 10^3 N/m^2 – 5×10^8 N/m^2
Damping Range	Tan δ (x1) 0.001 – 9.999 (x10) 0.0001 – 0.9999
Temperature Range	-150°C to +300°C
Scan Rates	Heating 1°C/10 min to 20°C/min Cooling 1°C/10 min to 15°C/min





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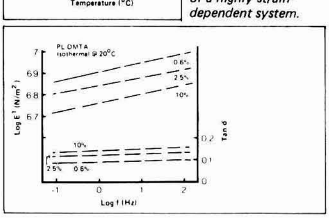
Quench cooled PET.

Left:
Poly(propylene) toughened with EPDM rubber.

Below:
Rubber with 30 pph carbon black is typical of a highly strain-dependent system.



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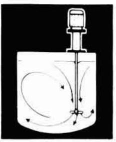
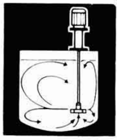
We have the mixer you need



Rapidex type PR

Propeller agitator
0.33—10.0 HP

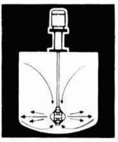
Stirring, suspending, dissolving.

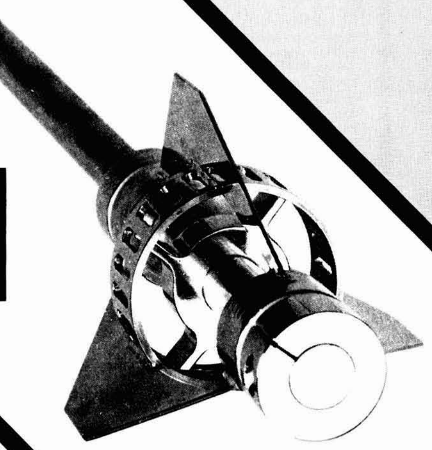


Rotostat type T

Mixer emulsifier
0.5—50.0 HP

Interchangeable stator screens available in a number of mesh sizes for emulsifying, homogenising, disintegrating, milling, suspending, difficult solubilising jobs. High shear mixing.

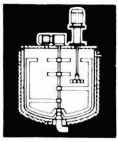


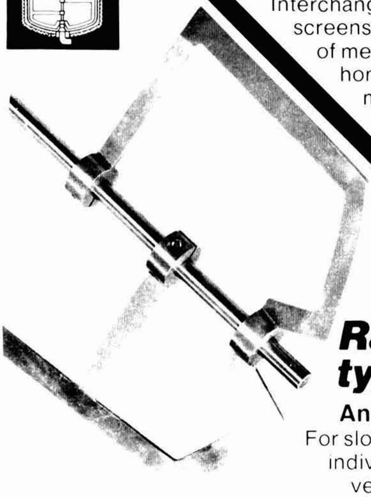


Rotostat type X

Disperser
0.75—100.0 HP

Dispersing, pigment-wetting, pre-mixing, disintegrating, grinding, difficult solubilising jobs. High shear mixing.

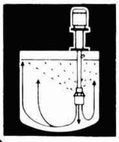




Rapidex type AR

Anchor stirrer

For slow stirring. Produced individually to fit any existing vessel. May be furnished with scrapers of f.inst. Teflon to prevent deposit of material on vessel wall.



Rotojet type Y

Axial jet mixer 0.5—20.0 HP

Highly effective mixing and agitation entirely without any air intrusion. Particularly suitable for dissolving crystalline materials and for mixing components varying widely in specific gravity or viscosity.

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JOHN GODRICH Consulting Engineer
Ludford Mill, Ludlow, Shropshire SY8 1PP.
Telephone: Ludlow (0584) 3153. Telex: 35275.

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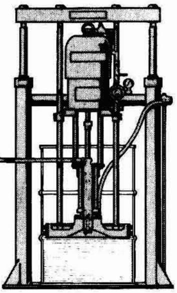

Manchester Section – Technical Discourse

"DISC"

A DISCOURSE IN SURFACE COATING

University of Lancaster
9.00 a.m. Friday 24 September 1982

The Manchester Section of OCCA is repeating the novel form of a one day technical meeting, pioneered in 1979, on Friday 24 September 1982 at the University of Lancaster. The technical discourse will be introduced and discussions led by well-known experts in the surface coatings industry and the University of Lancaster.

This will present participants with an opportunity to partake in a lively interchange of technical ideas and for everyone to achieve maximum involvement. Simultaneous discussions will take place in the morning and afternoon sessions and participants will be free to circulate and to take part in whichever discourse stimulates their particular interest.

Fees
Registration fees inclusive of coffee, lunch and tea are: OCCA member £20.00 + VAT, non-members £35.00 + VAT.

Overnight accommodation
Accommodation is available on the campus as follows: evening meal £3.50 + VAT, overnight accommodation £5.70 + VAT, breakfast £2.25 + VAT.

Further details and application forms are available from: **Mr E. J. Hurst, Ciba Geigy Plastics and Additives Company, Pigments Division, Ashton New Road, Clayton, Manchester M11 4AR. Tel: 061 223 1341.**

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