

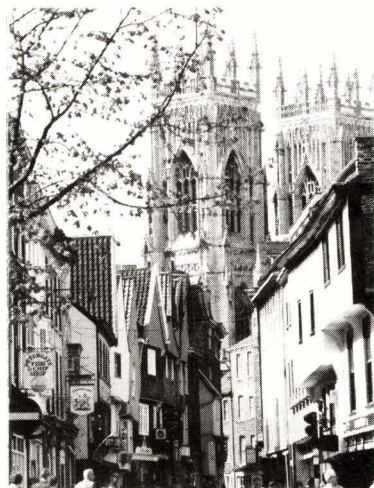


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Structural changes in polymer films. Part 2: the effect of the pigment zinc oxide on the electrolytic resistance and transition temperature; some comparisons with the pigment iron oxide and red lead

D. J. Mills and J. E. O. Mayne

Electrochemical impedance in coated metal electrodes. Part 5: Film thickness

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Micaceous iron oxide paints

D. M. Bishop and F. G. R. Zobel

The Railway Technical Centre, London Road, Wilmorton, Derby DE2 8UP, UK

1. Introduction

Micaceous iron oxide paints have been extensively used as undercoats and finishing paints for the protection of railway engineering structures all over the world. They were introduced into this country after the discovery of micaceous iron oxide ore in South Devon at the turn of this century¹. The protective qualities of these paints have been attributed to the orientation of the lamellar pigments parallel to the paint film surface, which reduces water penetration through the films (and hence increases corrosion protection^{2-16,43}) and reduces ultraviolet degradation of the paint film (increasing durability^{2,4,6,12,16,43}).

The first comprehensive tests on various paints and varnishes were carried out by R. Mallet¹⁷ between 1838-40 and he took out the first patent in 1841 on the use of a resinous material for corrosion protection¹⁸. The first patent involving the addition of red lead was in 1852 and white lead appeared in the following year. Until the last decade of the nineteenth century no further scientific work appears to have been carried out and many diverse paint compositions were introduced – some with disastrous results¹⁹. In 1898 *The Engineer* referred to tests carried out by Baucke with various oxides of iron pigments and stated that red oxides gave the best protection²⁰. Probably the most comprehensive tests were carried out at the very end of the century by H. Smith²¹, who concluded that the best protection for iron structures was given by one or two coats of genuine red lead followed by at least two coats of red oxide of iron paint. This was the state of painting specification for railway bridges in this country at the end of the century; a typical painting specification is shown in Appendix 1, to be followed by regular maintenance with the same paints.

With the advent of the naturally occurring grey micaceous iron oxide pigment it was possible to obtain the traditional colours by merely tinting with red oxide pigments. In the thirties it was possible to obtain various coloured micaceous iron oxide paints by the addition of natural and synthetic iron oxides (to produce red, brown, yellow and black shades), chromium oxide green, ultramarine blue, etc., possibly in combination with white lead or zinc oxide². Although there has been a tendency in this country to paint railway bridges in the traditional grey colour (or dark tints), micaceous iron oxide paints tinted with flake aluminium or white lead (at varying pigment levels) have been used over many years.

The availability of alternative micaceous iron oxide pigments to those approved for use in railway protective paints necessitated the physical and chemical characterisation of available pigments¹, followed by the evaluation of the effects of those differences on the corrosion protection and mechanical properties of the paint coatings, which is discussed in this paper.

2. Historical development of railway micaceous iron oxide paints

Although only two micaceous iron oxide pigments have been used in railway protective paints over the last 80 years, there have been significant changes in the media, extenders, additives, methods of manufacture, application methods, etc., all of which can greatly affect the corrosion protection. In general, over the years satisfactory corrosion protection has been achieved in a variety of environments.

In view of the importance of micaceous iron oxide paints in the protective paint systems for bridges, the significant changes in raw materials/formulations will be discussed in historical sequence, as far as the British Railways are concerned, since it is considered relevant to the performance of modern day protective paints. The events will be discussed as follows:

- (1) Raw materials (extenders, media, antisetling agents, etc.)
- (2) Micaceous iron oxide paints

2.1 Raw materials

2.1.1 *In the beginning there was red oxide pigment...*

Prior to the introduction of micaceous iron oxide pigments, undercoats and finishing paints were based on natural red oxide pigments which were available from many sources. Red oxide pigments had been used in bridge specification paints since the nineteenth century and it was usual for the undercoats to be tinted a chocolate-brown colour¹. The general painting specification used at this time was based on the familiar red lead/linseed oil primers, as shown in Appendix 1. It was not uncommon for all steel parts to be scraped, wire brushed and dipped in hot boiled linseed oil prior to erection; this was followed by a coat of red lead in linseed oil applied either before or after erection¹³. A second coat of red lead primer was applied after erection, followed by a coat of chocolate-brown undercoat and red oxide finishing paint.

2.1.2 *Micaceous iron oxide pigments¹*

From the turn of this century until 1964, when it became in short supply to the paint trade, the pigment came from the Ferrubron mines in South Devon, England. In 1964, alternative micaceous iron oxide pigments were examined and this resulted in the approval of that from Waldenstein, Austria; the accelerated corrosion test results are shown in Table 1.

2.1.3 *Extenders*

Extenders were originally introduced into micaceous iron

Table 1
Effect of micaceous iron oxide pigments on protection (1964 tests)*

Micaceous iron oxide (% w/w)					Water absorption (% w/w on dry paint film)	Order of merit (1 = best and 6 = worst)		
Coarse British grade (SS1711)	Fine British grade (SS47)	Austrian Standard grade	French	Extender (% w/w)		Corrosion test† (15 weeks)	SO ₂ /humidity test (15 weeks)	Evan's salt immersion test‡ (1 week)
62				6	22	2	3	3
	62			6	22	5	1	3
		47		22	16	3	4	1
47				22	22	6	2	1
			47	22	21	4	5	5
31			31	6	20	1	6	6

*Medium was long oil isomerised linseed oil/phenolic resin (50% solids w/w).

†Accelerating weathering (carbon arc and water spray) with intermittent exposure to SO₂/humidity at 35-40°C.

‡Scatched panel immersed in 3% salt solution.

Table 2
Micaceous iron oxide paint formulation variables 1900-1981

Date	Undercoat			Finish		
	PVC*	MIO† on pigment (w/w)	Extender	PVC	MIO on pigment (w/w)	Extender
1900-1930s	← same as finish →			30%	82%	mica, graphite
1945	← same as finish →			35%	75%	white lead, aluminium
1950	28%	85%	aluminium powder, zinc oxide	38%	96%	aluminium powder
1953-1966	45%	94%	china clay, leafing aluminium	47%	96%	leafing aluminium
1966-1970	← same as finish →			≈45%	not specified but probably as 1953-1966	aluminium and tinters
1970	← same as finish →			≈45%	80%	various

*PVC = pigment volume concentration, †MIO = micaceous iron oxide.

oxide paints as a cheap replacement for part of the more expensive lamellar pigment. Nowadays, extenders are acknowledged to contribute more than mere economy to a paint and can improve antisetling properties, sagging properties, paint build, etc.^{23,24} The extenders used in the railway micaceous iron oxide paints over the years are summarised in Table 2, their content of the total pigment varied between 4-25 per cent w/w. The original micaceous iron oxide paints (which were supplied by Griffiths Brothers & Co.) were extended with mica, graphite and barytes; various tints were used to get the required colour. This basic formulation probably continued into the thirties as shown by the analysis in Appendix 2. In the forties, *composition specifications* were introduced for micaceous iron oxide paints to be used for railway structures and this continued until 1966. The range of extenders was very restricted and only aluminium powder, basic lead carbonate (white lead), asbestine, china clay and zinc oxide were acceptable during this period (see appendices 3-5). From 1966 there was a change to *performance*

specifications with minimal guidance on composition details. The extenders in the micaceous iron oxide paints now include barytes, talc, china clay, titanium dioxide, etc., any of which can greatly influence the paint performance.

2.1.4 After linseed oil...

Until the forties, railway micaceous iron oxide paints were based on a medium prepared by adding litharge and umber to boiling linseed oil and heating until the lead and manganese salts had dissolved²⁵. This modification to linseed oil was established in the early nineteenth century producing a more viscous medium due to the combined polymerisation and oxidation induced by the heating, with faster drying due to the dissolved lead and manganese acting as driers.

The disadvantage of linseed oil-based coatings was the poor through drying of generously applied coatings, but

this was overcome in micaceous iron oxide paints by modifying the linseed oil with copal resins. Copal resins, which are hard, natural resins from tropical countries, are highly polymerised and insoluble in drying oils but by means of a thermal decomposition process (known as gum running) could be sufficiently degraded or de-polymerised to render them compatible with the drying oil, which was added hot to the molten resin. By 1935 the medium contained tung oil, which was found to have faster drying properties than linseed oil, but it was found necessary to add some rosin to make the chemical reaction more controllable in the varnish cooking process – remembering the primitive plant in use at that time; this medium, or variants of it, was used up to the sixties²⁹.

Linseed oil/copal resin was the approved medium for micaceous iron oxide paints supplied against the composition specification – British Railways Specification No. 35, covering “Materials for use on Bridges, Buildings and Structures” which was introduced in 1953 (see Appendix 5). In 1954 there was an interruption in supplies of copal resin from the Congo, which was the main source, necessitating a review of alternative resins. This resulted in the approval in 1963 of modified phenolic resins as the medium for micaceous iron oxide paints.

Rosin modified phenolic resins had been originally introduced as replacements for natural copals during the First World War and were frequently named “synthetic copals”. It is possible that this medium was used during the time interval between the shortage of Congo copal and the introduction of oil modified phenolic resins. Initially linseed oil was used as the modifying oil for phenolics, sometimes in conjunction with tung oil (or China wood oil, as it is often called), but in later years only tung oil has been generally used. This medium was the basis of micaceous iron oxide paints manufactured to meet the *performance requirements* of British Railways Specification No. 59, covering “Priming, Undercoating and Finishing Civil Engineering Paints for Protective Systems” (introduced in 1966) and British Railways Specification No. 70, covering “Paints for Civil Engineers”. The latter is the current specification having been introduced in 1970; tung oil modified phenolics are still used but modified urethane oils are gaining commercial preference.

2.1.5 Antisettling agents^{27,29}

Early micaceous iron oxide paints were characterised by rapid pigment settlement and poor through drying of heavily applied coatings. Various additives were tried over the years to overcome these problems. Aluminium stearate was used as an antisettling agent in 1930, when dissolved in drying oils it formed a gel the consequent viscosity increase reducing pigment settlement. It was common to “mature” micaceous iron oxide paints in a tank for several days to allow gel formation and improve the antisettling properties. A later modification was to add litharge (PbO) to improve the film through-drying properties and it was noted that “litharge had the unexpected effect of shortening the time of stirring in the tank to produce a satisfactory suspension of the pigment from 7 to 3 days!” Litharge slowly reacted with the acids from the drying oils to form lead soaps and the resulting gel (and increase in viscosity) reduced the pigment settlement but also gave rise to surface skinning and sometimes complete paint gelation. The need for “maturing” was eventually eliminated by making the gel in white spirit before incorporation into the rest of the paint mix. In the late thirties, a solution of rubber and cobalt oleate in white spirit became available (under the name Wettag) and its incorporation into a paint prevented hard pigment settlement. It was found that Wettag used in conjunction with

aluminium stearate greatly improved the antisettling properties. The introduction of strontium sulphate as an extender affected the drying times and litharge was re-introduced together with white lead, which produced the gel conducive to pigment stabilisation by reaction with the acids from the drying oils. A typical Ferrodor micaceous iron oxide paint in the late thirties contained:

Micaceous iron oxide	} antisettling agents
Strontium sulphate	
Litharge	
White lead	
Aluminium stearate	
Wettag	
Medium and driers	

In the early forties, Wettag was not available, probably because of rubber shortages during the war years, and precipitated calcium carbonate of extremely fine particle size (less than 15 microns) was introduced. The calcium carbonate pigment particles were coated with a layer of calcium stearate and prevented pigment agglomeration and facilitated wetting of these pigments by the medium. When properly dispersed, calcium carbonate pigments confer a gel structure to the paint which reduces pigment settlement. This was used for many years until evidence accumulated that the calcium carbonate could be leached from the paint film to the surface, under certain conditions, giving a shabby look to the paint.

Doubts arose in the fifties as to the necessity of retaining litharge and white lead in paint formulations in view of the disadvantages of excessive skinning and discoloration in sulphurous atmospheres. A railway specification dated 15 November 1950 (see Appendix 4) stated that in the finishing paint “to assist in the suspension of micaceous iron oxide, aluminium stearate and/or china clay may be incorporated into the paint provided the former does not exceed 1 per cent and the latter 10 per cent of the paint”. China clay, because of its chemical nature and particle size and shape, can reduce pigment settlement. It is assumed that pigment settlement was acceptable in the undercoat! In the late fifties and early sixties, preliminary trials with alternative antisettling agents showed that only two commercially available types were of use in micaceous iron oxide paints, namely precipitated calcium carbonate and Bentone. Bentones are light coloured powders (originally octadecyl ammonium montmorillonite) which in certain solvents produce a gel that can reduce pigment settlement. Surface active agents/suspending agents were included in British Railways Specification No. 35 dated November 1958 (see Appendix 5). The modern tendency is to use Bentone (of which there are now several types available) or hydrogenated castor oil, often in conjunction with china clay, etc.

2.2 Micaceous iron oxide paints

The original micaceous iron oxide paints used by the railways in this country were supplied by Griffiths Bros. & Co., which was formed as a paint company in 1869 and became established worldwide as suppliers of micaceous iron oxide paints under the trade name Ferrodor (now part of Goodlass Wall & Co. Ltd). It was considered that the essential requirements of these early paints were²⁸:

1. They must be free from all substances that can have any injurious effect on the metal.
2. They must as far as possible be impervious to all external influences.

3. They must be sufficiently elastic to allow for the expansion and contraction of the metals under varying temperatures.
4. They must be hard enough not to rub off or peel off.

The basic formulation of these paints conformed to the normal formulation of an oil paint of about 65 per cent w/w pigment and fillers, and 35 per cent boiled linseed oil and driers²⁹. Typical fillers were slate powder, barytes and fine silica. A typical liquid drier was terebine (or Japan drier), which was originally a quick drying varnish consisting of copal with linseed oil and litharge and thinned with turpentine but which later became more of a heavy bodied oil being generally prepared by saturating linseed oil with lead and manganese²⁵. The paints were supplied either in paste form or ready-to-use at 28/- (shillings) per cwt and 34/- per cwt respectively. When the paste was purchased it then had to be thinned in the proportion of 3 lbs paste to 1 lb thinner (special linseed oil) before application²⁸. It was recommended that the "brush should be dipped into the paint and not only touch the surface; this would tend to keep the paint stirred in the can and so ensure an even use of the ingredients." It must be remembered that at this period there were no structuring agents or surfactants available and micaceous iron oxide pigments sank almost as quickly in boiled linseed oil as they did in water. Arduous stirring was required before taking paint from the paint suppliers' containers. This basic paint formulation remained substantially unchanged for 25 years or so, as shown by a typical analysis of Ferrodor by the Paint Laboratory in Derby Carriage & Wagon Works dated 28 October 1928, and shown in Appendix 2. Pure American turps could safely be added (up to half a pint) when the correct thinner (boiled linseed oil) was not available.

It was strongly recommended that the undercoats should be either the natural dark steel grey or the "natural purple" Ferrodor paints. The latter were based on the Spanish natural purple during its availability but subsequently became a mixture of micaceous iron oxide and red oxide pigments. The only difference between the undercoats and finishes was the colour, since the finishing paints were made from the two undercoats with the addition of only the required colouring matter to produce the desired shades. Red oxide, Indian red, chocolate, purple, brown, slate, dark greens, etc. could be supplied and "very handsome decorative finishes could be produced by the addition of aluminium." Although these rudimentary paints gave excellent protection over many years they suffered from two major faults, namely rapid pigment settlement and poor through drying of generously applied coatings.

The change in the composition of the micaceous iron oxide paints from the original oil paint type to a form approximating to one in which the pigment volume concentration was around the critical point was due to the work of Bennett²⁹. In the early twenties Bennett had observed over several years that the linseed oil film originally covering the micaceous iron oxide pigment had eroded away and that it was the exposed lamellar pigment bound by the oil between the flakes that provided the long term protection. Experimental paints were made by pasting the micaceous iron oxide pigment in a variety of media available at that time and adjusting to a practical consistency by addition of solvent. As the pastes were made using a pestle and mortar it was probable that the pigment volume concentrations were below the critical value rather than above. Exposure tests at the Ferrodor factory at Bermondsey showed that the medium had little effect on the durability, and even the shellac and Manila

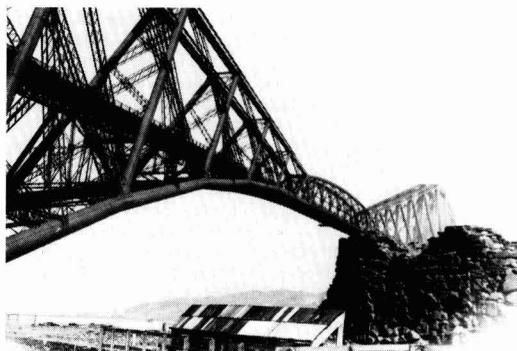


Figure 1. Early railway paint testing site – exposure rack at Inchgarvie Island (Forth Bridge)

copal media, which had alligatored on weathering, gave good protection between the cracks. These experiments gave a clear indication that, contrary to the accepted wisdom of the time, an all oil medium was not essential to long term protection in micaceous iron oxide paints. The prospective use of varnish gave promise of faster drying times and less "tender" films but not the elimination of rapid pigment settlement.

Originally micaceous iron oxide was offered as a primer pigment and since paints were sold by weight it was claimed that micaceous iron oxide paints were a better buy than those based on lead, because the buyer obtained twice as many gallons per hundredweight²⁹. Although Bennett's work had clearly shown that good protection could be achieved by using micaceous iron oxide pigments only, nobody who aspired to stay in business as a paint manufacturer could afford to use the pure pigment. A common comment of the time was "a paint manufacturer should raise his hat when passing a sack of barytes for there is his profit and livelihood." Whatever the merits of the "new" Ferrodor it had a lower weight per gallon than the previous 66:33 (pigment/oil) quality, and filler – now becoming known by the more respectable name of extender – had to be re-introduced to restore, to some extent, the status quo. The concern that the presence of amorphous pigments could affect the corrosion protection was eliminated by further experiments. Despite the faults and inconvenience of those early micaceous iron oxide paints, they became recognised worldwide as giving improved corrosion protection over the then existing paints.

2.2.1 Paint evaluation trials

These early micaceous iron oxide paints were assessed by the railway companies at various exposure sites, such as that at Inchgarvie Island adjacent to the Forth Bridge. This site, on which the first panels were exposed in 1936, was used by the London & North Eastern Railway to assess paints intended for use in marine conditions (see Figure 1). Records were kept at the London & North Eastern Railway's paint laboratory at Doncaster but both the test site and the laboratory have now disappeared.

2.2.2 Spondon Bridge³⁰

One of the frequently quoted trials of micaceous iron oxide paints was on the railway footbridge at Spondon, Derbyshire. The newly erected bridge was used in 1944 by the paint laboratory of the London, Midland & Scottish Railway to develop a painting scheme that would take full

advantage of the improved surface condition of flame cleaned steel. This was necessary because of the tendency of red lead in linseed oil primer to become brittle when applied to the warm steel surfaces and it was considered that alternative inhibitive pigments and/or media might be superior.

Loose millscale was removed by flame cleaning and each of the 23 panels forming the bridge was painted with a four coat process, each panel having a different primer. Two coats of the same primer were applied to each panel and the whole bridge was finished with two coats of the same micaceous iron oxide paints, probably formulated as shown in Appendix 3. Most of the primers were brush applied and the finishing coats were conventionally sprayed.

The striking results of this experiment were that the paint systems remained in excellent condition for over 20 years and that there was little to choose between them. This was attributed to three factors:

1. The total dry film thicknesses. A paint flake removed in 1951 varied between 270 and 415 microns, including 110-250 microns of primer.
2. The high standard of surface preparation.
3. The high quality of the paints used.

These trials also showed that a high level of protection could be achieved on a good surface using alternative pigments to red lead, in a synthetic medium, and opened the door for the eventual replacement of the oleo-resinous medium used in traditional red lead primers.

2.2.3 Composition specifications

When the railways were nationalised in 1948, the paint laboratory of the London, Midland & Scottish Railway became responsible for the issuing of composition specifications for the micaceous iron oxide paints to be supplied to the whole of the railway network (see Appendix 4). The objective was to replace the proprietary micaceous iron oxide paints with those purchased against specifications issued by the paint laboratory. In fact, it was to be several years before only specification micaceous iron oxide paints were to be used.

In 1953, British Railways Specification No. 35, covering "Materials for Use on Bridges, Buildings and Structures" was first issued and included composition specifications for micaceous iron oxide paints (see Appendix 5 for typical formulations). All paints were subjected to the standard accelerated corrosion tests of the day (such as SO₂/humidity, carbon arc/water spray, etc.) as well as being fully analysed for their pigment, resin and solvent components to ensure that the composition met the specification requirements.

Although the use of these specification paints spread, albeit sometimes reluctantly, through the railway network, there were still many who preferred to use proprietary micaceous iron oxide paints typified by Ferrodor.

2.2.4 Comparison of specification and proprietary micaceous iron oxide paints

At the request in December 1956 of the Chief Civil Engineer, British Transport Commission, an inspection of bridges painted with the proprietary Ferrodor micaceous iron oxide paints (supplied by Griffiths Bros & Co. Ltd)

and those purchased against Specification No. 35 was carried out on the London Midland Region. In order to obtain the most reliable information the inspections were confined to bridges painted in 1953, the year in which the specification became fully operative.

One hundred and ten bridges were inspected, ranging from London to Manchester and as far west as Bangor, and were selected as being typical of railway conditions generally. The general conclusions were that both Ferrodor and micaceous iron oxide paints supplied by approved manufacturers to the specification gave excellent protection even in a marine atmosphere. This comparability in performance was not surprising as both paint formulations were similar to that shown in Appendix 5, with pigment volume concentrations of about 45 per cent. The inspections revealed that the most important factor affecting the durability of both paint systems was the surface preparation. Where surface preparation had been correctly carried out, an additional durability of three to four years was obtained from the paint system compared with cases where cleaning had not been properly carried out.

The excellent and comparable corrosion protection given by both the Ferrodor and the specification micaceous iron oxide paints resulted in a gradual change to the use of the specification paints only. This *composition specification* continued in use until 1966, when it was replaced by a *performance specification*, No. 59, covering "Priming, Undercoating and Finishing Civil Engineering Paints for Protective Systems".

2.2.5 Performance specifications

Paint manufacturers were required to formulate paints to meet specified performance requirements and paint compositions were left to the manufacturers' discretion, except where indicated under individual items. Submitted paints were tested for both their liquid and dried film properties. The basic formulations used to meet the requirements of this new specification, not surprisingly, were based on the previously acceptable composition specification.

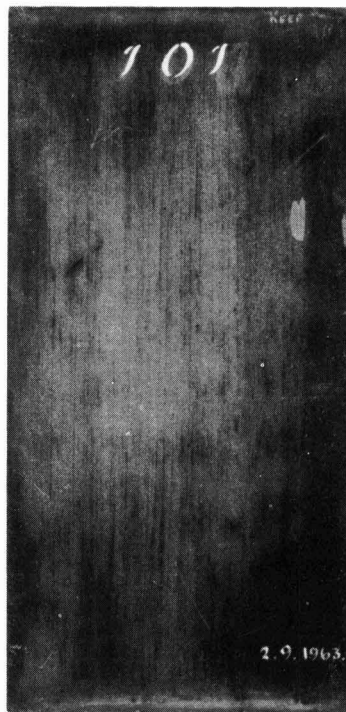
Until the early sixties micaceous iron oxide paints had been only brush applied, but the introduction of airless spray techniques for the painting of railway rolling stock led to the possibility of its use for large structures. The early problems of tip blockages due to coarse pigment particles were overcome¹ and, together with the development of Bentone as an antisagging agent for high build coatings, airless spray grade micaceous iron oxide paints were incorporated into a new performance specification, No. 70, covering "Paints for Civil Engineers". This was introduced in 1970 and is still the current specification. It differed from the previous performance specification in that there was more guidance on the pigments, resins and solvents to be used, and included additional accelerated test methods. A typical paint formulation to meet this specification is shown in Appendix 6.

2.3 Formulation variables from 1900-1981

The optimum coating performance regarding water permeability, corrosion protection, blistering, etc. is obtained when a paint is formulated at or near the critical pigment volume concentration³¹, which is defined as the pigment level in the dried film where there is just sufficient medium to fill the voids between the pigment particles. Above the critical pigment volume concentration there is not enough medium to fill the voids and there is a sharp decrease in corrosion protection, blistering, etc. and a sharp increase



Wire brushed rusty steel. One coat red lead primer to BR Specification 35 Item 8, one coat micaceous iron oxide undercoat to BR Specification 35 Item 61, one coat micaceous iron oxide finish to BR Specification 35 Item 62. Panel exposed in June 1960; all coats brush applied



Shot blasted mild steel. One coat red lead primer to BR Specification 35 Item 8, one coat micaceous iron oxide undercoat to BR Specification 35 Item 61, one coat micaceous iron oxide finish (silver grey) to BR Specification 35 Item 63. Panel exposed 2 September 1963; all coats brush applied. This system was used during the re-building of Euston Station

Figure 2. Long

in water permeability. The critical pigment volume concentrations are dependent on the nature of the pigment, its size (and size distribution) and shape, and this is reflected in the oil absorption of the pigment. Oil absorption is defined as the amount of oil necessary to produce a stiff paste with 100 grams of pigment; the lower the oil absorption the higher the critical pigment volume concentration³³. For micaceous iron oxide pigments (with oil absorption 18-19) the critical pigment volume concentration was found to be over 40 per cent in a tung oil phenolic or urethane oil medium but lower for other media examined. It is interesting to examine the pigment volume concentrations used in micaceous iron oxide paints over the last 80 years (see Table 2). The first Ferrodor paints had a pigment volume concentration of 30 per cent and remained substantially unchanged up to the forties, there being no differentiation between undercoats and finishes. These pigment levels are similar to those generally used in Holland and Germany, where concentrations of 25-35 per cent are used for micaceous iron oxide undercoats and 20-30 per cent for finishes³². There is some indication that in the forties the railway specification differentiated between the pigment volume concentrations for undercoats and finishes, namely 35 per cent and 30 per cent respectively. In a London Midland Region specification dated 15 November 1950 the pigment volume concentration was lower in the undercoat than in the finish, i.e. 28 per cent and 38 per cent respectively (see Appendix 4). Pigment levels were increased to about 45 per cent by the late fifties, there being no differentiation in the pigment levels

in undercoats and finishes (see Appendix 5), and have been maintained at this level up to the present time. The various pigment levels used in railway micaceous iron oxide paints have, however, been commensurate with the critical pigment volume concentrations of the lamellar pigment in the various types of media used over the years.

In general, micaceous iron oxide pigments are "diluted" with extenders, which can play an important part in paint performance depending on their physical and chemical properties, oil absorptions and how they pack with the lamellar pigments. The critical pigment volume in practice will depend on the quantity and quality of the extenders used, the medium, and the method of paint manufacture.

3. Factors affecting corrosion protection

The corrosion protection given by micaceous iron oxide paints over the 80 years, whether formulated to meet the railways composition or performance specifications, has in general been good (see Figure 2). The protective qualities of these paints have been attributed to the orientation of the very thin platelets or lamellae parallel to the paint surface. Cross-sectional analysis of outdoor exposure panels dating from the sixties and coated with micaceous iron oxide paints in various media, using various extenders, applied by different techniques, and manufactured by dispersion, ball milling, etc., have shown that the lamellar pigments have always orientated parallel to the paint surface. Samples of current paints were pre-



One coat red lead primer to BR Specification 35 Item 8, one coat micaceous iron oxide undercoat to BR Specification 35 Item 61, one coat micaceous iron oxide finish to BR Specification 35 Item 62. Panel exposed 1 January 1964; only primer was brush applied other coats were sprayed

One coat quick drying inhibitive pigment, one coat micaceous iron oxide undercoat to BR Specification 35 Item 61, one coat micaceous iron oxide finish to BR Specification 35 Item 62. Panel exposed 1 January 1964; only primer was brush applied other coats were sprayed

tests at Derby

pared for cross-sectional examination by spraying strippable lacquer onto a suitable substrate and applying the micaceous iron oxide paints onto the lacquer. The strippable lacquer (together with the paint) was peeled off the substrate, frozen in liquid nitrogen and fractured by bending. Using this technique, more realistic photographs were obtained than by the usual polishing technique. The photographs shown are representative of a large number examined.

that are a blend of lamellar/granular particles appear to be randomly distributed (as shown in Figures 4.5 and 4.6) with inferior corrosion protection to the pure lamellar pigments. There are further indications that the particle shape and size are important since the pigments with the lowest oil absorptions (and in theory the highest critical pigment volume concentrations) should have given good protection at higher pigment levels than those used in these tests³³. In fact, these pigments gave very poor corrosion protection,

3.1 Nature of pigments

The corrosion protection of currently available micaceous iron oxide pigments was evaluated by incorporation into a urethane oil modified alkyd. This coating was then subjected to an ammonium sulphate/sodium chloride salt spray test with wet and dry cycling, and outdoor exposure tests as single coat systems at dry film thicknesses of 50 microns. The results are summarised in Table 3 and typical panels are shown in Figure 3. These clearly show that the lamellar pigments from South Devon, France and Austria gave the best protection; cross-sectional analysis showed that the lamellar pigments were orientated parallel to the paint surfaces (see figures 4.1-4.3).

Granular pigments, with diameters and thicknesses up to 100 microns, could protrude through the surfaces of paint films of conventional dry film thicknesses and accelerate corrosion by capillary flow of water along the pigment surface to the substrate (see Figure 4.4). Pigments

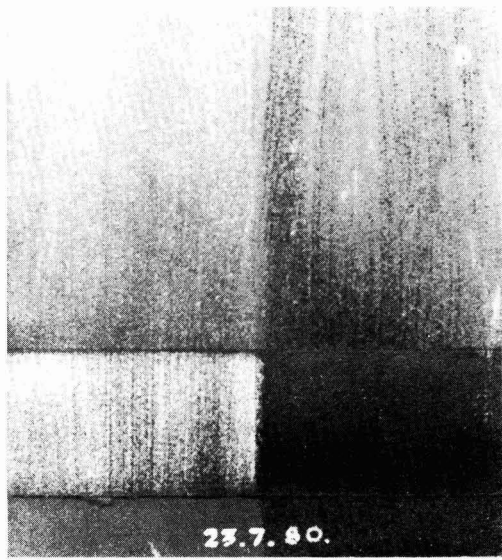
Table 3
Effect of ore on protection

Ore	Test		Corrosion protection		
	Particle shape	Oil absorption	20%	30%	40%
British	micaceous	18	good	good	good
Austrian	micaceous	19	good	good	good
Spanish	granular	16			poor
French	micaceous	19			good
S. Australian	micaceous	13			poor
Indian	micaceous	15			poor
S. African	granular	23			poor
W. Australian	granular	16			poor



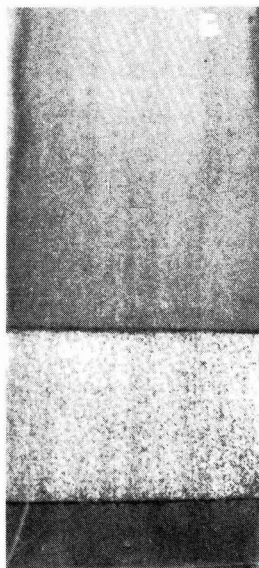
French

South African

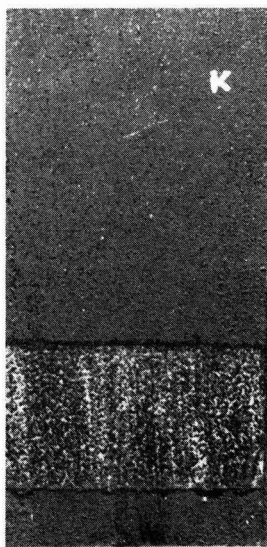


Spanish

Indian



British



Western Australian



Austrian

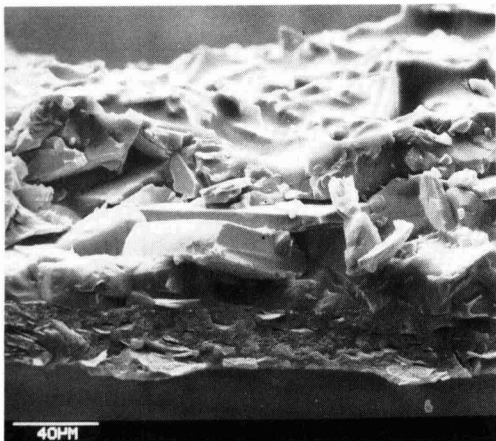
Figure 3. Effect of different micaceous iron oxide pigments on corrosion protection. Urethane oil/alkyd medium, PVC \approx 40%, dry film thickness \approx 50 microns. Panels grit blasted before painting and exposure at Derby

which could be attributed to their much smaller particle size since chemical analysis showed no significant corrosion accelerators in these pigments.

3.1.1 Effective levels of micaceous iron oxide pigments

Over the years outdoor exposures have shown that paints containing high proportions of micaceous iron oxide pigments on the total pigment level (80 per cent w/w or more) generally give good corrosion protection; these paints were formulated at pigment volume concentrations of

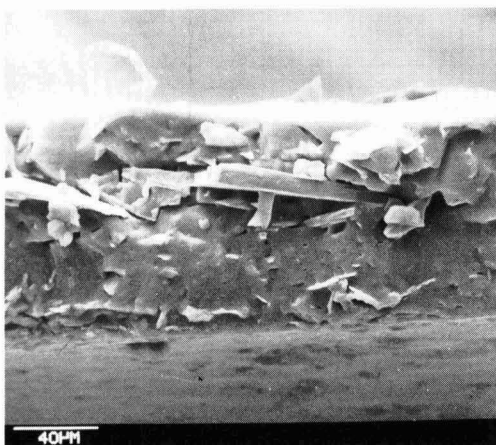
about 45 per cent. Eight year exposure tests in the mid-sixties showed that replacement of 50 per cent w/w of the micaceous iron oxide pigments by extenders (such as talc, barytes, etc.) resulted in a marked decrease in the level of corrosion protection when tested as single coats and applied over a coat of red lead primer to British Railways Specification 35 Item 13. Similar results were obtained after three years outdoor exposure with the "dilution" of micaceous iron oxide pigments with silica graphite; it was found that even 25 per cent w/w replacement resulted in a decrease in the corrosion protection.



4.1 Ferrubron GRA



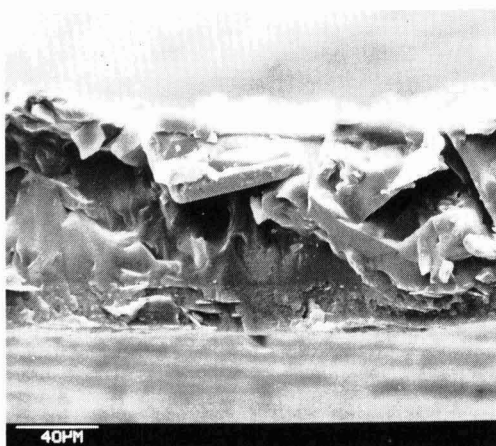
4.2 Austrian Standard grade



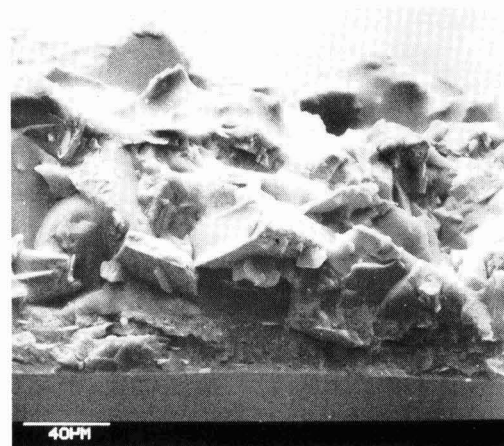
4.3 French



4.4 Spanish

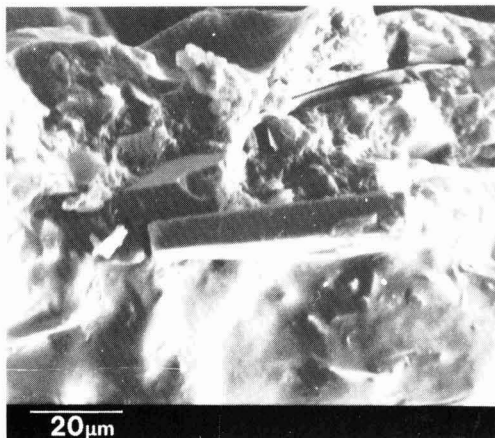


4.5 South African

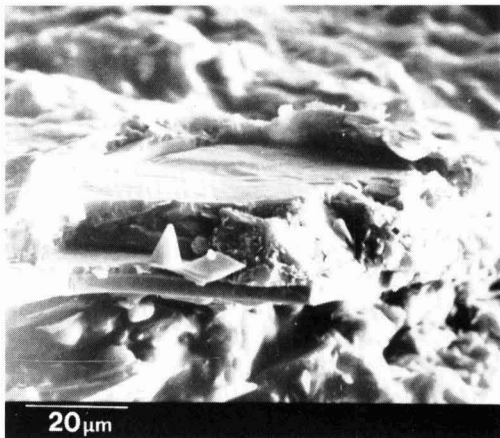


4.6 Indian

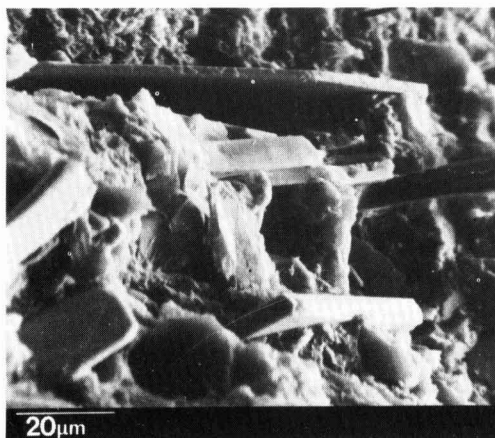
Figure 4. Effect of pigment type on orientation (magnification $\times 500$)



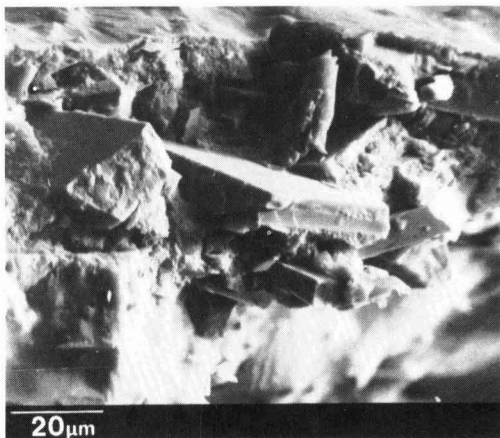
Tung oil modified phenolic



Urethane oil/alkyd



Two-pack polyurethane



Two-pack epoxy/polyamide

Figure 5. Effect of medium type on pigment orientation (magnification $\times 1,000$)

3.2 Media

In current formulations there is a tendency to use urethane oil/alkyds instead of the more expensive tung oil phenolics. By urethane oil modified alkyds it is meant those that contain high proportions of urethane oil (probably not less than 67 per cent w/w) in a physical blend with a suitable alkyd (or their equivalents in a chemical blend) since it is only at these levels that water permeation through the paint films is at a minimum³⁴. Over the years micaceous iron oxide paints, normally based on oxidising media, have given satisfactory protection to bridges and this has been confirmed by long term exposure tests carried out at Derby over various primers (see Figure 2); the best protection is given by the recommended painting schedule of a coat of primer and two coats of micaceous iron oxide paints. Chlorinated rubber-based paints have also been successfully used since 1936 when first used on the Ravensglass Viaduct. Outdoor exposure tests have also shown that two-component paints such as epoxies and polyurethanes can give very good corrosion protection.

In the variety of oxidising media used over the years, the lamellar pigments have always been found to pre-

ferentially orientate parallel to the paint surface (see Figure 5). Chemical curing in systems such as polyurethanes and epoxies with faster solvent evaporations, etc., do not appear to affect pigment orientation (see Figure 5).

3.3 Pigment volume concentration

It has already been stated that the corrosion protection given by a paint film is greatly influenced by its pigment volume concentration. The trend in railway specifications has been to formulate paints at pigment levels of about 45 per cent in either tung oil phenolic or urethane oil modified alkyd media. Corrosion tests have shown that the critical pigment volume concentration for lamellar micaceous iron oxide pigments was between 40 and 50 per cent in a urethane oil modified alkyd, as shown in Figure 6, using the Austrian Standard pigment; similar results were obtained for the English GRA grade pigment. This test also showed that below a pigment volume concentration of 20 per cent there was reduced corrosion protection. Corrosion tests in other oxidising media have shown that the critical pigment volume concentration varies according to the medium (see Table 4) and the correct pigmentation

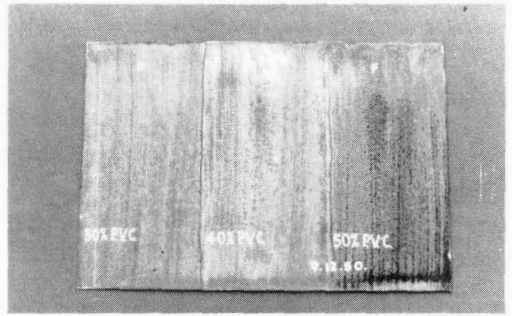
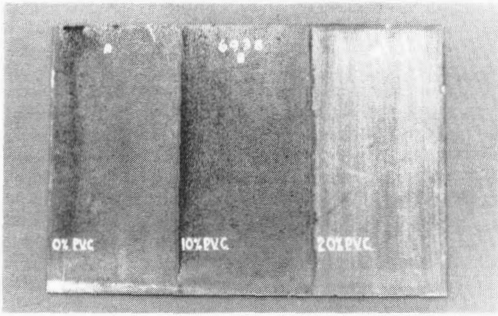
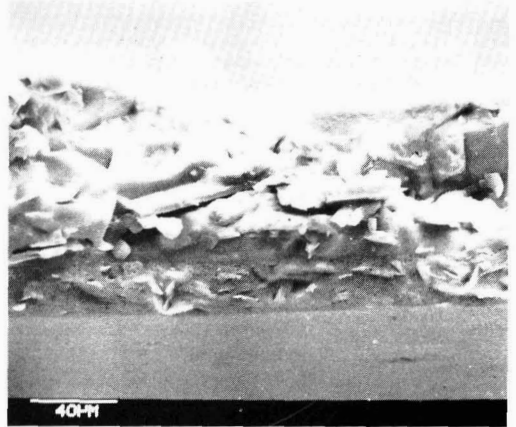


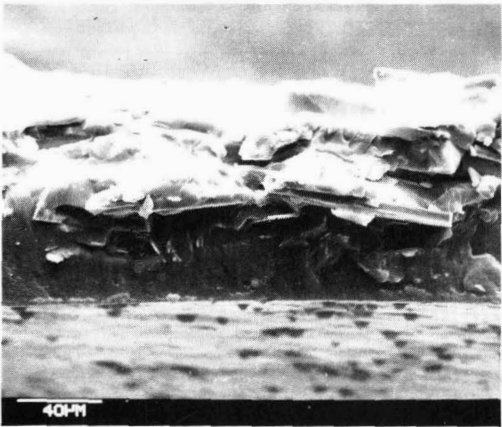
Figure 6. Effect of PVC on corrosion protection. Urethane oil/alkyd medium, dry film thickness \approx 50 microns; panels exposed at Derby



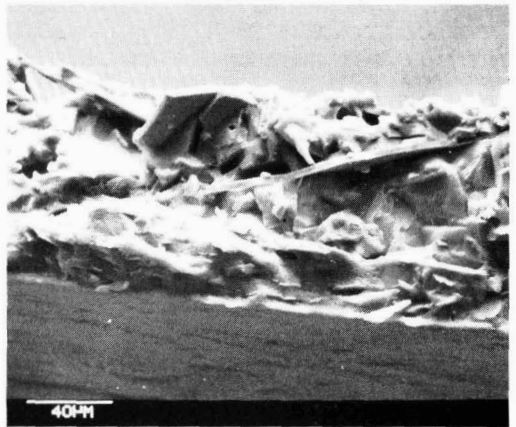
10% PVC



30% PVC



40% PVC



50% PVC

Figure 7. Effect of PVC on pigment orientation (magnification \times 500)

must be a matter for experimentation. This is in agreement with other published data which also found that the critical pigment volume concentration could, with various media, change following paint storage³¹.

The effect of pigment volume concentration on the orientation of lamellar pigments, shown in Figure 7, is that

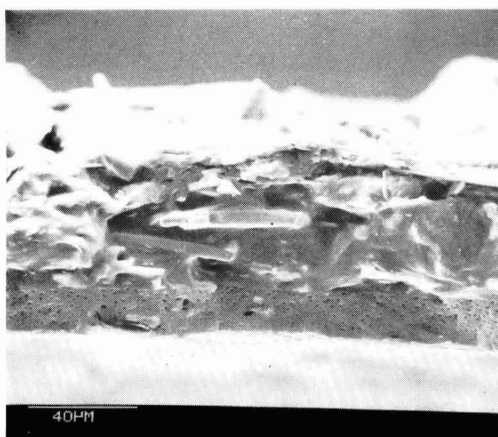
at levels of up to 50 per cent there is no apparent effect on pigment orientation. The only difference as the pigment volume concentration increases, other than the obvious increase in pigment density, is that the thickness of the clear layer on top of the pigment decreases (see Figure 7); above 40 per cent there was no apparent resin layer. This means that any extenders incorporated into micaceous iron oxide paints with high pigment levels will be

Table 4
Effect of medium on critical pigment volume concentration

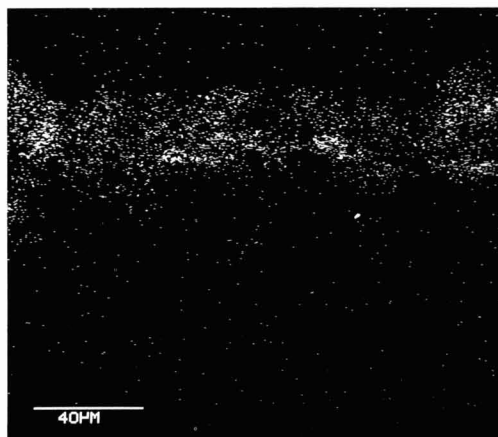
Medium*	Critical pigment volume concentration† (%)
Long oil alkyd (soya)	35
Medium oil alkyd (linseed)	35
Vinyl toluenated alkyd	35
Tung oil modified phenolic	40
Urethane oil	40

*The corrosion protection and critical pigment volume concentration will depend on the quality of the medium, i.e. the supplier and chemical compositions of the medium.

†Determined by natural weathering and/or accelerated corrosion tests. Dry film thickness \approx 50 microns.



Scanning electron micrograph



Aluminium X-ray distribution analysis of above micrograph

Figure 8. Surface layering of aluminium in micaceous iron oxide paints (magnification \times 500)

susceptible to atmospheric attack at the paint surface since there will be no protection from the medium. A classic example is the attack of aluminium tinted micaceous iron oxide paints at pigment levels of 40-45 per cent. The aluminium, being a light pigment, floats to the surface (see Figure 8) and since there is not enough medium to protect the pigment it is highly susceptible to sulphurous attack. Although only a surface defect, it produces an unacceptable aesthetic appearance. Decreasing the pigment level, together with suitable extenders and media (with reduced chalking), could give improved performance similar to that of the coloured micaceous iron oxide paints, at a pigment volume concentration of 30 per cent, as used in the thirties².

3.4 Extenders

Exploratory work has shown that the nature of the extender can greatly influence the corrosion protection given by micaceous iron oxide pigments. There are many extenders available differing in chemical composition, particle size and shape, and it would be impossible to evaluate them all. It is apparent that different supplies of some extenders can show significant differences in colour, which is probably indicative of their purity and/or particle sizes which are factors that can greatly affect the corrosion protection of the major pigment.

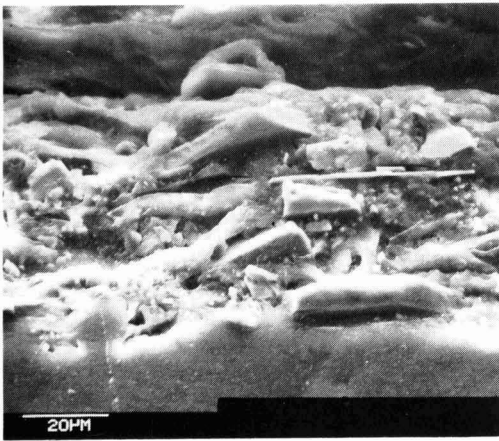
Typical extenders such as barytes, talc, titanium dioxide, mica, china clay, etc., have been used over the years in paints of varying pigment levels, the micaceous iron oxide levels normally being very high, and there appears to be no effect on the lamellar pigment orientation, as shown in Figure 9, or on the corrosion protection. Typical results with various extenders are shown in Table 5, the pigment levels being at 45 per cent and the medium used a urethane oil/alkyd. The zinc phosphate and talc pigments used in the tests had high oil absorption values compared with the micaceous iron oxide pigments and probably reduced the critical pigment volume concentration sufficiently to reduce the corrosion protection. The zinc phosphate particle size was comparable to the micaceous iron oxide pigments and did not give such "tight" packing as did the smaller barytes, titanium dioxide etc. These latter extenders have lower (or comparable) oil absorptions than micaceous iron oxide pigments, have much smaller particle sizes and can fill the voids between the lamellar pigments. This results in less oil demand and a higher critical pigment volume concentration with more free resin and greater corrosion protection than with extenders which do not readily pack²². Figure 10 shows the difference in packing with zinc phosphate and barytes. The micrographs and X-ray distribution analyses

Table 5
Effect of extender on corrosion protection

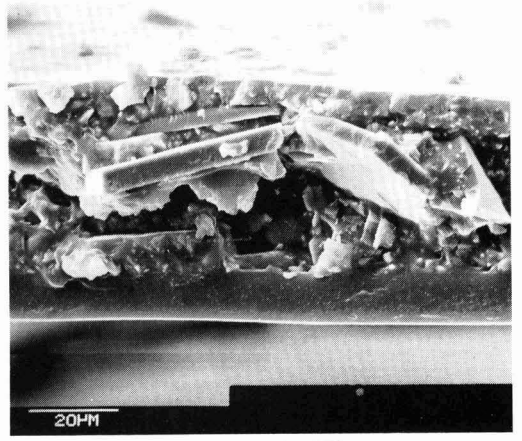
Extender*	Corrosion protection†
Talc	poor
Zinc phosphate	fair
Rutile titanium dioxide	good
Barytes	good
China clay	good

*The extenders used were randomly selected and it should not necessarily be taken as indicative of the performance of the whole "family", but rather that care must be taken in selecting the most suitable grades of extenders to optimise the corrosion protective properties of the lamellar pigments.

†Determined by natural weathering and accelerated corrosion tests. Dry film thicknesses \approx 50 microns using a urethane oil/alkyd media; PVC \approx 45%.



Paint applied in 1921



Paint applied in 1980s

Figure 9. Layering of micaceous iron oxide pigments in paints applied to railway bridges (magnification $\times 1,000$)



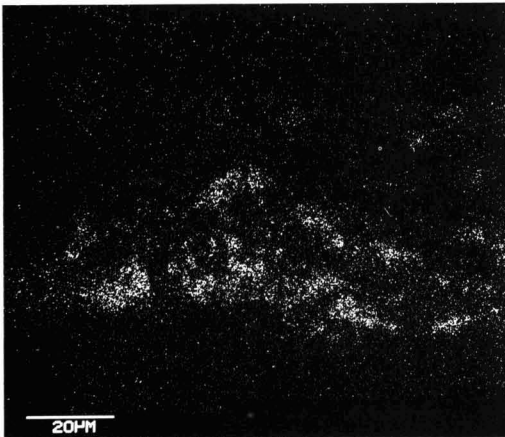
Scanning electron micrograph

Barytes

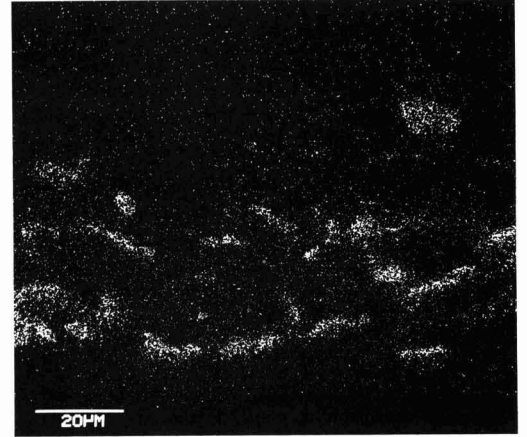


Zinc phosphate

Scanning electron micrograph



Barium X-ray distribution analysis of above micrograph



Zinc (of zinc phosphate) X-ray distribution analysis of above micrograph

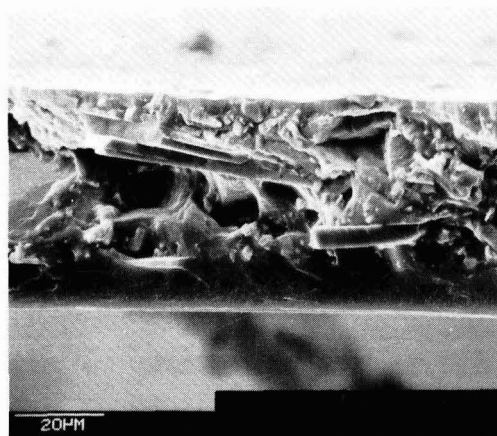
Figure 10. Packing of extenders in micaceous iron oxide paints (magnification $\times 1,000$)



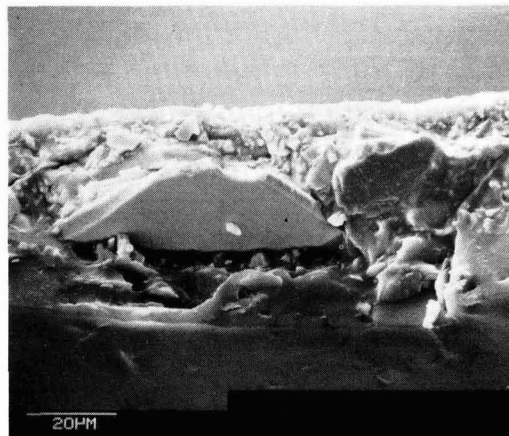
80:20 (w/w) micaceous iron oxide/barytes



75:25 (w/w) micaceous iron oxide/barytes



60:40 (w/w) micaceous iron oxide/barytes



50:50 (w/w) micaceous iron oxide/barytes

Figure 11. Effect of pigment/extender ratio on orientation (magnification $\times 1,000$), urethane oil/alkyd medium, PVC $\approx 45\%$

were carried out on a scanning electron microscope. It can be seen that the smaller barytes packs more readily between the larger micaceous iron oxide pigments than do the zinc phosphate pigments; alternative zinc phosphate pigments are available differing in particle size, shape and chemical composition, which could improve the packing and corrosion protection³⁶.

Diluting the micaceous iron oxide pigments with extenders appears to have no effect on the lamellar orientation down to levels of 60:40, micaceous iron oxide/extender, as shown in Figure 11 for barytes, the pigment volume concentration being 45 per cent. At 50:50 there appears to be some disorientation and this has been observed with other extenders. Short term corrosion tests have shown that there is no decrease in the corrosion protection down to 50 per cent w/w but that diluting the micaceous iron oxide significantly, causes increases in the level of chalking.

In practice, several different types of extender will be incorporated into a paint and the performance will depend on the types used, their oil absorptions, particle sizes, proportions, as well as the method of paint manufacture.

3.5 Water permeability

Typical water permeability curves, obtained by the Payne Cup method³⁵, are shown in figures 12 and 13 and agree with other published data on micaceous iron oxide paints⁴. The water permeability will depend on paint formulation (types of resin, oil lengths, driers and their proportions, method of manufacture, etc.) as well as on the drying conditions (and hence the retained solvents) and film thicknesses. All resins used in these tests utilised the driers (and their levels) recommended by the resin manufacturers; all paint films were aged one month in the laboratory before water permeability tests were started. It can be seen that minimum water permeability was obtained at pigment levels between 10-15 per cent, there being a slight decrease compared to the clear medium; at pigment levels above 25-30 per cent there was a very rapid increase in water permeability. At the current pigment levels of about 45 per cent the water permeability (in a urethane oil modified alkyd) was about $20 \times 10^{-4} \text{ g cm}^{-2} \text{ h}^{-1}$, whereas at the 30 per cent levels it was about $4 \times 10^{-4} \text{ g cm}^{-2} \text{ h}^{-1}$. The similar chemical and physical properties of the English and Austrian pigments¹ were reflected in their similar permeability curves. Water per-

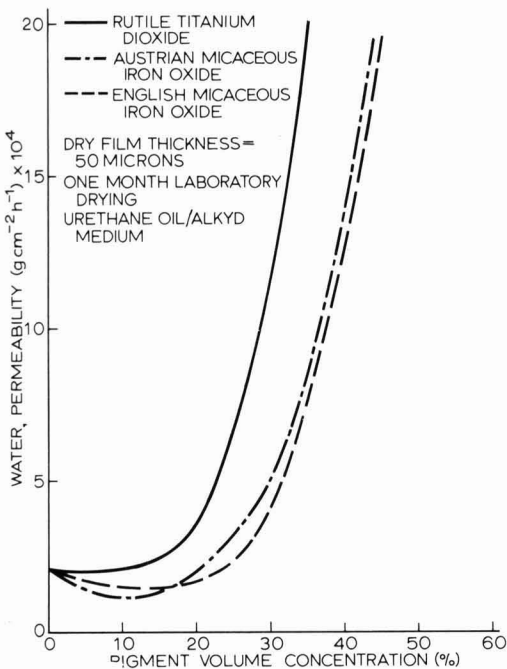


Figure 12. Effect of pigment type on water permeability

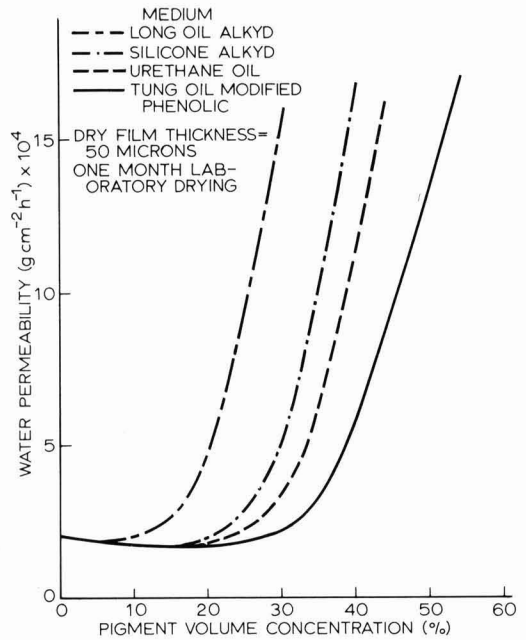
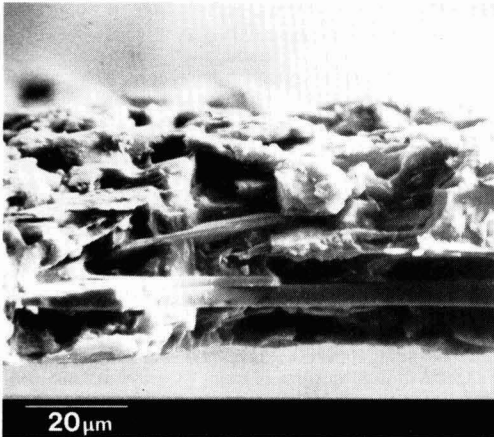
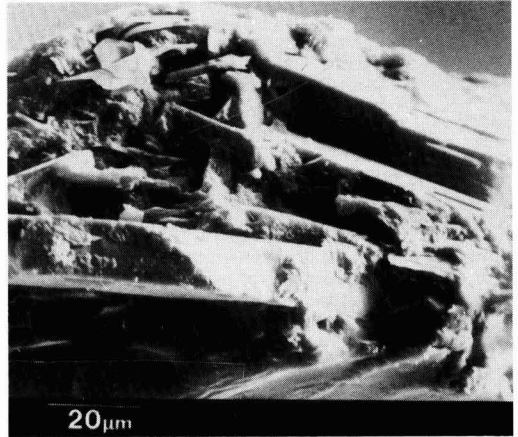


Figure 13. Effect of medium type on water permeability



Brush



Airless spray

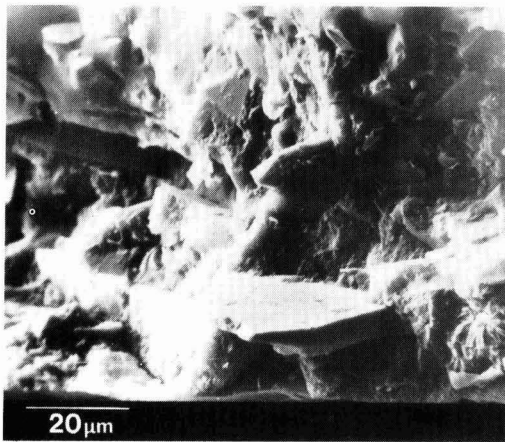
Figure 14. Effect of method of paint application on pigment orientation (magnification $\times 1,000$)

meability curves of various media pigmented with the Austrian Standard micaceous iron oxide pigment are shown in Figure 13, and the pigment level above which there was a rapid increase in water permeability was different for each medium. For the long oil alkyd the critical pigment level was about 10 per cent, and about 25 per cent for the tung oil phenolic; for the remaining media examined the critical level was about 15 per cent. The pigment volume concentrations at which the water permeabilities were at a minimum were much lower than the critical pigment volume concentrations determined by the corrosion tests, and there are doubts as to whether permeability data obtained from the free paint films are representative of supported films⁴². In order to obtain satisfactory application properties, film build, etc.,

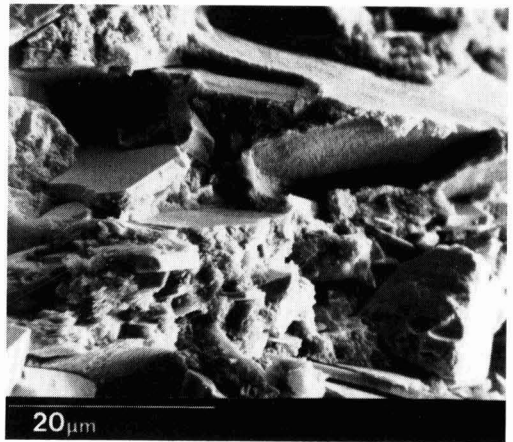
micaceous iron oxide paints have been formulated around 40-45 per cent in tung oil phenolic or urethane oil/alkyd media⁴³.

3.6 Method of paint application

Up to the mid-sixties these paints were brush applied, but after this date airless spraying was introduced to the railways as an alternative method of paint application. The method of application had no apparent effect on the corrosion protection, providing the specified dry film thicknesses were obtained, nor on the pigment orientation (see Figure 14). In general, thicker wet coatings are applied by airless spraying than by brushing, but no



Applied wet film thickness \approx 100 microns



Applied wet film thickness \approx 200 microns

Figure 15. Effect of paint film thickness on pigment orientation (magnification \times 1,000)

difference has been observed in pigment orientation when micaceous iron oxide paints are applied at different film thicknesses (see Figure 15).

4. Weathering

It has been claimed that the layering of lamellar micaceous iron oxide pigments in paint films reduces the ultraviolet attack on the film, thus increasing its durability^{2,4,6,12}. Comparison of the effects of weathering on the surface topography of paints formulated with different micaceous iron oxide pigments tends to substantiate this claim (see Figure 16). There is little apparent erosion of the surface of the lamellar micaceous iron oxide paint, but the surfaces of paints based on the Indian and Spanish pigments have been considerably roughened (due to chalking) and this is probably due to the combined efforts of stress cycling (due to surface temperature variations and water movement through the film) and ultraviolet attack. Craters were formed on the surface of paints based on granular pigments because erosion of the medium exposed the pigments which were only loosely bound to the weathered paint surface. Further, weathering would result in these pigments being removed from the paint surface with a substantial decrease in dry film thickness (because the granular pigments have diameters of up to 100 microns) and hence a reduction in the corrosion protection. The Indian pigment, which contained "fines" and only a small amount of lamellar structure, also produced craters on the paint surface. The lamellae of the Austrian pigment have layered on the paint surface and the surface topography has changed little on weathering; any loss of pigment would result in only a few microns reduction in film thickness.

Attempts were made to measure the rates of oxidation/changes in the thermal properties of paint films on weathering by extensibility tests on attached films and differential scanning calorimetry.

4.1 Extensibility tests^{37,38}

The paint films were applied to chromated soft aluminium substrates, which eliminated the difficulties of preparing detached films as well as being considered to give a realistic test. Extensibilities at which the paint films first

exhibited any cracking were measured by direct tensile tests and were found to decrease as paint films oxidise/crosslink on weathering. Results for titanium dioxide and micaceous iron oxide pigmented paints are shown in Figure 17 and indicate that paints based on the lamellar pigments have a reduced rate of change.

4.2 Differential scanning calorimetry³⁹

This is a technique for studying the thermal behaviour of materials as they undergo physical and chemical changes during heating or cooling. A typical thermogram obtained for a micaceous iron oxide paint is shown in Figure 18 from which the glass transition temperature of the paint sample can be determined. The weathering of paint films can be followed by measuring the change in glass transition temperature as the paint film oxidises, as shown in Figure 19 for micaceous iron oxide paints of different pigment volume concentrations. It can be seen that increasing the pigment volume concentration by up to 20 per cent has a profound effect in reducing the rates of change; increasing the pigment volume concentration above this level appears to have little effect on the rates of change. A typical decorative paint (pigment volume concentration 40 per cent) has a glass transition temperature of over 20°C after a similar period of accelerated weathering.

5. Conclusions

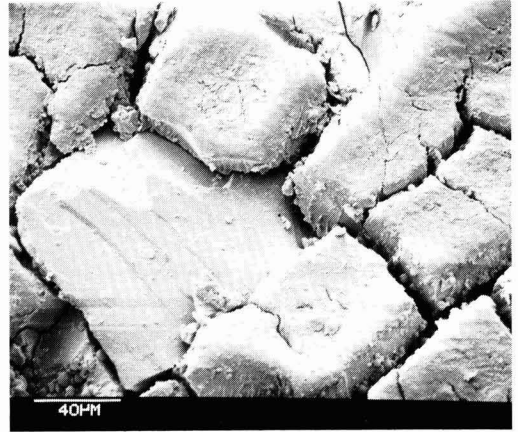
This work has clearly shown that commercially available pigment samples afford greatly differing levels of corrosion protection to steel structures:

- (i) Paints based on lamellar pigments gave the best corrosion protection.
- (ii) Paints based on granular and/or fine pigments gave inferior corrosion protection and cannot be considered comparable to the accepted standards.

It has also been shown that the lamellar pigments preferentially orientate parallel to the paint surface in a wide variety of media, and pigments showing this characteristic have good corrosion protection and weathering properties.

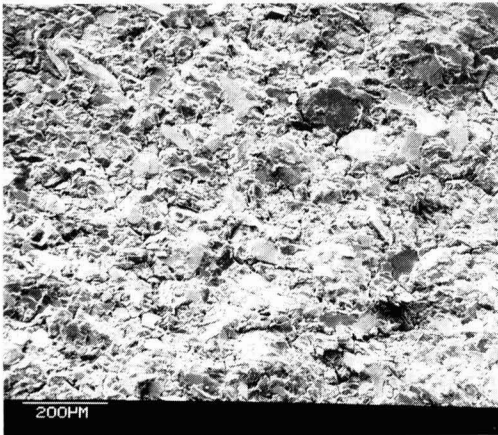


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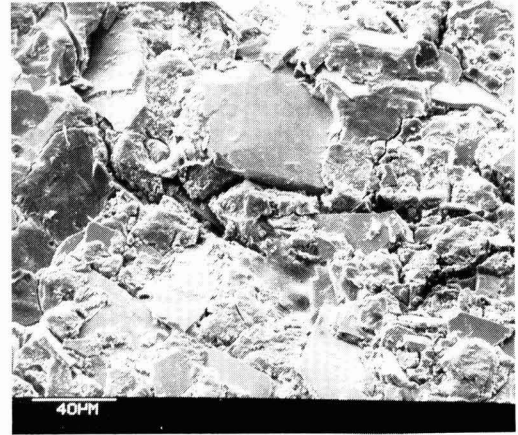


magnification $\times 500$

Spanish pigment

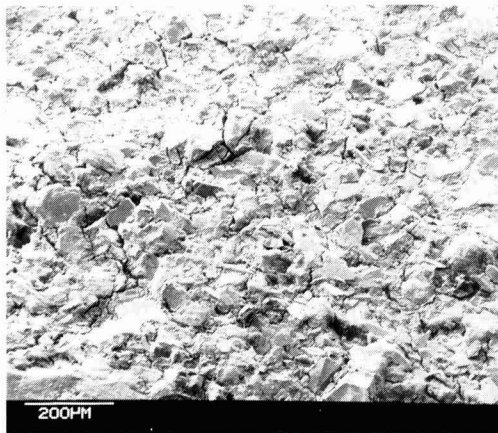


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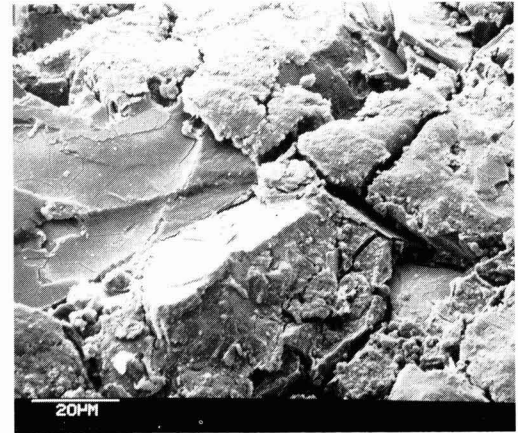


magnification $\times 500$

Austrian pigment



magnification $\times 100$



magnification $\times 500$

Indian pigment

Figure 16. Effect of different micaceous iron oxide pigments on the surface topography of weathered paint films (two years outdoor exposure)

Good protection and weather resistance have been achieved in the past with pigment volumes around 40 per cent, with the micaceous iron oxide level around 80 per cent w/w on the total pigment using barytes, titanium dioxide, mica and talc etc as extenders.

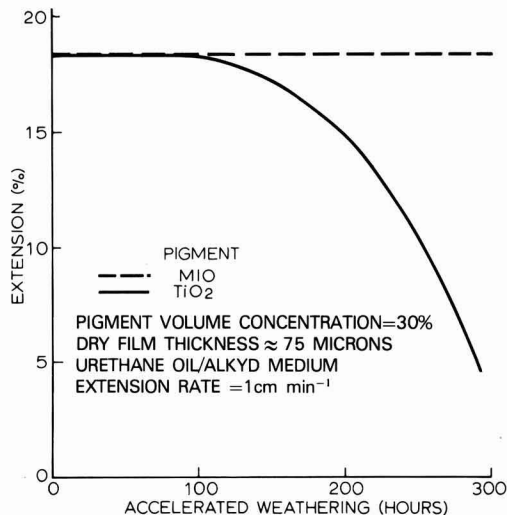


Figure 17. Effect of pigment type on weathering

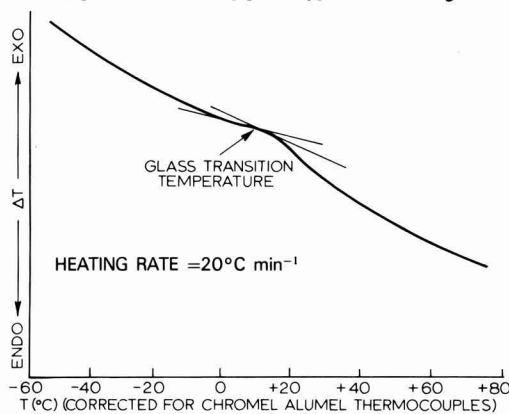


Figure 18. A differential scanning calorimetry thermogram of an MIO in urethane oil/alkyd medium film, unweathered (20% PVC)

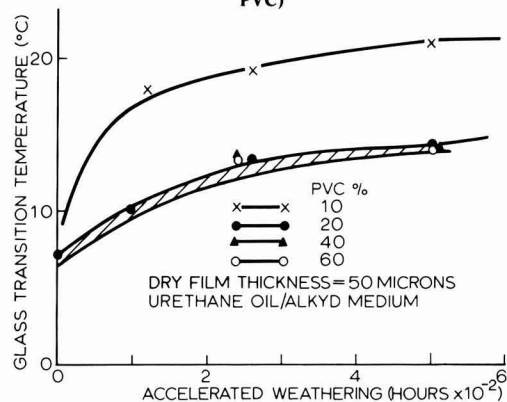


Figure 19. Effect of PVC on weathering

However, some of the evidence presented suggests that equally good or possibly better results could be obtained by reducing both the level of micaceous iron oxide in the pigment and the pigment volume concentration. Careful choice of the medium and extender, to minimise effects of chalking in particular, and possibly method of manufacture would be necessary in this case.

6. Acknowledgments

The authors would like to thank the raw material and paint industries for the information and assistance that was readily given, and their analytical colleagues at the Railway Technical Centre, J. Jarvis and D. A. Williams, for their scanning electron microscope expertise. The authors acknowledge the permission of the Director of Research, British Railways Board, to publish this paper.

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Alkyd/linseed oil formulation

Micaceous Iron Oxide	75 grams
Aluminium powder	5
Basic carbonate white lead	20
Paralac 15	25
Stand oil	10
White spirit	9.5
Drier	9.5

Pigment volume concentration \approx 35%.

Appendix 1. Early railway bridge painting specification

Extracted from *Engineering*, 28 February 1890, and gives details of the original paint process used on the Forth Bridge.

"All plates, bars, angles and other parts belonging to the superstructure, received as they had passed through the shops or yards a thorough scraping with steel scrapers and steel wire brushes, and afterwards a coat of boiled linseed oil applied as hot as possible. As soon after erection upon the structure as could conveniently be done, and in many cases also before they were put up, they received a coat of red lead paint, and subsequently a second coat of red lead. The paint finally decided upon for the bridge is an oxide of iron paint, of which two coats are applied over the two coats of red lead already laid. The first is called a priming coat of dark chocolate brown; the last is a finishing coat of a bright Indian or Persian red, which, however, darkens considerably in a short time.

The above are for outside painting only, the inside of the tubular members receiving one coat of red lead and two coats of white lead. It is calculated that inside and out, the amount of surface to be painted is equal to 145 acres."

Appendix 2

Analysis of Ferrodor Micaceous Iron Oxide Paint carried out in the Paint Laboratory of Derby Carriage & Wagon Works, dated 18 October 1928.

DS/9966 LZ/403	Ferrodor Paint	18.10.28
Works Superintendent, Derby		
Oil	30.5% w/w	
Volatile Thinners	6.1%	
Pigment	63.4%	
Fineness	App: 9%	retained by the 200 1 mm standard screen

Volatile thinners appear to be app: 20% genuine turps, and 80% White Spirit.

Pigment consists of 81.9% Oxide of Iron, and the remainder a low grade Graphite containing a fair proportion of Mica. From the analysis of this paint one would not expect it to wear any better than the Red Oxide now used in the Dept. Practical tests show this material goes on rather badly when applied, being deficient in body, which would appear to necessitate additional coats to afford the same degree of protection as other paints(1).

Note

Calculated pigment volume concentration = 30%.

Appendix 3

Approved Micaceous Iron Oxide Paint Formulation
Ex. Paint Laboratory,
London Midland & Scottish Railway, 1945.

1983(3)

Appendix 4

London Midland Railway Specification For Micaceous Iron Oxide Finishing and Undercoating Paints. 15th November 1950.

Item 1. Undercoat (Brush)

Micaceous Iron Oxide	42.5% w/w
Aluminium Powder	6.0
Zinc Oxide	1.5
Medium (1)	30
White Spirit	20

Pigment volume concentration \approx 28%

(1) Treated vegetable oils, resins and driers.

Item 2. Finishing Paint (Brush)

Micaceous Iron Oxide (2)	60% w/w
Aluminium Powder (2)	2.5
Medium (1)	22.5
White Spirit	15%

Pigment volume concentration \approx 38%

- (1) Treated vegetable oils, resins, and driers.
- (2) To assist in the suspension of the micaceous iron oxide, aluminium stearate and/or China Clay may be incorporated into the paint, provided the former does not exceed 1%, and the latter 10% of the paint. The total pigment content was to be between 60-65% w/w including suspending agents.

Appendix 5

Extract from British Railways Paint Specification No. 35 covering "Materials For Use On Bridges, Buildings and Structures", November 1958.

Item 61. Undercoating Micaceous Iron Ore Paint (1)

Micaceous Iron Ore	55-60 lbs.
China Clay, Grade 1, to B.S. 1795	3 lbs.
Leafing Aluminium Paste, to B.S. 388 (Part 2).	0.5 lbs.
Boiled Linseed Oil to B.S. 259	6 lbs.
Stand Oil (15 poise)	8-10 lbs.
Medium Oil Length Varnish	4- 6 lbs.
White Spirit to B.S. 245	4-10 lbs.
Liquid Driers	5- 7 lbs.

Pigment Volume Concentration \approx 45%

Item 62. Finishing Micaceous Iron Ore Paint (Natural) (1)

Micaceous Iron Ore	60-65 lbs.
Leafing Aluminium Paste, to B.S. 388 (Part 2)	2.5 lbs.
Boiled Linseed Oil to B.S. 259	6 lbs.
Stand Oil	8-10 lbs.
Medium Oil Length Varnish	4- 6 lbs.
White Spirit to B.S. 245	2- 3 lbs.
Liquid Driers	5- 7 lbs.
Aluminium Stearate	0.5 lbs.

Pigment Volume Concentration \approx 47%

- (1) Surface active suspending agents may also be incorporated but must not exceed 0.5% by weight of the total pigment.

85

Appendix 6. Suggested present-day paint formulation⁴⁰

Micaceous Iron Oxide	50 (parts by weight)
Extender*	6
Antisettling agent†	1
Air drying medium (solids)‡	18
Mineral spirits	24
Driers and antiskinning agents	1
	<hr/>
	100

Volume solids = 50%

Pigment volume concentration = 40%

*Many extenders are available (e.g. barytes, talc, asbestine, mica, china clay etc.) differing in chemical composition, particle size and shape. Water-soluble salts must be kept to a minimum.

†Such as montmorillonite clay-like mineral or hydrogenated castor oil.

‡Air drying media such as:

- Tung oil modified phenolic resin or tung oil/linseed modified phenolic resin. 60-70 per cent oil length.
- Modified alkyds (i.e. urethane oil or vinyl modified).
- Alkyds. 20-25 per cent phthalic anhydride 55-65 oil length.

Copolymerisation of polyunsaturated fatty vinyl monomers with styrene

B. S. Sitaramam, P. C. Chatterjee and M. A. Sivasamban

Regional Research Laboratory, Hyderabad-500 009, India

Summary

Vinyl esters of mixed fatty acids, and acrylic and methacrylic esters of mixed fatty alcohols derived from safflower and linseed oils were bulk copolymerised with styrene using benzoyl peroxide as the initiator. Some of the copolymers exhibited excellent coating characteristics. They gave hard, glossy films with excellent flexibility, good impact resistance and very good water, acid, alkali and solvent resistance.

Introduction

The results of investigations into the emulsion polymerisation of polyunsaturated fatty vinyl monomers have been reported in earlier communications^{1,2}. The oligomers obtained had very good characteristics as coatings but yields of the oligomers were rather low (ca. 65-70 per cent). The solution copolymerisation of linseed and safflower acrylates and methacrylates with vinyl acetate has also been studied³. Here too the copolymers were obtained in low yields and failed to give hard films even on baking. The present paper reports the results of studies on the bulk copolymerisation of some polyunsaturated fatty vinyl monomers with styrene. When copolymerised in appropriate molar ratios, the acrylic and methacrylic esters yielded copolymers, almost in quantitative yields, that gave hard glossy films with excellent flexibility, good impact resistance and very good water, acid, alkali and solvent resistance.

Experimental

Materials

Vinyl esters of mixed fatty acids of linseed and safflower oils were prepared by refluxing one mole of the acid with six moles of stabilised vinyl acetate monomer for three hours in the presence of the catalysts mercuric acetate and 40 per cent hydrofluoric acid⁴.

Acrylic and methacrylic esters of the mixed fatty alcohols derived from linseed and safflower oils were prepared by Rehberg's procedure⁵. This involved alcoholysis of methyl acrylate or methyl methacrylate in

the presence of an acid catalyst such as naphthalene-2-sulphonic acid and a polymerisation inhibitor such as hydroquinone.

Each monomer was purified by one or two distillations under reduced pressure (0.01–0.1 mm Hg) over 0.1 per cent copper rosinate. The distillate was pure enough (≈ 99 per cent) to respond satisfactorily to the polymerisation technique adopted in the study. The monomers were characterised by IR (Perkin Elmer Model 221) and NMR (Varian 60 MC) spectroscopies, and their purity was checked by chromatographic techniques.

Styrene was distilled at reduced pressure in an atmosphere of nitrogen. The vinyl monomers as well as the styrene were stored in a refrigerator.

Dibenzoyl peroxide (May and Baker) contained about 12 to 13 per cent moisture by weight. The material was purified by dissolving it in chloroform at room temperature and adding twice its volume of methyl alcohol⁶. On storing in a refrigerator overnight, pure benzoyl peroxide separated out as transparent needles which were filtered, dried and stored in a cool dark place.

Polymerisation and film properties

All polymerisation reactions were carried out in bulk. Monomers in appropriate molar ratios and the requisite amount of initiator (0.5 per cent on the weight of monomer) were weighed into a tube (having a constriction near its open end so as to enable rapid sealing of the tube) which was purged thoroughly with nitrogen. Pure nitrogen was gently introduced into the tube to provide a blanket and the tube was sealed at the constriction. The sealed tube was placed for the required period in a water bath maintained at $70 \pm 0.1^\circ\text{C}$. The course of the reaction was followed by taking the tube out at regular intervals and visually observing the change in viscosity of its contents. Towards the end of the reaction period the contents of the tube attained a high viscosity, approximately greater than that Z-6 on Gardner's scale.

At the end of the reaction period the tube was cooled to room temperature, neatly cut and opened slightly below

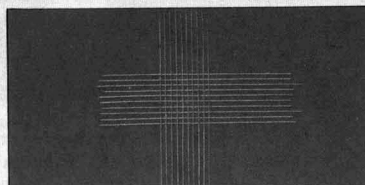
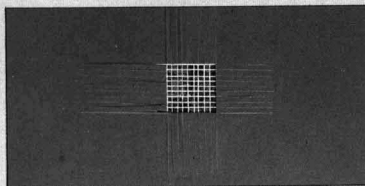
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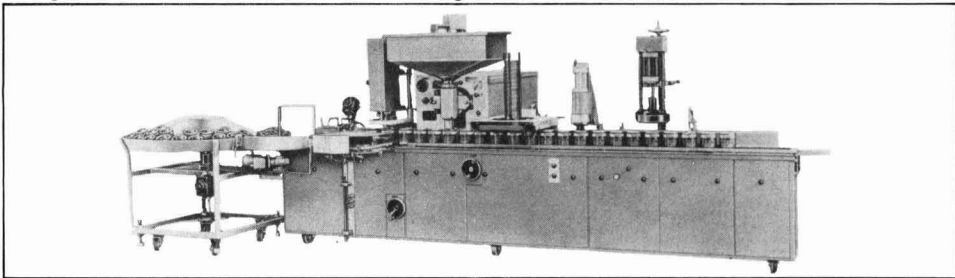
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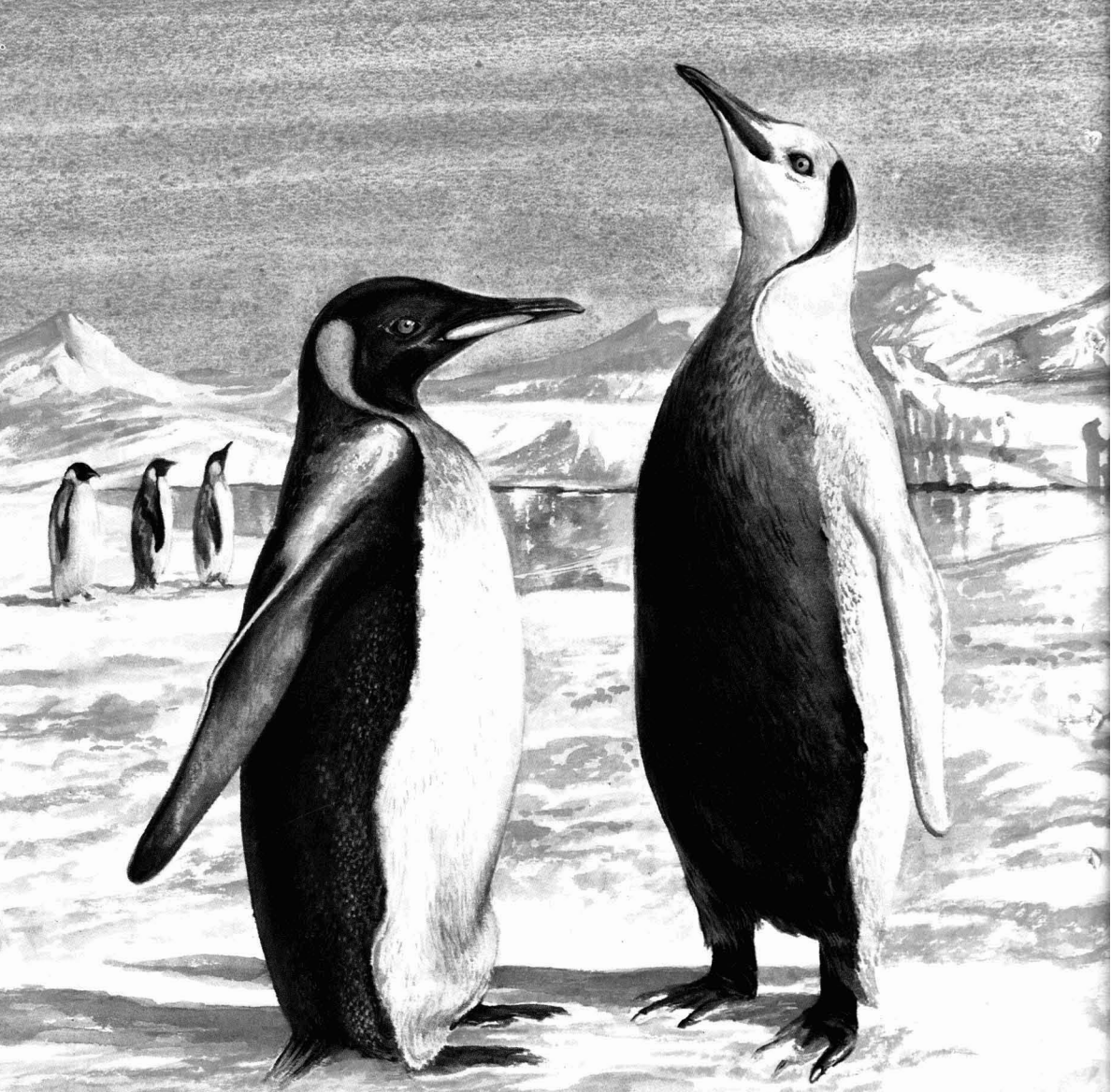
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Table 1
Copolymerisation of polyunsaturated fatty vinyl monomers (M_1) with styrene (M_2)

M_1	$M_1:M_2^*$ (molar ratio)	Reaction time†(h)	Viscosity of the reaction product‡	Conversion (%)	Film properties																							
					Scratch hardness (g)	Other properties																						
SA	1:2	36-38	W - Y (50% solution in xylene)	85 - 95	1,800 - 2,000	Films were clear and had good gloss. They passed: (a) 1/8 inch conical mandrel bend test, (b) cross-cut adhesion test, and (c) impact resistance test (DEF 1053 (17a). Further, the films were not affected by water, 5% sulphuric acid (w/v), 5% NaOH solution, xylene, <i>n</i> -butanol or white spirit for 72 hours. However, they failed in chloroform within 1 - 2 minutes.																						
	1:3	32-34																										
	1:4	27-29																										
SM	1:2	25-26					U - V (undiluted)	30 - 55	2,200 - 2,400	Films were hazy, tacky and brittle. Further tests were not necessary.																		
	1:3	23-24																										
	1:4	20-21																										
LA	1:2	29-30									reaction stopped after 96 hours	30 - 55	2,000 - 2,200	Films were hazy, tacky and brittle. Further tests were not necessary.														
	1:3	27-28																										
	1:4	26-28																										
LM	1:2	24-26													reaction stopped after 96 hours	30 - 55	2,300 - 2,500	Films were hazy, tacky and brittle. Further tests were not necessary.										
	1:3	22-24																										
	1:4	19-21																										
SVE	1:2 1:3 1:4	reaction stopped after 96 hours	U - V (undiluted)	30 - 55	2,300 - 2,500	Films were hazy, tacky and brittle. Further tests were not necessary.																						
LVE	1:2																		reaction stopped after 96 hours	U - V (undiluted)	30 - 55	2,300 - 2,500	Films were hazy, tacky and brittle. Further tests were not necessary.					
	1:3																							reaction stopped after 96 hours	U - V (undiluted)	30 - 55	2,300 - 2,500	Films were hazy, tacky and brittle. Further tests were not necessary.
	1:4						reaction stopped after 96 hours	U - V (undiluted)	30 - 55	2,300 - 2,500																		

SA = safflower acrylate, SM = safflower methacrylate, LA = linseed acrylate, LM = linseed methacrylate, SVE = safflower vinyl esters and LVE = linseed vinyl esters

*Larger proportions of styrene produced copolymers that gave hazy, brittle films with poor properties. Larger proportions of vinyl monomer(s) led to longer reaction times and gave tacky copolymers with poor film properties. †Reaction times can be considerably reduced by using greater amounts of initiator, but it becomes difficult to control gelation. ‡Measured in Gardner Bubble Viscometer at 30°C.

the constriction (so that the polymer could be dissolved in benzene, which was usually necessary to facilitate flow) and the contents poured into a large excess of methanol under constant stirring with a glass rod. The precipitated copolymer was transferred into a weighed flask, freed from solvent under vacuum and weighed. Conversion efficiencies were calculated from the weight of the precipitated polymer. The methanol was distilled and re-used.

Each copolymer was dissolved in an appropriate mixture of xylene and butyl acetate until the desired viscosity was attained. The solids content of various copolymer solutions ranged from 40-55 per cent. The driers added were 0.03 per cent cobalt and 0.3 per cent lead, as naphthenates, on the weight of the copolymer.

Films were cast on mild steel panels (150 mm × 100 mm × 0.9 mm) and on tinned mild steel panels (150 mm × 50 mm × 0.315 mm). In each case the panels were lightly abraded with a fine emery paper and swabbed with xylene before applying the films. The panels were baked at 120°C for one hour. The films, of dry film thickness 1-2 mil. (1 mil. = 1 inch × 10⁻³), were tested for their properties 48 hours later.

Results and discussion

While the vinyl esters could not be successfully copolymerised with styrene, the copolymers of the acrylic and methacrylic esters with styrene gave clear, glossy films having excellent flexibility and adhesion on metal substrates. The coated panels remained unaffected when subjected to: (a) 1/8 inch conical mandrel bend test, (b) impact resistance test (10.5 lb, 25 inches fall), and (c) cross-cut adhesion test using adhesive tape to pull off film from the squares. The films also exhibited excellent

scratch hardness (IS-101(1961)). In general the methacrylates gave harder films than the corresponding acrylates. The films remained unaffected in water, 5 per cent sulphuric acid (w/v), 5 per cent sodium hydroxide solution, white spirit, xylene and *n*-butanol. However, they failed in chloroform within 1-2 minutes. Salient features of the copolymerisation reactions and the important film characteristics of various copolymers are given in Table 1.

Conclusion

The present study has indicated that useful coating compositions can be developed by copolymerising polyunsaturated fatty acrylates and methacrylates with styrene. It is, in fact, more appropriate to state that styrene can be internally plasticised by acrylic and methacrylic esters of fatty alcohols to obtain such properties as are desired in good coating compositions. The process is simple and economical as styrene is one of the low cost coating ingredients, also the copolymers have excellent coating characteristics. These two facts indicate that these compositions have good potential for industrial exploitation.

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Structural changes in polymer films. Part 2: the effect of the pigment zinc oxide on the electrolytic resistance and transition temperature; some comparisons with the pigments iron oxide and red lead*

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Summary

An examination has been made of the effect of zinc oxide on the transition temperatures of films cast from three vehicles: a pentaerythritol alkyd, a phenol-formaldehyde tung oil and an epoxy polyamide.

It was found that, in the range 0–50°C, only in some cases was the transition temperature affected and then it rose less than 5°C.

The changes in ionic resistance were also measured and found to be almost unaffected by pigmentation at 25°C.

However, pigmentation was found to affect the ionic permeability of the films, thus the percentage of permeable D areas increased upon pigmentation and there was some evidence that the value fell slightly before rising to 100 per cent as the CPVC (critical pigment volume concentration) was approached.

The effect of temperature on the ionic resistance was also examined.

Finally the results are discussed and shown to be similar to those obtained with iron oxide and red lead.

Introduction

In a previous paper¹ it was shown that in the case of clear varnish films transition temperatures occurred in the temperature range 0–50°C. The values of these transition temperatures could be determined most accurately by dilatometry but they could also be followed by monitoring the I type resistance and water uptake as a function of temperature. An investigation has now been made of the effect of the pigment zinc oxide on the transition temperature. Movement of transition temperatures with pigmentation can be used as a method of investigating polymer-pigment interaction, an advantage of the method being that the dried film is studied.

An important factor from the point of view of protection is the electrolytic resistance of the film, and the effect of zinc oxide on this parameter was investigated. The results have been compared with those obtained earlier with iron oxide and more recently with red lead.

Experimental

Three vehicles were used; a pentaerythritol alkyd, a phenol-formaldehyde tung oil and an epoxy polyamide.

Details have been given in an earlier paper². Pigmented films were cast from paints prepared by dispersing known weights of pigment in the vehicles by means of a ball mill containing steatite balls. The zinc oxide was a calcined grade of high purity and it consisted of spherical particles, average diameter 2 microns. Ball milling was continued for 24 hours at which time the biggest aggregates were less than 5 microns, as checked by a Hegmann gauge. Driers were then added and subsequent casting and drying was the same as for clear films¹. Details on the preparation of iron oxide pigmented films have been published³. The red lead pigmented films were prepared in a similar way to the zinc oxide films. The red lead was Type 1 BSS 217, 1961.

When pigmenting the epoxy resin the pigment was ground into the more viscous material (Beckalide), the less viscous (Epikote) being added later. This limited the maximum PVC (pigment volume concentration) attainable. All the zinc oxide films cast on glass plates could be stripped from the plates after a short soak in water. The PVC is defined as:

$$\frac{\text{Volume of pigment}}{\text{Volume of vehicle and pigment}} \times 100$$

The transition temperatures were obtained using a dilatometer in exactly the same way as for the clear films. To calculate α (the cubical coefficient of expansion of the vehicle), the volume of vehicle is required and hence accurate values of the density are needed. The values used here were obtained from the PVC, the density of ZnO (5470 kg/m³) and the clear film densities (1160, 1050 and 1090 kg/m³ for the alkyd, tung oil and epoxy respectively). This assumes no shrinkage or expansion of the vehicle due to the pigment. Observed values using the dimensions method were slightly different so this probably limits the accuracy of the value of α to ± 5 per cent. It is assumed that the contribution of zinc oxide to expansion is negligible.

The ionic resistance of the film was investigated by mounting small (100 mm² exposed area) pieces of film in small glass cells filled with potassium chloride solution. The resistance of a piece of film in 0.001 M and 3.5 M KCl classified the conduction in the film as D (direct) or I (inverse) type. About 20 pieces of film, free from visible defects, were measured from each cast and the number of pieces giving D type behaviour divided by the total number investigated (i.e. both D and I type) multiplied by 100 gave the percentage D type of the film. This is similar

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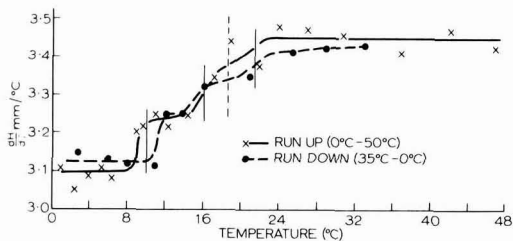


Figure 1. Dilatometer run, 5 per cent ZnO in alkyd (annealed)

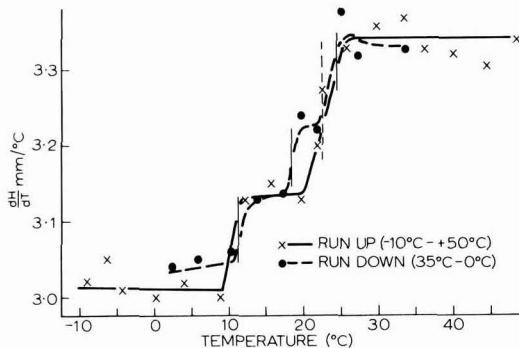


Figure 2. Dilatometer run, 25 per cent ZnO in alkyd (annealed)

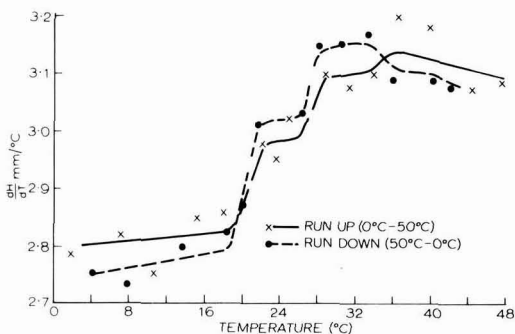


Figure 3. Dilatometer run, 5 per cent ZnO in tung oil (annealed)

to the method used previously²⁴ to characterise the resistance behaviour of detached films. The method used to investigate the effect of temperature on the ionic resistance of D and I type films pigmented with zinc oxide was the same as that used for clear films¹.

Results

Structural transitions

A total of six zinc oxide pigmented films have been examined - two levels of PVC in each of the three systems (alkyd, tung oil and epoxy polyamide). Dilatometer runs gave the results shown in figures 1-6. The transition temperatures from the graphs, values of α and densities are found in tables 1 and 2. These tables also include the results for clear films¹ for comparison. Measurements

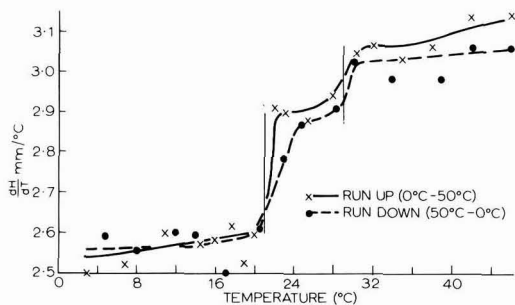


Figure 4. Dilatometer run, 30 per cent ZnO in tung oil (annealed)

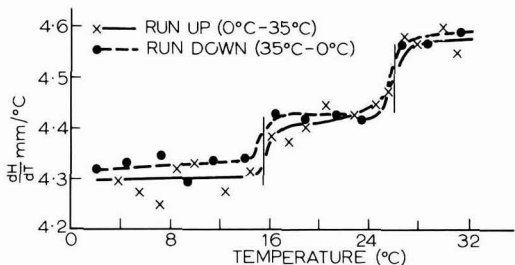


Figure 5. Dilatometer run, 5 per cent ZnO in epoxy (annealed)

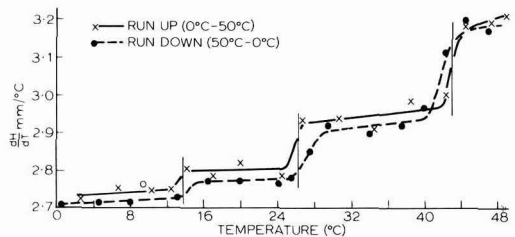


Figure 6. Dilatometer run, 10 per cent ZnO in epoxy (annealed)

were made over the range 0-50°C for all films except the 5 per cent zinc oxide epoxy, when the run did not extend sufficiently high to cover the backbone transition.

The asterisks attached to the T_g values for the pigmented alkyd films in Table 1 indicate that these transitions were rather ill-defined. They might be better represented by two transitions (e.g. 17°C and 21°C for the 5 per cent ZnO in alkyd, and 18°C and 24°C for the 25 per cent ZnO in alkyd). This is represented by the solid lines in figures 1 and 2. The lower transition remains the same but with a decreased gradient change. The values of α suggest that the original 10°C transition could have split to give a residual transition at 10°C and a new one at 17°C. However, it may be that the upper (backbone) transition is not very sharp. Whatever the interpretation, the upper transitions rise slightly and continue to rise with increasing pigmentation. In the tung oil films both the transitions observed in the clear film rise a few degrees centigrade on initial pigmentation. The lower transition then remains constant at 30 per cent PVC, the upper transition continues to rise slightly with increasing pigmentation. The values of α below the lower and above the upper transition are consistent although the bulk of the

Table 1
Transitions in alkyd and tung oil phenolic films pigmented with zinc oxide

	Lower transition			Upper transition		
	T_{gg} (°C)	α_1	α_2	T_g (°C)	α_2	α_3
Clear alkyd	10.5	0.31	0.45	19.3	0.45	0.52
5% ZnO in alkyd	10.0	0.30	0.38	20*	0.38	0.50
25% ZnO in alkyd	10.8	0.32	0.38	22*	0.38	0.52
Clear tung oil	18.4	0.31	0.42	26.3	0.42	0.54
5% ZnO in tung oil	20.5	0.34	0.45	27.5	0.45	0.52
30% ZnO in tung oil	21.0	0.28	0.43	29.0	0.43	0.53

α values are given as $ccs/°C/cc \times 10^3$
*Values ill-defined, see text.

Table 2
Transitions in epoxy polyamide films pigmented with zinc oxide

	Lower transition						Upper transition		
	T_{gg} (°C)	α_1	α_2	T_{gg} (°C)	α_2	α_3	T_g (°C)	α_3	α_4
Clear epoxy	15.4	0.27	0.31	26.0	0.31	0.36	39.4	0.36	0.45
5% ZnO in epoxy	15.5	0.28	0.32	26.0	0.32	0.38	not measured		
10% ZnO in epoxy	14.5	0.30	0.33	26.5	0.33	0.38	43	0.38	0.49

α values given as $ccs/°C/cc \times 10^3$.

gradient change occurs at the upper transition for the clear film and at the lower transition for the pigmented films.

In the epoxy system three transitions were observed in the clear films. The lower two remain at the same temperature in the pigmented films (up to 10 per cent PVC), the upper one rises a few degrees. The gradients are consistent throughout.

Ionic resistance

Table 3 gives the value of percentage D type, $\log R_i$ and $\log R_D$ for thin (35-45 microns) zinc oxide pigmented films at 25°C for the three vehicles. The effect of temperature on the ionic resistance ($\log R_i$ in 3.5 M KCl) of three pigmented ZnO films is shown in figures 7, 8 and 9. These are for a 5 per cent ZnO in alkyd, a 5 per cent ZnO in tung oil and a 10 per cent ZnO in epoxy. They serve as examples of the effect seen with ZnO in the three systems. Other degrees of pigmentation gave similar results. Changes in slope occur at certain temperatures for all I type films. It appears that conduction is highly activated at the higher temperatures and less so as the temperature falls.

Some pigmented D type films were also examined, however D type conduction was found to be less activated with no significant change in slope between 0°C and 50°C. These results are analogous to those obtained for clear films⁴.

Table 3
Resistance behaviour of zinc oxide pigmented films

PVC	% D Type	$\log R_i$	$\log R_D$
Pentaerythritol alkyd			
0	54	11.3 (± 0.15)	6.7 (± 0.7)
1	57	11.8 (± 1.0)	7.5 (± 1.0)
5	40	11.8 (± 0.3)	7.5 (± 0.8)
8	42	11.5 (± 0.5)	7.7 (± 0.5)
16	53	11.2 (± 0.5)	7.4 (± 0.4)
25	55	10.1 (± 0.3)	7.9 (± 0.5)
37	56	9.5 (± 0.3)	7.0 (± 0.6)
Phenol-formaldehyde tung oil			
0	72	12.3 (± 0.3)	6.8 (± 0.7)
2	82	12.1 (± 0.2)	7.1 (± 0.7)
5	60	12.4 (± 0.3)	6.7 (± 0.5)
10	80	12.0 (± 0.3)	7.1 (± 0.6)
20	75	11.8 (± 0.4)	6.9 (± 0.7)
30	100		6.3 (± 0.7)
Epoxy polyamide			
0	77	11.3 (± 0.2)	6.8 (± 0.7)
1	80	11.6 (± 0.3)	7.1 (± 0.7)
5	85	11.5 (± 0.2)	6.6 (± 0.5)
10	96		6.8 (± 0.7)
20	100		6.6 (± 0.8)

Discussion

Ionic resistance

The effect of zinc oxide on the ionic resistance as shown in Table 3 particularly on the percentage D type will be discussed first. The importance of the percentage D type of a film in assessing its protective ability has been established for clear films⁴. The lower the number of D areas the better the protection afforded by the film.

The top set of graphs in Figure 10 shows how percentage D type is affected by pigmentation with zinc oxide. Although error bars are not given on the graph for clarity, the statistical nature of a percentage D type result (picking up small defects in a continuum) means that the expected error is quite large (standard error is ± 20 per cent of actual value, or ± 10 per cent as percentage D type for a 50 per cent D type film with 20 pieces of film measured). This means that there is a 50:50 chance that a sample value of 50 per cent has come from a population with a value of 58 per cent or 42 per cent. There is a one in 20 chance that a sample value of 50 per cent has come from a population whose actual value is 30 per cent or 70 per cent. Hence caution must be exercised in interpreting results, and differences between pairs of readings of less than 20 per cent may not be significant. At higher values of percentage D type (e.g. 80 per cent) the error becomes less and differences of greater than 15 per cent could be considered significant. The sample values obtained are consistent with population values as shown by the broken lines on the graphs. However, there is some evidence that the percentage D type in a given batch decreased slightly

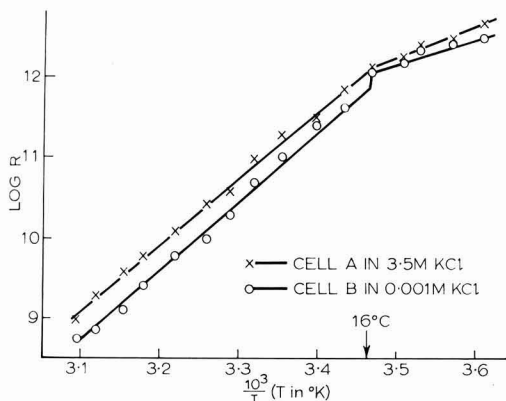


Figure 7. Arrhenius plot for I type resistance of 5 per cent ZnO in alkyd film

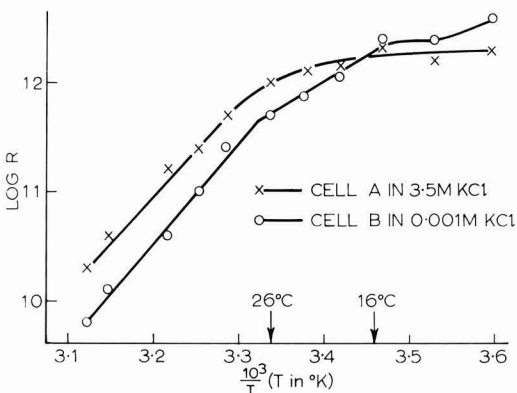


Figure 8. Arrhenius plot for I type resistance of 5 per cent ZnO in tung oil film

in the region of 5 per cent pigmentation in the case of all three vehicles.

The effect of pigmentation on the value of the ionic resistance is also shown in Table 3, from which it can be seen that $\text{Log } R_D$ was not affected significantly by pigmentation in any of the three systems. $\text{Log } R_I$ was unaffected by pigmentation with zinc oxide in the tung oil and epoxy systems, but was reduced significantly at high PVCs in the alkyd system.

The effect of temperature on the ionic resistance of pigmented films, figures 7, 8 and 9, was very similar to that observed for clear films (reference No. 1, figures 1, 2 and 3) and this suggests that following the effect of temperature on conduction could be a method of locating structural transition temperatures. However the values may not occur at exactly the same temperatures but this is to be expected due to water plasticising the film. Also the similarity of the results to those for clear films indicates that the mechanism of conduction is essentially unchanged by pigmentation and theories developed for clear films² are still valid.

The fall in $\text{Log } R_I$ of the highly pigmented alkyd films can be explained by the observed high water uptake of these films (up to 10 per cent compared with 2 per cent for the clear alkyd). Highly pigmented tung oil and epoxy

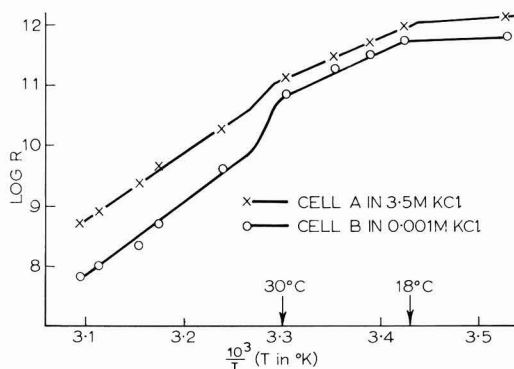


Figure 9. Arrhenius plot for I type resistance of 10 per cent ZnO in epoxy film

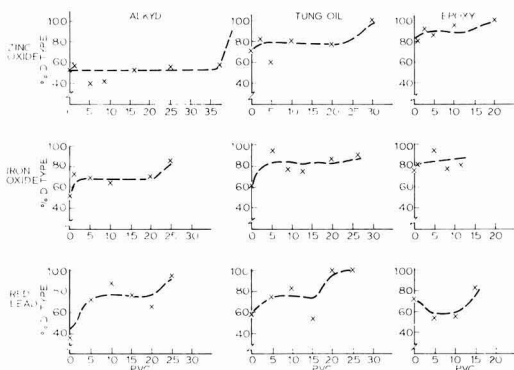


Figure 10. Graphs of percentage D type versus PVC for the three pigments in the three vehicles (x is experimental sample point, ----- is expected population lines)

films do not take up much more water than clear films. Hence there is much less effect on I type resistance.

Transitions

Study of the results in tables 1 and 2 shows that pigmentation with zinc oxide has not caused a change in the backbone transition temperature of greater than 5°C in any of the three systems. Also the values of α below the lower and above the upper transition are relatively unchanged by pigmentation. This indicates that there is no great change in crosslinking being brought about by the pigment in the bulk of the polymer. There may be slight chain stiffening caused by the pigment adsorbing certain groups so that the effective number of $-\text{CH}_2$ groups between crosslinks is reduced. This leads to a slight rise in the backbone transition. Galperin⁵ gave a similar explanation for the changes he observed in transition temperatures when incorporating titanium dioxide into an epoxy vehicle. At 40 per cent PVC he found the upper transition had risen by 10°C. However, Kwei and Kumins⁶ working with the same system found no change in the backbone transition up to 12 per cent PVC. In contrast, Kumins⁷, working with titanium dioxide dispersed in Vynilite VYHH, observed a large decrease in T_g upon initial pigmentation and a rise as pigmentation increased; however, the solvent retention of films of VYHH is very large and this may account for the initial fall.

The subsidiary transitions (T_{gs}) present in the clear films are also present at the same temperatures in three out of four cases in the pigmented films, although the gradient change at the transition is sometimes altered. This is again indicative of no great change in polymer structure being effected by the pigment. Scantlebury³ studied the effect of iron oxide on the 10°C alkyd and 15°C epoxy transitions and observed no change in the transition temperature on pigmentation.

Relation between structure and percentage D type changes caused by zinc oxide

The number of D areas present in a polymer film is important in resistance inhibition⁴. The size and possible causes of these D areas have been discussed recently⁹. One conclusion was that they represent only a very small fraction of the bulk polymer (in a normal highly cross-linked polymer film perhaps only 1:1,000 to 1:10,000 of the film is D type material). Nonetheless they represent regions where the crosslinking is considerably less, and where they traverse the film they cause a drop in resistance of as much as 10^8 times in 3.5 M KCl on an area basis. An explanation which is consistent with the facts is that D type areas in a dried film are caused by polymerised material present in the resin before application. It is suggested that they are composed of large low functionality gel-like molecules which fail to crosslink further on drying.

The present results for transition temperature changes show that zinc oxide had a relatively small effect on the main polymer structure. However, the pigment has affected the number of D areas particularly in the tung oil and epoxy systems.

A measurement like transition temperature change reflects a property of the bulk polymer whereas the number of D type films observed relates to the effect of the pigment on a small fraction of the polymeric material in the film. Hence no attempt should be made to correlate directly movement of transition temperatures and percentage D type. Nonetheless polymer-pigment interaction must be affecting the changes observed in percentage D types and the small changes in transition temperatures do give some clues as to the nature of this interaction.

It is generally agreed that a pigment will adsorb preferentially either certain groups if it is chemically active or certain molecular weight fractions if it is an inactive pigment. Zinc oxide is a basic pigment and thus would be expected to react with acid groups such as $-\text{COOH}$, which are present in the alkyd system, and consequently adsorption of these groups occurs. It can be assumed they are present in gel molecules and mainly low molecular weight material because if they were present in the higher molecular weight material in the bulk polymer then the backbone transition would be expected to rise more than observed. This chemical adsorption leads to some improvement in the percentage D type when the pigment particles are relatively far apart as this breaks the continuity of some D type areas. At higher PVC the gel-like areas become continuous again and the film is no better (with respect to percentage D) than an unpigmented film.

In the tung oil and epoxy systems the overall effect is for the pigment to increase the number of D types, although there is some evidence that it has caused a slight decrease at around 50 per cent pigmentation. Presumably the adsorption in these systems is again mainly of low molecular weight material but not necessarily gel molecules. Jettmar's¹² work may throw some light on this and is discussed below.

Comparison with other pigments

The results obtained by Buller⁸ with red lead and those by Scantlebury with iron oxide³ dispersed in the three vehicles are shown in the bottom and middle set of graphs in Figure 10. Several of Scantlebury's results for iron oxide have been repeated. The values obtained were essentially the same except for the tung oil films when highly pigmented, where significantly higher percentage D types were obtained. This may have been due to the effect of thickness because it has been shown⁹ that thickening the film reduces the percentage D type dramatically, consequently the values given in Figure 10 are all for films in the region 35-45 microns.

Although the results are not given here, there was no significant change in the values of $\text{Log } R_D$ and $\text{Log } R_I$ with PVC for films pigmented with red lead and iron oxide in any of the three systems, only zinc oxide in alkyd showed any variation of $\text{Log } R_I$ with PVC. Furthermore, the changes in water uptake with PVC in the case of those films pigmented with red lead and iron oxide were not as great as that for zinc oxide dispersed in the alkyd resin; the increase in the latter case was probably due to the formation of soluble soaps.

In general the effect of pigmentation was to increase the number of D areas followed by a slight fall then a rise again, the only exceptions being red lead dispersed in the epoxy-polyamide vehicle and zinc oxide in alkyd. The latter has been discussed above. It is suggested that for all the other systems upon initial pigmentation those portions of the polymer containing active centres segregated around the pigment particles. Consequently the percentage of D areas increased since ions could traverse the film more easily via the ionogenic adsorbed layers. This explanation is in accordance with the views expressed by Rothstein¹⁰ and Sherwood and Rybicka¹¹, who concluded that upon pigmentation low molecular weight material tended to segregate around pigment particles.

Upon further pigmentation, that is to say in the region 5-15 per cent, there is some evidence that the percentage D areas tended to decrease. This effect, if not due to statistical variation, may be due to the fact that the quantity of active material contained in the polymers is limited and as pigmentation increases complete coverage of the pigment particles by the active material does not take place. The ionogenic adsorbed layers are incomplete and ionic penetration is thereby rendered more difficult. However, upon further pigmentation the percentage D type of the film increases again and at the CPVC films become 100 per cent D type. Jettmar¹² has suggested that the adsorption of low molecular weight material onto the surface of the pigment can reduce the solubility of the higher molecular weight material and produce gelled areas of high molecular weight polymer containing only small amounts of pigment. This is probably the reason why at higher PVCs (but short of the CPVC) the percentage D type tends to increase.

In the case of red lead dispersed in the epoxy-polyamide resin, the initial rise in the percentage D areas does not appear to occur. This may be attributed to the interaction of red lead with the residual polyamide, which may initially suppress the adsorption of the active fractions of the polymer; however, as the pigmentation increases the free polyamide becomes exhausted and active polymer segregates around the pigment particles, with a consequent rise in the percentage D areas.

Conclusions

An examination has been made of the effect on three vehicles, a pentaerythritol alkyd, a phenol-formaldehyde tung oil and an epoxy polyamide, of pigmentation with zinc oxide.

It was found that in all cases films contained both I and D areas and that the ionic resistance of the films was not affected significantly by pigmentation, except in the case of the pentaerythritol alkyd vehicle, when the resistance was reduced at high pigment loadings.

The effect of temperature on the ionic resistance has been measured and found to be very similar to that of the unpigmented film, thus indicating that the mechanism of conduction was essentially unchanged by pigmentation. The effect of zinc oxide on the transition temperatures of the polymers has been determined by dilatometry and it has been established that pigmentation brought about a relatively small change, less than 5°C, and this occurred only in some cases.

This is in contrast to the effect produced by pigmentation on the percentage of D type areas in the film, which rose, sometimes appreciably, upon pigmentation and there was some evidence that it later fell slightly before rising to 100 per cent as the CPVC was approached.

The results obtained with zinc oxide have been compared with those obtained with iron oxide and red lead when dispersed in the same three vehicles and it was found that, in general, they all behaved in a similar way.

The work also shows that none of these three pigments brings about any dramatic decrease in the number of D type areas. Hence single coat films made from these

vehicles and pigments would not be expected to prevent corrosion solely by resistance inhibition. Other factors that can be changed by the pigment and that affect the ability of a pigmented film to protect the substrate are the formation of inhibitive materials and adhesion. Further work is required to make a full assessment of these factors.

Acknowledgements

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Electrochemical impedance in coated metal electrodes. Part 5: Film thickness*

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Summary

Impedance techniques and potential measurements were carried out on relatively thick films of a vinyl lacquer on mild steel immersed in artificial sea water. During the initial stages of immersion the impedance data and the potential measurements failed to correlate with the corrosion observed on the specimens. Further, abrupt changes in potential correlated with substantial changes in the impedance response. When the specimens had reached the final stages of breakdown the impedance response was characteristic of porous coatings.

Introduction

Previous papers in this series¹⁻⁴ have examined various aspects of the impedance response of relatively thin lacquers containing a number of holidays on a mild steel substrate. The impedance response consequently contained a large contribution from these pores. The low impedance

areas associated with these regions effected the corrosion pattern occurring in areas away from the holidays, i.e. the corrosion was concentrated at point sites which were subject to preferential attack, and the anode to cathodic area was consequently disproportionate. In the work reported herein, care was taken using a multi-coat technique to produce relatively thick lacquers which were as free as possible from holidays. The results obtained were markedly different from any of those reported previously.

Experimental

The materials and techniques used were identical with those reported previously³, with the exception that coatings were produced by a spinning technique. Each specimen was spun coated four times to give a total dry film thickness of 100 ± 15 µm. Each individual coat was allowed to dry for a period of seven days at 33°C under a

*Parts 1 to 4 of this paper were published in *JOCCA* earlier: *JOCCA*, 1981, **64**(2), 83; *ibid.*, 1981, **64**(3), 119; *ibid.*, 1981, **65**(4), 140; *ibid.*, 1982, **65**(1), 11; respectively

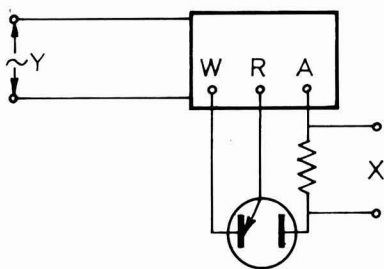


Figure 1. Circuit diagram for high input impedance measurements

stream of dust free air. Each panel was then cut in half to produce two "identical" test pieces. From the range of specimens thus prepared, the most similar pairs were selected for exposure such that each specimen presented one exposed area of 34 cm² to the solution.

Because of the extremely high impedance of this type of specimen, it was necessary to connect the Y input of the frequency response analyser directly across the generator in order that none of the current flowing between the auxiliary and working electrode of the potentiostat could flow through the relatively low input impedance of the analyser's Y input. This arrangement is shown in Figure 1. It had the disadvantage that phase shift occurring in the potentiostat could now influence the response obtained, especially at high frequencies (above 1 KHz). However, this phase shift was minimised by careful selection of the count resistor.

The polarisation technique employed was that described previously² whereby the rest potential of the electrode was measured and the impedance data obtained while the specimen was held at the measured potential using a potentiostat. The specimen potential was followed in this manner rather than set at a predetermined level as the purpose of this investigation was to examine the variations in the impedance response apparently occurring on "identical" specimens. To force the potential to a pre-set value would have had the effect of reducing any variations that naturally might occur; however it should be borne in mind that sometimes the act of measuring the potential does seem to have some disturbing effect on the specimen potential even using the highest impedance instrumentation.

The progress of corrosion occurring on the specimens with time was monitored photographically.

Results and discussion

The photographic evidence indicated that all four specimens corroded essentially in a similar manner throughout the period of exposure. The appearance of the specimens after four days exposure showed a fine haze of very small, closely spaced underfilm brown rust sites having diameters of the order of 0.1 mm, with the occasional larger spot surrounded by a rust free area. The appearance of the specimens after 74 days exposure to artificial sea water showed that no new sites had developed, the original sites having extended laterally under the film in a manner similar to that observed in filiform corrosion⁵. Occasional rust spots had a darker colour rust associated with them. The subjective differences between the four specimens were slight. This visual similarity was not reflected in the electrochemical data.

Table 1
Potential versus time data for the four coated specimens in artificial sea water

Time (days)	Potential (-SCE)			
	A	B	C	D
0	NSP	NSP	NSP	600
1	670	NSP	NSP	610
4	610	NSP	545	NSP
5	675	NSP	600	665
7	680	NSP	670	690
13	680	NSP	720	720
20	685	NSP	680	635
43	680	NSP	690	610
47	680	600	700	610
74	680	580	680	650
89	680	640	690	665

NSP = no stable potential

Measurement of potential showed that the rate at which each specimen took up a stable rest potential varied considerably, see Table 1 and Figure 2. Specimen B took 45 days to reach a stable rest potential but was the specimen which showed the most obvious macroscopic underfilm corrosion during the first few days of immersion. Specimen A, however, had similar but less pronounced features but took up a stable potential after one day immersion.

In the remaining two specimens the shapes of the potential versus time curves were similar to those reported by Kendig and Leidheiser⁶, who observed a positive going potential peak in the first few days immersion. After this peak the potential gradually settled to a potential of -610 mV (SCE). Similar initial potential deviations were observed by Wormwell and Brasher, but in this work a negative going peak was observed after the first 20 days immersion. In both these studies it was concluded that these changes were a result of changes in the corrosion process occurring beneath the coating. As stated earlier in this paper, the authors were unable to detect any such changes in the observed corrosion pattern but, as will be referred to later, there were as yet unexplained changes in the impedance curves.

Variations in potential also had variations in impedance data associated with them. When no stable rest potential could be measured, the impedance data exhibited considerable scatter, the higher frequency points showing mainly capacitive behaviour. In these specimens, when a rest potential became measurable the impedance response consisted of a high frequency semicircle followed by low frequency behaviour characteristic of a non-linear Warburg impedance, figures 3 and 4, the impedance plots being similar in shape but different in size. A possible explanation is that the same fundamental process was occurring on both specimens but over a different area in each case, as the capacitive and resistive contributions vary directly and inversely respectively with area. This type of behaviour is commonly observed and has been reported by the present^{2,3} and other workers⁶. The high frequency semicircle is generally considered to be attributable to the parallel combination of the coating resistance and its associated capacitance. The general trend of the change in the impedance curves with time for these two specimens was similar to that observed during work on thinner more defective films that has been reported previously³. However, during the period of observation,

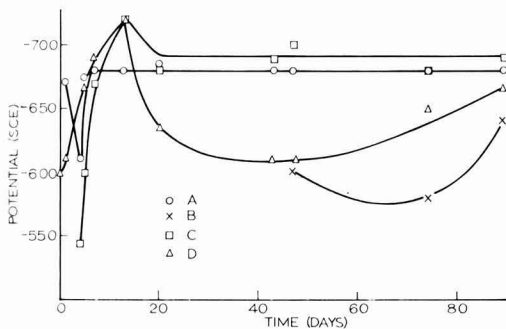


Figure 2. Potential versus time data for the four coated specimens in artificial sea water

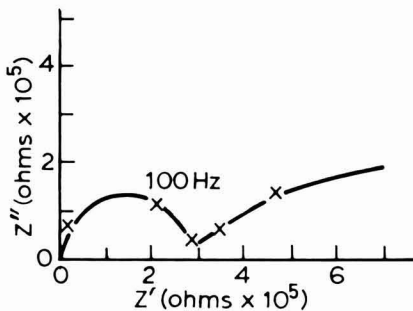


Figure 3. Impedance diagram for specimen C at four days carried out at the rest potential, -545 mV (SCE)

from time to time impedance data was obtained that did not fit in with the general family of curves, in that the high frequency semicircle disappeared and the response was of the type associated with a leaky capacitance, i.e. having a very large capacitive component in parallel with a large but finite resistive component, Figure 5. Previously such data have been regarded as suspect, but co-workers in the authors' laboratory have also observed this phenomenon and its appearance seems to be capable of being correlated with spontaneous changes in specimen potential.

The remaining two samples also exhibited non-characteristic impedance behaviour. Specimen D only exhibited a semicircle of the type previously associated with coated metals after 13 days immersion. Prior to this either Warburg or depressed semicircle impedance data had been obtained. Specimen A did not exhibit this high frequency semicircle at any time, the response being a depressed semicircle over the majority of the period of exposure.

In the final stages of immersion all four specimens settled to an impedance response of the type shown in Figure 6. This kind of response had previously been observed in thinner specimens after the initial transient stages had been passed through and new pore initiation had ceased².

Conclusions

1. The impedance data obtained during the initial stages of exposure of mild steel coated specimens, the coatings having thicknesses of the order of 100 μm , do not directly relate to the observable corrosion phenomena.

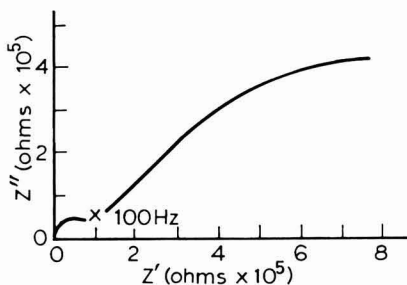


Figure 4. Impedance diagram for specimen B at 47 days carried out at the rest potential, -600 mV (SCE)

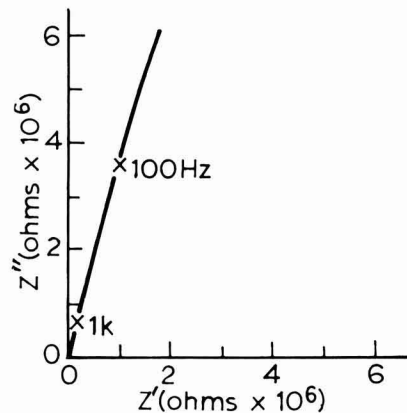


Figure 5. Schematic impedance diagram showing typical "leaky capacitance"

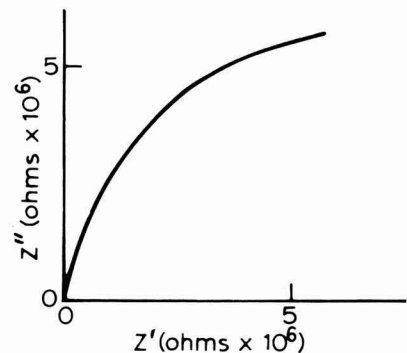


Figure 6. Impedance diagram for specimen C at 47 days carried out at the rest potential, -680 mV (SCE)

2. Potential measurements also fail to correlate directly with the observable corrosion.

3. Specimens that exhibit variations in potential also exhibit variations in the impedance data that do not easily fit the general trend of the curves.

Acknowledgements

The authors wish to thank Dr W. W. Harpur, Dr P. D.

Philpot and Dr G. C. Googan of International Paint for their encouragement and financial support without which this work could not have been carried out.

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6. Kendig, M. W. and Leidheiser, H., Jr., *J. Electrochem. Soc.*, 1980, **123**, 982.
7. Wormwell, F. and Brasher, D. M., *J. Iron Steel Inst.*, 1950, **164**, 141.
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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 April issue:

The surface finishing of exterior plywood by *T. B. Dearling and G. A. Smith*

Fractional precipitation of lac. Part I: integral fractionation by *A. Kumar*

Instrumental assessment of application properties of latex paints by *A. Rudin and J. Baas*

Adhesion and the gap between theory and practice (short communication) by *W. Funke*

occa meetings

Irish

Alternative methods of pigmentation

The first lecture of the new session was given by Herr G. Dam in the Clarence Hotel, Dublin on Thursday 14 October 1982. Herr Dam is the technical service manager of Sachtleben Chemie GmbH of Duisburg, West Germany.

The subject was the use of zinc sulphide opacifying pigments and barium sulphate extenders and how these can be used with good economic effect in conjunction with titania. (The concept of "pigment area concentration" was introduced as the calculating factor to be used rather than pigment volume concentration.) There are three good reasons for looking again at these products which many regard as "old fashioned":

- (a) Increasing price of titania
- (b) The latest types of micronised lithopones and blanc fixe now available
- (c) The changes that have taken place in paint technology during the last 30 years, when considerable quantities of these materials were used.

The properties of the pigments and extenders were described:

Advantages – Excellent rheology because of low surface area, low oil absorption, soft texture

Information regarding membership of OCCA is obtainable from the Association's offices, see contents page for address.

Excellent dispersibility because of micronisation and good particle size distribution

No flocculation

Dense film packing

No absorption in near UV range

Disadvantages – Lithopone has lower tint reduction than titania

High SG

Some of the uses to which these materials can be put were outlined as follows:

- (a) Emulsion paints – By judicious replacement of titania with lithopone a raw material saving of about 5 per cent by volume can be achieved.
- (b) Zinc phosphate/chromate primers – Use of lithopone in these formulations can improve corrosion resistance. This could be the answer to the ecological restraints placed on the use of chromates.
- (c) Alkyd gloss paints and silk emulsions – The replacement of 10 per cent of titania with micronised blanc fixe can be achieved with no loss in gloss or opacity. No change in colour takes place although there could be a brightening effect.
- (d) UV curing – Curing by means of UV is not possible with titania pigment in most circumstances because of

absorption of energy. Using zinc sulphide will give optical opacity without inhibiting the cure.

Questions from the floor centred on the experience of members when using lithopone in past years, e.g. mercurial fungicides and copper wood preservatives. The speaker pointed out that for ecological reasons most of these types of materials were not now used. During the past 30 years the paint industry had "formulated out" the elements that are detrimental when used with zinc sulphide.

A vote of thanks was given by David Godden who suggested that the ideas gave much food for thought.

R. C. Somerville

Thames Valley

UV curing – operational aspects in metal decorating

The theory of UV curing and its relevance to operational experiences in metal decorating were discussed by J. B. Emmerson of Metal Box plc on 18 November 1982 at the Crest Motel, Beaconsfield. The mechanisms of ionic and free radical polymerisation were contrasted and the operation of a standard electrode UV lamp system was described.

General reference was made to the methods of evaluation of typical ultraviolet curable inks in the laboratory, and health and safety considerations were described from both material and equipment viewpoints.

Metal Box production installations were described and the unique role of the company as manufacturer, supplier and user of UV curing equipment was emphasised. The features of the new Metal Box short lamp drier were outlined and a unit was made available for inspection.

R. L. Stephens

London

Wood preservation

On Thursday 21 October 1982 members and guests heard Mr E. Pearce of Fosroc Ltd give an illustrated talk on "Wood preservation" at the Princess Alice, Romford Road, London E7.

Mr Pearce introduced his subject by saying that the problems of wood decay were very old and he referred to "resinous" wood being used to build the ark.

The problem has always been with us but particularly so since World War II when faster grown plantations of timber, with a higher proportion of sapwood, were used in housing. The situation can be aggravated due to the poor building practice of exposing primed joinery to all weathers on site, and cutting primed joinery on site leaving the particularly vulnerable untreated end grain exposed. Fungal decay is related to moisture content and can readily take place when this exceeds 25 per cent.

**occa
meetings**

The importance of using three minutes immersion or vacuum treatment with organic solvent-based preservatives was stressed. Problems relating to product formulation, uptake, biocidal activity and water repellancy were discussed, together with problems that arise in ensuring compatibility with adhesives used in joinery construction and with paints.

In the discussion period it was clear that many of the questioners were speaking from personal experience of timber decay and were seeking advice. Interest was expressed in paste-like products containing insecticides or fungicides that can be applied to existing timber. Application method is by injection into holes drilled into the timber in the vicinity of joints. Over a period of time the active ingredients can penetrate into the adjacent wood. Clearly there is no alternative to the replacement of decayed wood but the method offers a means of reducing decay in existing timbers.

After question time Mr H. Worsdall in his vote of thanks suggested that we must be careful not to close the door after the horse has bolted. The vote of thanks was warmly endorsed by the audience.

K. H. Arbuckle

Manchester

Carbon black

Herr Achmed Elbrechter, assistant manager, Technical Service Department, Pigments Division, Degussa AG, Hanau, West Germany, gave his lecture to our Section on Monday 10 January 1983. The venue was the All Saints Lecture Theatre, Manchester Polytechnic, All Saints, and 35 members and their guests were in attendance.

Following on from the Section Chairman's (Frank Redman's) introductory remarks the lecturer presented data which may be summarised thus:

<u>Carbon black</u>	<u>Production and usage</u>
Degussa production	200,000 tonnes per annum
Paints/plastics	10-20 per cent
Rubber	80-90 per cent
Various types	Furnace black Channel black Lamp black

The production process details were as follows:

- Lamp black – Chinese production method 2,000 years old
Hydrocarbon liquid – incomplete combustion – coarse particles
- Channel – Natural gas – incomplete combustion

occa meetings

Furnace – Advanced – 95 per cent of carbon black production

Gas + oil + compressed air – burnt – water quench.

Carbon black characteristics:

<u>Physical</u>	<u>Coloristic</u>
Particle size	Jetness
Specific surface	Shade
Area	Tint strength
Structure	Hiding power

Dispersibility:

The primary particle size of Carbon Black is 10-100 nm. Values for surface area can be partly due to internal surface area. The lecturer stressed the difference between rubber blacks and pigment blacks and then went on to list the advantages of channel black in coatings as follows: 1. ease of dispersion, 2. better stability, 3. higher gloss, and 4. less flocculation.

The surface chemistry involved in oxidation processes was discussed and Herr Elbrechter advised that only oxidised grades should be used in high jetness level finishes based on acrylic and polyurethane binders. His recommendations on pigmentation levels were of the order of 3-5 per cent by weight on the vehicle solids.

Dispersing equipment discussed included:

For beaded carbon black – bead mill/ball mill

For fluffy carbon black – all types of equipment

The tinting strength of carbon black compared to titania and iron oxides was very high, e.g. ten times that of black iron oxide. He then illustrated with slides the variations in undertone obtained with: (a) differing carbon black, (b) differing titania, and (c) differing PVC values.

The lecture was followed by a lively discussion period when subjects discussed included the following: (i)

undertone – furnace black gives bluish type, (ii) for QC purposes always use same grade titania, (iii) oxidation process, and (iv) which grades to use for water-thinnable systems. It was stated that channel blacks were better for long term stability but that there was no rule of thumb dictating choice.

The lecture was concluded by a vote of thanks proffered by Ken Wright which was acknowledged enthusiastically.

F. B. Windsor

West Riding

Aspects of modern analytical techniques

A lecture meeting was held on Tuesday 7 December 1982 at the Mansion Hotel, Leeds. Dr Brian Davies of Perkin-Elmer Ltd gave a paper on the above topic.

Dr Davies remarked that in the last 4-5 years there had been a considerable number of developments made in analytical equipment to solve many otherwise difficult problems. The role of the computer in these developments was highlighted.

The main analytical techniques discussed were UV, IR, atomic absorption, gas and liquid chromatographies, thermal analysis and finally fluorescent analysis.

Each technique was discussed in detail. Gas chromatography was said to be often used to measure trace quantities of pollutant or toxic chemicals in the industrial atmosphere. Dr Davies pointed out that liquid chromatography was often used in the oil industry for measuring and also controlling the composition of petroleum mixtures.

The speaker went on to introduce the relatively modern analytical technique, fluorescent spectrophotometry. He suggested that this analytical tool could be used to detect compounds that are not detectable by IR or UV analysis.

Finally, Dr Davies introduced the recent developments in IR spectroscopy. Again the computer was said to play a significant role in making the job of the analytical chemist easier.

After a very enlightening question period, the vote of thanks was proposed by Mr Hugh Young.

D. V. Maltman

news

New chemicals trading company

S & W Berisford has launched a new subsidiary, Berisford Chemicals Ltd.

The company will trade initially in specialty chemicals required by the

Further information on any items mentioned below is obtainable by completing the Reader Enquiry Service form at the back of the Journal.

surface coatings, polymer and allied industries, and has plans to expand into additional areas.

Dr J. B. Warren has been appointed managing director of the new company. Prior to taking up this appointment he was research director of Diamond Shamrock Europe and of Lankro Chemicals. His earlier experience was with the Mond Division of ICI. One of his major contributions has been the pioneering work involved in establishing Diamond Shamrock's radiation curing

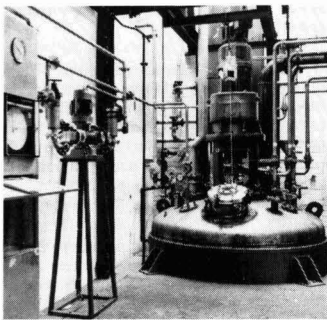
business, which is now a major force both in Europe and the USA.

Reader Enquiry Service No. 31

Kirklees to distribute Methocel

Kirklees Chemicals is to distribute the Methocel range of cellulose ethers in the United Kingdom for Dow Chemicals. Kirklees will be concentrating on supplying paint and adhesive manufacturers.

Reader Enquiry Service No. 32



Scott Bader's £100,000 investment in new manufacturing plant

New Reactor at Scott Bader

Scott Bader Company Ltd recently installed a new reactor system for use in the manufacture of water-soluble polymers.

The system, which consists of a ten tonne reactor and associated equipment, will enable the company to increase its manufacturing capacity by 5,000 tonnes a year.

Reader Enquiry Service No. 33

Restoration at the Tate

The photograph on the right shows an unusual application for one of Kremlin Spray Painting Equipment Ltd's J3 type spray guns. A protective varnish is being applied to a painting, done by the English artist Legros, in the Conservation Department of the Tate Gallery, London as part of the restoration procedure.

In restoring old paintings, the yellowed varnish is removed and also any earlier restorations. The painting is then re-varnished before any re-touching is carried out (re-touching makes good any losses where the original artist's paint has fallen away). The protective varnish applied must be easily removable as well as non-yellowing. These are usually made up by the Conservation Department using methacrylate copolymers (e.g. Paraloid B72) dissolved in xylene, or polycyclohexanone resins (e.g. Laropal K80) dissolved in white spirit to give a 5-10 per cent solids varnish. Occasionally natural damar resin is used dissolved in white spirit.

With such a large percentage of xylene being used, the Conservation Department's spray room was completely rebuilt to meet health and safety requirements, with full air extraction, enclosed spray masks and all electrical equipment meeting BASEEFA standards.

The Department also re-equipped itself with Kremlin spray guns, using the J3 for most work, but also an M18 gun for larger works including the application of protective lacquers to polished metal sculptures.

Reader Enquiry Service No. 34

New President of Paint RA

At the Paint RA's 57th annual general meeting held on 24 November 1982, Dr T. E. Groves was installed as its President. The Immediate Past President, Mr Leslie Silver, remains on the board of management.

Dr Groves worked with British Petroleum for ten years, initially in technical development and subsequently in production management in the oil refining division. He then joined British Resin Products, part of the Distillers (Plastics) Group, and for six years was technical manager responsible for the technical and process development of the company's wide product range of resins, moulding powders, polyvinyl chloride and polystyrene compounds. He was then chief chemist at Sissons Brothers, part of the Reckitt and Colman paint division. Dr Groves' wide experience is now appreciated by Manders Paints, where for some years he has been the senior executive responsible for paint, resin and process development.

Dr Groves' sound understanding of paint technology should greatly benefit the Paint RA.

Reader Enquiry Service No. 35

Stearates

A subsidiary of the Lambson Group known as Dart Chemicals has announced that it is now representing Breyer-Chemie of Holland for that company's full range of metallic stearates in the UK.

These versatile products are used in coatings as flattening agents, dispersing aids, thickening agents (due to gelling properties), fillers etc., and are said to



improve the brushability, workability and other properties of varnishes, paints and inks.

They are also used in other industries such as rubber, plastics, paper, cosmetics, foundries and light engineering.

Reader Enquiry Service No. 36

Wengain becomes Mooney agent

Wengain Ltd has been appointed sole UK agent for Mooney Chemicals Inc. of Cleveland, Ohio.

According to Wengain, Mooney Chemicals was established in 1946 and has gained a high reputation for its advanced ranges of metal carboxylates and related performance chemicals for paints and printing inks. In recent years Mooney has pioneered the development of complexed water-dispersible drier catalysts with their Hydro-Cure and Hydro-Cem ranges, also manufacturing anti-skinning agents, dispersing agents and fungicides.

The Mooney plant occupies a 55 acre site in Franklin, Pennsylvania. There is over 105,000 square feet of manufacturing space and a tank farm of nearly three million gallons capacity. The company is owner managed and operates a unique profit sharing plan whereby all employees are "partners" in the business.

Reader Enquiry Service No. 37



Protective varnish being applied to a painting by Legros. Part of the restoration work done by the Tate Gallery in its Conservation Department

news

Stress rheometer from Sheen

Sheen Instruments is now marketing the new Carri-Med controlled stress (CS) rheometer.

The high precision rheometer is said to greatly simplify the determination of yield value, plasticity, visco-elastic properties as well as conventional viscosity, both in research and in production.

Sheen also claims that the unique controlled stress system enables direct measurement of the stress required to deform a system up to the yield point. Subsequent flow properties can then be measured with greater precision.

Reader Enquiry Service No. 38

new products

International's new "European" paint

Acryline is a new system described by International Paint as the most advanced car refinishing system ever developed. The comprehensive two-pack system, from the Vehicle Finishes Division of International Paint, will match up to the increasingly demanding standards of the large car dealers and specialist bodyshops.

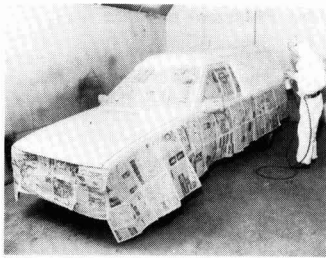
It is believed that Acryline, regarded as the first of the second generation two-pack acrylics, is the nearest yet that a repair material has come to equalling the performance of the original paint that is applied on the production line and baked at high temperatures.

Acryline was introduced to the market in the north west of England in September and has since been progressively launched region by region to International Paint's 150 approved distributors throughout the UK.

The product has also been launched simultaneously by International's sister companies in Italy and Spain. Acryline is eventually intended as the flagship in a push into other European markets to expand International's distributive network.

Kevin Hayward, director and general manager of the Vehicle Finishes Division of International Paint, said:

"Acryline represents a big step forward in our offer to the car repair and re-spray markets. It is a high performance product, combining easy application and economy in use with superb appearance



Acryline — according to International Paint: the most advanced car refinishing system ever developed

and outstanding durability. We believe that, in acryline, we have matched each of the best virtues of our competitors' two-pack acrylics all in one system!"

A new plant with advanced production concepts has been commissioned at International's Ladywood factory. According to International, the plant uses techniques that point the way ahead in paint making and incorporates a very high level of control over every operation; in particular the standards of cleaning lead to a degree of quality control that is at least the equal of any paint production unit in Europe.

Acryline is the fruit of three years of joint development by International Paint chemists in the UK, Italy and Spain.

Reader Enquiry Service No. 39

New sizing equipment

Fritsch has announced an addition to its range of particle sizing equipment. The Fritsch Analysette 20 scanning photo-sedimentograph will automatically size particles in suspension of 2 to 200 microns, and in certain circumstances particles of 1 to 500 microns can be measured.

The equipment consists of a sedimentation tank, a single beam (halogen) light source and a programmed micro-processor which presents the particle size distribution on graph paper. The beam of light scans the solution in the sedimentation tank and a photometer records the changes in light intensity which result from the particles falling to the base of the tank. The built in micro-processor calculates from these values the particle size distribution according to Stokes' Law.

A feature of the equipment is the speed at which samples can be measured. It is reportedly simple to operate because the instrument carries out all the measurements automatically once the data is fed into the microprocessor. It is also said to be extremely easy to get comparative measurements. The equipment can, it is claimed, cope with low concentrations of the suspensions, and is said to be very compact. High definition and reproducibility are also said to be features of this instrument.

Reader Enquiry Service No. 40

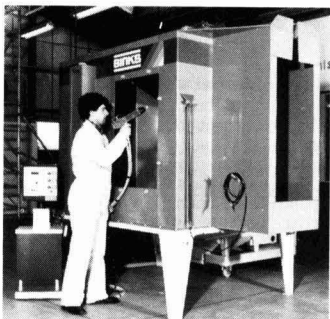
New pigments and additive from BASF

BASF recently placed a number of new pigments and an additive on the market. Seven of the pigments are highly concentrated preparations based on cellulose nitrate known as Enceptur C preparations. They are particularly suitable for use in printing inks containing ethanol/ethyl acetate.

The three other new pigments are in the Heligen range, two, a green and a blue, being described as suitable for all binder systems. The third, a blue pigment, is intended for offset printing inks.

Lastly, the additive, BASF Wax EVA 1, is a polyethylene wax. It is based on an ethylene/vinyl acetate copolymer and according to BASF is suitable as an antistetting and orientation agent and gellant in two-coat metal effect finishes; as an antiblocking agent and gellant in wood and metal finishes; as a binder and dispersing agent in pigment masterbatches (particularly carbon black); and as a wax component in hot melts.

Reader Enquiry Service No. 41



Binks-Bullows' new plastic booth. An efficient filter system means air can be exhausted into working areas

New plastic booths for powder coating

Binks-Bullows Ltd has introduced a new range of powder coating booths. These booths are available in three principal sizes, six, nine and twelve feet in length, and are manufactured from fire retardant polypropylene.

This construction is claimed to allow electrostatic powder coating to be more efficient because the plastic walls of the booth repel the electrostatic charge. The steel floors of the booth allow the electrostatic charge on surplus powder to be dissipated before powder is collected in fluidised bed cones for recycling.

A major advantage of the booths is said to be an efficient filter system which provides clean air which can be exhausted into working areas. Filtration is provided by an integral unit which allows surplus powder to be recycled to the powder feed hopper.

Reader Enquiry Service No. 42

Breathing aid

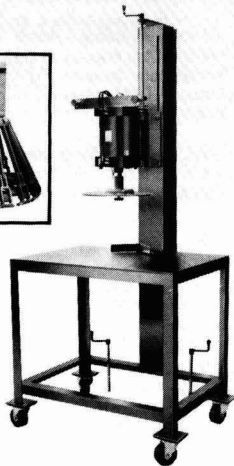
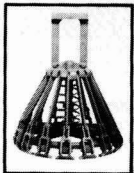
A refined version of the Breathing Aid Industrial breathing set package has been launched by Thorite Pneumatics. The new unit is said to deliver clinically clean air for use with full face or half face masks for either one or two operatives.

The new breathing aid has a capacity of 16 cubic feet per minute and conforms to BS4275 for oil, oil odour and dirt removal.

The three stage filter package includes a sintered bronze Norgren element (to screen out particles of down to five microns and remove water using a cyclonic action), a coalescing filter (to remove sub-micron particles and oil aerosols) and an activated carbon element (to aid oil odour extraction).

A visual indicator shows up oil contamination and warns of the need to change filter elements. The appliance is described as light and easily transportable for floor standing or wall mounted positioning.

Reader Enquiry Service No. 43



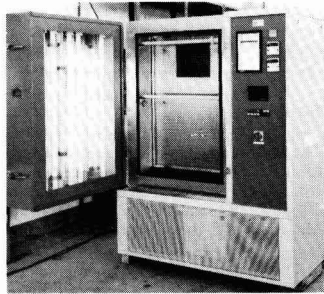
Beltron's lid closer for plastic pails, 2-5 gallons, or, using the optional crimper head (inset), for steel pails, 1-7 gallons

Lid closer

A new model SPC lid closer for plastic and steel pails is being manufactured by Beltron. Two buttons, located on either side of the air cylinder head, must be pressed within 0.03 of a second and held to activate the head. The operator can neither "fool" the system nor rewire the unit to override the pneumatic logic.

The SPC operating on an air supply of only 50 p.s.i. can close a five gallon plastic pail. It will close 2 to 5 gallon pails and fitted with an optional crimper head (inset) will close 1 to 7 gallon steel pails.

Reader Enquiry Service No. 44



New accelerated weathering machine from Weiss Technik which can accommodate specimens of surface area up to 8,000 cm²

Accelerated weathering machine

Weiss Technik has announced production of a new accelerated weathering machine for testing light fastness and resistance to weathering. With this new unit only the actinic part of global radiation in the spectral region $\lambda < 450$ nm is simulated. According to Weiss Technik, specimens with a surface area of up to 8,000 cm² and a thickness of up to 10 cm can be exposed over the entire natural temperature and humidity range.

Reader Enquiry Service No. 45

New six pen plotter available from ICS

Instrumental Colour Systems, who claims to be a world leader in colour instrumentation for colour measurement and control, can now supply a six pen multi-colour plotter as an optional extra to its colour instrumentation systems. The company has previously offered a single pen plotter as an optional extra and in supplying the new equipment has recognised the need for customers to be able to easily recognise individual plots on a multi-plot graph.

The plotter, which is microprocessor-based provides A4 sized plotting at three inches per second with 0.005 inch resolution.

When connected to an ICS colour system the plotter provides hard copy of the graphical information displayed on the VDU.

The plotter draws and identifies its own graph paper, which eliminates the need for special paper and also the need for precise paper positioning. Labelling of each plot is carried out automatically.

The plotter can produce a solid line plot in up to five colours (the sixth colour is used for the grid), if it is required to add further to the graph, the plotter will sequence back through the colours, plotting with a dotted line.

The plotter is used in conjunction with the ICS colour systems to plot log K/S, K/S or reflectance curves.

Reader Enquiry Service No. 46

news

Automatic cartridge filler

An automatic cartridge filling service for high viscosity mastic adhesives is now being offered by Industrial Adhesives Ltd. The company's first pneumatically operated machine, with an output of 10,500 cartridges per day, in sizes from 300 - 380 cm³, has recently been commissioned at its Chesham factory.

The new facility will handle products produced by the company, but will also be available for sub-contract filling work to other adhesive manufacturers. Although capable of processing a wide and varied range of adhesives, it will be employed initially on products for the building industry. Typical examples are adhesives for fixing panels to studding in dry-wall lining, acrylic water-based sealants for gap filling around floors or windows, and special fast setting stair nosing and carpet gripper compounds.

Cartridges are filled, sealed and batch numbered in one cycle, and the accurate control mechanism ensures products wastage is minimised.

Reader Enquiry Service No. 47

New traverse system from Mindon

Mindon Engineering (Nottm) Ltd has introduced a new traverse vertical paint spraying machine for use with metals, plastics or timber.

The new Mindon high speed traverse has been specially designed to be used in conjunction with existing spray plant and conveyors, or integrated within fully automated systems.

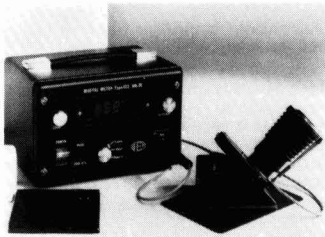
Typical applications include domestic radiators, refrigerator and washing machine panels, structural steelwork, sheet steel pressings and a wide variety of related items.

Operating from a standard factory airline, the new Mindon traverse is pneumatically driven to eliminate judder and to ensure smooth operation. Stroke length and position adjustment is said to be simplicity itself, achieved by the sliding of two proximity switches within a range of 300 to 1,500 mm.

The manufacturer says the new machine is designed as a self contained unit, the Mindon traverse will accommodate most manufacturers' spray painting guns including electrostatic and airstatic systems.

Reader Enquiry Service No. 48

news



Sheen's new low cost colorimeter

Colorimeter for non-continuous use

Sheen Instruments Ltd has made available its colorimeter for non-continuous use in process control. The model is comparatively low priced and described as miniature. Sheen recommend the instrument as an alternative to the more expensive and sophisticated instrumental techniques.

Reader Enquiry Service No. 49

literature

Standard for reflection haze

The amount of haze in an image is the most important attribute considered in visually rating a glossy paint finish for the quality of images reflected by its surfaces. To measure this haze, Standard D 4039, Standard Test Method for Reflection Haze of High Gloss Surfaces, was developed by ASTM.

The standard is under the jurisdiction of ASTM committee D-1 on Paint and Related Coatings and Materials, and its sub-committee on Optical Properties.

According to ASTM, prior to the development of this test method there were many standards evaluating other coating qualities but none existed in this area. As a result of this recent standard development, the paint and coatings industry, as well as industries which use these coatings, now have a universal standard with which to test haze.

This test method uses two specular gloss measurements made at two angles from the verticle, namely 60° and 20°. The difference between the two measurements gives a haze index for evaluating the haze in clear finishes on non-glossy substrates and in reflected images produced by the surfaces of opaque glossy pigmented finishes.

Reader Enquiry Service No. 50

meetings, etc.

Period paint

The Institute of Industrial Archaeology is to hold a one day short course at the Ironbridge Gorge Museum on Tuesday 19 April 1983 entitled "Period Paint: the Materials and their Matching".

The course, organised in conjunction with the Paint Research Association, is a successor to the heavily over-subscribed course "Period Paint", run in May 1982. It will develop the main theme that emerged in the proceedings: how craftsmen and conservators can match the colours and types of finish originally used on historic buildings or objects. The forthcoming programme will consider in more detail, techniques of analysis of paint layers, of colour matching and of application and finishing.

The course is of relevance to curators and conservators in many types of museums, heritage and craft organisations, as well as to the paint industry itself. Architectural interiors, painted furniture and other woodwork, and carriages and cars will be amongst the range of surfaces and objects being considered. There will be contributions from Ian Bristow, Crown Paints, and the Paint Research Association as well as from craftsmen and conservators.

For further information, bookings and a brochure contact Michael Stratton (architect and historic building consultant), The Institute of Industrial Archaeology, Ironbridge Gorge Museum, Ironbridge, Telford, Shropshire TF8 7AW, Tel: 095 245 3522, Ex. 32.

ICorrST conference

The North East Branch of the Institution of Corrosion Science and Technology is holding a conference on "Coatings and Surface Treatments for Corrosion and Wear Resistance". The conference will be held from 12-15 April 1983 and will be structured around four main subject areas: 1. Polymeric coatings and linings, 2. Inorganic coatings/high temperature, 3. Metallic coatings, and 4. Advanced coating techniques.

For further information and offers of papers contact: Professor K. N. Strafford or P. K. Datta, School of Materials Engineering, Newcastle upon Tyne Polytechnic, Newcastle upon Tyne NE1 8ST, Tel: 0632 326002.

people

Mr Tony Stroud has been appointed commercial developments manager by Cookson Group plc (formerly Lead Industries Group). Located at the com-

pany's City headquarters, he will report to the Group's Board Committee.

The Cookson Group has a turnover of £430m with 50 subsidiary and associated companies around the world.

★ ★ ★

The chairman and chief executive of Evode Group plc, **Andrew Simon**, has announced a Group restructuring to create three main business divisions.

The new divisions are responsible for the Group's activities in paints and plastics, adhesives and sealants, and roofing and insulation.

Mr David Winterbottom has been appointed divisional managing director of the new Paints and Plastics Division - which comprises Evode Plastics Ltd, Evode Industries Ltd and Postans Ltd. Mr Winterbottom also retains his present post as group financial director and company secretary.

Mr Vasck Vohralik has been appointed divisional managing director of the Adhesives and Sealants Division and retains responsibility for the activities of Evode Ltd, Vik and Evacor.

Evode Roofing, Joint Sealing, and Tekurat Insulations Ltd comprise the new Roofing and Insulation Division with **Mr Anthony Cobbold** as divisional managing director.

All three divisional managing directors report directly to chairman Andrew Simon.

★ ★ ★

The directors of Ault & Wiborg Group plc have announced the appointment of **Gordon Phillips** as group managing director.

In this new role Mr Phillips will be directly responsible to **Mr C. F. Strang**, the group chairman, for the operation of Group companies both in the UK and overseas.

Gordon Phillips joined the Ault & Wiborg organisation in 1973 as operations director of Ault & Wiborg Paints Ltd. He was appointed managing director of the company in 1976 and became a member of the Ault & Wiborg Group Board in 1977.

The Ault & Wiborg Group reported a turnover of £55m in its last published report covering the 1981 financial year.

★ ★ ★

Vinyl Products Ltd has announced the appointment of **Mr Joseph Fairless** as technical manager, paint and building, to head the company's research and application work on polymer emulsions for these two industries. Mr Fairless, who is an ATSC, brings with him a wealth of experience drawn from a working life that began with British Paints in Newcastle;

he then worked at English China Clays Loving Pochin Ltd of St Austell, before transferring to International Trading Corp. of Baltimore, marketing fillers in Europe and the Far East. Immediately before joining Vinyl Products he was with Air Products Inc. as technical service manager, Europe, and latterly in the Central Technical Services Laboratories, Allentown, Pennsylvania.

Vinyl Products also announced that **Dr David Wilson**, who has been technical manager, paints and building, since 1981, is now marketing manager, Scandinavia, while retaining his marketing responsibilities in Ireland. Before joining the company in 1981 Dr Wilson was with an associate company, Urachem International Ltd, with marketing responsibilities in the Far East; prior to that he had been with Letraset UK Ltd.

★ ★ ★

Ellis & Everard plc, a leading UK

Information regarding membership of OCCA is obtainable from the Association's offices, see contents page for address.

professional grade

At the meeting of the Professional Grade Committee held on 23 February 1983 the Committee authorised the following (section shown in italics):

Admitted as Associates

Allen David Frank (*Irish*)
Gibson Anne McArdle (*Scottish*)

chemical distribution company, has announced that **Ken Hough**, fine chemicals division's managing director, has been appointed chairman of the export division.

Peter Wood, Ellis & Everard's group finance director, has also joined the export division's board.

Nigel Braye, a director of the export division, continues to be responsible for the day to day running of the company.

Ellis & Everard's chairman, **Simon Everard**, remains a director of the export board. He was previously the chairman. **Geoff Sykes**, another main board director, has resigned from the export division board as he is moving to the United States to look after the company's interests there.

It was also announced that the Export Division will be relocating its operations from Greenwich in South London to the

news

company's Billericay site in Essex, where it will share premises with the company's fine chemicals division. The move will take place in May.

★ ★ ★

Geoff Targett of Burbage, Leicestershire has been appointed field sales manager, north, for the Vehicle Finishes Division of International Paint. He will be responsible for volume sales in the northern sales area, which covers mid-north Wales, the Midlands and the north of England. This appointment reflects International's restructuring of its marketing and sales teams.

OCCA news

Important amendment to the Licentiateship Regulations

At the Council meeting held on 23 February 1983 it was resolved that Regulation 5 for the Licentiateship should be amended by substituting the words "written evidence" for the existing words "a dissertation". The object of this amendment is to allow candidates to submit reports, projects and other written evidence on subjects directly associated with the science and technology of surface coatings or allied materials in place of a specially prepared dissertation on a topic. It is felt that this will be of benefit to students following a course of

study, and those candidates who have already applied for LTSC but have not yet submitted their dissertations may use this method of application. The written evidence will be assessed and the candidates will still have to attend for viva voce examination. Will all senior members of the Association who have younger personnel on their staff please encourage them to apply for the Licentiateship. Forms of registration are obtainable from the Association's office.



Shown from left to right at the London Section's ladies' night are (first row) Mrs Henman, Mrs Wright, Mrs Tennant, Mrs Morris, Mrs Gilliam, Mrs Redman, Mrs Kimber, Mrs Fowkes, (second row) Mr Henman, Mr Wright, Mr Tennant, Mr Morris, Mr Kimber, Mr Gilliam, Mr Redman, (third row) Mr Fowkes, Mr Hamblin

London Section

Ladies' night

The London Section's 1982 ladies' night was held on Friday 3 December at the Royal Chace Hotel, Enfield, Middlesex.

Present as top table guests were the President and the chairmen of the Bristol, Thames Valley, Manchester and Midlands sections and their wives, and the Director & Secretary. The Section also welcomed as top table guests Mr P. Henman, President of Mitcham Polymers Club, and Mrs Henman, and Mr R. Tennant, President of Birmingham Paint, Varnish and Lacquer Club, and Mrs Tennant.

The toast to the ladies was proposed by Mr Ian Gilliam, Section Chairman, and the response made by Mr Don Morris, OCCA President.

In his speech, Mr Morris commented on the practice of running sweepstakes on the length of speeches. People now tend

occa news

to complain about the brevity of the speeches rather than the content.

After an excellent meal, dancing commenced to the music of a very talented group called Rise.

A tombola organised by Mrs Gilliam, aided and abetted by committee members and their wives, was a great success.

Dancing continued until 1.00 a.m. A most successful and enjoyable evening was had by all present and credit must go to the Section's Social Secretary and toastmaster, David Sharp, for organising the event.

B. A. Canterford

bsi news

British Standards

684:
Methods of analysis of fats and fatty oils
684: Part 2: Section 2.3: 1983 Determination of insoluble impurities 4 page A4 size Gr 2
The soluble material is dissolved in a suitable solvent and the residue is collected by filtration, dried and weighed. =ISO 663. Supersedes BS684: Section 2.3: 1976. (ISBN 0 580 13038 X)

5711:
Methods of sampling and test for glycerol
5711: Part 17: 1983 Limit test for lead 2 page A4 size Gr 1
Determines whether a sample contains greater than, equal to or less than 1 mg/kg of lead. No current standard is superseded. (ISBN 0 580 13146 7)

6337:
General methods of chemical analysis
6337: Part 1: 1983 Method for determination of traces of sulphur compounds by reduction and titrimetry [=ISO 6228] 8 page A4 size Gr 6
Applicable to amounts of sulphate between 4.5 and 450 g either in solution or in the test portion. The sulphate can be present as such or can be produced by suitable pre-treatment. No current standard is superseded. (ISBN 0 580 13150 5)
6337: Part 2: 1983 Method for determination of silicon content (reduced molybdosilicate spectrophotometric method) [=ISO 6382] 8 page A4 size Gr 6



Shown above are those who attended a luncheon during the FSCT annual meeting in Washington, DC, on 4 November 1982. Standing left to right: Toshihiko Nakamichi, JSCM, Nori Kawashima, JSCM, Fred Daniel, FSCT, A. Clarke Boyce, FSCT President-Elect, John C. Weaver, FSCT, John Green, FSCT, John J. Oates, FSCT, Joseph A. Bauer, FSCT, Naoyuki Katoh, JSCM, Percy E. Pierce, FSCT, Terry Johnson, FSCT Treasurer. Seated left to right: Frank J. Borrelle, FSCT Executive Vice-President, Charles M. Hansen, SLF, Andre Toussaint, FATIPEC President, Howard Jerome, FSCT President, Kenji Uecki, JSCM President, Donald J. Morris, OCCA President, William Griffiths, OCCA Australia

The publications listed below and their prices are obtainable from: BSI Sales Counter, 195 Pentonville Road, London N1 9ND (personal callers), BSI Sales Department, 101 Pentonville Road, London N1 9ND (orders by post). Telephone: 01-837 8801. Telex 23218.

Applicable to the determination of quantities of silicon, expressed as SiO₂, between 2 and 200 g in the aliquot portion of the test solution taken for the determination. Reference should be made, for the preparation of the test solution to the standard relating to the product being analysed, which should also give any modifications. No current standard is superseded. (ISBN 0 580 13151 3)
6337: Part 3: 1983 method for determination of iron content (1,10-phenanthroline spectrophotometric method) [=ISO 6685] 4 page A4 Size Gr 4
Applicable to test solutions from which an aliquot portion can be taken containing between 10 and 500 g of Fe in not more than 60 ml. Reference should be made, for the preparation of the test solution, to the standard relating to the product being analysed, which should also give any modification. No current standard is superseded. (ISBN 0 580 13152 1)

Proposed for confirmation

BS 2782: PLC/17
methods of testing plastics

Method 123A: 1976 Determination of the melting point of synthetic resins (capillary tube method)
Method 123B: 1976 Determination of the melting point of polyamides
Method 123C: 1976 Determination of the melting point of semi-crystalline polymers using polarized light

Part 4: Chemical properties
Method 432B: 1976 Determination of the acid value of unsaturated polyester resins

Part 5: Optical and colour properties, weathering

Method 530A: 1976 Determination of yellowness index
Method 530B: 1976 Determination of the colour of near-white or near-colourless materials
Method 540A: 1977 Determination of resistance to change upon exposure under glass to daylight

Standards withdrawn

3900:
Methods of test for paints
3900: Part A4: 1966 Notes for guidance on paint application
Obsolete
3900: Part F7: 1973 Determination of resistance to water (water immersion method)
Superseded by BS 3900: Part G5: 1976

Draft standards for public comment

*82/56028 DC BS 2782 Methods of testing plastics. Part 7 Rheological properties. Method 730A Guidelines for the standardisation of methods for the determination of viscosity number and limiting viscosity number of polymers in dilute solution (ISO/DIS 1628/1) PLC/17

New ISO Standards

ISO 787:
General methods of test for pigments and extenders
ISO 787/24: 1982 Determination of relative tinting strength of coloured pigments and relative scattering power of white pigments - Photometric method 11 page G

ISO 1387: 1982
Methanol for industrial use - Methods of test 7 page E
±BS 506

OCCA CONFERENCE

15-18 June 1983

The Viking Hotel, York, England



The efficient use of surface coatings

Session I "Formulation including manufacture"

Thursday 16 June 9.15 a.m.–12 noon

Keynote address

Surface coatings in relation to external insulation

The need for speed and accuracy in the formulation and production of efficient surface coatings

Automated paint manufacture

Linear polymonosulphide and polysulphide polymers – general survey recent developments and applications (paper presented on behalf of FATIPEC) By Prof. Brossas (University of Louis Pasteur)

Chairman: Mr J. R. Taylor (Hon. Research & Development Officer)

By Mr R. A. Fidler (International Paint PLC)

By Dr M. Wilkinson (Blundell Permoglaze Ltd)

By Mr R. J. McCausland (Bayswell Consultants)

By Mr W. Ollett (Crown Decorative Products)

By Dr A. Carrick (Kratos Ltd)
By Dr M. Marshall (MQAD)
By Dr A. Gamble (J & C Ink Co. Ltd)

Session II "The use of computers and other advanced techniques in surface coatings"

2.00 p.m.–4.30 p.m.

Introduction to computer technology

Solving paint problems with computers

Introduction of microprocessors in surface coatings

The use of NMR in the characterisation of polymers used in surface coatings

Efficiency and change in metal decoration

Chairman: R. B. Tennant

By Mr G. T. Eady (Ault & Wiborg Paints Ltd)

By Mr H. J. van der Stoep (Sikkens Ltd)

By Dr A. Carrick (Kratos Ltd)

By Dr M. Marshall (MQAD)

By Dr A. Gamble (J & C Ink Co. Ltd)

Session III "Maintenance of quality and prediction of performance"

Friday 17 June 9.15 a.m.–12 noon

Quality control and standardisation in the titanium pigment industry

Prediction of performance of exterior wood coatings

Prediction of salt spray results from formulation parameters (paper presented on behalf of FSCT)

Acoustic emission – further unpublished results of the new technique for the study of paint performance during environmental exposure tests

Wood protection – the interaction between substrate and product and the influence on durability (paper presented on behalf of SLF)
By Mr K. Kleive (A/S Jotungruppen)

Chairman: Mr T. Graham

By Mr R. Blakey (BTP Toxide Ltd)

By Dr E. R. Miller (Building Research Station)

By Dr F. L. Floyd (Glidden Inc.)

By Mr T. A. Strivens (ICI Paints Ltd)

By Mr K. Kleive (A/S Jotungruppen)

Session IV "The efficient use of coatings application"

2.15 p.m.–4.15 pm

Quality control of application of coatings and technical developments which have occurred

The use of modern application equipment and its efficiency

Paint finishing in the car industry

Fire retardancy of coatings systems and application techniques

Chairman: Mr F. H. Palmer

By Mr D. Bayliss (ITI Ltd)

By Mr M. Eaton (Kremlin Spray Painting Equipment Ltd)

By Mr Quick (Talbot)

By Dr F. G. R. Zobel and Mr D. Bishop (British Railways)



York is probably the most beautifully preserved historic city in Britain and is expected to prove popular and interesting to delegates. The social programme arranged for the Conference will afford delegates an opportunity to visit places of interest including York Minster, the world famous Castle Museum and the National Railway Museum. Coach tours have been arranged to Castle Howard, Harewood House and the City of York, together with a river cruise from the hotel's landing stage.

REGISTRATION FEES

Council has fixed the registration fees payable at the same level as for the 1981 Conference: £80 for members, £25 for partners and £110 for non-members. Council has again made a concession for Retired Members and Registered Students of the Association in fixing a reduced fee of £40, the same rates as in 1981. Accommodation in the Viking Hotel is being held for the Association only until 1 April 1983, and early application is strongly advised. If desired, those attending the Conference may make their own hotel accommodation arrangements, but this must be stated on the registration form (included with this Journal).

DAILY REGISTRATION

Daily registration will be available, again at the same rates as in 1981, to members of the Association at £45 per member per day for Ordinary and Associate Members (£25 for Retired Members and Registered Students of the Association), which will include copies of the preprints, but not facilities for attending the social functions.

Those wishing to attend the Conference should complete the registration form included with this Journal and send it, together with the appropriate fee(s) as well as a REMITTANCE TO COVER ALL THE ITEMS in which they wish to participate (but NOT the cost of hotel accommodation), to the Director & Secretary, OCCA, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, UK.

ACCOMMODATION

Delegates attending the Conference will be accommodated in the Viking Hotel; the daily rates including VAT being as follows: single room £48.30, twin bedded room £40.80. For children under the age of 14 sharing their parents' room there is no charge for the extra bed; children occupying their own room will be charged at £12.

GENERAL

At the beginning of June 1983, members and non-members who have registered for the Conference will receive preprints of the papers to be given, together with a Conference folder, which will contain a Conference badge, a descriptive leaflet of York, street map, details of allocation of rooms, etc.

ONLY BRIEF DETAILS ARE SHOWN ABOVE (SEE THE JANUARY ISSUE OF JOCCA FOR SUMMARIES OF PAPERS AND BIOGRAPHIES OF AUTHORS) AND A REGISTRATION FORM ENCLOSED. ANYONE WHO WOULD LIKE A COPY OF THE CONFERENCE BROCHURE CONTAINING FULL DETAILS SHOULD CONTACT: THE DIRECTOR & SECRETARY, OCCA, PRIORY HOUSE, 967 HARROW ROAD, WEMBLEY, MIDDLESEX HA0 2SF, UNITED KINGDOM.

CLASSIFIED ADVERTISEMENTS

SITUATIONS WANTED

**Permanent or Temporary
Employment Sought**

Due to an early retirement, member with 27 years experience of pigment evaluation is available for temporary or permanent employment.

Replies in confidence to Box No. 527

Technical Manager

Member with 16 years experience in the decorative paints industry seeks challenging new position, preferably in the North West.

Experience includes R & D, Technical Service, Technical Marketing, and Works Production Control. *Reply in confidence to* **Box No. 530**

Position of Responsibility Sought

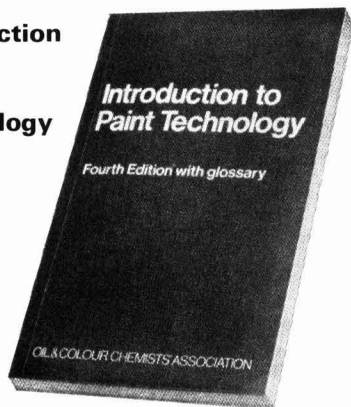
Industrial chemist (MSc, CChem, MRSC, ATSC) and member seeks position of responsibility with supplier or user of raw materials of Paint, Surface Coatings, Ink and Allied Industries.

Reply in confidence to **Box No. 528**

Overseas Managerial Position Sought

Paint chemist (ATSC) with 25 years experience in formulation, production etc., seeks overseas managerial position.

Please reply in confidence to **Box No. 529**

**Introduction
to
Paint
Technology**

The Introduction to Paint Technology, of which over 25,000 copies have been sold, forms an excellent introduction to the whole field of surface coatings and related technologies. The fourth edition contains a glossary of terms together with explanations of their derivations.

Copies of this book are available at £5.00 each (prepayment only), post free by surface mail, from: OCCA, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, UK.

★ ★ ★ ★

OCCA Exhibition 1984

**is now being planned and details will be announced in
this Journal as soon as possible.**

**Organisations wishing to receive a copy of the
Invitation to Exhibit on publication should contact
(letter or telex) the Director & Secretary who will also
be interested to learn of the proposals by exhibitors
for lectures of the type successfully introduced at the
1982 Exhibition. The number of lectures which can be
given is naturally limited so that it is in the interest of
any organisation wishing to present a lecture to
forward this information as soon as possible.**



Reprinted from the brochure in the December issue of JOCCA
 "THE EFFICIENT USE OF SURFACE COATINGS"
 For details of sessions and papers see January JOCCA pages 28 - 36

TO BE RETURNED TO THE DIRECTOR & SECRETARY NOT LATER THAN 1st APRIL, 1983

YORK CONFERENCE—REGISTRATION FORM

To: R. H. HAMBLIN, M.A., F.C.I.S.,
 Director & Secretary,
 Oil & Colour Chemists' Association,
 Priory House,
 967 Harrow Road,
 Wembley, Middlesex, HA0 2SF.

FOR OFFICE USE ONLY

Serial No.

Date rec'd

Rec. No.

DATE

NAME FORENAMES

(BLOCK CAPITALS, PLEASE)

ADDRESS

.....

SECTION CLASSIFICATION OF MEMBERSHIP

1. ACCOMMODATION. Please reserve the following accommodation for myself and:—†

.....

(Please state forenames for badges)

Type of Room i.e. Single/Twin	Price per day

†If any of your party are children, please state ages and if sharing room with parents.

Would you kindly state whether you are willing to share a twin-bedded room with another member

(If 'Yes' please suggest the name of the person with whom you are willing to share)

Date of arrival: Date of departure:

N.B. Normal date of arrival 15th June and for departure 18th June.

If you would prefer to make your own arrangements for accommodation, please indicate accordingly.

2. PARKING. Make, c.c. and registration number of car

PLEASE COMPLETE THIS SIDE AND THE REVERSE SIDE BEFORE SENDING IN YOUR FORM

3. **ASSOCIATION DINNER AND DANCE.** At the Association Dinner on Friday, 17th June, I wish to be seated near: (Block capitals please)
(N.B. Tables are normally arranged to seat 10 persons but please see also page 6).

4. **GOLF TOURNAMENT.** If you wish to participate in the Golf Tournament please insert the word 'GOLF' in this box.

Green fees to be paid to the Club direct, see page 5. I shall/shall not* require refreshments.

5. **REGISTRATION FEES.** I enclose registration fee(s) of
(Members £80 plus £12 VAT = £92.00; Non-Members £110 plus £16.50 VAT = £126.50; Wives £25 plus £3.75 VAT = £28.75; Registered Students and Retired Members £40 plus £6.00 VAT = £46.00; Daily rate for Ordinary and Associate Members £45 plus £6.75 VAT = £51.75; Registered Students and Retired Members £25 plus £3.75 VAT = £28.75 PER DAY.

£ | p

Daily Registration. Please quote date applicable
Please enter the word COACH in this box if you wish to be notified of any coach party organised by your Section.

Note: The rate of VAT quoted are those in force November 1982. If there is any change in rate before your application is sent, please adjust figures accordingly.

6. **COACH TOURS.** Please reserve me seats for the Coach Tour to Harewood House @ £6.00 each inclusive of admission charge and gratuities on Thursday, 16th June.

Please reserve for me seats for the York City Tour @ £3.50 each inclusive of entrance fees, gratuities and refreshments in the medieval guildhall on Friday, 17th June.

Please reserve for me seats for the Coach Tour to Castle Howard @ £5.00 each inclusive of admission charge and gratuities on Friday, 17th June.

7. **RIVER TRIP.** Please reserve for me places for the River Trip @ £3.00 per person on Thursday, 16th June.

TOTAL REMITTANCE ENCLOSED

***PLEASE DELETE WHERE INAPPLICABLE TO ENSURE CLARITY**

8. **THEATRE.** The programmes for the theatre were not finalised when this brochure was printed (November 1982) but if you would like to be sent details of the theatre programme for the evening of Thursday, 16th June, when this is available, please put 'Theatre' in this box.

Note: If you wish to be informed of theatre programme for night of Wednesday, 15th June also, please tick this box.

	15th JUNE
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9. **NATIONAL RAILWAY MUSEUM.** If interested in visiting the museum on Thursday, 16th June, please insert the word 'Railway' in this box.

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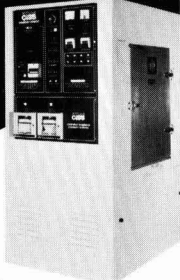
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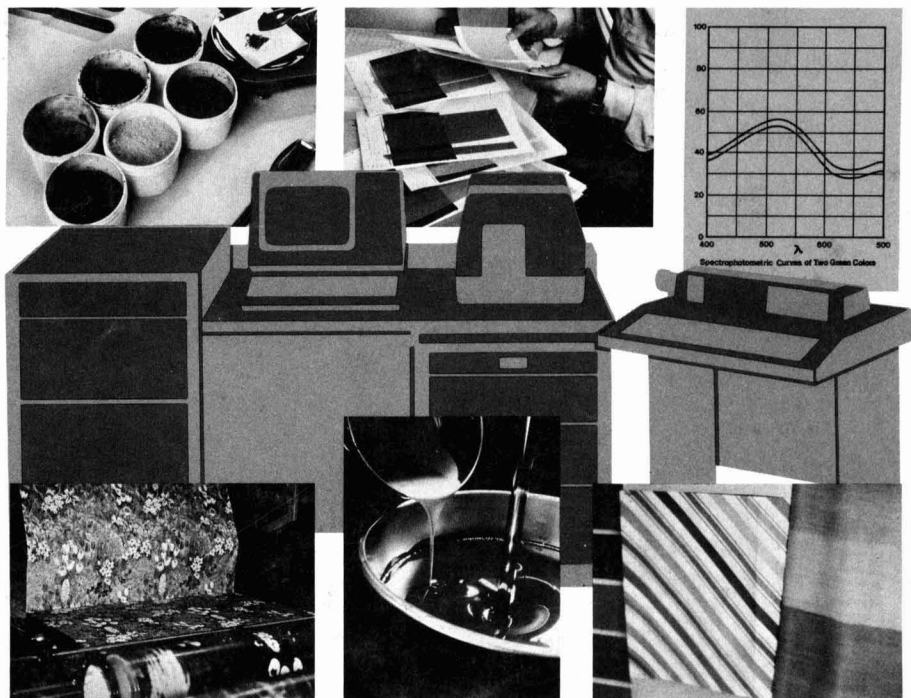
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