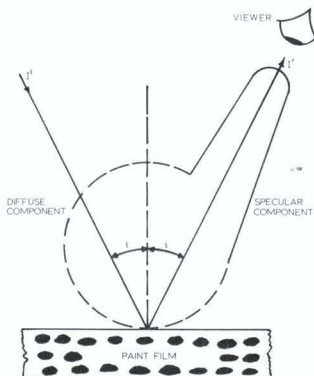
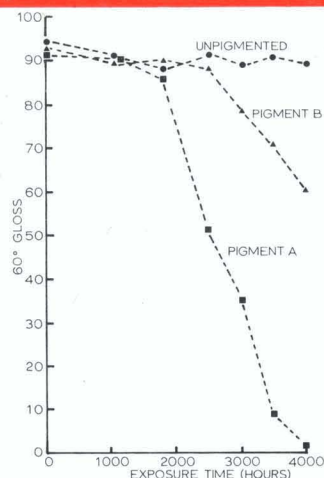




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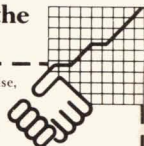
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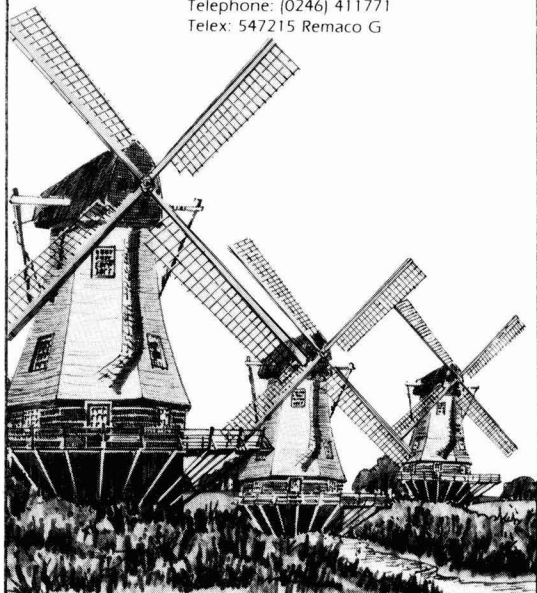


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Influence of titanium dioxide pigment on the surface roughness of organic coatings

L. A. Simpson

Toxide UK Ltd, Central Laboratories, Portrack Lane, Stockton-on-Tees, Cleveland, England

Synopsis

Organic coatings are often pigmented with titanium dioxide in order to produce opacity. However, the presence of titanium dioxide at the surface of the coating can affect its micro-roughness, which will influence properties such as specular gloss and metal marking. In addition, titanium dioxide pigment is photoactive, which means that during weathering, it will contribute towards the breakdown of the organic binder, and therefore the surface roughness of the coating will increase with exposure time.

This paper illustrates that in order to minimise the effect of titanium dioxide on the surface roughness of a coating, it is important to ensure that the correct grade of pigment is used, and that maximum dispersion is obtained.

1 Introduction

Titanium dioxide pigment has a higher refractive index than any other white inorganic pigment, and therefore it is widely used for producing opacity in white and tinted paints, printing inks, plastics, paper, and other products. Apart from its effect on opacity, titanium dioxide pigment can also influence the surface roughness of the product, which in turn can affect certain optical/decorative properties such as gloss¹, gloss retention during weathering², and metal marking³. In order to reduce the effect of pigment on surface roughness, it is important to ensure that the state of pigment dispersion is good, and that the photoactivity of the pigment is low since this will minimise the topographical changes that occur during weathering.

Thus pigment selection is important since depending on the type of titanium dioxide pigment used, differences in dispersion and durability will exist. The purpose of this paper is to illustrate the extent to which titanium dioxide can affect the above mentioned properties with particular reference to certain organic coatings.

2 Gloss and surface roughness

Specular gloss, which is a measure of brightness of a reflected image, is a function of the refractive index of the reflecting surface, the angle of incident light, and the surface roughness (see Figure 1 where I^i = intensity of incident beam, and I^r = intensity of reflected/specular beam of light). If the reflecting surface/coating is optically smooth, then the intensity of the reflected image, for a given angle of incident light, can be predicted using the following modified Fresnel equation:

$$\frac{I^r}{I^i} = \frac{1}{2} \left\{ \left(\frac{\cos i - \sqrt{n^2 - \sin^2 i}}{\cos i + \sqrt{n^2 - \sin^2 i}} \right)^2 + \left(\frac{n^2 \cos i - \sqrt{n^2 - \sin^2 i}}{n^2 \cos i + \sqrt{n^2 - \sin^2 i}} \right)^2 \right\} \quad (1)$$

where i = angle of incidence

and n = refractive index of the coating.

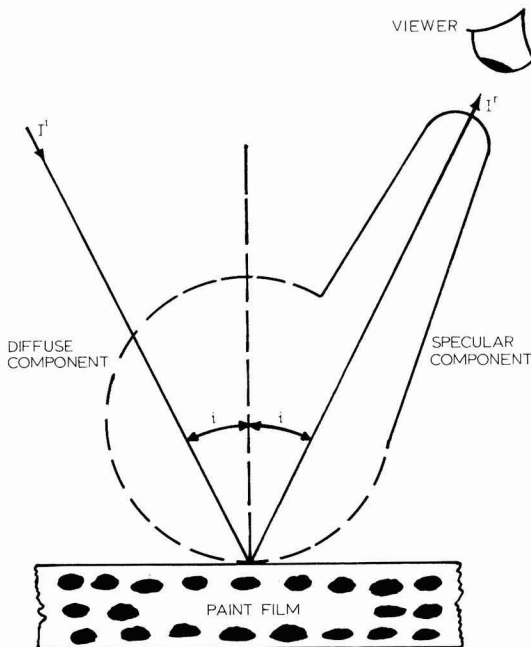


Figure 1. Distribution of light from a white glossy film. Angle of incidence i .

It is evident from this equation that for a given angle of incidence, I^r/I^i increases with increasing refractive index, and similarly, for a given refractive index, I^r/I^i increases with increasing angle of incidence. In essence, specular gloss involves measuring I^r/I^i for the coating under study (at a fixed angle of incidence) and comparing the value with that of a smooth black tile of known refractive index. The angle of illumination is generally one of three angles (20° , 60° or 85°) depending on the gloss of the coating. Thus specular gloss (G) is defined as follows:

$$G = \frac{(I^r/I^i)_{\text{Coat}}}{(I^r/I^i)_{\text{Tile}}} \times 100 = \frac{I^r_{\text{Coat}}}{I^r_{\text{Tile}}} \times 100 \quad (2)$$

(where Coat = coating).

In practice, only two measurements (i.e. I^r_{Coat} and I^r_{Tile}) are required in order to calculate G . Further details regarding the measurement of specular gloss are given in the British Standard specification BS3900: Part D5: 1980, the American ASTM D523 and International Standard ISO 2813-1978.

The specular gloss of an optically smooth coating can therefore be calculated if its refractive index is known.

This paper was presented at the Macro Group/OCCA joint symposium, held in London on 5 December, 1984.

However, if the coating exhibits surface roughness then the specularly reflected light will decrease in intensity. The surface roughness of a coating can be considered to consist of two fractions, namely macro-roughness and micro-roughness. Macro-roughness is the result of surface defects of the order of 1 μm or more in height, whereas micro-roughness is attributable to defects of the order of the wavelength of light and less (i.e. less than 0.6 μm).

If a paint film exhibits only macro-roughness, as shown in Figure 2, the incident beam sees a surface which varies with regard to angle of incidence and thus, the reflected light diverges. Consequently, the specular gloss will be lower than expected since some of the light which should have been reflected in the mirror-image direction, is in fact distributed about the peak reflectance value. Surface defects which cause this type of image distortion are large and are often related to the rheological behaviour of the coating (e.g. poor flow and levelling of a paint such that brush/roller marks are retained in the dry film). Alternatively, defects in the substrate such as poor sand blasting of a metal surface could also affect the macro-roughness of the coating.

In contrast to macro-roughness, micro-roughness is the result of very small surface defects, which are comparable in size with titanium dioxide particles which are of the order of 0.2 μm in diameter. In this case, the decrease in intensity of the specularly reflected light is due to diffraction which occurs at the surface of the coating. Also, because these surface defects can be pigmentary, the incident light will be scattered at the surface and this will result in image distortion on a very fine scale. The effect of micro-roughness on gloss was derived by Rayleigh⁴ who gave some indication of the tolerable error in the geometrical accuracy of a plane reflecting surface. If one considers a simple step-function defect of height D , illuminated at an angle of incidence i , by light of a wavelength λ , the tolerable value for D given by Rayleigh was:

$$D = \frac{\lambda}{8 \cos i} \quad (3)$$

If, for example, $\lambda = 0.5 \mu\text{m}$, and $i = 20^\circ$, it follows from Equation 3 that the tolerable defect is about 0.07 μm .

Although the above equation indicates the size of surface defect that affects gloss for a given angle of incidence, it does not show the extent to which gloss is affected. A theory which has been successfully used by the author, and which is based on diffraction, was established by Bennett and Porteus⁵ and further developed by Toporetz⁶. The expression developed is as follows:

$$G = G_T \exp - \left(\frac{4\pi\sigma \cos i}{\lambda} \right)^2 \quad (4)$$

where G = specular gloss

G_T = maximum possible theoretical gloss, which is calculated using the Fresnel equation

i = angle of incidence

λ = wavelength of light used

and σ = root mean square roughness, defined as the root mean square deviation of the surface from the mean surface level.

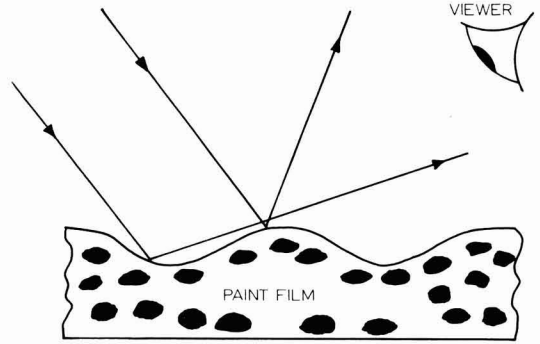


Figure 2. Light reflected from a surface exhibiting macro-roughness.

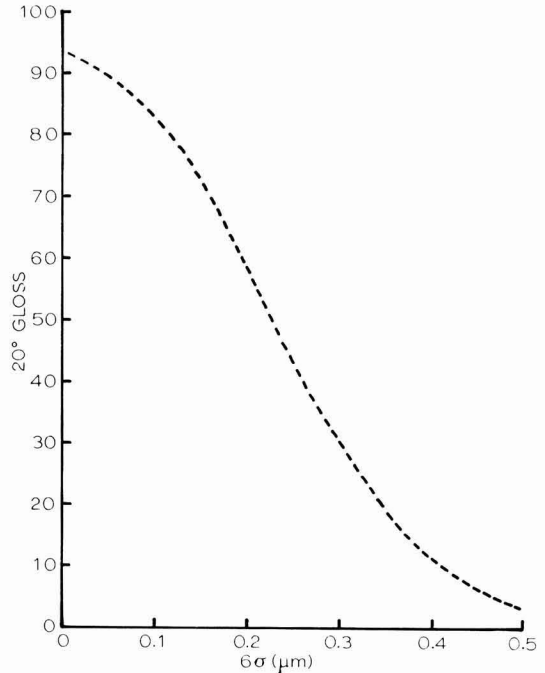


Figure 3. Theoretical plot, based on the Bennett and Porteus⁵ model of gloss versus maximum surface roughness (6σ).

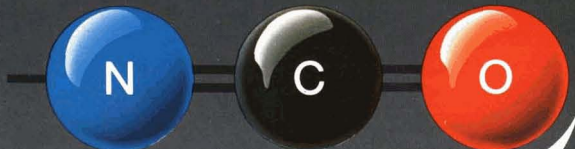
Since Equation 4 is based on a model which assumes that the distribution of heights of surface irregularities is Gaussian about the mean, it follows that 99.7 per cent of the surface defects are less than 6σ in height.

In Figure 3, G is plotted against 6σ using Equation 4, where $i = 20^\circ$, $\lambda = 0.55 \mu\text{m}$ and $n = 1.50$ (typical value for a pigmented paint film). It can be seen from this plot that surface defects less than 0.1 μm in height have little effect on gloss (cf Equation 3) whereas for increasing values of 6σ in excess of 0.1 μm there is a deterioration in gloss until the maximum surface roughness is about 0.4 μm . It also follows from Figure 3, that only small changes in surface defects which are in excess of 0.1 μm in height need occur before gloss is markedly affected.

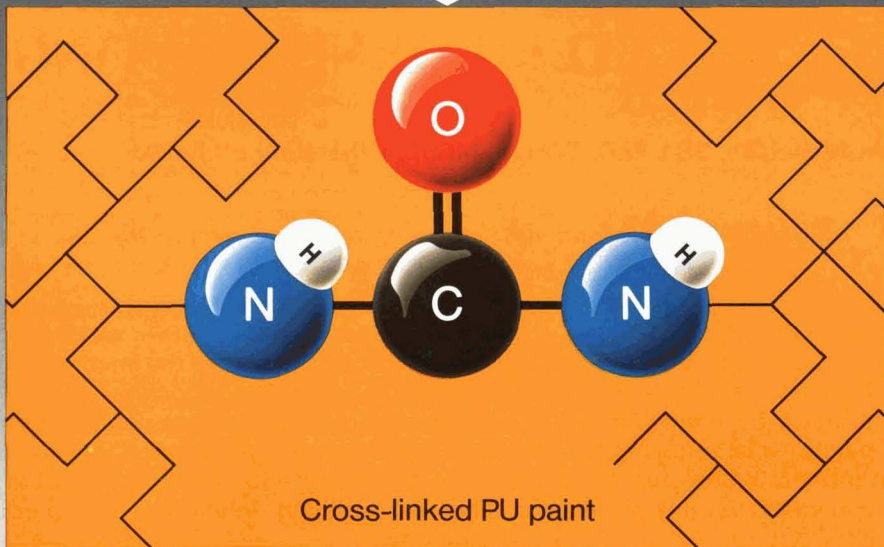
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In order to measure the surface roughness of a coating, Equation 4 can therefore be used if the gloss and refractive index of the coating, the wavelength of incident light and angle of incidence are known. To obtain these measurements, a goniophotometer¹, which enables one to measure the angular distribution of reflected monochromatic light for different angles of incidence, is required. In addition the refractive index of the coating can be determined⁷ using the Brewster angle technique. However, if a goniophotometer is not available, then surface roughness can be quantified using a mechanical/electrical profile meter. This type of instrument consists of a fine stylus (approximately 2 μm in diameter) which traverses the surface under examination. The mechanical movements of the stylus are converted into electrical impulses to produce either a profile of the surface, or a meter reading which gives a quantitative measure of the surface roughness. One parameter which is used to give an indication of the surface roughness is centre-line average (CLA) which is defined as the arithmetical average value of the departure of the surface profile above and below a reference line; a perfectly smooth surface has a CLA value of 0. Further details about this type of measurement are given in the British Standard specification BS1134: Parts 1 and 2: 1972. Although the quantitative measurement of surface roughness using a mechanical/electrical profile meter is quicker than the goniophotometer method, care should be taken when using the former technique, since with certain organic coatings penetration of the surface by the stylus is likely to occur. As a result, the CLA value is lower than perhaps expected.

3 Effect of pigmentation on gloss

Since the size of surface defect which has a detrimental effect on specular gloss is comparable with that of titanium dioxide pigment particles, it follows that in a coating where pigment is present at, or very close to the surface, gloss may be significantly affected. Thus, depending on the coating, the grade of pigment and its concentration are important factors.

3.1 Pigment loading

The primary function of incorporating titanium dioxide into, for example, a paint is to produce opacity. Unfortunately, increasing the amount of pigment to produce an increase in opacity causes the gloss to fall. This decrease is particularly noticeable in emulsion paints where pigment is present at the surface, unlike that of an alkyd or polyurethane paint where a clear layer may exist (see Murley and Smith⁸). However, increasing the pigment volume concentration (pvc) in a paint causes the refractive index of the film to increase, which increases the potential gloss of the paint film. This effect is illustrated in Figure 4 where the measured 20° gloss of an emulsion paint based on 100 per cent acrylic copolymer and titanium dioxide pigment is plotted against pvc. Figure 4 also gives the theoretical gloss of each film determined from measured refractive index values. It is evident that the theoretical gloss (based on the assumption that the film is optically smooth) increases with increasing pvc although the actual gloss decreases. This is because as the pvc increases the presence of titanium dioxide at the surface causes the surface roughness to increase, which has a greater effect on gloss than the increase in refractive index. The effect of increasing pvc on surface roughness and 20° gloss for a similar series of paints is shown in Figure 5; the CLA value is used to give a measure of surface roughness. It can be

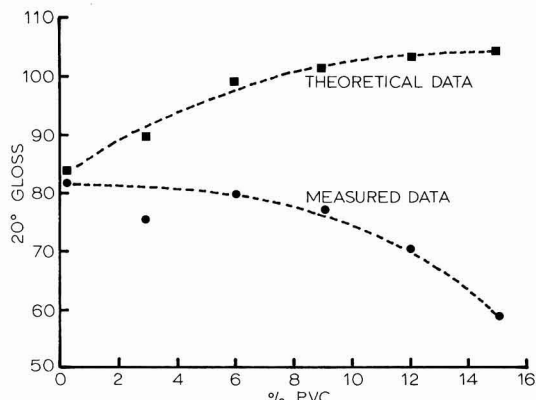


Figure 4. Comparison of measured and theoretical 20° gloss values as a function of pvc for an emulsion paint.

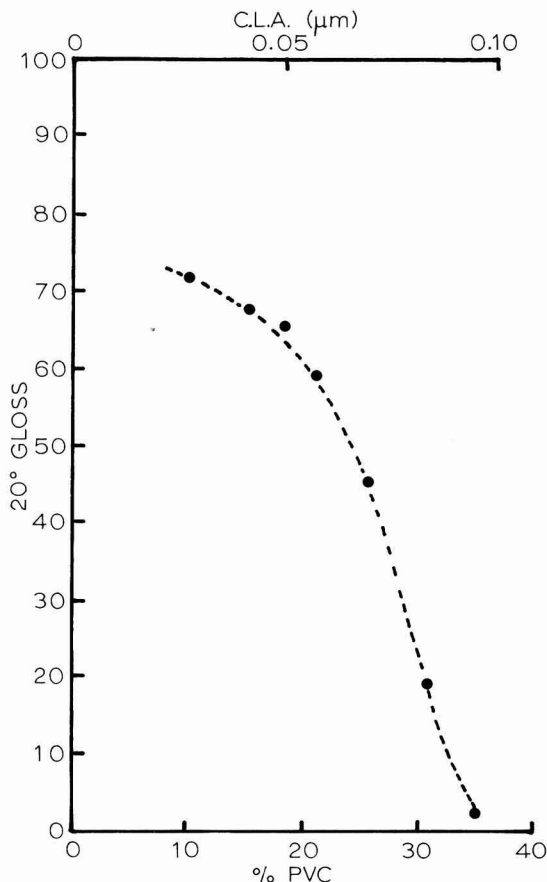


Figure 5. Effect of increasing pvc on gloss and surface roughness (CLA) for an emulsion paint.

seen from Figure 5 that the relationship between gloss and surface roughness is similar to that given in Figure 3, and that at a pvc of about 15 to 20 per cent, the gloss is still relatively high. Since a compromise between gloss, opacity and raw material cost is often required, then if high gloss is needed, it is evident from Figure 5 that the emulsion paint should have a maximum pvc of 20 per cent.

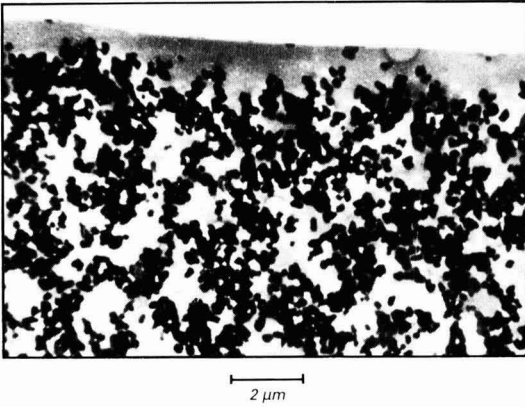


Figure 6. Electron micrograph of a section of an air-drying polyurethane paint film, illustrating a clear surface layer.

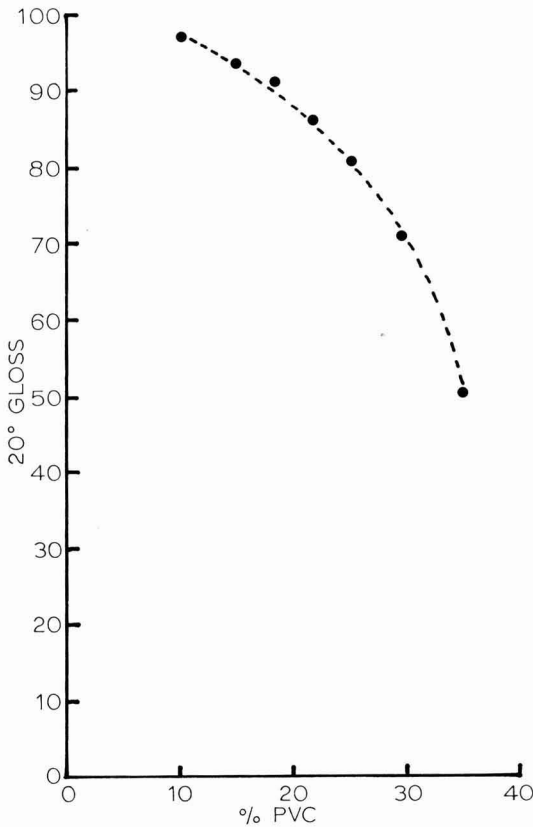


Figure 7. Effect of pvc on gloss for an air-drying alkyd paint.

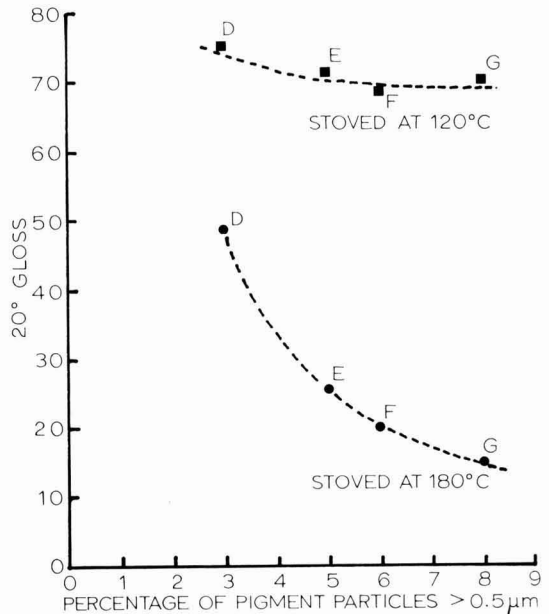
For paints which exhibit a clear surface layer such as the one illustrated in Figure 6, the effect of increasing pvc on surface roughness and gloss is not so pronounced. This effect is shown in Figure 7, where 20° gloss is plotted against pvc for an air-drying alkyd paint which has a clear layer thickness of about 0.2 μm. It is evident from this plot that at a pvc as high as 30 per cent relatively high gloss is sustained.

3.2 Pigment dispersion

Since titanium dioxide affects the surface roughness of a paint it is important to ensure that it is as well dispersed as possible in the dry film so that surface irregularities are kept to a minimum. The process of dispersing pigment in a paint can be considered to consist of the following three stages: 1. wetting; 2. disruption; and 3. stabilisation of the pigment, and all three aspects are important with regard to affecting gloss, although stage 3 is probably the most important. However to achieve an acceptable degree of dispersion, the paint formulator must consider all three stages, and with this in mind many grades of titanium dioxide are coated⁹ with inorganic oxides such as alumina and silica, and treated with organic polyols and amines in order to improve the dispersibility of the pigment. (NB The other reason for coating a pigment is to improve its durability, and this will be discussed in some detail in the next section).

To illustrate the importance of pigment selection/dispersion with regard to gloss development, four different coated rutile grades of titanium dioxide pigment were incorporated into a thermosetting alkyd/melamine formaldehyde paint. Pigment D was a super-refined grade of titanium dioxide; E and F were refined grades; and G was an experimental grade of titanium dioxide. The paints were formulated such that the pvc was 20 per cent, and the resulting films were stoved for (a) 30 minutes at 120°C (standard stoving schedule) and (b) 60 minutes at 180°C. The 20° gloss of all films was measured, and an indication of the degree of dispersion of each pigment in the wet paint was obtained by measuring the percentage of oversize pigment particles (greater than 0.5 μm) using X-ray sedimentation. In Figure 8, gloss is plotted against oversize, and it is clear that at the lower stoving temperature, the grade of pigment selected has little effect on gloss. By contrast, at the higher temperature, gloss is significantly

Figure 8. Influence of stoving temperature and pigment type on gloss for an alkyd/melamine formaldehyde paint.



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affected by the grade of pigment used, and it decreases with increasing oversize. During stoving there is solvent evaporation and polymer cross-linking, which result in film shrinkage. Increasing the stoving temperature of such a paint system not only serves to increase the degree of cross-linking but also produces an increase in film shrinkage. Thus, in the case of the films which were stoved at 180°C, the titanium dioxide pigment which is close to the surface of the coating is having a greater effect on surface roughness compared with the lower stoving temperature, due to greater film shrinkage. It therefore follows that the importance of pigment dispersion increases with increasing stoving temperature.

4 Gloss retention during weathering

When pigmented paint films are subjected to weathering they undergo oxidative destruction due to incident ultraviolet radiation in the presence of oxygen and water. This results in a progressive loss of gloss, mass loss and chalking. Two degradation mechanisms are responsible for the breakdown of the binder in a paint system which exhibits the above phenomena, one of which is direct photochemical degradation by ultraviolet radiation, and the other is attributable to the photoactivity of titanium dioxide pigment. With both mechanisms, pigment plays an important role although the relative importance of each mechanism is primarily determined by the type of binder used. Thus, the interaction between pigment and binder significantly affects the durability of a paint film.

4.1 Photochemical degradation

Photochemical degradation of a binder is primarily an oxidation process whereby ultraviolet radiation provides the energy and oxygen is taken from the atmosphere.

In order for oxidation to occur, molecular bonds in the binder have to be broken and this is achieved by quanta or photons colliding with electrons associated with the bonds. The greater the energy of a photon, the greater the effect. Obviously, the energy of a photon required to break a molecular bond will depend on the bond, so different binders will exhibit different rates of breakdown.

In Figure 9, a simple model of a paint film containing titanium dioxide pigment, illustrates the changes that occur at the surface when only photochemical degradation occurs. Assuming pigment plays an inert role, binder is slowly removed during weathering which results in the pigment particles protruding above the surface. Obviously during this breakdown, the state of pigment dispersion will affect the overall surface roughness and gloss. If erosion continues, then eventually the pigment particles will be released at the surface, resulting in a phenomenon which is called chalking.

4.2 Photocatalytic degradation

Titanium dioxide is a strong absorber of ultraviolet radiation (see Figure 10 for a typical reflectance profile) and therefore to some extent it can protect the binder. However, titanium dioxide is photoactive and as a result it can catalyse breakdown of the binder.

When rutile titanium dioxide is irradiated, provided that the wavelength of radiation is less than 405 nm (i.e. quantum energy equal to or in excess of 294.3 kJ/mole)

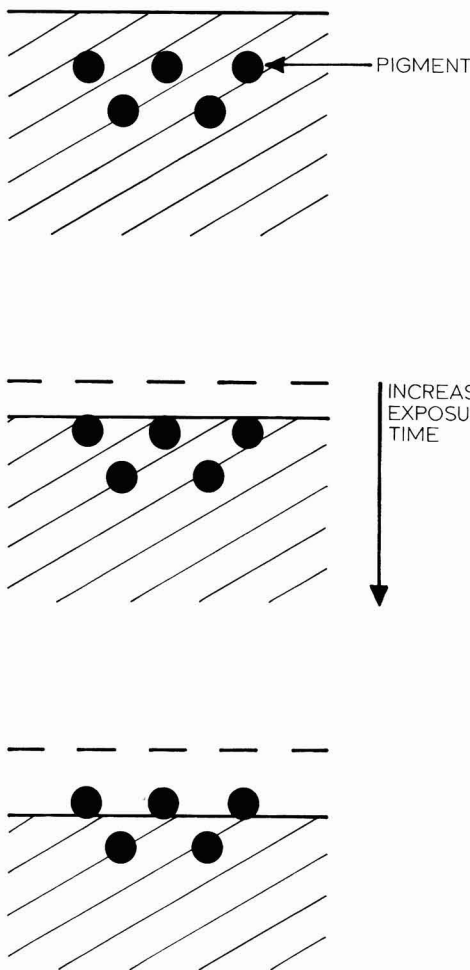
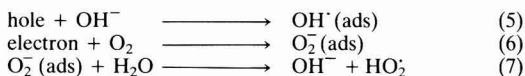


Figure 9. Schematic representation of photochemical degradation.

electrons are excited from the valence band to the conduction band leaving positive holes in the valence band. Both the excited electrons and holes are free to move within the crystal lattice of titanium dioxide where they can recombine. However, some electrons and holes do reach the surface of the titanium dioxide crystal where they are capable of initiating chemical reactions in the surrounding medium resulting in degradation. Thus, on reaching the crystal surface, positive holes react with surface hydroxyl groups to form adsorbed hydroxyl radicals, whilst electrons react with adsorbed oxygen to form the O_2^- ion which then attacks a water molecule to form the HO_2 radical:



Either the hydroxy OH^\cdot , or perhydroxy HO_2^\cdot radical will initiate breakdown of the binder. It is evident from the above reactions that both oxygen and moisture are essential for photocatalytic degradation to occur.

To reduce the degree of photocatalytic degradation, pigment manufacturers dope the titanium dioxide crystal

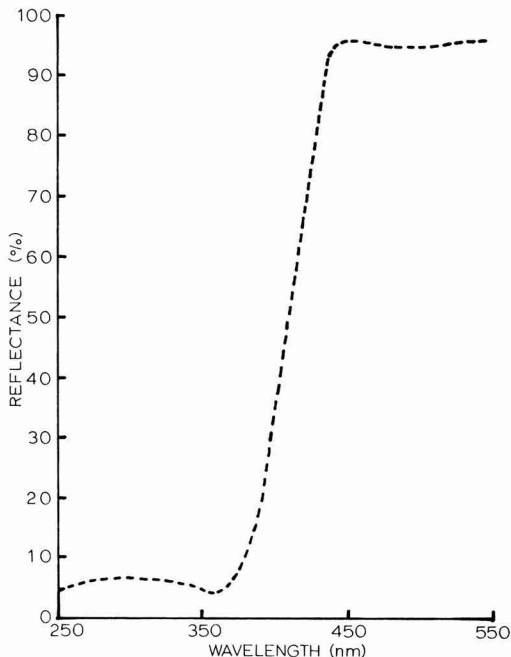
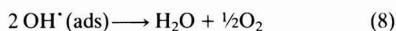


Figure 10. Reflectance profile for rutile titanium dioxide.

with transition metals such as zinc or aluminium which act as electron and hole recombination centres; in addition the crystal is coated with oxides such as alumina, zirconia, and silica which help destroy the hydroxy radical by providing an 'active' area for recombination. Thus:



It follows that for a real system, the model given in Figure 9 is oversimplified since the ultraviolet absorption/photoactive characteristics of the pigment have not been taken into account. Since photocatalytic degradation only occurs in the vicinity of the pigment particles which are absorbing ultraviolet radiation (i.e. those which are close to the paint film surface) this will result in a characteristic hole formation which was initially reported by Kaempf et al¹⁰. A schematic diagram of this degradation process together with that of photochemical breakdown is given in Figure 11. Apart from its effect on surface roughness/gloss retention, photocatalytic degradation will result in the loss of adhesion between pigment particles and binder, and therefore chalking will also be prevalent during the early stages of weathering.

4.3 Influence of pigment type on gloss retention

It is evident from Figure 11 that the degree of hole formation, its distribution and the state of pigment dispersion will all play a part in affecting the surface roughness of a coating during weathering. In addition, the type of binder used will also determine the extent to which the two breakdown processes operate. For example, if the durability of the binder is high, then by definition, photochemical breakdown will be low, and therefore photocatalytic degradation will dominate. Conversely, if the binder is non-durable, then photochemical degradation

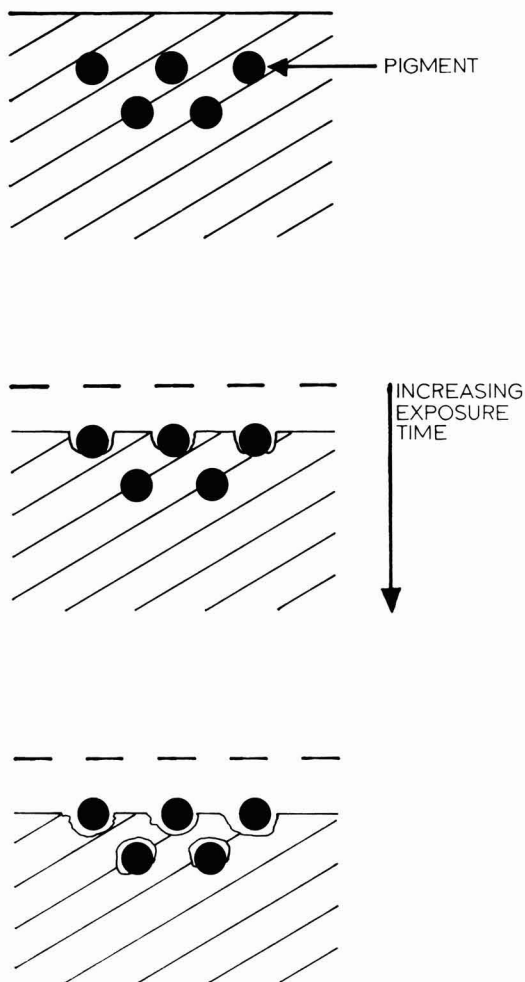


Figure 11. Schematic representation of photochemical and photocatalytic degradation.

will dominate, although photocatalytic breakdown will also occur.

In order to illustrate the significance of pigment selection on gloss retention, two coated rutile grades of titanium dioxide (i.e. pigment A rated as durable, and pigment B rated as superdurable) were incorporated into a durable polyester/isocyanate resin system such that the pvc was 15 per cent. In addition, an unpigmented paint was prepared. All three paints were weathered using an enclosed carbon arc artificial weathering machine and 60° gloss was measured at periodic intervals. In Figure 12, gloss is plotted against exposure time and it is evident that the unpigmented paint is exhibiting very good gloss retention compared with the two pigmented paints. It can also be seen that the gloss retention of the paint containing pigment B (superdurable grade) is superior to that shown by the paint based on pigment A. Obviously, in the case of the unpigmented paint, there is no hole formation during weathering and therefore the photochemical breakdown, which is only slight is having minimal effect on surface roughness. In contrast, the difference between the two

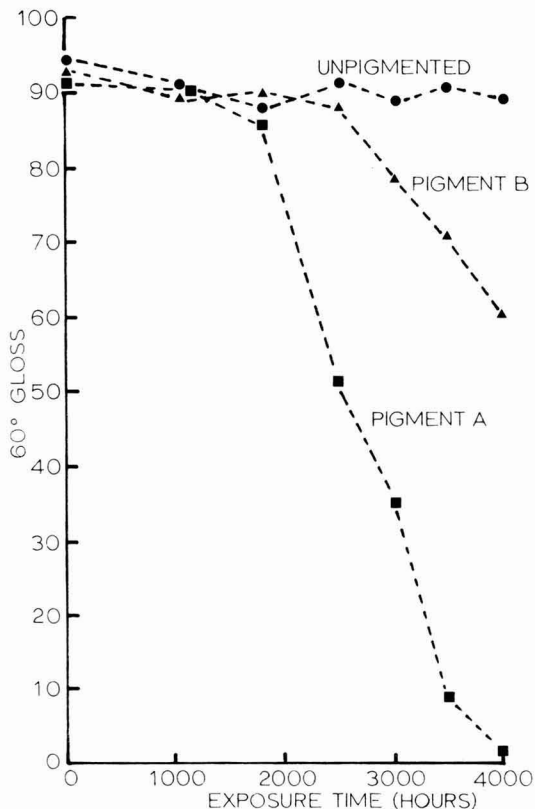


Figure 12. Gloss behaviour for three polyester/isocyanate paints, as a function of exposure time.

pigmented paints is mainly attributable to differences in the degree of hole formation, which as mentioned above is directly related to the photoactivity of the pigments. Further evidence to support these findings is given in Figure 13, where scanning electron micrographs of the surfaces of all three paints after 3,500 hours weathering are given. It is clearly evident that for the unpigmented paint, the surface is featureless and relatively smooth, whereas with the paint containing pigment A there is a significant amount of localised breakdown, resulting in hole formation, and in the case of pigment B, there is very little hole formation.

Since a durable resin system was selected above, then photocatalytic breakdown will dominate and therefore the photoactivity of the pigment will play a major role in affecting the surface roughness of a coating during weathering. However, it has been shown² that in the case of a non-durable binder, pigment primarily protects the resin, and therefore the state of pigment dispersion is the major factor with regard to gloss retention, but nevertheless, the photoactivity of the pigment will play a part in influencing surface roughness/gloss retention during weathering.

5 Metal marking

The ability of an organic coating to withstand streaking or marking when a metal object is dragged across the surface of the coating is referred to as metal marking or ring resistance. In essence, metal marking is the result of hard

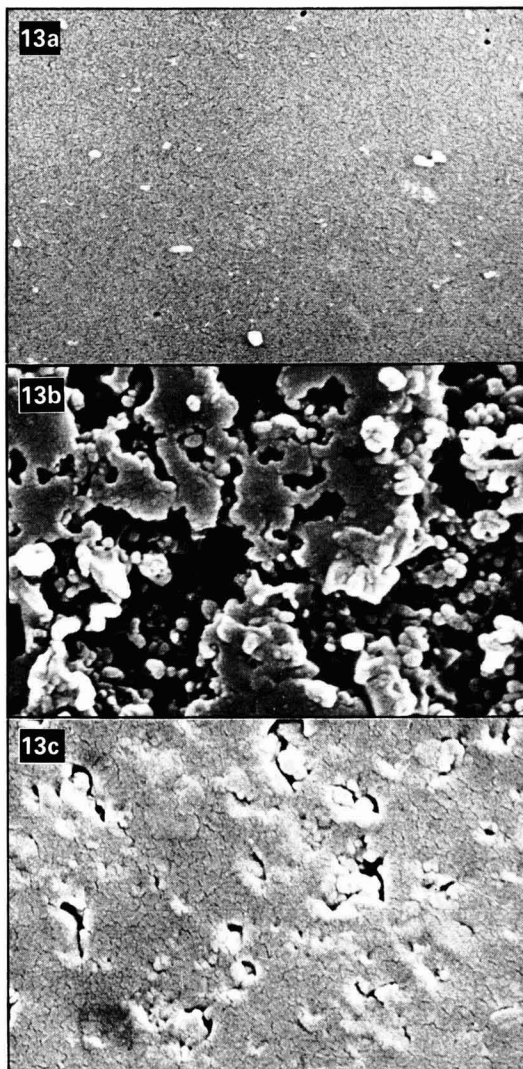


Figure 13. Scanning electron micrographs of (a) unpigmented (b) pigmented—grade A and (c) pigmented—grade B, polyester/isocyanate paints, after 3,500 hours weathering in a twin carbon arc machine.

asperities such as titanium dioxide particles situated at the surface of a coating, which indent, groove and then cut material out of the metal object. The decorative appearance of the article is affected because a small amount of the metal has been transferred to the coating. Examples of potential metal marking are: rubbing one's belt buckle or ring against a car; a child sliding a metal toy along a wall; or a housewife dragging a metal wash basket from the top of a washing machine.

Since the organic coating is the abrasive element which is responsible for metal marking, there are several formulation variables which could contribute to this abrasivity, one of which is titanium dioxide pigment since it is relatively hard (i.e. Mohs hardness of 5-5.5 for anatase and 6-6.5 for rutile).

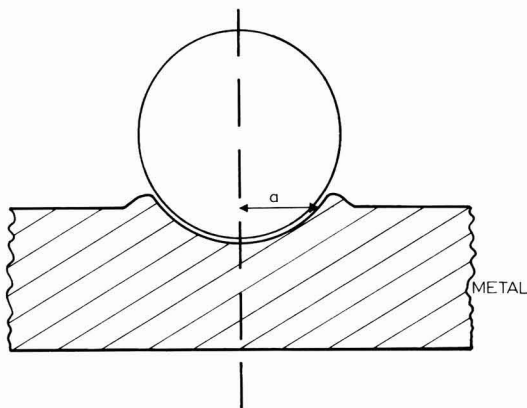


Figure 14. Indentation of a metal surface by a sphere.

When two surfaces such as a metal object and an organic coating are brought together they only touch at the tips of the highest asperities. Thus, the real area of contact, which is the important factor from a wear point of view, is only a small part of the apparent area of contact. Since it is difficult to assess the distribution of real areas of contact between an organic coating and a metal object, one must consider the simple case of a spherical particle (representing a titanium dioxide crystal protruding above the surface of the organic binder) indenting a smooth metal surface (Figure 14). An indication of the degree of penetration can be obtained using the following Hertz¹¹ equation:

$$a = \left(\frac{4KR}{3E} P \right)^{1/3} \quad (9)$$

where a = radius of the circular area of contact
 R = radius of the titanium dioxide crystal
 P = load applied to the titanium dioxide crystal
 E = Young's modulus of the metal
 and K = constant depending on the Poisson ratios of the titanium dioxide and metal surfaces

Archard¹² has shown that when an indenting particle is subjected to a dynamic force, the amount of metal removed (δV) at any one point of contact is:

$$\delta V = \gamma a^3 \quad (10)$$

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

$$W \propto \sum \frac{\delta V}{2a} \quad (11)$$

where the summation is carried out for all the individual areas constituting the total area of contact. Thus, using Equations 10 and 11 it follows that:

$$W \propto \sum \frac{\gamma a^2}{2} \quad (12)$$

Equation 12 therefore shows that the wear rate of metal, which is related to the degree of metal marking, is proportional to the square of the area of contact.

Let us now assume that at the surface of a coating, the titanium dioxide particles are well dispersed, and each one

is bearing a load, P . If the pigment particles become flocculated, then the number of points of contact with the metal surface is likely to be reduced, which means that for a given total load, the load applied to each of the flocculates will increase. In addition, the mean radius of the penetrating titanium dioxide particles will have increased. Thus, it follows from Equations 9 and 12 that an increase in either P or R will produce an increase in metal marking. Obviously, an increase in R will result in an increase in surface roughness.

5.1 Effect of pigment dispersion on metal marking

In order for titanium dioxide to have a significant effect on metal marking it must be either very close to or at the surface of the coating. If, for example, the paint system under study was similar to the polyurethane paint which is illustrated in Figure 6, then the clear resin layer at the surface would prevent metal marking. Thus, to show the effect of pigment dispersion/surface roughness on metal marking, an alkyd/urea formaldehyde based paint was selected, a typical cross-section of which is given in Figure 15. Three coated rutile grades of titanium dioxide (pigments X, Y and Z) which were known to exhibit differences in dispersion in this paint system were chosen, and the paints produced (pvc = 20 per cent) were stoved on glass for 30 minutes at 120°C.

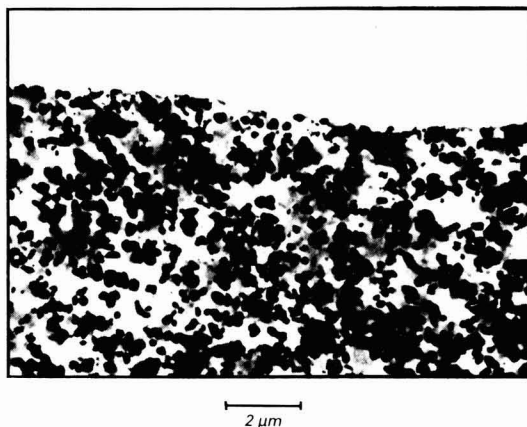


Figure 15. Electron micrograph of a section on an alkyd/urea formaldehyde paint film.

The degree of metal marking was assessed using a technique developed by Simpson⁷, which involves marking each coating using a loaded metal stylus. The extent of the marking is assessed visually in relationship to a photographic reference standard which is based on a series of standard marks ranging from 0 to 6, where 6 represents maximum metal marking and 0 no marking. In some cases, a metal mark rating falls between two of the standard ratings (e.g. 2 and 3) and therefore an intermediate rating (e.g. 2+) is given. Thus, a total of 13 ratings are available using this particular standard.

In Table 1, the metal mark ratings, using a 200 g load on a brass stylus and CLA values for all three paints are given. It can be seen that although there are only small differences in surface roughness they are sufficient to affect the degree of metal marking such that metal marking has increased with increasing surface roughness.

Table 1

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

Pigment	Mark rating* (200g brass stylus)	CLA (µm)
X	2+	0.027
Y	3	0.033
Z	5	0.038

* 6 = Severe marking, 0 = No marking

It is well-known that the presence of an acid catalyst in an acid catalysed alkyd/urea formaldehyde stoving paint can affect the shelf life of the paint by flocculating the pigment. From the above findings it would be deduced that the degree of metal marking would also be affected. Therefore, an acid catalysed alkyd/urea formaldehyde paint containing 10% paratoluene sulphonic acid based on weight of urea formaldehyde resin was formulated using pigment X at a pvc of 20 per cent. After the addition of acid, the paint was drawn down on glass and stoved for 30 minutes at 120°C. The paint was then allowed to age for five hours and 24 hours, and after each period, the paint was drawn down and stoved as above. Surface roughness measurements were carried out on the films to give an indication of the pigment dispersion at the surface of the coating, and metal marking was rated using a 200g loaded brass stylus. In Table 2 the results show that the effect of ageing the paint, which resulted in pigment flocculation, has caused the metal marking to increase slightly.

Table 2

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

Age of paint (hours)	Mark rating* (200g brass stylus)	CLA (µm)
Fresh	3+	0.059
5	4	0.074
24	4+	0.232

* 6 = Severe marking, 0 = No marking

Other factors associated with titanium dioxide pigment such as the amount used in the coating, and whether it is anatase or rutile, also play a part in affecting metal marking. Further information regarding these aspects of formulation are discussed in detail by Simpson³.

6 Conclusion

It has been shown that titanium dioxide pigment influences the surface roughness of an organic coating, and as a result certain optical/decorative properties such as gloss and resistance to metal marking are affected. In addition, the photoactivity of titanium dioxide catalyses the breakdown of a coating during weathering which in turn affects its surface roughness and hence gloss retention.

Careful attention has therefore to be given when selecting the grade of titanium dioxide pigment since it is

important to ensure that its durability is adequate for the particular application, and that its dispersion is as good as possible in order to keep micro-roughness to a minimum.

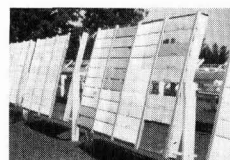
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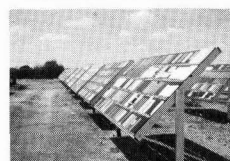
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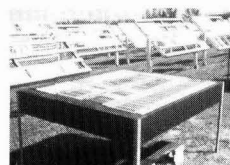


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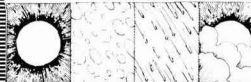


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A classification system for anti-fouling paints based on a dynamic flow test

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Abstract

In this paper a classification system for anti-fouling paints is presented. Paints are classified with regard to two criteria: anti-fouling performance after dynamic ageing on a rotor and toxicity to man and environment. To be classified paints must also meet some minimum paint technological requirements. The framework of the system has been tested with about 30 commercial paints. Of most of these paints the anti-fouling performance has been investigated, their leaching rates have been determined and their composition analysed.

It appeared that reliable classification by fouling tests is often difficult because of the variation of the anti-fouling performance of the paints. This problem has been overcome by determining the leaching curves of the paints, from which the leaching rate can be calculated. This shows whether the amount of toxins leaving the paint film at the time of testing was sufficient. Thus paints could be classified satisfactorily, giving a clear indication of differences in quality.

With regard to toxicity paints were classified on the basis of the results of the analysis of the elements by röntgen micro-analysis. This gives an indication of the kind of hazardous materials present and their concentrations. However, when all toxic materials present should be detected, a more detailed and complicated analysis procedure is necessary.

- The lifetime of the dried paint film in relation to adhesion, blister formation, wear, etc.
- The toxic properties in relation to occupational-health and environmental problems.

Taking all these properties as criteria into account, would mean to design a very complicated classification system, which is badly manageable in practice and in our opinion not necessary. Apart from the lifetime with regard to anti-fouling activity, the toxic properties seem to be most important as a criterion for classification. The consequences of the toxic properties for labourers and environment are very well known these days and legislation is increasing accordingly. This legislation will make conditions as to the use of the paints and will forbid their use in a number of cases.

Though anti-fouling activity and toxic properties are the most important criteria for classification, it does not mean that the other properties mentioned are unimportant.

For instance a paint must have good application properties and must adhere well to the substrate. These are requirements to be met, otherwise the classification is meaningless. A procedure for classification should therefore be started with an investigation into these properties. Detrimental phenomena such as lack of adhesion, blister formation, etc., can be studied during the tests of the anti-fouling activity.

3 Framework of the classification system

3.1 Anti-fouling activity

As has already been outlined some time ago¹ there does not exist one uniform practice with regard to the life-time of an anti-fouling paint.

The life-time depends on:

- The time a ship is sailing relative to the time it lies stationary.
- The seawater composition.
- The sailing route, determining the kind and amount of fouling encountered.
- Pollution of harbours, etc.

Because these conditions vary for each ship, classification of anti-fouling paints by ship trials is very difficult, if not impossible. Therefore simulation of the ageing process on a ship's hull under controlled conditions is necessary.

This should be done under dynamic flow conditions followed by a stationary test for fouling resistance^{1, 2} for the following two reasons:

1 Introduction

For a shipowner it has always been a problem to decide what kind of anti-fouling paint to use on his ship in order to achieve optimal protection. When new paints are offered the normal procedure is to start ship trials. These trials appear more difficult to keep under control and it takes a long time before the results are known. Furthermore the results are not always applicable to other ships in his company, with other sailing patterns. By the time the results are known paint manufacturers may have developed better products, which suggest that former results are obsolete.

In recent years the problem has become very pressing, due to the successful introduction of the so called "self polishing" anti-fouling. Therefore it has been decided to set up a "classification scheme" as a guide for the owner to make his selection.

In this paper a description of the scheme will be given. Furthermore the results of the investigation of some 30 paints are discussed. The investigation has been carried out to test the scheme and to improve it.

2 General considerations

Classification of an anti-fouling paint comprises in principle not only the duration of the anti-fouling-activity of the dried paint film, but also a number of other properties e.g.:

- Those of the wet paint, spraying characteristics, drying time, etc.

1. Leaching of toxins from anti-fouling paints is much higher when water flows along the surface (ship sailing) than under stationary conditions²⁻⁴.
2. Fouling preferably takes place under stationary conditions⁵⁻⁷.

For these reasons anti-fouling paints in our laboratory are aged in seawater on a rotor apparatus and subsequently tested on a raft against algal and barnacle fouling. Furthermore samples are taken and measurements performed to analyse the solution rate of the toxins in seawater, which occurs either by leaching or erosion.

The latter is done to support the fouling test results, considering that there is a direct relation between leaching rate and fouling prevention.

Rotor procedure including a picture of the rotor equipment, analysis of toxins and raft test have already been described^{1, 8, 9}.

The above mentioned test procedure simulates a situation in which long periods of sailing are alternated with short stationary periods in which fouling can occur. Because these are the severest conditions for ageing (solution of toxins in seawater) and fouling, it must be expected that in practice the life-time will be longer. "The procedure as described shows which paint gives the best relative anti-fouling activity *under the same circumstances*. It gives furthermore an indication for the real life-time to be expected". Only when the circumstances in practice are quite different from the rotor-test conditions, a prediction based on the latter may be erroneous. This may happen in a few cases e.g. in the case of copper paints in the Baltic, with a lower salt concentration. The rotor-test does not guarantee the life-time in practice, because so many factors (pollution, bad application, etc.) are not considered.

3.2 Toxic properties

Classification according to toxic properties forms a special problem, because there are many toxic substances of which it is unknown how harmful they are and in which concentration. However, there are some guidelines which might be helpful:

- Classify paints with toxins, of which the harmful character is well-known, suspected, or do not accept them for classification. This applies for instance to paints containing mercury, lead, arsenic, antimony, PCB, PCT and DDT, which are all hazardous materials.
- Classify paints with high toxicity at low concentrations and vice versa. In doing so a premium is put on the use of lesser amounts of toxins.

3.3 Description of the system

Thus it seems that the most significant system would be:

1. A *main classification* on the basis of the results of the anti-fouling performance, as has been obtained after rotor-ageing followed by a raft test. In case of doubt, leaching- and erosion-curves can give additional evidence for the final decision.
2. A *sub classification* on toxic properties, determined by analysis of the toxic chemicals present.

Table 1

Main classes: Anti-fouling activity

Class	Foulfree after:
1	One fouling season on a raft or 50 days on the rotor followed by a raft test
2	100 days on a rotor followed by a raft test
3	200 days on the rotor followed by a raft test
4	300 days on the rotor followed by a raft test
5	350 days on the rotor followed by a raft test
6	400 days on the rotor followed by a raft test

Table 2

Sub-classes: Toxic material

Class	Description
1	Paints containing Hg, As, Sb or chlorinated products like PCB, PCT or DDT
2	Paints containing more than 55 weight percent toxic material calculated on the dry paint, not falling under heading 1
3	As class 2, but containing 25-55 weight percent toxic material
4	As class 2, but containing less than 25 weight percent toxic material

The main and sub classification classes are described in Tables 1 and 2. Paints will be tested for resistance against algae and barnacles because these organisms are most important. A classification for both species will be given. The number of classes can be extended if necessary. Before starting the experiments concerned it will be investigated whether the paints meet a number of minimum paint-technological requirements as sprayability, drying, thickness to be applied in one coat and recoatability. Furthermore the paints will be analysed for identification.

4 Testing of the system

To test the system described in the previous paragraphs, 31 anti-fouling paints have been selected from those offered for sale on the international market. For this purpose not only paints with a claimed long service time have been chosen, but also with a medium and short time of performance. Furthermore, apart from classical contact leaching types, also modern erodable paints have been investigated. From these 31 paints, 22 have been tested according to the system; nine have been used to carry out more detailed investigations to answer questions especially with regard to the erosion aspect.

To test the anti-fouling activity the paints have been applied to the anti-corrosive substrate as recommended by the manufacturer. As far as could be observed all the paints did meet the minimum paint technological requirements, though no detailed tests were carried out. The paints have been rotated as a circumferential speed of 10 knots for times according to the class boundaries and tested then for their fouling resistance. The leaching has been determined by chemical and röntgen micro-analysis, erosion by thickness decrease. To investigate the toxic properties the dry paint films have been analysed also by röntgen micro-analysis.

Table 3

Algal resistance

Paint no	After ageing on rotor (days)*					
	0/50	100	200	300	350	400
1	1(B)	1(G)	4(G)	1(G)	0	2
2	1(G)	0	4(G)	4(G)		
3	3(G)		4(G)			
4	1(B)		4(G)	2(G)	4(G)	
5	0	1(G)	0	0	1(G)	4(G)
6	3(G)					
7	0	1(G)	0	1(G)	4(G)	
8	1(G)	0	4(G)	4(G)	2(G)	
9	0	1(G)	1(G)	1(G)	1(G)	2(G)
10	0	0	0	1(G)	0	4(B)
11	0	0	0	1(G)		1(G)
12	0	0	0	0		1(G)
13	0	0	1(G)	0	1(G)	1(G)
14	1(B)	1(B)	2(G)	1(B)	0	0
15	0	1(B)	1(G)	4(B)	1(G)	1(G)
16	0	0	1(G)	0	1(G)	0
17	1(G)	0	0	0	0	1(G)
18	0	1(B)	1(G)	1(G)	1(G)	2(G)
19	0	1(B)	2(G)	1(G)	2(G)	1(B)
20	0		1(G)	0	3(G)	0
21	0	0	1(G)	0		
22	0	0	0	**		

(G) = Green algae (B) = Brown algae

* 0 = 0% of surface covered

1 = 0-10% of surface covered

2 = 10-20% of surface covered

3 = 20-40% of surface covered

4 = > 40% of surface covered

** extensive detachment

Table 4

Barnacles resistance

Paint no	After ageing on rotor (days)*					
	0/50	100	200	300	350	400
1	0	0	0	0	0	3
2	2	1	3	3		
3	3	1	2			
4	0	1	1	0	0	
5	0	0	1	0	0	1
6	1/4	4				
7	0	0	0	0	0	
8	0	0	0	0	0	
9	0	0	0	0	0	2
10	0	0	1	0	0	2
11	0	0	0	0	0	1
12	0	0	0	0	0	1
13	0	1	0	0	3	3
14	0	1	1	0	0	0
15	0	1	1	0	1	1
16	0	0	0	0	0	0
17	0	0	0	0	0	0
18	1	1	1	1	1	0
19	0	0	1	1	1	0
20	0	0	0	0	0	0
21	0	0	0	0	0	0
22	0	0	0	**		

* 0 = no fouling observed

1 = 0-10 barnacles per dm²2 = 11-25 barnacles per dm²3 = 26-50 barnacles per dm²4 = > 50 barnacles per dm²

** extensive detachment

4.1 Anti-fouling results

In Tables 3 and 4 the results of the anti-fouling behaviour of 22 paints are reported.

Empty spaces in the tables indicate that no tests were carried out. All tests were executed until a non-toxic panel was completely fouled.

Notable in both tables is in many cases the variation of the results with rotor-time, especially for algae. Such a variation has been observed also on panels of the same paints which have been exposed continuously on the raft up to four years, without rotor-ageing. The variation observed is well known¹⁰ and takes place also on non-toxic substrates¹¹.

Analysis of all the information available has shown that the variability observed is neither increased nor induced by the rotor procedure (including application, drying, etc.). Anyhow the variation phenomenon makes unambiguous classification difficult.

4.2 Leaching rate

An indication for the anti-fouling resistance of a paint film is the rate by which the toxins dissolve in seawater, from which algal zoospores, barnacle-larvae, etc. take them up. Minimum rates are necessary to prevent settling. Because these are rather well known for the toxins normally used, a leaching curve can be of great help in classifying. Such a

curve should include the toxins leaving the paint-film by diffusion and/or erosion. Therefore the leaching of the paints from the 22 series has been determined for copper and tin, originating from the most important toxins present (cuprous oxide, organotin derivatives). In Table 5 the average leaching rate in a 200 days rotor period is reported. From this table it is clear that some paints can not have any resistance to fouling, because no leaching occurs at all. Most of the others have averages in the neighbourhood of the minimum rates and their resistance to fouling is doubtful, at least after 200 days.

A better insight into the life-time to be expected is obtained from Figures 1 (algae) and 2 (barnacles). In these figures the average amount of fouling observed in the 200 days period is plotted against the average leaching rate. If copper and tin were both present, the leaching rate of tin was always very low and has therefore been neglected. In the figures furthermore the minimum leaching rates are indicated, necessary for fouling protection. The minimum leaching rates for copper are slightly different from what normally is accepted in the literature (10 µgr Cu/cm²/day). The values are based on our experience and reflect better the well-known difference between algae and barnacles. For tin the values have been taken as found for tributyl tin fluoride⁸. For triphenyl tin fluoride, another well-known tin toxin, the values are most probably much lower¹². It appears that for algae most of the paints have average leaching rates below the minimum values. Most of them therefore foul. For barnacles the copper leaching is in most cases greater than the minimum rate and therefore no

Table 5

Average leaching rates over a 200 days rotor period

Paint no	Toxicant	Average leaching rate*		
		by diffusion	by erosion	total amount
2	Cu	0		0
3	Cu	8		8
6	Cu	0		0
8	Cu	12		12
1	Cu	0		0
	Sn	5.5		5.5
5	Cu	12		12
	Sn	1		1
7	Cu	12		12
	Sn	2		2
9	Cu	18		18
	Sn	2		2
11	Cu	11		11
	Sn	1		1
12	Cu	13		13
	Sn	2		2
13	Cu	11		11
	Sn	0.2		0.2
16	Cu	45		45
	Sn	0.3		0.3
19	Cu	17		17
	Sn	0.2		0.2
20	Cu	12		12
	Sn	0.3		0.3
21	Cu	12		12
	Sn	0.7		0.7
22	Cu	32		32
	Sn	0.1		0.1
4	Sn	0.6		0.6
10	Sn	1.2	0.5	1.7
14	Sn	3.3		3.3
17	Sn	2.5	2	4.5
15	Sn	1.1	3.2	4.3
18	Sn	1.3	1.1	2.4

* in $\mu\text{gr}/\text{cm}^2$ day

fouling occurs. For tin the leaching is too low to prevent settling of barnacles as well as algae.

Apparently fouling occurs now and then, though the leaching rate is higher than needed according to the minimum leaching rates. This may be due to the fact that averages have been plotted. However, X-ray microanalysis has also shown that in these cases the leaching on one and the same paint-film may be different on different places and therefore may be sometimes too low.

In most of the cases¹⁶ the leaching rate results confirm the fouling tests as discussed in Section 4.1. Deviations nearly always occur with algae data.

4.3 Toxins

In order to determine the kind and amount of toxins, dried paint-films have been investigated by röntgen microanalysis. By this method in principle all the elements

Fouling (arb. scale)

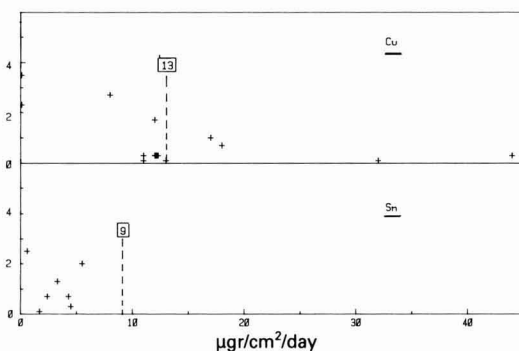


Figure 1. Fouling with algae in relation to copper or tin leaching (average result in a 200 days rotor-period).

Fouling (arb. scale)

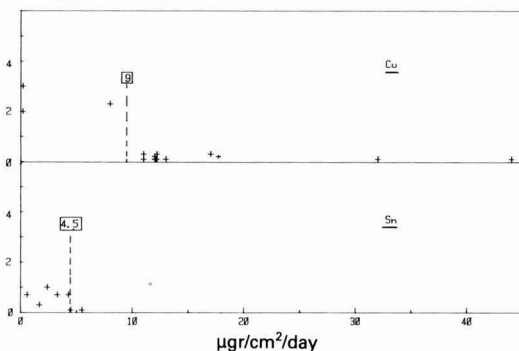


Figure 2. Fouling with barnacles in relation to copper or tin leaching (average result in a 200 days rotor-period).

between number 5 and 92 can be detected. The amounts of copper, tin and zinc have been determined with the help of a standard paint. In Table 6 the results for the most important elements in 25 paints are reported. Next to these silicon, aluminium, magnesium, calcium and titanium were found, in amounts of 0-10%.

Obviously no elements like mercury, arsenic, antimony or lead, pointing at hazardous toxins, are present. The method, however, is not suitable to detect organic compounds like PCB, PCT, etc. No other method has been applied at present to look for these materials. The most important toxic materials used seemed to be cuprous oxide and organo-tin derivatives. In some paints (10, 15, 17, 18, 23 through 25) the tin is, as tributyl tin oxide, attached to an acrylic polymer. These have erodable properties. The presence of sulphur sometimes means (1, 2, 6, 10, 14, 23 through 25) that an organic algicide has been used. However, in other cases (15-1, 15-2 and 18-2) sulphur is, as copper, obviously present in copper thiocyanate. In this respect it is noteworthy that in two subsequent fouling seasons copper thiocyanate as such has shown no anti-fouling properties in a special test on our raft.

Further it has to be noted that nitrogen could not be detected. For this element a slightly different method has to be used. Therefore algicides containing nitrogen, remained unnoticed.

Table 6

Elements* in the dried paint film

Paint no **	Cu	Sn	S	Zn	Fe
1	68.3	1.2	2.3	3.3	
2	53.0		2.5	6.1	4.0
3	13.7			16.4	5.7
4		1.7		38.1	3.7
5	32.0	1.9		24.6	5.0
6	64.1		1.8		4.4
7	48.8	2.4	0.7		2.3
8	52.8			14.2	
9-1	1.1	5.6		34.1	
9-2	34.6	1.6		25.8	6.6
10-2	0.9	3.0	6.3	43.4	5.2
11	46.1	3.8		6.0	3.6
12	36.1	3.4		6.1	3.6
13	61.5	1.4	0.5		2.6
14		15.9	6.3		9.5
15-1	17.4	11.8	11.0		
15-2	19.3	11.3	12.0		
16-1	60.7	1.1		5.1	
16-2	57.3	1.3		8.6	
17-1		13.2		42.0	
17-2		12.6		43.7	
18-1	69.1	6.0	1.3		6.6
18-2	29.7	9.1	18.1		
19	54.1	1.1	0.8	5.8	0.4
20-1	43.2	0.8		16.0	5.9
20-2	43.8	1.2		13.7	3.7
21	42.6	4.1		2.8	4.5
22	50.2	1.6			4.3
23	5.7	3.4	7.0	41.1	4.1
24	5.6	3.1	9.6	41.4	
25	6.7	2.5	7.6	49.7	

* % by weight

** 9-1, 15-1 etc, means first coat of paint system
9-2, 15-2 etc, means top coat of paint system

4.4 Identification of paints

Basic for good functioning of the system is identification of the paints to be classified. This is necessary in order to determine whether the same paint as classified is offered by the manufacturer at a later date. Complete analysis for this purpose takes much time and is not necessary. Sufficient would be a "fingerprint-technique" by which the paint is unambiguously characterised.

For this purpose two such techniques are available.

In the first place X-ray micro (REM-RMA)-analysis, as mentioned in Section 4.3, which determines the pigment composition. For identification it is sufficient to compare the X-ray spectrum of a new sample with that of a former one.

With the second technique, infrared spectroscopy, mixtures of polymers, plasticisers, etc, as used in paint media, are identified. In this method the pigments are separated from these materials, which remain in solution. From the solution a film is spread onto potassium bromide discs to produce the infrared spectrum. As in the case of the pigments it is sufficient to compare the spectrum of a new sample with the one formerly taken.

5 Classification

On the basis of the results in the foregoing paragraphs 21 paints have been classified. Because paint 22 showed loss of adhesion during the rotor-tests this product was not considered. A number of paints were still foul-free after their test period. They have been placed in the corresponding class. However, on extending the rotor-test, they could have scored higher.

5.1 Anti-fouling activity

Classification (using Table 1 notation) has been carried out on the basis of the results in Tables 3 and 4. In doing so one should remember that a qualification 1 with regard to fouling means that 0-10% of the surface is covered with algae or that 0-10 barnacles per dm² occur. In both cases this will give a friction increase along the surface, which is not acceptable.

As can be observed from Tables 3 and 4 this guideline is often not easy to handle, because of the variation in the fouling results. To decide whether the fouling observed was just a coincidence or not, the leaching rate was used as a second guideline.

The following rules were adopted to classify the paints:

- A paint will be placed in the class, before the one in which for the first time fouling occurred.
- When fouling is qualified with a rating 1, this will be neglected when later on no fouling took place, on the condition that the leaching rate is not lower than the minimum rates discussed in Section 4.2.

Classification in relation to algal and barnacle fouling is reported in the following table:

Class	Algae	Barnacles
Not classified	1, 2, 3, 4, 6, 14	2, 3, 6, 18
1	8, 9, 15, 18, 19	4, 14, 15
2		10, 19
3	7, 10, 11, 16	
4	5, 12, 13, 20, 21	11, 12, 13
5	17	1, 5, 7, 8, 9
6		16, 17, 20, 21

As can be observed from this table the paints are reasonably well dispersed over the classes, which means that a difference in quality can thus be indicated. Classification in this way is only in a few cases somewhat doubtful.

5.2 Toxic properties

In this case classification (using Table 2 notation) has been done on the basis of the results reported in Table 6.

Furthermore the following rules were adopted:

- Copper was considered to be present as cuprous oxide, unless it was clear that copper thiocyanate was used. In this case the amounts of copper and sulphur have been neglected, because CuCNS is not a toxin.

- Tin has been calculated as tributyl tin oxide.
- When sulphur is present as part of an algicide, the amount present has been multiplied with the average factor of five to find the percentage of that algicide.
- The amounts of toxic materials have been taken together, without taking into account their specific toxicity.

Subclassification in relation to the amount of toxic materials is reported in the following table:

Sub class	Division
1	—
2	1, 2, 6, 7, 8, 11, 13, 14 16-1, 16-2, 18-1, 19, 21
3	5, 9-2, 10-2, 12, 15-1, 15-2, 17-1, 17-2, 20-1, 20-2
4	3, 4, 9-1, 18-2

This table shows that many paints contain a high amount of toxin. Though a number of toxins cannot be detected using the method of analysis so far carried out (see Section 4.3); the system seems to give a rough but satisfactory impression of toxicity.

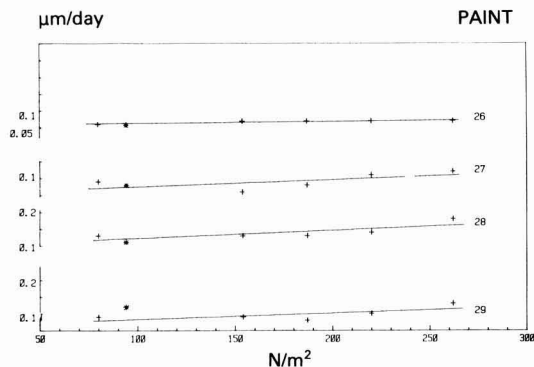
6 Influence of some of the test conditions

6.1 Circumferential speed of the rotor

Testing has been executed so far with a circumferential speed of the rotor of 10 knots. It has been shown earlier³ that at higher speeds the leaching of conventional contact-leaching paints is not increased. However, for modern erodable anti-foulings the erosion may be dependent on the water-flow rate. In such a case a paint film would be eroded at an earlier stage and therefore give a shorter period fouling protection.

For this reason the erosion of four erodable anti-fouling paints were determined on a spinning disc⁹. The results are shown in Figure 3. Instead of the varying speed the corresponding theoretically calculated friction has been plotted as independent variable. At the same time the erosion of the paints on the rotor has been determined at 17 knots. This has also been plotted in Figure 3.

Figure 3. Erosion on a smooth disc: circ. speed = 27 knots, temp. 20°C, + = disc, * = rotor (17 knots).



As can be observed there is not a significant relation between erosion and friction. At least the effect of the friction will not be very high.

Nevertheless it seems sensible to increase the rotor-speed to 17 knots, so that the friction in that case is at least within the range encountered on the disc. This range may also be expected on the ship's hull⁹. To check this, the erosion of five erodable paints has been measured on the rotor at 17 knots as well as on a container ship. For the latter purpose the paints have been applied to panels which have been attached to the bilge keel. The paints have been exposed on the forward part of the bilge keel as well as on the rear end. Both places were about 60 m apart. The erosion on the rotor has been followed for a period of three months, on the ship for about nine months. In the following table (* = µm/day) the results of the comparison of erosion on rotor and ship are presented:

Paint	Bilge keel*		Rotor*
	Front	Rear	
18	0.19	0.11	0.14
28	0.27	0.25	0.24
29	0.17	0.15	0.21
32	0.42	0.31	0.28
33	0.23	0.20	0.23

As can be seen they are very well in agreement. Only in one case, in the front end, was the erosion rate higher than on the rotor.

6.2 Rough surfaces

The question has been raised whether the roughness of a surface affects the erosion rate. For that purpose erosion measurements were done on the smooth part of the bilge-keel panels (see Section 6.1) as well as on the artificial rough surface parts (peak to valley 500 µm).

The results have been summarised in the next table (* = µm/day):

Paint	Smooth*	Rough*
18	0.14	0.12
28	0.26	0.26
29	0.17	0.16
32	0.37	0.36
33	0.26	0.22

As is shown, the differences between rough and smooth are only of minor importance.

6.3 Seawater condition during rotor tests

For the tests natural filtered seawater is used, with a pH of about eight and a salinity of about 2.8‰; pH and salinity are continuously monitored. The temperature of the seawater is at a constant 20°C. The water is furthermore renewed continuously. The system may in some cases lead to erroneous results when the salinity is different from the figure quoted (see Section 3.1). The problem is restricted to cuprous-oxide containing paints. Lower salinities will occur in some seas and in estuaries.

Unless ships are always sailing in these areas, a constant deviation from the leaching rate found during the classification procedure will not occur. Thus the life-time will not deviate considerably. At higher salinities the leaching is not so much affected³ and therefore also in this case the life-time will remain almost unchanged.

For contact leaching anti-foulings, no influence of the temperature on leaching was found by the author³, though this was not in agreement with other findings^{13, 14}.

In principle the erosion rate may also be influenced by the temperature. To the author's experience this is not the case, though no extensive experiments were carried out.

Continuous renewal of seawater is necessary to avoid accumulation of toxins in the rotor drum. Renewal takes place at a rate of 300 l/hour, which is 60% of the rotor's content. This rate keeps the concentration far below critical concentrations, which could affect the leaching rate.

Conclusions

With the system as described in this paper, commercial anti-fouling paints can be classified in an adequate manner. Thus insight is obtained into anti-fouling life-time differences and into the kinds and amounts of toxins.

The decision for anti-fouling classification in general is taken on the sole basis of the results of the fouling tests. However, a reliable classification can in many cases only be obtained when leaching-curves are available.

For a more reliable classification as regards toxicity, it would be necessary to determine also nitrogen, so that algicides containing this element are detected. Furthermore hazardous materials like PCB, PCT, etc. should be determined. No doubt this can be done. However, this asks for a more detailed and complicated analysis, of which the necessity at present is not clear. The same applies to the chemical structure of the algicides present.

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New binders for cathodic electrodeposition from epoxy resins

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Summary

Electrodeposition as a newer method of applying an organic coating to a metal surface has assumed importance during the past two decades. The epoxy binders modified with partially blocked isocyanates of phenol/cardanol for cathodic electrodeposition were developed and the film properties of the electrodeposited coatings such as flexibility, scratch hardness, adhesion, impact resistance and resistance to chemicals/solvents were studied. The epoxy binder modified with cardanol blocked isocyanate showed excellent film properties.

Introduction

The high cost of petroleum solvents which are also prone to fire and health hazards and also contribute to atmospheric pollution have resulted in the development of water-soluble polymers suitable for formulating paints that replace the conventional solvent based paints. Another reason for their popularity is that the water-soluble paints can be applied to metal substrates by conventional methods as well as by electrodeposition.

Electrodeposition is a novel method of application of paints to metallic substrates and has gained world-wide importance especially in the automotive and industrial appliances field because of automation, and of its low level of pollution, high level of coating utilisation and ability to coat the recessed portions of complex shaped articles. Electrodeposition is of two types, anodic and cathodic, of which the latter is gaining importance in recent years. In cathodic electrodeposition the article to be coated is made the cathode.

Cathodically electrodepositable binders containing amino/amide groups and onium compounds as well as those based on dispersions of non-ionic resins using cationic surfactants have been described by J. Mazia¹. An acrylic copolymer prepared from amino alkyl esters of acrylic or methacrylic acid, substituted unsaturated vinyl compounds like vinyl benzene and various acrylates was further modified with phenolic, alkyd or epoxy resins to give a satisfactory vehicle for cathodic deposition². Wizmer and Moffatt³ have described water-soluble epoxy system capable of giving excellent film properties such as corrosion resistance, adhesion and flexibility. A binder for cathodic electrodeposition was prepared from epoxy resin and Mannich bases⁴.

Though there has been, in recent years, some development in water-soluble binders, most of the information on cathodic binders developed particularly from epoxy resins is contained in patents. Hence a study was undertaken to develop epoxy resins modified with phenol/cardanol blocked isocyanates to serve as binders for water-soluble vehicles. The present paper deals with the development of modified epoxy-amine binders and the evaluation of their film properties.

Experimental

Materials

Epoxy resin: Araldite 6071 (Ciba Geigy), mol. wt. 900-1,000, epoxy eq. 450-500.

Diethanolamine: (Ranbaxy Chemicals, India), Mol. wt. 105, b.p. 268°C.

Cardanol: This monophenol with C₁₅H₂₇ side chain in the meta position was obtained by distillation of cashew-nut shell liquid under vacuum. It has mol. wt. 300, and b.p. 240°C at 4 mm Hg.

Phenol: (Ranbaxy Chemicals, India), Mol. wt. 94.11, b.p. 182°C.

2, 4-Toluene diisocyanate: (E. Merck) Mol. wt. 174.

Glacial acetic acid: (IDPL, India) L. R. grade.

Methyl ethyl ketone: Extra pure (E. Merck) b.p. 79.5°C.

Xylene: (BDH) b.p. 138°C.

White spirit: (Burmah Shell) b.p. range: 150-200°C.

Butanol: (Sarabai M. Chemicals, India) b.p. range: 116-118°C.

Deionised water

Emery paper: (Carborundum Universal Ltd, India) Emery paper of grade numbers 180, 220, 320, 400 (in increasing order of fineness) silicon carbide water proof paper.

Mild steel discs: Mild steel discs of diameter 32 mm were punched out of plate of gauge 20 (0.9 mm), abraded with emery paper of increasing order of fineness in white spirit medium, swabbed successively with xylene and butyl cellosolve and finally degreased with methyl ethyl ketone for two hours. The residual solvent from the degreased specimen was removed in a vacuum desiccator.

Mild steel panels: Mild steel panels of size 150 × 100 mm were cut from a plate of gauge 20 (0.9 mm) abraded with emery paper of increasing order of fineness in white spirit medium and swabbed with xylene and butyl cellosolve.

Mild steel rods: Mild steel rods of 10 cm length and 0.5 cm diameter were abraded with emery paper of increasing order of fineness in white spirit medium and swabbed with xylene and white spirit.

Tin coated mild steel panels: Panels of size 150 × 100 mm were cut from electrolytically tinned mild steel (0.315 mm). The tin coated panels were lightly abraded with a fine emery paper and swabbed with xylene and finally with butyl cellosolve.

Methods of preparation of media

To obtain water soluble cathodic binders, the epoxy-amine adduct was prepared with Araldite 6071 and diethanolamine which was modified with partially blocked isocyanates of TDI with phenol/cardanol in order to obtain better film properties.

I Preparation of epoxy-amine adduct

The adduct designated as binder 'A' of low free amine content was prepared by reacting epoxy resin with calculated amount of diethanolamine using methyl

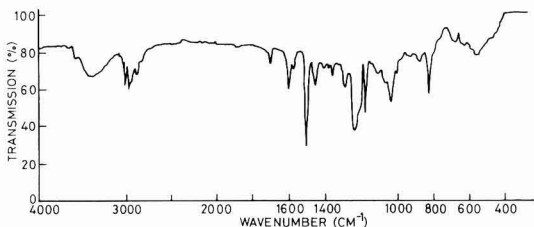


Figure 1. Infrared spectrum of epoxy amine adduct.

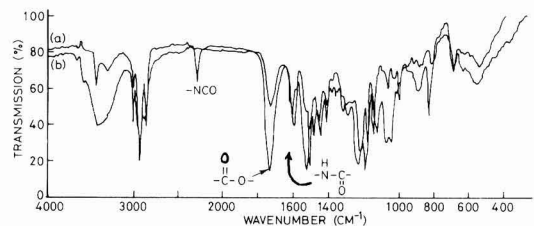


Figure 2: (a) Infrared spectrum of partially blocked TDI with cardanol, (b) Infrared spectrum of modified epoxy amine adduct with partially blocked TDI of cardanol.

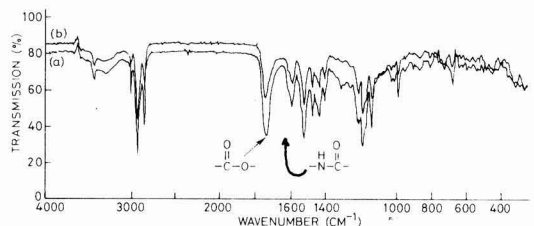


Figure 3: (a) Infrared spectrum of fully blocked isocyanate of TDI with cardanol (before curing), (b) Infrared spectrum of fully blocked isocyanate of TDI with cardanol (after curing).

cellosolve acetate as a solvent. The unreacted free amine was estimated according to the method described in AOCS Official Method Section-D-Tf 1b-64. The product was characterised by the IR spectrum (Figure 1).

2(a) Preparation of partially blocked isocyanates

Partially blocked isocyanates of toluene diisocyanate (TDI) were prepared by reacting 2,4- toluene diisocyanate with phenol/cardanol in 1:1 mole ratio at 60°C for a period of 1½ hours. The product was characterised by the IR spectrum (Figure 2).

2(b) Preparation of fully blocked isocyanate

Fully blocked isocyanate of cardanol was prepared from cardanol and 2,4- toluene diisocyanate by reacting them in 2:1 mole ratio at 60°C for a period of 1½ hours. The product was characterised by the IR spectrum (Figure 3).

3 Preparation of modified amine adduct with partially blocked isocyanate

The binders suitable for electrodeposition were obtained by reacting epoxy amine adduct with partially blocked isocyanate at 80°C. The modified epoxy-amine adduct from partially blocked isocyanate of phenol was designated as

Table 1

Electrodeposition: Effect of variation of time and voltage on film thickness of binders

Sample No.	Time (min)	Voltage	Dry film thickness (microns)	
			Binder A	Binder C
1	2	10	5	5
2	1	10	5	5
3	2	20	8	7
4	1	20	7	6
5	2	30	12	9
6	1	30	10	8
7	2	40	15	12
8	1	40	15	10
9	2	50	20	15
10	1	50	20	12

binder 'B'. The modified epoxy-amine adducts from partially blocked isocyanates of cardanol were named as binders C, C1, C2 and C3 which have the OH/NCO ratios of 6.8, 3.4, 2.3 and 1.8 respectively. The products were characterised by their IR spectra and their solubility in acidified water.

Electrodeposition

The electrodeposition bath consisted of a stainless steel anode and replaceable cathode made of mild steel panels, discs, rods or tin coated mild steel panels immersed in a solution of binder obtained by dissolving the binder in acidified water (water and acetic acid). The pH of the bath was maintained between 5 and 6.

The results of electrodeposition of the binders (A, B, C, C1, C2 and C3 used separately) with variation of immersion time and voltage on film build up are given in Table 1. The various physico-chemical characteristics of the electrodeposited film were evaluated and the results are presented in Tables 2 and 3.

Film properties such as scratch hardness of coatings on mild steel panels, flexibility of coatings on tin coated mild steel panels were determined as per IS: 101-1964. Impact resistance of coatings on mild steel panels were also determined as per DEF: 1053 specification. Resistance to chemicals/solvents of coatings on mild steel rods were determined as per modified IS: 101-1964. The results are listed in Table 2.

For the adhesion test, the mild steel discs were coated by electrodeposition. The coated discs were bonded using epoxy resin adhesive (Ciba Araldite and Hardener) between stainless steel doublets and these were kept for two days in parallel rod jigs for alignment. Then the bond strengths were measured by sandwich pull-off technique using a Hounsfield Tensometer⁵⁻⁶. The results are given in Table 2.

Results and discussion

It is observed from Table 1 that the deposited film was uniform and smooth when the solid content of the bath was 10% at pH 5-6. The dry film thickness was found to vary from 15 to 20 µm at 50V and an immersion period of two minutes. Hence, for evaluation of film properties, the above set conditions were adopted.

Table 2

Physico-chemical properties of electrodeposited and baked binder films*

Sample No.	Type of binder	OH/NCO ratio	Flexibility ¼" mandrel	Scratch hardness (g)	Practical adhesion values (kg/sq cm)	Impact resistance (10½lb, 23")	
						Direct	Indirect
1	A	0.0	F	2600	70	P	F
2	B	6.8	F	2200	230	P	F
3	C	6.8	P	2600	390	P	P
4	C1	3.4	P	2500	310	P	P
5	C2	2.3	P	2300	262	P	P
6	C3	1.8	P	2100	210	P	P

* P = Pass, F = Fail

Table 3

Solvent/chemical resistance of electrodeposited and baked binder films*

Sample No.	Type of binder	OH/NCO ratio	H ₂ O (48 hrs)	Acid (2% H ₂ SO ₄) (18 hrs)	NaOH (1%) (4 hrs)	Butanol (4 hrs)	White spirit (4 hrs)	Xylene (4 hrs)
1	A	0.0	A	A	NE	A	NE	NE
2	B	6.8	A	NE	NE	NE	NE	NE
3	C	6.8	NE	NE	NE	NE	NE	NE
4	C1	3.4	NE	NE	NE	NE	NE	NE
5	C2	2.3	NE	NE	NE	NE	NE	NE
6	C3	1.8	NE	NE	NE	NE	NE	NE

* A = Affected, NE = No Effect

As seen from Table 3, the isocyanate modification of epoxy-amine adduct has resulted in an improvement of alkali, water and solvent resistance, perhaps due to complexity of the structure of the molecule. It is also found from Tables 2 and 3 that the products obtained by modification with phenol/cardanol blocked isocyanates have improved film properties over the amine adduct itself. Both the modifications have shown similar performances (except in water resistance) with regard to resistance to chemicals and solvents.

In the case of the phenol modified product, the blocked isocyanate group is released during baking (150-160°C)⁷ and reacts with the available -OH group of the amine adduct making the products more complex and less flexible; hence, the binder failed in the flexibility test (Table 2). However, those of the cardanol blocked isocyanate product showed good flexibility and impact resistance under the similar conditions of the test (Table 2). This could be attributed to the cardanol remains as an integral part of polymer even after curing, providing the plasticising effect due to its long aliphatic side chain, thus making the cured films flexible.

It is also observed from the infrared spectrum of the fully blocked isocyanate of TDI with cardanol (Figure 3) that the free cardanol was not released after heating the fully blocked isocyanate of TDI with cardanol at 165°C for half an hour, while it is well known that the phenol gets liberated and evaporates at the curing temperature⁸.

The scratch hardness of the cardanol blocked isocyanate

binder depends upon the OH/NCO ratio. The scratch hardness decreases as the OH/NCO ratio decreases. The greater hardness of binder C (OH/NCO ratio = 6.8, Table 2) is due to cardanol isocyanate acting as a mild plasticiser on the final product.

The adhesion of different binders as shown in Table 2 indicate that the practical adhesion value is lowest for the epoxy-amine adduct (i.e. 70 kg/sq cm). While the blocked isocyanate modification results in an increased practical adhesion value due to urethane linkages. As the obtained failure is cohesive in nature, this shows that the adhesion to the substrate is higher than the measured value of practical adhesion. The adhesion to the substrate is better when cardanol blocked isocyanate is used instead of phenol blocked isocyanate (Binder B and C to C3, Table 2). This may be due to cardanol forming part of resin structure producing some sort of plasticizing effect (Binder B and C, Table 2). The increase in cardanol content gives more plasticization to the binders and hence the adhesion value goes on decreasing (Binder C to C3, Table 2). The adhesion value in the case of cardanol modification is maximum when OH/NCO ratio is 6.8, and minimum when it is 1.8.

Conclusion

Satisfactory epoxy binders for cathodic electrodeposition can be prepared by modifying them with blocked isocyanates of phenol and cardanol. These binders have good resistance to chemicals and solvents. They have also excellent adhesion to mild steel substrates. The epoxy binder has the highest adhesion value of 390 kg/sq cm when

it is modified with cardanol blocked isocyanate having an OH/NCO ratio of 6.8.

Acknowledgement

One of the authors, M. Ramasri gratefully acknowledges the financial assistance given to her in the form of a fellowship from the Council of Scientific and Industrial Research, New Delhi for carrying out research work.

[Received 23 April 1985]

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8. Hudson, G. A., et al., *Official Digest*, 1960, **32**, 213.

next month's issue

The Honorary Editor has accepted the following papers for publication in the October issue:

The influence of associative thickeners on coatings performance: III. Variation in percent non-volatiles by R. H. Fernando, W. F. MacDonald and J. E. Glass, North Dakota State University, USA

Control of substances hazardous to health draft regulations: The implications for the paintmaker by M. J. Leveté and W. E. G. Moffat, Paintmakers Association of Great Britain, London, UK

Characteristics of a Nigerian kaolinitic clay mineral extender for paints by T. O. Odozi, G. E. Akpokodje and J. O. E. Otaigbe, University of Port Harcourt, Nigeria

Fire and explosion in the paint industry by D. J. Reynolds, Berger Jenson and Nicholson Ltd, Dagenham, UK

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Akzo UK expansion

Akzo Coatings has completed its second stage of growth in the UK decorative paints market with acquisition of Blue Circle Sandtex Ltd. The new group, to be called Akzo Coatings plc, comprises Permoglaze Paints, Sikkens and Sandtex. It will have a turnover exceeding £50 million and employ over 800 employees making it one of the largest paint suppliers in the UK. The head office of Akzo Coatings plc will be based at Didcot, the current Sikkens site.

Macpherson's new corporate identity

Macpherson Plc of Bishop's Stortford, formerly the Donald Macpherson Co Ltd, are introducing an integrated corporate identity for all their operating companies and working divisions. Each company will be identified by a qualifying word or words after the name Macpherson (see below). Mr Charles Wenham, Chief Executive of Macpherson, stated that the new corporate identity will allow customers to see that all the companies and working divisions are part of the same entity.



Name change for BP Additives

BP Chemicals (Additives) Ltd has announced that it is adopting the trade name ADIBIS. BP Chemicals (Additives) Ltd was registered as a new and separate company when BP Chemicals Ltd purchased the 50% shareholding in Orobis from the Chevron Chemical Company at the end of 1985.

Sandoz anniversary 1886-1986

Sandoz of Basle, Switzerland, celebrates its hundredth anniversary and in doing so have produced a colour booklet on the firm's history and a review of its chemicals division. In 1885 a businessman, Edouard Sandoz and a colour chemist, Alfred Kern, set up a company in Basle for the manufacture and sale of synthetic dyes. The new partnership, under the name "Chemische Fabrik Kern & Sandoz" began production on 1 July, 1886, at a site on the left bank of the Rhine where the group's headquarters are still located today. The new factory (photo above) employed a total of 15 people. From the modest dyestuffs factory



Sandoz factory site 1886

Sandoz has grown into a worldwide chemical concern. A pharmaceuticals section was formed in 1917, and in 1929 a chemicals department was added, followed later by an agrochemicals department. The most recent acquisitions of Sandoz involve Sodyeco and Master Builders in the pharmaceuticals and chemical sector. Today, annual sales of Sandoz are about 8,500 million Swiss francs and the group has 40,000 employees.

Sheen — Haeffner link up

Sheen Instruments of Teddington has appointed H. Haeffner of Chepstow as Agents for the Sheen range of instruments for the surface coatings industry. Haeffner, long established chemicals/equipment suppliers, are now authorised to sell Sheen products worldwide.

Burmah Speciality Chemicals USA expansion

Burmah Speciality Chemicals has reached agreement with Reichhold Chemicals Inc of the USA to acquire its Chicago-based subsidiary, National Wax Company, for approximately \$11 million. National Wax is the leading US wax blender, serving a wide range of domestic consumer industries. National Wax will become part of Burmah Speciality Chemicals' Coatings Division.

Inmont award

Inmont of Wolverhampton, a major automotive paint manufacturer, has been awarded the 1986 British Safety Council Safety Award. Competing against Safety Council member companies throughout the UK, Inmont has won the award for the past five years in recognition of an outstanding health and safety record.

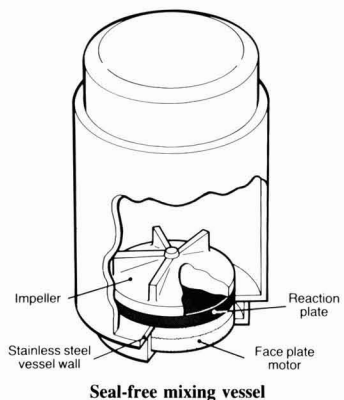
tance in water-based inks. It is designed for use as a let down vehicle for use with pigment bases made on LS18. *Reader Enquiry Service No. 21*

Luminous paints

Jalite UK Ltd of Basildon has added a new series of water-based photoluminescent safety paints to its range of "glow-in-the-dark" coatings. Designated system 100 and 310 respectively, the paints are available in two colours, lime green and fluorescent yellow, and are suitable for coating wood, plaster and concrete surfaces. They are designed as a safety aid. The paints have a silky matt finish and are non-toxic and non-flammable. The photoluminescent characteristic is produced from a safe inorganic pigment, and they are applied by normal brush, roller or spray methods. *Reader Enquiry Service No. 22*

Linear motor mixer

Davy Linear Motors Ltd of Loughborough has developed a mixing unit that dispenses with motors, gearboxes, drive shafts and shaft seals. This unit is a sealed mixing vessel in which the impeller has no mechanical connection with the drive motor. The *Face Plate Motor* (disc-shaped motor outside the mixing vessel, see figure below) uses the principle of linear motor drive to induce rotary thrust in a disc-shaped reaction plate through the wall of the sealed mixing vessel. The impeller is connected to reaction plate inside the vessel. *Reader Enquiry Service No. 23*



products

High gloss resins for water-based inks

Allied Colloids Ltd of Bradford has produced a new resin system for water-based inks. These two new chemicals in the Glascol series, are designated LS18 and LE17. LS18 is a low molecular weight styrene acrylic copolymer designed to give high gloss water-based inks. LE17 has been developed to give high gloss and heat resis-

Thermal analysis system

Perkin-Elmer of Beaconsfield announce another Thermal Analysis System—*Euro-lab 7*. This system will add a DSC capability to any laboratory already in possession of a Perkin-Elmer Model 3600/3700 Data Station. All eurolabs are based around the TADS series of instruments and offer DSC, TGA, TMA, DTA and DMA as options. Euro-lab 7 is based upon the

options. Eurolab 7 is based upon the DSC 4 differential scanning calorimeter with a temperature programmer, software and A4 plotter.

Reader Enquiry Service No. 24

literature

UK Chemical Industry

"Britain's Chemical Industry", a financial survey of the chemical industry, published by Jordan & Sons Ltd warns British chemical manufacturers that they are still not reacting closely enough to customer requirements on an international scale. The survey analyses 110 companies, providing information on each from the last three years' filed accounts, details of their types of business, immediate and ultimate holding companies, etc. The financial section includes comparison tables covering the top 30 British companies. This publication priced at £125.00 is available from: Jordan & Sons Ltd, Jordan House, Brunswick Place, London N1 6EE.

Safety Sign Wallchart

Focal Displays Ltd has published a new 1986 safety sign and pipeline identification

system wall chart. The colour chart, which includes over 100 new signs, features IMO-Sea and IATA-Air hazard warning signs, Hazchem storage and road tanker signs, and packaging labels for dangerous substances. For a free copy contact: Focal Displays Ltd, 12 Wandle Way, Mitcham, Surrey CR4 4NR.

meetings

FSCT Annual Meeting

Federation of Societies for Coatings Technology, 64th Annual Meeting 5-7 November, 1986, will be held at the Georgia World Congress Centre, Atlanta, Georgia. For further information contact: Federation of Societies for Coatings Technology, 1315 Walnut St, Philadelphia, Pennsylvania 19107, USA.

Chemical Storage

The Centre for Continuing Vocational Education, University of Sheffield is holding a one-day course on the "Safe storage of hazardous chemicals" on Wednesday, 26 November, 1986. For further details contact: Frances Wells, Centre for Continuing Vocational

Education, The University of Sheffield, 85 Wilkinson Street, Sheffield S10 2GJ.

HNC in Printing

The London College of Printing will be offering a Higher National Certificate in Print Planning and Production, commencing September 1986. The course should be of interest to those working in production and allied areas including ink and paper manufacture. For further details contact Dr Robert C. Thompson, Department of Science and General Studies, London College of Printing, Elephant and Castle, London SE1 6SB.

people

Mr C. L. Duggleby has been appointed Chemicals Sales Manager for BP Far East and will be based in Tokyo. Mr Duggleby was formerly Product Officer at the Hydrocarbon Solvents Division of BP Chemicals.

Peter Green has been appointed deputy Managing Director of Bink-Bullows Ltd of Walsall, the spray painting equipment specialists. Mr Green joined Binks as Export Sales Engineer in 1970 and was appointed Director in 1984.

occa news

Newcastle Section

Golf Tournament

The Newcastle Section Golf Tournament was played on Friday, 27 June, at Barnard Castle Golf Club. The competition was once again sponsored by Tioxide UK Ltd and the first prize was won by Reg Blakely who recently retired from Tioxide's technical department.

A replica cup for the leading visitor was won by David Thomas of Crown Paints Ltd.

Newcastle Section Golf Tournament: (on the left) Mr G. Carr (Chairman Newcastle Section) presenting the cup to Mr R. Blakely



In all 24 members and guests played in the tournament which took place in beautiful weather.

L. Morpeth

Northern Sections

1986 Northern Section's T. McWilliam Golf Tournament

On 27 May, 23 contestants braved the gale-force winds and blustery showers to compete for the T. McWilliam Team of Three Golf Trophy over the tough Pannal golf course.

After monopolising this event for the past six years the Manchester Section sportingly agreed to open up this competition and took on all-comers, their own best three scores verses the best three scores from all the other sections. This resulted in the narrowest of wins for the 'other' sections by a single Stableford point. Scores, R. Wells (West Riding) 27, R. Tennant (Midlands) 27, T. Wright (West Riding) 22. Total 76 points against Manchester Section's 75 points. J. Roberts 26, R. Ashton 25, D Clayton 24. These low scores aptly reflecting the difficult playing conditions.

The trophy and prizes were presented by Association President, Frank Redman and thanks to the generosity of many companies, all contestants received a prize as part recompense for the destruction of many a smooth golfing swing.

T. Wright

Scottish Section

Visit to Marks & Spencer

There was an excellent turn out of members and guests for the evening visit to Marks & Spencer on 16 April.

This proved to be a very interesting and informative evening which took the form of a cheese and wine buffet followed by a conducted tour round the various departments of the M & S Argyle Street, Glasgow, store. The visit included a behind the scenes look at the administration offices, staff facilities and canteen etc. There followed a lively question and answer session where the M & S management team were on hand to reply to the wide range of questions.

Overall the visit provided an interesting insight into the marketing policy of M & S.

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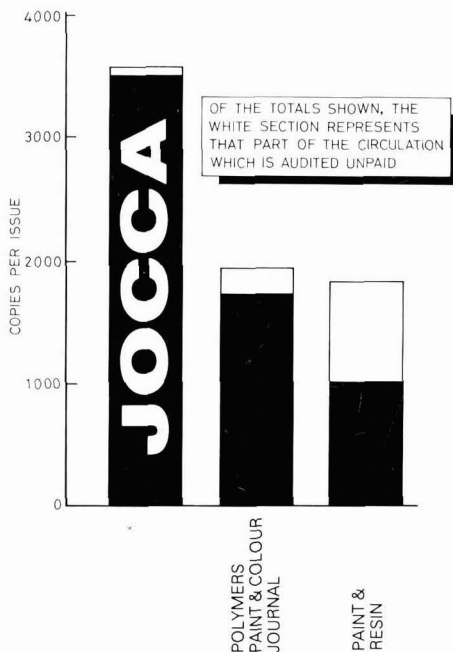
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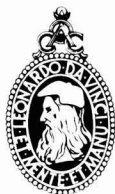
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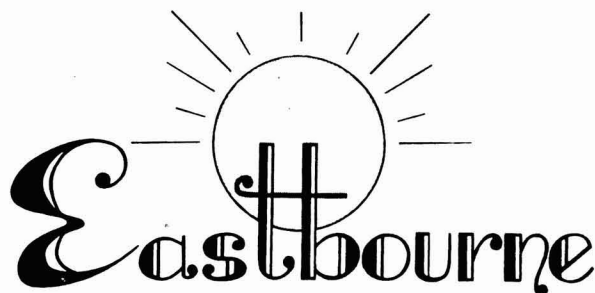
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OCCA CONFERENCE 1987

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17-20 JUNE, 1987

CALL FOR PAPERS

OCCA's next Biennial Conference will be held in Eastbourne from 17-20 June 1987. The theme for the Association's Conference, which in the past has attracted visitors from many parts of the world, will be "Advances and application of science and technology in surface coatings".

The objectives of the Conference will be to review the advances made in the science and technology of surface coatings in both the commercial and academic fields and it is intended to encompass as wide a field as possible in the paint, printing ink and allied industries. Attention will also be directed to future possible trends and implications in these industries.

The Honorary Research and Development Officer now invites offers of papers for presentation at this Conference. Anyone wishing to submit a paper for consideration should notify his intention as soon as possible to: **The Director and Secretary, Oil and Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, UK. (Tel: 01-908 1086, telex 922670).**

Golf Outing

The annual golf outing of the Scottish Section returned to the popular Aberdour Golf Course on the banks of the Firth of Forth on 9 May. After lunch members and guests spent an enjoyable afternoon negotiating the golf course, indeed some were not content with the golf course but preferred to include the neighbouring waters of the Forth.

However, as always this social event was a great success and was concluded with a meal and prizegiving. Prizes were awarded to:

Members

Whittaker Trophy: Brian Donaldson—nett 61.

Morris Ashby Quaich (Best Scratch Score): Tom Kirkwood—gross 76.

Tioxide Tankard (Most improved player): Nigel Baird (nine strokes).

Visitors

Visitors Shield: Ian Webster—nett 66.

R. A. Hunter

Bristol Section



The photograph above was taken by the Immediate Past Chairman of the Bristol Section and currently a Vice President (Mr Roger Saunders) on the occasion of the visit to the SS "Great Britain", arranged by Bristol Section in conjunction with the Association's AGM on 18 June 1986. A report of the visit appeared on p. 225 of the August issue of JOCCA

Cape Section

Cape OCCA ties

The Cape Section of the South African Division had now acquired a supply of embroidered OCCA ties and is requesting members in South Africa to wear the tie at OCCA functions. It has also been suggested that ties should be presented to important visitors and speakers. Available in blue or maroon, the ties are R16.50 each and may be obtained from the Cape chairman, Mrs C. J. de Villiers at PO Box 297, Paarden Eiland 7420, South Africa.

News of Members



Terry Say (left) being congratulated by Dick Philbrick, Chairman of Natal Section on becoming an ATSC

Terry Say, ATSC, Immediate Past Chairman of the Natal Section has been appointed Group Polymer Research

Manager for the RTZ Chemicals Group based at the Walsh Chemical Corporation, North Carolina, USA, where he will be responsible for the co-ordination and organisation of group research into polymers in the area of surface coatings. Mr Say was previously Technical Director for Bevaloid, SA (Pty) Ltd, a member of the RTZ Group.

David V. Maltman Grad. PRI, has been appointed Product Manager for Pigments and Additives by Floridienne (UK) Ltd trading as Micro Products. He will be responsible for the further development of Floridienne's interests in pigments and pigment preparations and additives for the paint and allied industries. His former appointments were with Vinyl Products Ltd, Durham Chemical Distributors and ICI Organics Division PLC.



D. V. Maltman

Douglas Graham, an ordinary member attached to the General Overseas Section, the International Marketing Manager with

the Colours Group of Sun Chemical Corporation, is relocating his office to Sun France Inc, Huningue, France, after seven years in Cincinnati, Ohio, USA.

Dr L. A. O'Neill has recently been awarded the Silver Medal by the Paintmakers' Association at their Annual Conference in Torquay for Meritorious Service, in recognition of his work for the industry over 50 years at the Paint Research Association. Dr O'Neill's contributions over this period have been threefold: the application of scientific research on paint media and properties to improve formulation; the development of analytical techniques for paints and their components, using the newly available instruments and principles; and, for the last 10 years in the information department, as an acknowledged expert on health and safety matters.

Jordan Award

The Jordan Award Committee now invites applications for the ninth award of £100. The rules of the Award are:

1. The Award will be made for the best contribution to the science or technology of surface coatings by a member of the Association of any nationality working in either the academic or industrial fields who is under the age of 35 at the date of the application.

2. The final date for submission of applications will on this occasion be 31 December 1986 and it is hoped to present the award at the Association's Conference in the following year.

3. The selection of the recipient of the Award will be made by the Jordan Award Committee under the chairmanship of the Association's Hon. Research and Development Officer.

4. There will be two methods of application. First, by submission of a paper describing original work by the candidate which is offered for publication in the *journal* or has been so published during application. The alternative method will be by recommendation of a superior for work which for reasons of commercial secrecy cannot be published; in this case the candidate will be expected to submit a dissertation on a topic relating to his work and demonstrating his superior knowledge of the principles thereof. The Award is for individual merit and clear evidence of the candidate's own contribution will be required if a paper is offered under joint authorship.

5. Applications should be addressed to the Director & Secretary at the Association's offices.

professional grade

At the meeting of the Professional Grade Committee held on 16 July 1986, the following admissions were made:

Transferred from Associateship to Fellowship

Hackney, Thomas (*Auckland*)
Pace, Graham (*Thames Valley*)

Admitted to Associateship

Summers, Sean Francis (*London*)
Zakaria, Anis (*Manchester*)

Transferred from Licentiateship to Associateship

Redpath, Neil Douglas (*Newcastle*)

Admitted to Licentiateship

Leonard, Mark (*Manchester*)

new members

The sections to which new members are attached are shown in *italics* together with the country, where applicable:

Ordinary members

Belding, P. N., BSc (*Transvaal*)
Dunn, M. A. R., BSc (*Auckland*)
Hodgson, P., BSc (*Newcastle*)
McGuinness, A., BSc (*Auckland*)
Middleton, J. D., BSc (*Transvaal*)
Munif, M. (*Auckland*)
Rothville, G. A. (*Auckland*)
Steele, G. V. J. (*Auckland*)
Voice, S. M. (*Auckland*)
Wilkie, P. J., BSc (*Auckland*)

Associate members

Campbell-Hall, G. D. (*Natal*)
Crocker, G. A. (*Auckland*)
Fabrizio, M. (*General Overseas—Italy*)
Fuller, H. S. (*Cape*)
Spencer, D. J. (*Natal*)

REPORT OF COUNCIL MEETING

A meeting of Council took place at 1.34 p.m. on 16 July 1986, at the Great Northern Hotel, London N1 9AN. The President (Mr F. B. Redman) was in the Chair and there were 26 members present.

Opening the meeting the President stated that since only one nomination, that of Mr Lionel Morpeth, had been received for the three elective places on Council, the first act of the Council would be to fill the two vacant places. More than two nominations from Council having now been received, it was necessary to hold a ballot, as a result of which Mr B. E. Myatt and Mr D. W. N. Clayton were declared elected.

The President then welcomed new members who were serving on Council for the first time and others who had returned after an absence.

A report was received on the very successful arrangements made by the Bristol Section for the social side of the AGM on 18 June with a Reunion Luncheon, visit to the SS "Great Britain" (see photograph on page 254) and a lecture on its restoration and the Council recorded its thanks to Mr Roger Saunders (Vice President and Immediate Past Chairman of Bristol Section) for the arrangements made.

At the AGM it had been announced that Mr J. R. Bourne had been appointed President Designate, Mr Lionel Morpeth had been elected as an Elective Council Member and that two new Honorary Officers had been elected (Mr A. J.

Newbould and Mr W. Borrell) to fill the vacancies by the resignation of Mr H. J. Clarke (Honorary Technical Education Officer) and Mr G. R. Robson (Honorary Overseas Secretary) respectively. A vote of thanks had been passed to retiring Council Members and to the Director and Secretary and his staff.

The dates for Council meetings for the forthcoming session were agreed.

The appointment of committees of Council were confirmed and these were published in the August issue of *JOCCA*. The Council considered vacancies which had arisen in the Association's representation on other organisations and suggestions were made for replacements.

Reports were received on the preparation for the Eastbourne Conference 17-20 June 1987, and the Conference at Chester, scheduled for 1989. The Honorary Research and Development Officer asked Council and Sections to forward to him or the Director and Secretary as many suggestions as possible for papers and lecturers so that the programme could be completed in the autumn.

The number of members in arrears with their 1986 subscription was tabled and Council was pleased to note that this was lower than in 1985.

A report was made on the sale of publications, including the new monographs and other books.

Details of the successful progress of the Paintmakers Open Tech Project were received and Council noted the possibility that those who completed the modules 1-8 could be urged to apply for the Association's Licentiateship in 1988. Senior members were asked to encourage younger personnel to become Registered Students during their training.

It was reported that the Professional Grade Committee had transferred two Associates to Fellowship, had admitted two Associates, transferred one Licentiate to Associateship and admitted one member as a Licentiate.

Full details on the recent Exhibition were discussed and preliminary plans agreed for a further exhibition at the Harrogate Conference Centre, with an extended area, 15-16 June 1988.

The President reported on correspondence with the New Zealand Division Chairman concerning the future of the Division and explained that the proposals already made would be discussed at the New Zealand Division's Convention at the end of July.

Further steps had been taken to consider the modernization and re-equipment of Priory House and the composition of a Working Group was agreed.

There being no further business, the President thanked members for their attendance and declared the meeting closed at 3.26 p.m.

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