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Transactions and Communications

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Transactions and Communications

The athermal theory of vehicle adsorption and the structure of pigmented paints

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Summary

This paper is intended to associate the practical problems of pigmented paint with the largely theoretical conception of adsorption. Because of the different levels of these two fields with respect to the theory of cognition, this connection cannot be directly accomplished. It rather requires a structural conception to be used.

The theory of adsorption has been established in closely following the experimental results. The authors have developed, therefore, a structural pattern of the pigmented paint that is in good agreement with both the logical consequences of the theory of adsorption and the practical behaviour of paints. Consequently, the structural pattern includes the generalization obtained from the theoretical work, in a way applicable to practical problems.

Examples of practical application are given. The application of the new structural pattern to practical problems is shown to have great heuristic power.

Keywords

Processes and methods primarily associated with:

analysis, measurement or testing
  adsorption

manufacturing or synthesis
  adsorption
  pigment dispersion

Properties, characteristics and conditions primarily associated with:

materials in general
  rheological property
  viscosity

bulk coatings and allied products
  pigment volume concentration
  stability

La théorie de l'absorption athermique de véhicle à l'égard de la structure de peintures

Résumé

L'intention de cet article est de relier les problèmes pratiques au concept largement théorique d'absorption. Toutefois, à cause de la lacune qui se trouve entre ces deux domaines on ne saurait achever ce liaison directement. On a besoin plutôt d'un concept structurel.

On a bassé la théorie d'absorption sur une considération étudiée des résultats expérimentaux. Les auteurs ont perfectionné un concept structurel de peintures qui s'accord bien aux conséquences logiques de la théorie d'absorption et à la fois au comportement en pratique de peintures. Par conséquent, dans une manière valable à la résolution des problèmes pratiques, le concept structurel comprend une généralisation dérivée de l'étude théorique.

On démontre que l'application de ce nouveau concept structurel aux problèmes pratiques possède de grandes possibilités au point de vue scientifique.

Die Athermale Theorie der Bindemitteladsorption und die Struktur Pigmentierter Lacke

Zusammenfassung

In der nachfolgenden Arbeit wird der Versuch unternommen, praktische Probleme des pigmentierten Anstrichstoffs mit der weitgehend abstrakten theoretischen Darstellung der Adsorption in Verbindung zu bringen. Diese Verbindung ist wegen der unterschiedlichen erkenntnistheoretischen Ebenen beider Gebiete nicht direkt zu vollziehen. Sie bedarf vielmehr der Vermittlung durch eine Strukturvorstellung. Die Adsorptionstheorie wurde in enger Anlehnung an die experimentellen Ergebnisse aufgestellt. Es gelang daher, aus ihr ein Strukturbild des pigmentierten Anstrichstoffs zu entwickeln, das sowohl mit den logischen Konsequenzen der Adsorptionstheorie als auch mit dem praktischen Verhalten der Anstrichstoffs in guter Übereinstimmung steht.

Das Strukturbild enthält somit die aus der theoretischen Arbeit erhaltene Verallgemeinerung in einer auf praktische Probleme anwendbaren Form. Es wurden einige Beispiele für die praktische Anwendung gegeben. Dabei erweist sich, daß die Anwendung des neuen Strukturbildes auf praktische Probleme eine große heuristische Kraft besitzt.

Introduction

Ref. 1-13

Adsorption is a phenomenon of great importance with regard to pigmented paint. For example, adsorption is generally known to exert an essential influence on the dispersion and the dispersion stabilisation of pigments. Therefore, many workers have dealt with problems of adsorption in paints and have studied them from several points of view.

Numerous data on the latter are given, for example, in references 1 and 5. Attention has also been paid to theoretical investigations into the adsorption of paint vehicles on to pigments; however, no great progress could be achieved in this field for a long time. Previously, the Langmuir isotherm had been used for the theoretical interpretation of vehicle adsorption, although most workers were aware of the inadequacy of this approach.[1-4] Difficulties are encountered mainly due to the fact that Langmuir's isotherm, on account of the presupposition in its derivation, is restricted to mixtures

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of components with molecules of equal size. The vehicles used in paints, however, usually have a molecular weight exceeding those of the solvents by at least a factor of ten. The thickness of the adsorbed layer of vehicle has been discussed in a number of papers[6-12] and found to be approximately 10nm. It is a reasonable assumption[5] that for such layers, which also contain large portions of solvent, the adsorption of individual vehicle molecules is improbable. Instead, the existence should be assumed of molecular assemblies, which contain a great number of vehicle molecules and a considerable amount of solvent, and whose diameter roughly corresponds to the thickness of the adsorbed layer. This makes the application of Langmuir's isotherm even more doubtful. In the authors' papers,[5, 9-12] it was not only the thickness of the adsorbed layer which could be determined from the data of the adsorption isotherm. This determination was verified also by measuring the rheological properties and the sedimentation volume of the pigment dispersions, so that the practical importance of the adsorbed layer could be explained. This view is confirmed by the fact that the present work was carried out on pigment dispersions, which employed pigment and vehicle concentrations at the levels normally used in paints.

In conjunction with the authors' experimental work a supplementary theory of vehicle adsorption has been developed[5, 13]. It takes into account the latest knowledge of the adsorbed layer and its practical significance, and correlates the properties of the vehicle solution with those of the pigmented paint. It provides, therefore, the basis for explanation of the structure of pigmented paints.

So far, the experimental work has been mainly with alkyd resins, so that the results presented here are largely related to solutions and paints based on these media.

The athermal theory of vehicle adsorption

Ref. 5

The experimental results suggest that the vehicle molecules become assembled in the solution to form large isodiametric molecular assemblies, which still contain a considerable amount of solvent. This makes the dimensional difference between the adsorbed particles and the solvent molecules even more pronounced than is apparent from the molecular weight ratio. The molecular assemblies respresenting the adsorbed particles are referred to as "globules". Experimental data[5] indicate that the molecular weight of the globules is usually 10^3 to 10^4 times that of the solvent molecules. Thus, it appears to be reasonable to use only an athermal equation of adsorption when considering vehicle adsorption.

Other athermal equations of adsorption

Ref. 14-25

Athermal equations of adsorption originated some time ago. As early as in 1937, a paper by Broda and Mark[11] dealt with the adsorption of chain molecules, and in 1939 Chang[15] reported on the arrangement of dimeric molecules in an interface. Once the theory of athermal solution had been developed, the problem of athermal adsorption was studied by many workers. Mackor and van der Waals[16], for example, derived adsorption equations for rigid rod-shaped molecules; Everett[17] reported an equation for the adsorption of rod-shaped molecules. Simha, Frisch and Eirich[18, 19] were the first to give a complete expression for the adsorption isotherms of flexible linear macromolecules from dilute solutions. In

a number of additional investigations, Frisch and Simha improved their theory and more recently the problem has been studied further by a considerable number of other workers.[20, 21]

Neither the model for rod-shaped molecules nor that for filamentary molecules in dilute solution is applicable to the problem of vehicle adsorption. The closest approximation was obtained using the equation given by Prigogine and Marechal,[25] although in this equation the thickness of the adsorbed layer is limited to the diameter of a solvent molecule, and this is inconsistent with the idea of globules. It became necessary, therefore, to derive a new athermal equation of adsorption which conforms with the experimental facts of vehicle adsorption.

Assumptions to be made in deriving the equation of adsorption

The methods of statistical thermodynamics were used in deriving the adsorption equation, and it was necessary, therefore, to make a number of assumptions which are summarized below.

1. The vehicle solution is considered as a two-component mixture; that is both the solvent and the vehicle consist of similar molecules. The "globules" are molecules of the vehicle.

2. The lattice model for liquids was used, and a solvent molecule and globule were assumed to take a lattice site and m^3 sites, respectively. The volume of a lattice cell in the adsorbed layer is identical to that in the solution.

3. The adsorption is considered to be a closed system; that is, the number of solvent molecules and the number of globules are known.

4. Due to adsorption, the molecules will lose their kinetic energy, and change their potential energy by the amount of adsorption energy. All other kinds of energy, which are independent of the above two energies, are not altered by adsorption.

5. The adsorption energy is present only in the lattice layer immediately adjacent to the adsorption surface and has an identical value on all lattice sites for all molecules of a component.

6. The interaction energies between molecules act between the nearest neighbours only.

7. Ideal behaviour of the interaction energies is assumed; that is, all configurations are equivalent in terms of energy.

Special features in the derivation and explanation of the isothermal equation

Ref. 5, 13, 26, 5

The derivation of the isothermal equation is based upon an athermal mixture. Owing to the above assumptions, the integral in the free energy term (represented by canonical distribution) becomes solvable. Equating the chemical potentials for the adsorbed layer to the remaining solution volume gives the isothermal equation. A detailed account of the derivation would go beyond the scope of this paper; it is dealt with elsewhere.[5, 13] Two special features of the

derivation should be mentioned however: the first is related to the calculation of the combination factors, when use was made of the "filling method" of Flory and Huggins.[26] This does not contradict the idea of a cooperative distribution of lattice sites, which is due to the fact that a globule occupies m^3 lattice sites. It is based on the assumption of random distribution of the globules and implies the separation of the statistics of the solution from those of the globules. In the athermal theory of high-polymer solutions, this is usually done in a different way; in deriving the isothermal equation, the globules are considered to be rigid. Allowance is made subsequently for the deformability.

The second special feature is related to the exchange conditions. On adsorption of a globule, not only do m^2 solvent molecules disappear from the adsorbed layer, but also the volume of the adsorbed layer changes. Whilst the m^2 solvent molecules are present in the first lattice plane above the adsorbent, the adsorbed globule will extend over m lattice planes. Analogously, there is a change in volume of the free solution. This change in volume associated with the adsorption of the two portions of solution, which are in a state of equilibrium, has been allowed for in the exchange conditions.

It is reasonable to state that an allowance for the first special feature will give a treatment of the solution sufficient for the experimental results, whilst to consider the second special feature will be to allow for the reality of the conditions existing in the adsorbed layer. The derivation will lead to the equation:

$$\frac{(1-A_N)^{m2}}{mA_N} = K\frac{(1-x_{2L})^{m2}}{x_{2L}} \cdot \exp(-x_{2L}M)\ldots\ldots1$$

where

A_N = degree of occupation of adsorbent area by the globules, expressed as a fraction of total area.

x_{2L} = volume concentration of globules in solution.

$m \approx$ diameter of globules (in the derivation exactly equal to length of the side of globules taken as cubes), expressed in solvent molecule diameters.

$M = m^3 - m^2 - 1 + 1/m$

K is the adsorption constant.

Essentially, the equation contains the partition functions of the translation of solvent molecules and the globule, and a factor which is due to deformability of the globules. In addition, K represents the adsorption energy, but compared with the other factors it is negligible. This corresponds to the athermal nature of the equation of adsorption. In most cases, K is very small. So far, $\log K$ has been found to range from 0 to -400. This wide range can be explained by the fact that even slight changes in the deformability of the globules will produce great alterations in the value of K.[5] When evaluating the isotherms, m is essentially of greater significance than K, since m corresponds to the thickness of the adsorbed layer; moreover, K is dependent on m. For higher values of m, the change in K will have a decreasing influence on the isotherms (Figs. 1-4).
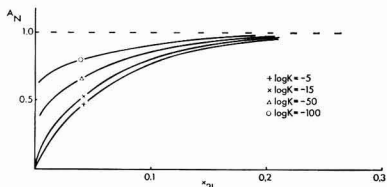
Fig. 1. Theoretical isotherms m = 15
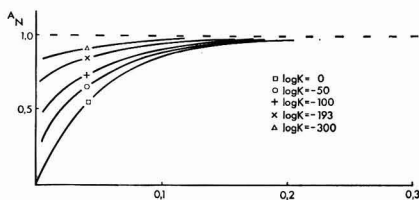
Fig. 2. Theoretical isotherms m = 20
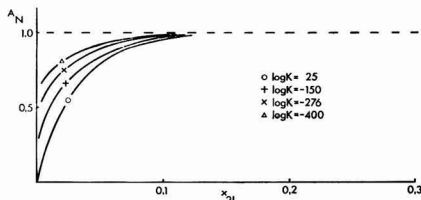
Fig. 3. Theoretical isotherms m = 30
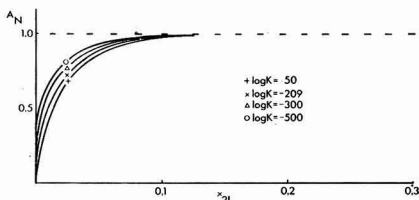
Fig. 4. Theoretical isotherms m = 40

Representation of the experimental isotherms by the adsorption equation

Ref. 9, 12, 9, 11

When the adsorption equation [1] is applied to experimentally determined isotherms, it should be noted that the quantities used in the equation are not identical with those used in the experimental representations and an appropriate conversion must be performed. When representing experimental adsorption isotherms (Figs. 5 and 6), it is common usage to give the vehicle concentration in solution C_G in terms of percentage by weight and the adsorbed amount of vehicle A in terms of an excess quantity as weight per unit surface area of adsorbent.

$$x_{2L} = \frac{\rho_o}{\rho_o + (C_A/C_G - 1).A} \ldots\ldots\ldots\ldots2$$

$$A_N = \frac{A}{a} + C_G/C_A \ldots\ldots\ldots\ldots3$$

Where C_A is the weight concentration of the vehicle in the adsorbed layer for complete occupation and corresponds to the composition of the globules. C_A can be determined from the point at which the isotherms intersect the abscissa (Fig. 5). a is the maximum amount of vehicle present in the adsorption space (for complete occupation $A_N = 1$) and is represented by the intersection of the extension of the linear portion of the isotherm with the ordinate (Fig. 5). ρ_A is the specific gravity of the vehicle solution having the concentration C_A, and ρ_0 is the specific gravity of the solvent.

It becomes evident that using the adsorption equation [1], certain demands are made on the experimental isotherms

C
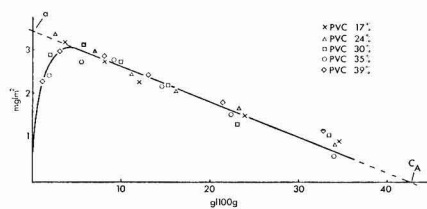
Fig. 5. Adsorption of Syntal 725 in xylene on to rutile TiO₂

due to conversion of the quantities. Whilst extrapolation on a is relatively simple, it is necessary to measure the isotherm over a wide range of concentrations to perform a reliable determination of C_A.

The adsorption equation [1] enables the experimental isotherms to be represented accurately, as can be seen in Figs. 7 and 8, which are derived from the curves shown in Figs. 5 and 6. The behaviour of the isotherm determined experimentally is shown as a solid line, whilst the theoretical values obtained from the given constants m and $\log K$ are plotted as points. The theoretical values are seen to be in excellent agreement with the experimental data. There is no doubt regarding the choice of the values of the constants m and K: that is, there is only one pair of values enabling a theoretical isotherm to be adapted to a given experimental isotherm. It is evident from Figs. 1 to 4 that for a given pair of values A_N and x_{2L}, there is in each case only one K-value suitable for one value of m. It can be seen from Fig. 9 that the curvatures of the isotherms with different values of m, passing through a given point, are markedly dissimilar; thus it is easy to choose unequivocally the correct m.
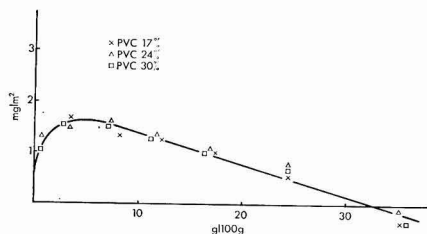
Fig. 6. Adsorption of Duxalkyd S 259 in xylene on to anatase TiO₂
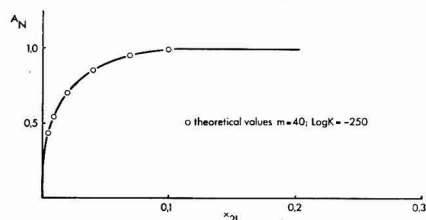
Fig. 7. Normalised representation of the isotherm shown in Fig. 5
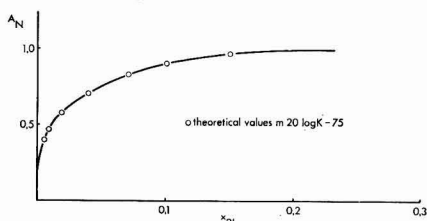
Fig. 8. Normalised representation of the isotherm shown in Fig. 6
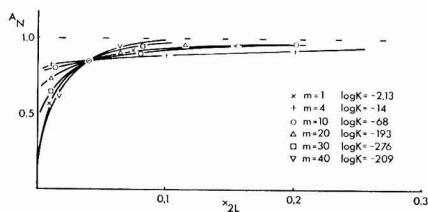
Fig. 9. Theoretical isotherms passing through the point $A_N = 0.85$
$x_{2L} = 0.04$

It is interesting to note the behaviour of the isotherm with $m = 1$; it is more similar to the cases where $m = 20$ and $m = 30$ than it is to $m = 4$. This finding explains how Langmuir's equation approximates reasonably well to the curves of the isotherms of vehicle adsorption, since equation [1] becomes Langmuir's equation when $m = 1$. Agreement between the curvatures of the experimental isotherm and the curves fitted to equation [1] can be obtained by selecting a definite value of m. However, m is an expression of the difference in size between the solution molecule and globule and, according to its definition, a direct measure of the thickness of the adsorbed layer. Thus, it is possible to determine the thickness of the adsorbed layer from the theoretical representation of the isotherm. Some examples are given in Table 1 and these are compared with the experimental

Table 1

Comparison of experimentally and theoretically determined thicknesses of adsorbed layer (D)

Solution	m	$\log K$	D (nm) theoretical	experimental
Duxalkyd SIIK in white spirit	40	—360	26.0	10.0
Duxalkyd SIIK in toluene	30	—150	16.8	10.4
Linseed oil/stand oil in white spirit	20	— 50	12.8	20.3
Syntal 725 in xylene	40	—250	23.6	8.0
Duxalkyd S 259 in xylene	20	— 75	11.8	6.5
Syntal 725 in xylene	30	—125	17.7	13.5
Linseed oil/wood oil/stand oil in xylene	20	0	11.8	6.4

determinations[9, 12]. Essentially, comparison between the theoretically and experimentally determined thicknesses of adsorbed layers should be considered from three aspects. Firstly, it should be pointed out that good progress has been made in the past by using Langmuir's isotherm when considered in the light of the conventional interpretation of vehicle adsorption. Roughly speaking, the deviations found lie within a factor of between 2 and 3. Proceeding as described above and using Langmuir's isotherm $(m = 1)$, theoretical values of the layer's thickness would be found to range around 0.6 nm. The deviations observed from the experimental values are characterized by the factor 20-30. Secondly, experimental uncertainty becomes involved in the consideration, namely in the experimentally determined thickness of the adsorbed layer due to pigment surface area, and in the theoretical values when the slope of the isotherm is determined. Thirdly, in deriving equation [1], a number of simplifying assumptions have been made, which are not exactly true in practice. Thus, for example, the vehicle solution has been considered as a two-component system, which can be true only as an approximation according to observations of

selective adsorption[9, 11]. It must be concluded, therefore, that in view of the theoretical and experimental conditions and assumptions, no better agreement of the two determinations of layer thickness could be expected.

Consequently, it can be stated that the adsorption equation [1] will very satisfactorily express the adsorption of vehicles on to pigments. In contrast to the interpretation of adsorption of vehicles usually obtained by using Langmuir's isotherm, the new equation offers a number of essential improvements:

1. The experimentally determined curvatures of the isotherm can be recorded with much greater accuracy than is the case when using Langmuir's equation.

2. Allowance can be made for the differences in size between vehicle and solvent molecules.

3. The correct magnitude of the adsorbed layer is evident from the adsorption equation.

4. The high solvent content in the adsorbed layer is in agreement with the assumption ma.:e when deriving the adsorption equation.

5. The large-size globule, occupying a volume hundreds of times that of a solvent molecule, accounts for the poor desorbability of the vehicles.

Equation [1] can be regarded as a true athermal adsorption equation for, compared with the difference in molecular size, the difference in adsorption energy is of secondary importance. Accordingly, the molecular assemblies can be adsorbed, although they do not have interaction energies relative to their nearest neighbours which differ from those of the solvent molecules. Thus, the athermal statement does not contradict adsorption. It can be claimed that the experimental conditions, the assumptions for deriving the theory, and the conclusions which can be drawn from it, do constitute a self-contained logical unit.

Conclusions regarding the structure of vehicle solutions

Ref. 5, 27, 28, 5

From the adsorption theory given above, essential conclusions can be drawn regarding the structure of vehicle solutions. Since the adsorption equation [1] has proved to be correct for representing the experimental isotherms, so the assumptions used in its derivation can be taken to be correct for the vehicle solution. Accordingly, the vehicle at low solvent concentrations is present as large-sized solvated associates, the "globules", which form an athermal mixture with the remaining solvent. In fact, this athermal mixture can exist only up to concentrations not exceeding that corresponding to the composition of the globules. Above this concentration, the vehicle must be considered as a swollen, free-flowing gel. The function of the adsorption theory is to characterize exactly the range of the athermal mixture. It indicates that the vehicle is dispersed, so to speak, in the solvent in terms of microgel particles. It allows the determination of size and composition of the microgel particles and enables the concentration to be determined at which the range of dispersion and the gel range of the vehicle solution would merge in one another.

According to this concept of the structure, Einstein's viscosity law for spherical suspensions should be applicable to the vehicle solution and, making use of the former, it should be possible to calculate the viscosity from the adsorption data. This was shown[5] actually to be true. Figs. 10 and 11 show the comparison between the experimentally determined viscosity and that calculated from adsorption data, using the solutions employed to obtain the data for Figs. 5 and 6. The calculations were carried out according to formulae reported by Eirich and Riseman[27] and Brinkman[28], which are extensions of Einstein's viscosity law concerning the range of concentrations. They can be used for volume concentrations up to approximately 10 per cent, that is up to weight concentrations of 4 per cent for the given example. Within this concentration range, the agreement obtained between experimentally determined and theoretically calculated viscosities is also reasonably good in other cases[5]. This result may be taken as satisfactory confirmation of the solution structure derived from the adsorption study. This confirmation is of particular value since it is completely independent of the adsorption.
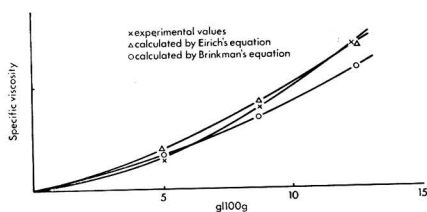
Fig. 10. Viscosity of Syntal 725 in xylene for the isotherm shown in Fig. 5
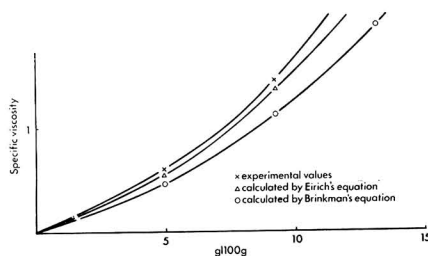
Fig. 11. Viscosity of Duxalkyd S 259 in xylene for the isotherm shown in Fig. 6

It is possible to calculate the viscosity of vehicle solutions from adsorption data, however, only if all of the vehicle were contained in the globules. This situation is not always encountered, and is referred to later.

The transition from the dispersion range to the gel range of vehicle solution can be determined from the viscosity behaviour as a first approximation (Fig. 12). In the dispersion range ($\approx < 33$ g/100 g), the solution viscosity is mainly determined by the solvent viscosity. It will, therefore, increase only at a slow rate with increasing vehicle content. It is when the volume concentration of the globules reaches values high enough to cause a considerable mutual steric hindrance (approximately 75 per cent by volume or 25 per cent by weight) that the viscosity will increase at an ever increasing rate, and steadily pass into the steep rise of the gel range.
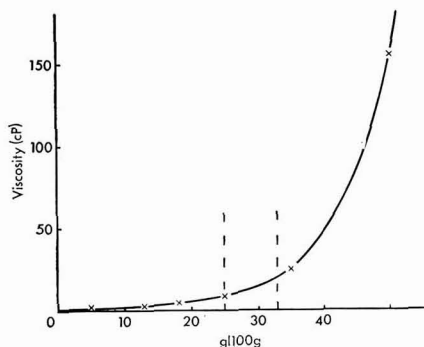
Fig. 12. Viscosity of solutions of Duxalkyd S 259 resin

The structure of pigmented paints

Ref. 5, 9-12, 5, 29

The results presented in the previous sections in conjunction with the results of the authors' experimental work[5, 9, 12], enable a comprehensive picture to be obtained of the structure of pigmented paints, in which adsorption plays a central part.

The considerations are based upon the volumetric distribution in the pigmented paint. There are essentially three volume components of the pigmented paint to be considered, namely: (i) the pigment volume, (ii) the volume of the adsorbed layer, and (iii) the volume of the remaining solution.

These volume components differ to a considerable extent, depending on the type of paint concerned. In most cases, the pigment volume will range from 5 to 40 per cent; that of the adsorbed layer from 1 to 20 per cent; whilst the volume of the remaining solution will be somewhere between 50 and 95 per cent. The adsorbed layer not only occupies a considerable volume, but is also of particular importance because of its spacial arrangement and its relationship to the solution structure. It is, for example, responsible for the fact that the pigmented paint can be assumed essentially, to be an athermal mixture such that the basic concepts of

the structural pattern of the pigmented paint given below can be taken as fundamental to the athermal theory.

1. The adsorbed layer causes the pigment particles to be screened energetically from each other and thus prevented from closely approaching one another, thereby conferring dispersion stability on the pigment suspension.

2. The adsorbed layer is characterized by mechanical strength and due to its volume will exert some influence on the essential paint properties. In terms of composition and thickness, the layer is constant over a wide range of concentrations of the vehicle solution, which may also extend beyond the concentration of the adsorbed layer.

3. The thickness and composition of the adsorbed layer are closely related to the structure of the vehicle solution, which can be derived from a study of the adsorption behaviour.

4. At sufficiently low concentrations (for alkyd resins somewhat less than 35 per cent), the vehicle is dissolved in the kind of globules which, together with the remaining solvent, form an athermal mixture. Size and composition of the globules can be derived from the thickness of the adsorbed layer.

5. With in the range of concentrations mentioned above, a pigmented paint is an athermal mixture of solvent, globules, and pigment covered by the adsorbed layer.

Diagrammatic representations of a pigmented paint with different pigment and vehicle volume concentrations (PVC and VVC) are shown in Fig. 13. It should be noted that the vehicle volume concentrations given in the Figures are assumed to be the concentrations of the globules, so that the actual VVC is essentially lower. The Figures have been devised such that the mean minimum particle spacing is correctly reproduced. The diagrams are based on a mean pigment particle diameter of 0.23 μm, and a thickness of adsorbed layer of 10nm. Under these conditions, the volume of adsorbed layer is approximately 30 per cent of the pigment volume. The Figures correspond to the suspension whose adsorption isotherm is plotted in Fig. 5; its sediment PVC and relative suspension viscosity are shown in Figs. 14 and 16, respectively. For this particular case, the simplified representation of pigment particles as spheres is fairly close to reality.
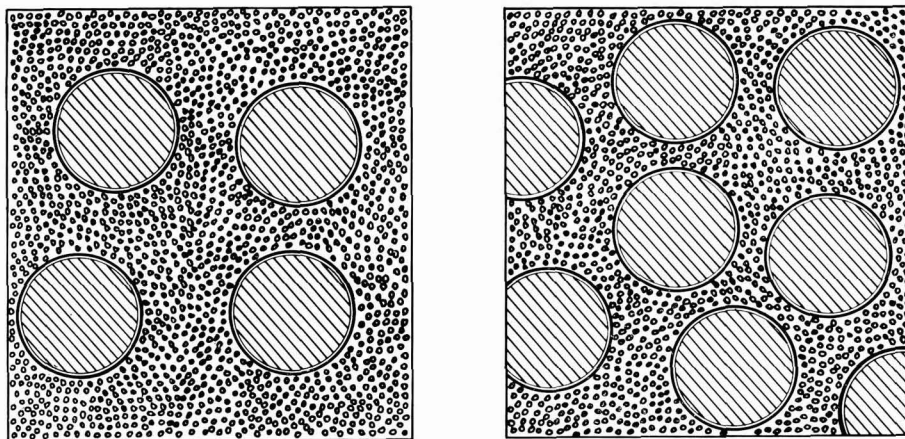
Fig. 13. Structure of pigmented paints

The figures reveal that, at sufficiently low vehicle concentrations, the pigmented paint exists as a dispersion of relatively large particles (the pigment particles plus the adsorbed layer) and relatively small particles (the dispersed gel particles of the vehicle) in the solvent. Due to its athermal nature this dispersion generally exhibits a high stability in spite of the great particle density. In fact, athermia implies an ideal behaviour with regard to the interaction energies between the particles. This consideration implies that it is only an athermal theory of adsorption which can describe exactly the phenomenon of vehicle adsorption on to a pigment. In view of the chemical structure of vehicles (especially that of alkyd resins), it is not conceivable that any adsorption based upon energetic preference could form a layer showing a perfect behaviour in terms of energies of interaction with the solution. Apart from the fact that such an adsorption theory could even not explain the actual adsorbed layers, the athermal nature of adsorption is an essential prerequisite for the dispersion stabilities observed. The best confirmation of the above is provided by the finding that for an incompletely developed adsorbed layer, no stable pigment dispersion could be obtained in the vehicle solution.

In experimental terms, the structural pattern of the pigmented paint presented so far has been correct in all its essential elements; however, it represents a fundamental pattern which involves much idealization and simplification. The necessary extension of this structural pattern and the deviations to be expected in practice will now be indicated.

Firstly, some comments should be made on the vehicle. So far, little attention has been paid to the heterogeneity of these substances. In order to develop the adsorption theory, vehicles have been assumed to be uniform substances. In fact, it is generally known that alkyd resins represent mixtures of substances, consisting of molecules differing both in size and composition. Doubtless, the formation of globules results in a reunification within the solution. However, it should not readily be assumed that all globules are identical. This results in the possibility of selective adsorption, leading to the view that the composition of the adsorbed layer may differ from that of the globules in the solution. Both the phenomena have been observed experimentally.

The determination of the composition of globules according to the present structural pattern, and independent of the determination of adsorption, is carried out by using the viscosity number. For this particular purpose, it is essential that all the vehicle be assumed present in the globules, which are consequently dispersed in pure solvent. Although this assumption would appear to be reasonably true in some cases, as is indicated, for example, by the agreement between calculated and measured viscosities shown in Fig. 10, it must not be taken as universally applicable. In view of the previously mentioned heterogeneity of alkyd resins, different solubilities of the individual vehicle portions must be assumed, so that as a general rule, there would always be some proportion of the dissolved vehicle outside the globules in the remaining solvent. This assumption, which strictly speaking is quite plausible, would also explain why the viscosity of the vehicle solution as calculated from adsorption data is considerably lower, in some cases, than the measured viscosity.[5] In the practical application of the so-called water-soluble resins, it is precisely this vehicle portion existing outside the globules which is of great importance. It will stabilize the globules in the solution. When it is removed from the solution by adsorption due to excessive pigmentation, the vehicle will precipitate.

Secondly the pigment should be considered. When the pigment particles are not isodiametric and of equal size, then because of their size and configuration, they will influence the relations between adsorption on the one hand and sediment volume and suspension viscosity on the other. If the particle configuration of the pigments is highly irregular due to aggregation, they can readily become so complex that they render any quantitative formulation of the relationships impossible.

In addition, attention should be drawn to the heterogeneity of the pigment surface, expressed, for example, by the varying surface areas obtained by different measuring techniques. Surely, it should not be supposed that those areas greatly varying in their action will have no effect on vehicle adsorption? It follows, for example, from the athermal nature of vehicle adsorption that the adsorption depends on the size of pigment particles. For particle size comparable with those of the globules, the adsorption is less pronounced. This was shown experimentally by establishing lower area-specific adsorption for pigments having a large specific surface area.[29]

It is certain that the development, and refinements presented here, of the uniform structural pattern of pigmented paints established at the outset, are not exhaustive. New aspects will be raised in future work. It is a reasonable assumption, however, that all of the extensions and deviations discussed above should harmoniously fit in to the fundamental pattern; based upon this pattern, they offer a logical interpretation of the experimental findings, thus verifying the structural pattern proposed.

Illustration of paint properties using the new structural pattern

In the structural pattern presented of the pigmented paint, the adsorbed layer plays a dominating part. It is characterized by exerting two essential effects. Firstly, it will reduce the forces of interaction between the pigment particles and, secondly, it will increase the solid volume of the suspension. It is primarily on the basis of these effects that many paint properties can be explained.

Pigment packing density

Ref. 8, 10, 12, 9

As a first example, the sedimentation volume, which is directly associated with the possible pigment packing density, will be considered. Some pigments consist of fairly regular isodiametric particles, which are nearly equal in size. Such a particle size distribution is often found, especially with the rutile pigments. Such a pigment should reach a volume concentration which corresponds to that of the random packing of spheres of equal size: this is 60.5 per cent. In fact, such a volume concentration cannot be achieved. The PVCs in the sediment are always considerably below this value. However, when the volume of the adsorbed layer is added to the PVC with the assumed particle distribution of the pigment, a volume concentration is always obtained which is consistent with the random closest sphere packing (Table 2). In those cases where different thicknesses of adsorbed layer occur, due to selective adsorption depending on pigmentation, the former will take effect in the sedimentation volume and, consequently, in the pigment packing density. In fact, this requires that the adsorbed layer be completely developed. If this is not so, agglomeration will be experienced due to interaction forces between the pigments, and such agglomera-

tion will hinder the closest packing. Therefore, at low vehicle concentrations, the PVC in the sediment will be lower (Fig. 14). Thus, the maximum obtainable pigment packing density can be increased by selecting conditions for a small adsorbed layer or for which the volume ratio of pigment to adsorbed layer is displaced to a greater extent towards a high proportion of pigment volume.

Table 2

Sediment parameters of different suspensions with rutile TiO_2

Vehicle	Long-oil alkyd resin		Short-oil alkyd resin	
Solvent	Xylene	Xylene + Butanol (8:2)	White Spirit + Xylene (4:6)	Xylene + Butanol (8:2)
Thickness of adsorbed layer (nm)	9.0	7.8	8.2	5.8
PVC in sediment	46.4	47.4	47.5	48.9
Volume concentration of pigment plus adsorbed layer	62.4	61.3	63.5	59.5
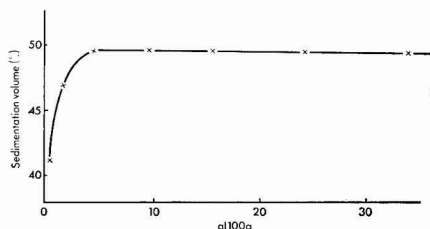
Fig. 14. PVC of sediments for a 30 per cent PVC suspension for the isotherm shown in Fig. 5

It should be pointed out, however, that a definite thickness of adsorbed layer is necessary for adequate stabilization of the dispersion. The minimum layer thickness is around 6nm for a 0.2 micron pigment particle diameter.[8] When the value is significantly lower, flocculation will be encountered as a result of poor shielding of the interaction between pigment particles; this effect considerably reduces the pigment packing density.[10, 12]

For pigments not consisting of spherical primary particles, for example, those containing aggregated particles of irregular shape, the grain configuration will have an effect on the pigment packing density that can be attained. In such cases, the maximum obtainable volume concentration of a pigment with an adsorbed layer is found to be lower than those for random sphere arrangement. In practical cases,[9] for example, values of some 55 per cent have been found. However, the effect of the adsorbed layer on the possible pigment packing density is still maintained in these cases.

Stabilization of dispersion

Ref. 8, 29

The part played by the adsorbed layers in the stabilization of the dispersion of pigments has been described by Crowl and Malati.[8] These workers provided experimental evidence of how the dispersion-stabilizing effect of the adsorbed layer depends on the pigment grain size. However, it was not until the appearance of the athermal theory of adsorption that it became possible to explain why no energetic interac-

tion can occur between the adsorbed layers and why pigmented paints, in spite of high particle concentrations, are capable of forming stable dispersions.

The athermal theory of adsorption reveals an additional relationship between pigment grain size and stabilization of dispersion. When the particle size of the pigments are so small to be comparable to the size of globules, adsorption will decrease.[29] This is mainly due to the mobility of the individual pigment particles becoming comparable with that of the globules and also due to the globules being hindered when oozing into the pigment agglomerates as a result of the dimensional conditions. This insufficient surface coverage is in accordance with the finding that with pigments such as carbon black and Milori blue, showing primary particle sizes of 20nm and less, difficulty is often experienced in dispersion. In most cases, vehicle solutions do not meet the requirements necessary for the stabilization of dispersion of such fine particles. For this, particles of smaller size are required, and this is normally true for the globules.

There is an essential question regarding the stability of dispersion, namely whether the globules would actually show the behaviour of athermal particles. In fact, the answer cannot always be "yes". The use of poor solvents can result in the formation of globules which do not exhibit an ideal behaviour in their interaction energies with regard to the solvent. Thus, the stability of solution in the dispersion range of the vehicle solution is not ensured. In such cases, for example with aqueous vehicle solutions, stabilization of the globules is often found to occur because of vehicle portions which are dissolved in the remaining solvent. However, such a stabilization is readily disturbed by pigmentation, so that such systems will always tend to be difficult to disperse. The existence of non-athermal globules is perceptible in terms of the anomalous viscosity behaviour of the vehicle solution (Fig. 15).
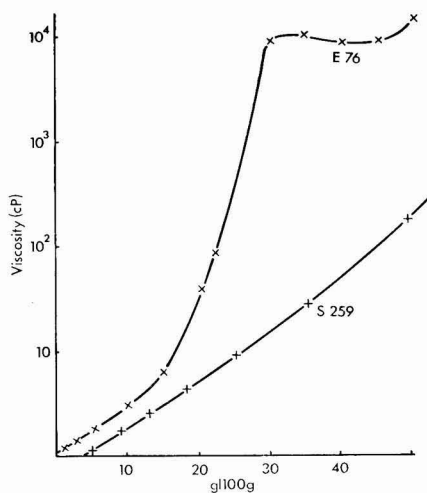
Fig. 15. Viscosity behaviour of water-soluble E 76 resin for Duxalkyd S 259 in xylene

The above indicates that apart from the pigment and the vehicle, the solvent too has a fundamental effect on the dispersion properties. Optimum properties of a pigmented paint can be obtained for a given pigment and vehicle by choosing a suitable solvent. Conversely, if the solvent is

specified, as is the case with water-soluble paints, the possibility of achieving optimum dispersion properties is greatly restricted.

Rheological properties

Ref. 10

The rheological behaviour of pigmented paints is greatly influenced by the adsorbed layer. The effect on the relative suspension viscosity, of the reduction in interaction between the pigment particles is clear from Fig. 16. At low vehicle concentrations, with an adsorbed layer not completely developed, the relative suspension viscosity (suspension viscosity/solution viscosity) is higher. It will decrease as the adsorbed layer builds up and maintain a constant value once the layer has been completely developed, provided the PVC is not excessively high.
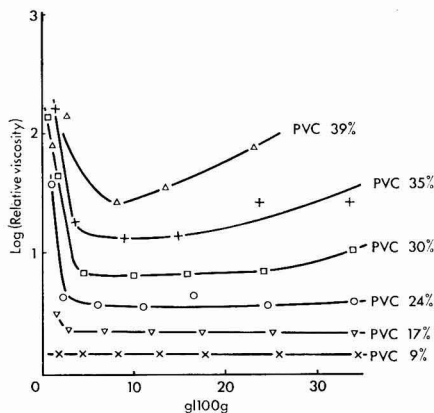
Fig. 16. Relative viscosities of the suspensions, on which the isotherm shown in Fig. 5 was measured

Likewise, the volume of the adsorbed layer has a marked effect on the suspension viscosity. Fig. 17 shows the relative viscosity of two suspensions, which contain an identical pigment, at 20 per cent PVC. The suspensions PX 20 and GX 20 have relative viscosities of 8 and 5, respectively. The corresponding thicknesses of adsorbed layer are 9nm and 6.4nm for PX 20 and GX 20. Further examples are given elsewhere,[10] showing that the same relative suspension viscosity occurs, independently of the vehicle, when the sums of pigment volume and volume of the adsorbed layer are equal. Thus, it is possible to reduce the suspension viscosity if a thin adsorbed layer is established, other conditions being identical. The rheological behaviour, of course, will be effected by the thickness of the adsorbed layer, which should not be less than the minimum value mentioned earlier; otherwise, a further increase in viscosity will result because of the interaction forces between the pigment particles. Particularly impressive evidence of the effects of the structural pattern developed is provided by the explanation of the rise in relative suspension viscosity with increasing vehicle concentration at high PVCs. Fig. 16 shows an example where the relative viscosity of the suspensions remains constant at low PVC but which varies at higher PVCs. In this Figure, the curve of 30 per cent PVC runs, after the initial slope caused by the incomplete built-up of adsorbed layer, almost parallel with the abscissa, whilst at 35 per cent PVC and 39 per cent PVC the relevant slopes are followed by a slight and a steep rise.
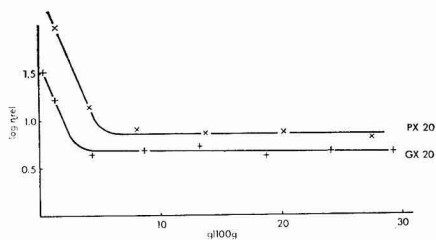
According to the structural pattern detailed earlier the constancy of the relative suspension viscosity is contingent on the adsorbed layer, depending on the vehicle concentration. Once fully built up, the adsorbed layer will eliminate the energetic interaction between the pigment particles and, in consequence, it too is independent of the vehicle concentration. At a higher PVC, the spacing between the pigment particles enveloped by the adsorbed layer will become so small to be comparable with the size of the globules. When the spacing becomes smaller than the globule size, the globules are jammed between the adsorbed layers, thus making the specific viscosity of the globules become apparent. The higher the vehicle concentration, the more will the globules become jammed in the gaps, and also the more will the viscosity of the solution in the gap differ from the normal solution viscosity, and the suspension viscosity is observed to increase as a result.

For the suspensions shown in Fig. 16 (the associated adsorption isotherm being shown in Fig. 5), the relationships are reproduced in Fig. 18. The mean minimum particle spacings according to random spherical packing are plotted for 30, 35 and 39 per cent PVC. Around the pigment particles, assumed to be of spherical shape, the adsorbed layer is shown by shading. On shearing, the minimum particle spacings become smaller. For the purpose of calculating the minimum particle spacing for shear, a simple cubical packing was assumed. The corresponding spacings are shown as dashed lines. The size of globules was derived from the adsorbed layer. They were drawn as spheres having the same volume as a cube with sides just equal in length to the thickness of adsorbed layer. This implies that the globule diameter is 1.25 times the thickness of adsorbed layer. At 30 per cent PVC, it is clear that the spacing is essentially wider than the globule, whilst at 35 per cent PVC they are just equal in size, and at 39 per cent PVC the spacing is substantially smaller than the globule, which is exactly represented by the behaviour of relative suspension viscosities shown in Fig. 16.

The viscosity behaviour of the suspension follows the structural pattern presented in an exact manner, so that it is possible to determine quantitatively the thickness of adsorbed layer and, consequently, the size of the globules solely from their relative viscosities. From this, it is conclusive that (i) the structural pattern is correct, and (ii) it can be applied to actual problems.

Fig. 17. Relative suspension viscosity for different thicknesses of adsorbed layer
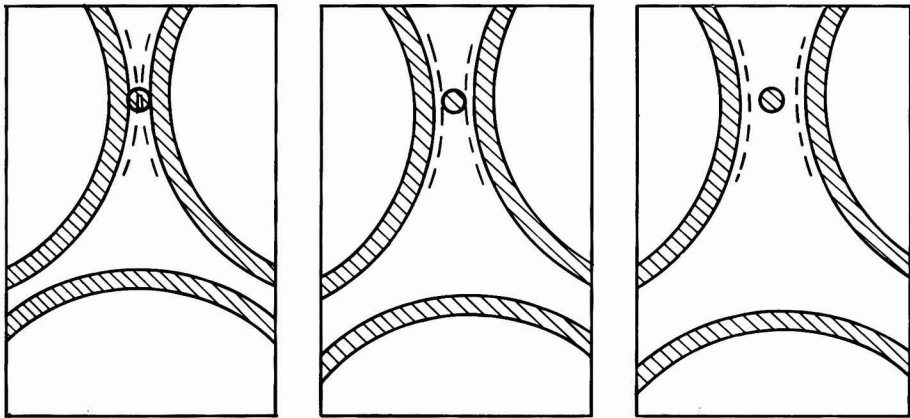
Fig. 18. Shear in pigmented paint

Conclusion

An athermal theory of vehicle adsorption is described, which has been developed on the basis of new experimental results. This theory not only enables the experimental results obtained on adsorption to be interpreted very satisfactorily; it also yields new findings regarding the structure of vehicle solutions.

Thus, it becomes possible to establish a structural pattern of a pigmented paint. In accordance with this structural pattern, the pigmented paint must be considered essentially as an athermal mixture consisting of three volume portions, namely the pigment volume, the volume of adsorbed layer, and the volume of the remaining solution. The essential details of the structural pattern for practical application are given. This new structural pattern enables paint properties largely to be explained. The effects of different vehicles, solvents and pigment properties on the structural pattern can be explained, which provides a valuable aid, therefore, in determining optimum paint properties.

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Relative permittivities of some printing ink pigments

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Summary

A method has been devised for determining the relative permittivities of non-conductive or poorly-conductive pigment powders at 25 kilohertz. The powders are compressed into pellets, which are then silvered, and located between metal electrodes in a sample holder, the capacitance of which is measured on a specially designed AC bridge. Standardisation of the results is by comparison with pellets of sucrose and potassium nitrate.

Keywords

Raw materials: prime pigments and dyes

  pigments

Equipment primarily associated with analysis measurement or testing

  electrical equipment

Les permittivités relatives de certains pigments pour encres d'imprimerie

Résumé

On a perfectionné une méthode pour déterminer à une fréquence de 25 kilohertz les permittivités relatives de certains pigments non conducteur ou faible conducteur sous forme de poudre. Les boulettes des poudres comprimés sont argentées et ensuites elles sont introduites dans un porte éprouvette que l'on pose entre les électrodes métalliques. Au moyens d'un pont au courant alternatif et spécialement conçu, on a déterminé la capacité. La normalisation des résultats s'effectue en faisant une comparaison auprès de ceux rendus par les boulettes de sucrose et de nitrate de potasse.

Dielektrizitätskonstante einiger Druckfarbenpigmente

Zusammenfassung

Eine Methode wurde zur Bestimmung der Dielektrizitätskonstanten von bei 25 Khz nichtleitenden oder schlechtleitenden Pigmentpulvern ausgearbeitet. Die Pulver werden zu Pillen gepresst und versilbert, alsdann in eine Zwinge zwischen Metallelektroden plaziert, deren Kapazitanz mit Hilfe einer speziell hierfür entworfenen AC Brücke gemessen wird. Normung der Ergebnisse erfolgt durch Vergleiche mit Saccharose-und Kaliumnitratpillen.

Introduction

Ref. 1-5

During a programme of investigation of printing ink pigments, Chapman[1] suggested that it might be useful to know the dielectric constants (or relative permittivities) of the pigment powders, partly as an aid in interpreting X-ray measurements of structure, and partly because the results would prove of general use in the printing industry for assisting in the identification, purification and classification of pigments, in that it should be possible to obtain the dielectric constant of a commercial pigment for comparison with the known value of a pure material, thereby obtaining a measurement of the quality of the pigment about to be used in a printing process.

Further, a knowledge of the value of the dielectric constant is necessary, as reported by Birkett and Elsayad,[2] in studying the quality of inks used in electrostatically assisted gravure printing.

Preliminary work on the powders at 20MHz using a *Q* meter (Marconi Instruments type TF886B) indicated that the value of relative permittivity obtained was very much dependent on the state of compaction of the pigment powder, so that in order to obtain consistent and repeatable results, the pigments in later work were compressed into pellets using pressures of order 4,000 psi (27.6MNm⁻²), and the relative permittivities of the materials in these pellets were measured. Compaction of pigments into pellets has recently been investigated by Smith[3], with whom the authors agree in observing large differences between powders with respect to the change of bulk volume which occurs when pressure is applied, the spread of results for the relative permittivity for different specimens of a given pigment being sometimes apparently markedly influenced by this effect. Some of the difficulties of measuring the relative permittivities of solids, for example conductivity, electrode effects, traces of water etc, have been pointed out by Davies[4]. In the measurements described below, conductivity was relatively unimportant in the pigment samples, whilst electrode effects, such as the effect of small airspaces, were eliminated by silvering both sides of the pellet. Several of the pigments used have been discussed by Patterson[5].

Experimental

Ref. 6, 7

Pellets were made in a 16mm die (Beckmann RIIC Limited type KBR) by compression at 4,000 psi in a manually operated hydraulic press (Epco Ltd), using a simple piston-type vacuum pump for lowering the pressure to a few torr in the die. To prevent the pellet sticking to the metal inserts, with the risk of producing internal cracks in the pellet upon removal, the polished faces of the inserts were smeared with

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a trace of oil before each pellet was made, whilst as a pre-
caution against contamination, the pellets were carefully
wiped with tissue paper before silvering. A jig was used
which, with a little practice, enabled pellets to be made only
of thicknesses in a chosen range, between 1 and 2mm.
Pellets of thickness beyond this range were excluded. The
reasons for this were twofold. In pellets of thickness less than
1mm, errors in estimating the thickness could occur due to
variations across the cross section, which were of order
0.1mm in the least suitable powders. These, and possibly
errors due to penetration of the silvering paste into the
pigment material, were considered to be likely to give too
great a percentage error for thicknesses of less than 1mm.
In pellets of thickness beyond 2mm, on the other hand,
errors due to an "edge" effect in the capacitance measurement
were anticipated. Von Hippel[6] states that the increase of edge
capacitance when the specimen is inserted between two
circular disc electrodes of a parallel plate capacitor "can be
practically eliminated by making the diameter of the specimen
less than that of the electrodes by two times the thickness".
Since the specimen diameter in the present work was 16mm,
and the electrode diameter 19.8mm, the limiting thickness of
pellet permissible is a little less than 2mm. Further increase
of electrode diameter was not practicable, since it would give
too great an air capacitance to be subtracted from the
measured capacitance of the sample holder with the pellet
inserted.

After wiping, the thickness of the pellets was measured
with a micrometer screw gauge, the average of eight readings
at different places on the cross section being taken as the
mean thickness. The pellet was then coated on both sides
with silver, using Silver Dag (Acheson Colloids Ltd.) applied
with a fine brush. Great care was taken to avoid applying
any silver to the curved sides of the specimen.

Drying occurred within a minute or two, after which the
silvered pellet was placed in a small central recess, approx-
imately 0.25mm deep, in the lower brass electrode of the
capacitance measuring assembly. The upper brass electrode
was then dropped gently into place, after which the fine,
flexible wire approximately 1 centimetre long and attached
to the upper electrode was soldered to the screened lead at A
(Fig. 1). The recess was designed to be a loose fit on the
16mm disc of the pellet. Accordingly, the slight increase in
size due to the silvering operation did not give rise to any
uncertainty whether or not the pellet would slide fully into
the recess, and slight pressure and sideways thrust was
applied manually to make quite certain that fitting into the
recess had taken place. Location of the metal electrodes was
by an outer polythene tube into which they were a sliding fit.
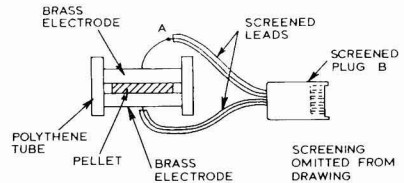
Fig. 1. A diagrammatic sketch of the capacitance measuring assembly

With the pellet in place, the capacitance (usually between
4.5 pF and 10 pF, with an air capacitance to be subtracted
which was usually between 2 and 3.5 pF) was measured on a
25 kHz bridge, designed so that neither electrode of the
sample capacitor was earthed, although screening was
provided which was earthed to the chassis of the bridge.
Provision was made for balance of any leakage resistance
greater than a few megohms, and for additional series
resistance up to 100 kΩ when required. A block diagram of
the bridge circuit is given in Fig. 2. The series arms, apart
from the pellet holder, are in separate screening boxes. The
range is from 0.005 to 100 pF. To avoid expense, the anode
current of one valve is maintained at a constant value using
a variac. The alternative is a stabilising transformer. Before
each measurement, a standard 75 pF capacitor attached to an
exactly similar plug and screened lead to that used on the
pellet holder was plugged into the bridge, setting this at
75 pF, and balancing using a pre-set gain control on one
side of the differential amplifier. The lead from the pellet
holder was then plugged in, and a clip lead from the screen
attached to chassis, whereupon the capacitance C_{pellet} of the
electrodes with the pellet in place, was measured quickly
before any changes of bridge conditions could occur. Initial
calibration of the bridge was against a Q meter (Marconi
Instruments Ltd. type TF886B) by transfer of fixed capaci-
tances.

Preliminary calibration of the sample holder, without the
pellet, was carried out using paper spacers of diameter 2mm,
cut with a leather punch, to separate the electrodes in place
of the pellet. Spacer thicknesses ranged from 0.05 to 1.4mm.
Three spacers of a given thickness were placed on the outer
brass rim surrounding the depression in the lower electrode.
The measured capacitance was corrected for the presence of
the spacers to give C_{air}, the capacitance with the electrodes a
known distance apart and separated only by air. The cor-
rection, which was worked out assuming a relative permit-
tivity of 2.2 for paper, varied from 3 to 4 per cent of the total
air capacitance (for 1.7mm and 1.0mm pellets, respectively).
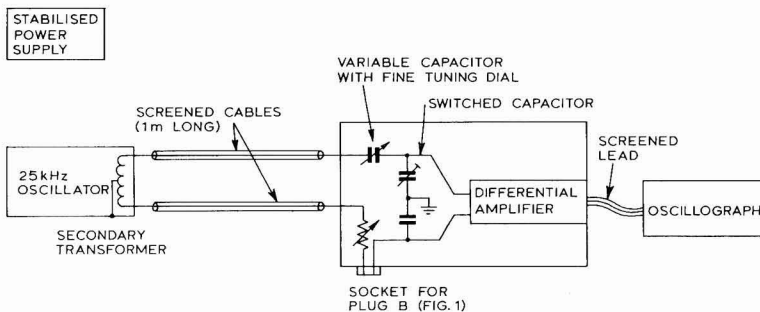
Fig. 2. Block diagram of the bridge circuit

Thus any error in the value assumed for the relative permittivity of paper would be relatively unimportant, of order 1 or 2 per cent at most. To complete a graph of C_{air} against spacing, porcelain beads were used at spacings corresponding to 3.7 and 4.7 mm pellets, well outside the permissible range of pellet thickness, where C_{air} was 1 pF or less, the correction for the spacers being only about 0.2 pF, assuming a relative permittivity of 5.6 for porcelain. The accuracy of the calibration was checked by measuring separately the relative permittivity of dry pellets of sucrose, and potassium nitrate. Results for these materials, given below, were in good agreement with values quoted by Weast et al[7].

Where necessary, the moisture content was checked by measuring the resistance of the silvered pellets on an Avometer $100 \times$ ohms range. The resistance of dry pellets normally exceeded 30 megohms.

The formula used for calculating the relative permittivity ε_r of the pellet material was:

$$C_{pellet} - C_{air} = 8.854 \times 10^{-3} (\varepsilon_r - 1) \, \pi r^2/t$$

where C_{pellet}, C_{air} are the capacitances (in pF) of the sample holder with and without the pellet inserted, whilst r and t are the radius and thickness of the pellet in mm. On an average, six determinations were made for each material, and the average values are given in Table 1.

During the course of the work it was suggested to the authors that a possible correction to be made to ε_r was that of a Mosotti-type relationship based on the density of the pellet compared to the density of the crystals from which the pellet was made.

The measured density of the pellets was approximately 1 to 4 per cent lower than that of the crystals. The authors felt, however, that no meaningful results could be obtained in this manner as the density measurements of the pellets and the crystals were both subject to errors, so that it would have been unrealistic to compare them or apply them in the Mosotti formula, even if it were relevant for these particular materials.

Hence the results presented here are simply for the relative permittivity of the pellets made in the manner and at the pressure indicated.

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Table 1
Results

Material	Average ε_r	Standard deviation ($\pm$)
Sucrose	3.3	0.05
Potassium nitrate	5.0	0.2
Irgalite Yellow G	4.0	0.1
Irgalite Yellow 10G	3.55	0.15
Irgalite Red (RLY)	4.3	0.1
*Phthalocyanine (Monastral Blue)	4.6	0.15
GNC Purple (Phos-Moly)	6.1	0.03
TNC Green (Phos-Moly)	6.25	0.15

*A. Moser and F. Thomas, "Phthalocyanine Compounds" (Reinhold 1963), quote a value of 4.85 obtained by A. Voet using a different method.

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Practical evaluation of anti-fungal paints in the tropics*

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Summary

A series of paints based upon a variety of paint media and pigments and including a range of fungicides were exposed for two years at Lae, New Guinea. The paint media varied considerably in their inherent resistance to fungal attack. Most of the fungicides were ineffective but Mystox and Orthocide 83 showed some promise. Zinc oxide markedly improves the fungal resistance of linseed oil paints, the chalking type being superior to the chalk-resistant type, but the efficiency of this compound in other media remains to be established. It appears that for a zinc-containing material to be effective the zinc must become available in a water-soluble form at or near the surface of the film and that this state may be promoted by chalking although the latter does not, in itself, inhibit fungal growth.

Keywords

Une évaluation pratique des peintures fongicides sous les tropiques

Résumé

Une série de peintures basées sur divers milieux et pigments y compris une gamme de fongicides a été exposée à Lae en Nouvelle Guinée, pendant deux années. Les milieux se variaient dans une manière importante à l'égard de leur résistance inhérente à l'attaque mycélienne. La plupart des fongicides sont inefficaces, mais d'ailleurs Mystox et Orthocide 83 démontraient certaines possibilités. L'oxyde de zinc augmente sensiblement la résistance mycélienne des peintures à l'huile de lin dont le type farinant étant supérieur au type résistant au farinage, cependant l'efficacité de ce composé en autres milieux reste à être établie. Il semble qu'un compose zincifère ne puisse être effectif que dans le cas où le zinc se trouve à la surface ou dans sa proximité sous forme d'un composé soluble dans l'eau et que cette circonstance puisse être favorisée par farinage, bien que celui-ci lui-même n'inhibe pas la prolifération de végétation mycélienne.

Praktische Bewertung von fungiziden Anstrichmitteln in den Tropen

Zusammenfassung

Eine Anzahl von aus verschiedenerlei Bindemitteln und Pigmenten bestehenden Anstrichmitteln, die eine Reihe von Fungiziden enthielten, wurde zwei Jahre lang in Lae, Neu Guinea exponiert. Der den Bindemitteln innewohnende Widerstand gegen Pilzangriff war jeweilig ganz verschieden. Die meisten Fungizide waren wirkungslos, Mystox und Orthocide 83 erwiesen sich als wahrscheinlich brauchbar. Zinkoxid verbessert die Widerstandsfähigkeit gegen Pilzbewuchs erheblich bei Leinölfarben, wobei die kreidende der nichtkreidenden Sorte überlegen ist, die Wirksamkeit dieser Verbindung in anderen Bindemitteln muss jedoch erst nachgewiesen werden. Es scheint, dass zinkhaltige Erzeugnisse, um wirksam zu sein, davon abhängig sind, dass Zink in einer wasserlöslichen Form an oder nahe der Filmoberfläche verfügbar wird, und dass dieser Zustand durch Kreiden gefördert wird, obwohl dieses an sich Pilzwuchs nicht verhindert.

Introduction

In tropical areas, such as parts of Queensland, Papua and New Guinea, paints are rapidly disfigured and their effective life shortened by fungal growth. There is thus a requirement for paints which are resistant to fungal attack. Information on the susceptibility of different types of paints to mould growth and the efficiency of different fungicides is incomplete and frequently conflicting. A series of paints formulated at Defence Standards Laboratories was therefore exposed at Lae on the northern coast of New Guinea where fungal growth is severe. The object of the trial was to reveal information on the following:

(i) the inherent susceptibility of a range of paint media to fungal growth,

(ii) the effect of chalk-resistant zinc oxide,

(iii) the effect of type and amount of zinc oxide,

(iv) the mode of action of zinc as an anti-fungal agent, and

(v) the efficiency of a number of fungicides.

At the same time, a request was received from the British Chemical Inspectorate for the tropical exposure of paints on its behalf since attempts in England to evaluate fungicidal paints and varnishes by field trials had proved abortive. The Chemical Inspectorate trials were designed to gain information on the susceptibility of various paint media to fungal growth and the effect of various fungicides. The media and fungicides were, for the most part, different from those examined by DSL.

This report is the first of a series of similar trials concerning anti-fungal paints.

Defence Standards Laboratories (DSL) paints

Paint media

The reference paint (No. 1), selected to be susceptible to fungal attack, had linseed oil as its vehicle and was pigmented essentially with rutile titanium dioxide and blanc fixe.

Five other paints (Nos. 2-6) were made by replacing the linseed oil medium by four different alkyd resins and a linseed-tung oil-phenolic resin, whilst still retaining the same pigment-volume concentration.

Effect of chalk-resistant zinc oxide

The literature contains numerous references to the fungistatic properties of zinc oxide, but its value as a practical solution to the fungal problem in tropical areas had not been established. A series of paints (No. 19 and Nos. 7-11) was made replacing 45 per cent by volume of the total pigment in paints 1-6 with chalk-resistant zinc oxide.

Effect of type and amount of zinc oxide

The amount of zinc oxide in a paint film might be expected to affect its fungal resistance, and it was felt too that fungal resistance might be influenced by the nature of the zinc oxide; in particular by its reactivity with the vehicle and its chalking properties. A series of paints (Nos. 17-20) was made, therefore, by replacing 15, 30, 45 and 60 per cent of the pigment volume of the reference paint with chalk-resistant zinc oxide and in a second series (Nos. 21-24) corresponding amounts of chalking zinc oxide were used. Two other paints (Nos. 25 and 26) were made by replacing 45 per cent by volume of the pigment in No. 1, the reference paint, by chalk-resistant acicular zinc oxide (for 25) and by a chalking type colloidal zinc oxide (for 26).

Mode of action of zinc as an anti-fungal agent

It is not known whether the anti-fungal property of zinc oxide is due to the presence of zinc or to some intrinsic property of the oxide. To assist in answering this question various zinc compounds of differing basicity and solubility were included in a series of paints. In two paints (Nos. 27 and 29) the pigment in the reference paint (No. 1) was replaced by zinc tetroxychromate to give a zinc content equivalent to 45 per cent by volume of zinc oxide, and in a third paint (No. 28) basic zinc chrome was introduced in like

manner. In another paint (No. 31) the titanium dioxide and blanc-fixe in the reference paint was replaced by lithopone, giving a paint with a zinc content equivalent to 26 per cent of zinc oxide by volume; this is the maximum that could be used without altering the ratio of pigment to vehicle. In another paint (No. 51) zinc naphthenate was added to the reference paint formulation to give a zinc content of 2 per cent.

The anti-fungal action of zinc might be due to the formation of zinc soaps in the paint film. Therefore, a series of paints (Nos. 12-16) was made using the same formulation as paints Nos. 7-11 but after reducing the acid-value of the alkyd vehicle to zero by treating with diazo methane.

Some evidence was available suggesting that paints containing chalking zinc oxide were superior to those containing the same proportion of chalk-resistant zinc oxide, but it was not clear whether the difference was due to chalking or to some other property of the zinc oxides. Therefore, a free-chalking paint containing no zinc (No. 30) was made by replacing 70 per cent of the rutile in the reference paint by anatase titanium dioxide. In a second paint (No. 32) 45 per cent by volume of the pigment in No. 1, the reference paint, was replaced by chalk-resistant zinc oxide and anatase titanium dioxide replaced rutile to give a free-chalking paint containing a chalk-resistant zinc oxide rather than a chalking zinc oxide.

Effect of fungicides

A series of paints (Nos. 33-50) was prepared by incorporating in the reference paint (No. 1) the linseed oil paint, the following fungicides in the concentrations shown:

	Per cent		
Copper 8 quinolinolate	0.15	0.3	0.6
Phenyl mercury acetate	0.03	0.09	0.3
Phenyl mercury oxime	0.03	0.09	0.3
Pentachlorophenol	0.3	0.6	1.5
Tributyltin naphthenate	0.03	0.09	0.3
Nuodex 321	0.3	0.6	1.5

Further information on the formulations of these paints is given in Appendix A.

Chemical Inspectorate paints

Paint media

The reference paint (No. 1016) was of the same formulation as the DSL reference paint; that is, it was based on linseed oil and was pigmented essentially with rutile titanium dioxide and blanc-fixe. Paint No. 1028 was chlorinated rubber based and pigmented with rutile titanium dioxide. Paint No. 1035 was a rutile titanium dioxide pigmented long oil linseed alkyd gloss paint and paint No. 1044 plasticised polyvinyl acetate emulsion pigmented with rutile titanium dioxide with a proportion of extender pigments.

Effect of fungicides

Treating the four paints mentioned above as control paints, fungicidal versions of them were made by adding to them (a)

2 per cent and (b) 4 per cent, calculated on the non-volatile content of the paint, of the fungicides listed below:

Mystox

Paratoluene sulfonamide

*Cadmium dehydroacetate

Orthocide 83 (N-trichloro-methylmercapto-
4-cyclohexene-1:2 dicarboximide)

Further information on formulations of the Chemical Inspectorate paints are given in Appendix B.

Experimental

Ref. 1

Test panels

The test panels were of Parana pine (Araucaria Brasiliana) and measured 300mm × 150mm × 15mm. The surfaces to be exposed were planed, sanded and the edges rounded. Because algae and fungi had been often observed growing vigorously under window-sills of houses which had painted walls, a small ledge, 100mm long 15mm thick and projecting 25mm from the surface, was fitted to each panel 75mm from the top edge by morticing and glueing. This ledge on the panel simulated a projecting still and provided a shaded area beneath it and a run off of rain water at each side. The backs of the panels and the edges were given a coating of aluminium paint which also extended over the rounded front edges.

Application and drying of paints

Three coats of each paint were applied to three test panels with at least 72 hours being allowed for drying between each coat. One panel of each set was painted at Maribyrnong, Victoria and the other two were painted at Lae, New Guinea. The reason for this was to determine whether there would be any difference in the mould growth and durability between panels painted in a temperate climate and allowed to harden before being despatched to the tropics and those painted under humid conditions and exposed immediately.

The paints were applied by brushing to give the following wet film thicknesses per coat:

(a) linseed oil based paints   45 μm to 55 μm

(b) long oil alkyd based paints   37 μm to 50 μm

(c) polyvinyl acetate based paints   50 μm to 75 μm

(d) chlorinated rubber based paint   40 μm to 50 μm

Details of exposure

The panels were exposed in May, 1960. They were placed in a vertical position on racks which were at an angle of 70° to the horizontal and faced northwest. Sunlight fell on the upper face of the panels from 11.30 am onwards. The ledge, which projected out 25mm from the surface shaded the lower face of the panel until about 1.30 pm. The region immediately under the ledge rarely received any sunlight because by 4 pm, at which time this area should have been illuminated, clouds nearly always gathered.

*Supplied by British Drug Houses.

There were nine racks arranged in two rows, and the panels were randomly distributed over the racks.

Each rack carried five horizontal rows of panels, the lowest of which was 4ft from the ground to avoid splashing. The rows of panels sloped backwards, with the lowest row at the front, so that there was no run off of rain water from an upper panel onto a lower one. Wires placed above and slightly behind the upper row of panels served as more attractive perches for birds than the panels themselves so that the latter escaped bird dropping.

Climatic conditions

Average climatic data for Lae are shown in Appendix F. It receives an average of about 4.5m of rain a year, which falls on 265 days; the monthly distribution of rain is fairly uniform, but is greater from July to September. The absolute maximum and minimum temperatures ever recorded were 34°C and 20°C. The average relative humidity is very high; the lowest ever recorded was 66 per cent. Lae is only 6° 43' south of the equator so that the length of day remains close to 12 hours. Sunshine varies between 6.5 hours in October and November and 4 hours in July and August. Cloud coverage, therefore, varies from 5.5-8 hours per day; staff who visited Lae generally agreed that the mornings were bright and sunny, but that clouds appeared in the afternoon and rain fell almost every night.

Rating methods and procedures

The first inspection of the panels was made after seven months exposure. The operator rated all the panels and arranged to have one of the series, which was painted at Lae, returned to Maribyrnong. Panels from the other two series which showed extensive mould growth were also withdrawn at this time. These ratings were supplemented by detailed examination of all panels returned to Maribyrnong by the original and two other operators.

The panels were rated for film failures by the methods given in DSL Circular 10[1]. Briefly, each panel is rated on a numerical scale from 10 to 0 where 10 denotes no failure and 0 complete failure for the particular property concerned. An attempt was made to rate separately for (a) area covered by fungus and (b) the intensity of fungal growth but this proved too difficult and eventually a single numerical rating was given where 10 denotes that no fungus is present and 0 means complete and dense coverage.

The panels remaining on the racks were assessed again after 15 months exposure. The remaining panels of the series painted at Lae were withdrawn and returned to Maribyrnong for assessment by two additional operators. After two years the remaining panels, which belonged to the series painted at Maribyrnong, were returned for rating.

Results and discussion

The ratings for paint failures after 24 months exposure together with those for mould growth and information on the incidence of rot in the panels is given in Appendix C for DSL series and in Appendix D for the Chemical Inspectorate series. Ratings made after 7 and 15 months are compared and commented upon in the text where they are of interest.

DSL paints

Paint media

The results given in Table 1 show that the linseed oil based paint was much less resistant to fungal growth than those based on varnish media and that there was no significant difference between those based on the latter. This conclusion is supported by the results obtained when a different pigmentation was used in the same media Table 2 and when the acid values of the media were reduced to zero.

Table 1

Paint media—mould ratings

Treatments paint medium			Mould rating		
			7 months	15 months	24 months
Linseed alkyd	..	..	7	7	7
Safflower penta	..	..	9	6	7
Linseed penta	..	..	6	7	7
Safflower glycerol	..	..	9	6	6
Linseed tung oil/phenolic		..	9	8	5
Linseed oil	..	..	0	—	—

There was some evidence to suggest that the paint based on the linseed tung oil/phenolic varnish chalked earlier than paints based on alkyd media. The results in Appendix C show that the phenolic based paints had developed severe integrity failure after two years' exposure.

Effect of chalk-resistant zinc oxide

Table 2 gives the mould and chalking ratings at 7, 15 and 24 months of paints Nos. 19 and 7-11 in which 45 per cent of the total pigment in paints 1-6 was replaced with chalk-resistant zinc oxide.

After fifteen months, there was an indication that the replacement of some of the titanium dioxide by chalk-

resistant zinc oxide improved the mould resistance of the varnish based paints slightly, but this effect was no longer evident nine months later. On the other hand, incorporation of chalk-resistant zinc oxide markedly improved the mould resistance of the linseed oil vehicle. Varnish media in which part of the titanium dioxide has been replaced by zinc oxide are better for mould resistance than the oil medium with the same replacement.

Replacement of titanium dioxide by zinc oxide significantly increased the chalking of most of the varnish based paints after 24 months but this increased chalking did not reduce mould growth.

Effect of type and amount of zinc oxide in linseed oil vehicle

Table 3 gives the mould and chalking ratings of the series of linseed oil paints containing various amounts of different zinc oxide pigments, together with ratings of the reference paint.

The improvement in fungal resistance noticed earlier in the exposure, obtained by replacing part of the reference paint with zinc oxide, whether chalking or chalk-resistant, was still evident to the same extent after two years. The chalking zinc oxide and particularly the colloidal variety, was continuing to have a greater effect in reducing mould growth than the chalk-resistant type. Paints that contained appreciable amounts of chalk-resistant zinc oxide, including the acicular zinc oxide, were chalking much more after 24 months than at 15 months, but the mould ratings showed little change.

Integrity failures were shown by most of the paints; paints containing chalk-resistant zinc oxide tended to crack and flake and those containing chalking type zinc oxides checked with some cracking.

Mode of action of zinc as a fungicide

The mould ratings of the varnish based paints in which the acid value of the varnishes had been reduced to zero did not differ significantly from paints made from the untreated

Table 2

Effect of chalk-resistant zinc oxide

Media		Treatments										
		titanium dioxide pigmentation						CR zinc oxide pigmentation				
		7 months		15 months		24 months		7 months		15 months		24 months
		Mould	Chalk	Mould	Chalk	Mould	Chalk	Mould	Chalk	Mould	Chalk	Mould	Chalk
Linseed alkyd	.. ..	7	Not rated	7	7	7	5	9	8	8	4	8	2
Safflower penta alkyd	..	9	,,	6	8	7	6	9	10	7	7	7	2
Linseed penta alkyd	..	6	,,	7	7	7	4	9	7	8	6	6	2
Safflower glycerol alkyd	..	9	,,	6	7	6	3	9	10	8	6	7	2
Linseed tung oil/phenolic		9	,,	8	4	5	2	9	4	9	4	4	2
Linseed oil	.. ..	0	10	+	+	+	+	3	9	3	8	5	2

+ Panels withdrawn after 7 months

F

Rutile replacement concentration	Chalk-resistant zinc oxide						Chalking zinc oxide						Acicular zinc oxide					
	7 months		15 months		24 months		7 months		15 months		24 months		7 months		15 months		24 months	
	Mould	Chalk	Mould	Chalk	Mould	Chalk	Mould	Chalk	Mould	Chalk	Mould	Chalk	Mould	Chalk	Mould	Chalk	Mould	Chalk
0	0	10	—	—	—	—	0	10	—	—	—	—	0	10	—	—	—	—
15	3	8	3	9	3	9	5	8	5	6	5	2	—	—	—	—	—	—
30	4	9	4	7	4	3	6	3	6	3	6	2	—	—	—	—	—	—
45	3	9	3	7	5	2	8	3	8	4	7	2	3	9	3	8	3	4
60	2	10	5	5	—	—	9	3	7	4	7	2	—	—	—	—	—	—

vehicles at any stage of the exposure. This indicates that the presence of zinc soaps of long chain fatty acids in concentrations likely to be found in normal varnishes does not inhibit mould growth.

After seven months' exposure it was concluded that chalking does not intrinsically prevent fungal growth, but that it may reduce its incidence. It was also thought that for a zinc-containing material to be effective the zinc must become available in a water soluble form, such as the low molecular weight zinc soaps produced as the oil film degrades.

It is interesting to review these suggestions in the light of the complete results of the exposure trial. Table 4 gives the mould and chalking ratings of the series of paints used in this study after 7, 15 and 24 months' exposure.

Colloidal and chalking zinc oxide showed good mould resistance throughout the trial. Both pigments are capable of forming water soluble zinc soaps by reacting with products

Table 4

Ratings for standard paint with various zinc compounds and a chalking type zinc free paint

	Mould ratings			Chalk rating		
	7 months	15 months	24 months	7 months	15 months	24 months
Colloidal zinc oxide 45% replacement of pigment in reference paint	9	9	9	3	3	2
Chalking zinc oxide 45% replacement of pigment in reference paint	8	8	7	3	4	2
Pigment replaced by 45% chalk resistant zinc oxide the rest of the rutile replaced by anatase E	5	7	6	3	3	2
Pigment replaced by basic zinc chromate to give zinc (as zinc oxide) 45%	9	4	5	9	9	9
Pigment replaced by zinc textroxy chromate to give zinc (as zinc oxide) 45%	9	4	4	10	9	6
Chalk resistant zinc oxide 45% replacement of pigment in reference paint	3	3	5	9	8	2
Acicular zinc oxide 45% replacement of pigment in reference paint	3	3	3	9	8	4
Reference paint	1	—	—	10	—	—
Rutile titaniun dioxide and blanc fixe in reference paint replaced by lithopone	0	—	—	3	—	—
Reference paint and 2% zinc naphthenate	0	—	—	10	—	—
Seventy per cent rutile replacement by anatase E in reference paint	2	—	—	3	—	—
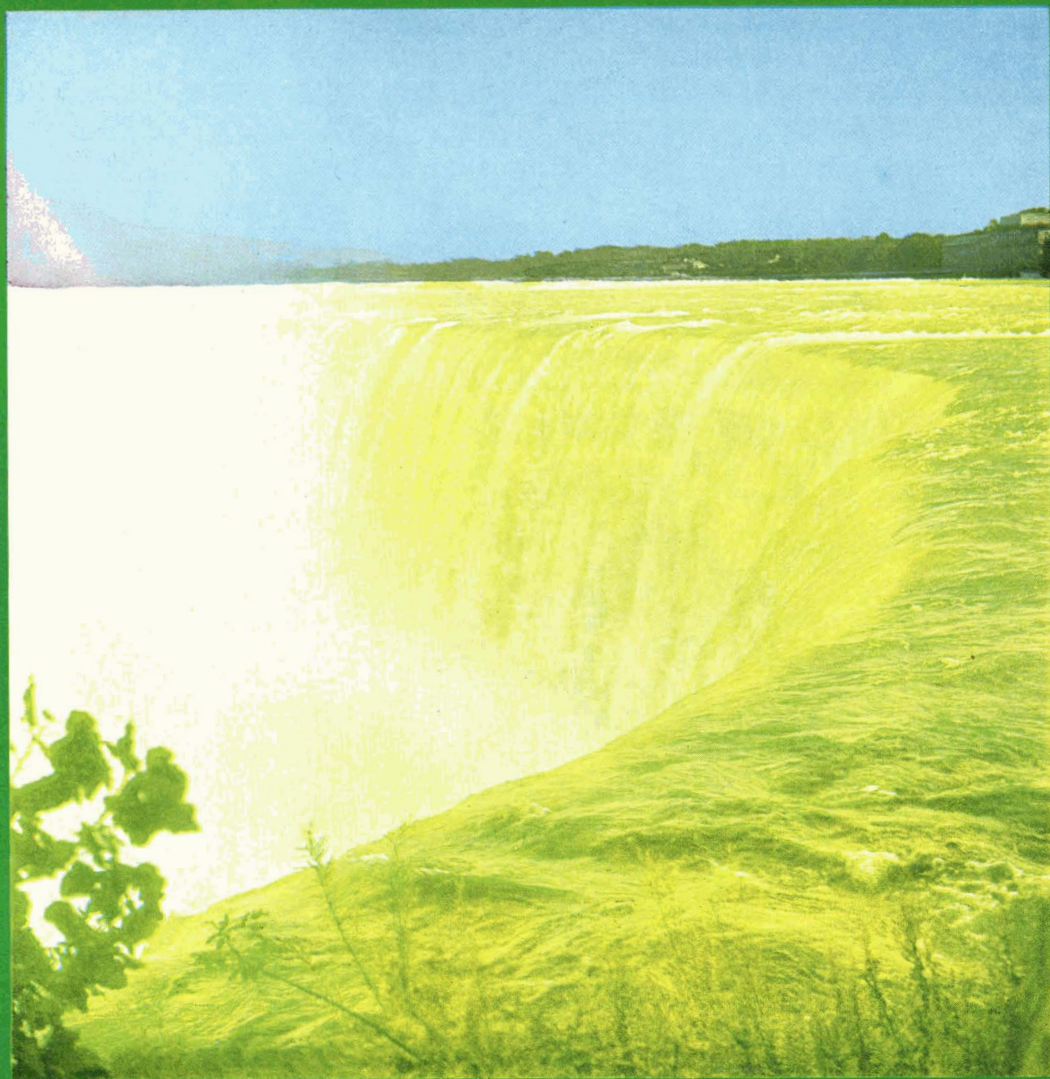
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Colloidal zinc oxide					
7 months		15 months		24 months	
Mould	Chalk	Mould	Chalk	Mould	Chalk
0	—	—	—	—	—
—	10	—	—	—	—
—	—	—	—	—	—
—	—	—	—	—	—
—	—	—	—	—	—
—	—	—	—	—	—
9	—	9	—	9	—
—	3	—	3	—	2
—	—	—	—	—	—
—	—	—	—	—	—

formed during the breakdown of linseed oil; the high rate of chalking suggests that this breakdown was occurring.

Zinc chromate and zinc tetroxy chromate showed good mould and chalk resistance at seven months, but were showing considerable mould growth after 15 months. The decline in mould resistance could be due to most of the water soluble zinc compounds originally present in the chrome being leached from the surface layers of the film. The films remained reasonably chalk-resistant so that little water soluble zinc compounds would be available from film breakdown.

The chalk-resistant and acicular zinc oxides were inferior in mould resistance to the chalking type zinc oxide throughout the exposure period and also to the chromes in the early stages of exposure. They chalked freely only at 24 months and their ability to form water soluble zinc compounds would be retarded by the slow rate of degradation of the films, indicated by the absence of chalking in the earlier stages of exposure. Consistent with this is the improved fungal resistance afforded by the chalk-resistant zinc oxide when early breakdown is induced by the presence of anatase.

The paints containing lithopone and anatase titanium dioxide chalked freely but had poor mould resistance, zinc sulfide is sparingly soluble and would not react with the degradation products of linseed oil. Zinc naphthenate is relatively insoluble in water and the paint containing it in small quantity showed poor mould resistance.

Zinc chloride has been reported to confer good fungal resistance to paints[2] and this perhaps supports the theory regarding water solubility.

It may be, however, that zinc oxide particles near the surface of the film and uncovered by vehicle degradation are fungistatic, whilst titanium dioxide and lithopone particles, similarly laid bare, are not.

Effect of fungicides

After 7 months' exposure all the paints containing fungicides had a mould rating of zero indicating that the fungicides were ineffective in the concentration used in the linseed oil paints.

Chemical inspectorate paints

The ratings for mould growth after 7, 15 and 24 months' exposure are given in Table 5.

The main conclusions drawn from the earlier assessments at seven and fifteen months were:

1. Chlorinated rubber paints showed the best and linseed oil the worst fungal resistance. The linseed oil based paints all showed heavy mould growth before the fifteen-month assessment and were not rated further. The mould ratings of the alkyd and pva based paints were similar to each other and slightly lower than those of the chlorinated rubber paints.

2. Of the fungicides, Orthocide 83 showed definite improvement in the linseed oil medium at seven months but was ineffective after fifteen months. There was no difference in the mould ratings of the paints based on the other three media containing fungicides and their respective control paints after seven months; after fifteen months paints which contained Mystox or Orthocide 83 were slightly better in fungal resistance than their control paints.

The mould ratings of the chlorinated rubber, polyvinyl acetate and alkyd based paints after 15 and 24 months' exposure were analysed statistically, each concentration of fungicide being considered as a different treatment.

It was found that there was no significant difference between the mould ratings at 15 and 24 months. The analysis also showed that chlorinated rubber is more resistant than the other two vehicles and there are some indications that the polyvinyl acetate is more resistant than the alkyd vehicle. Mystox and possibly Orthocide 83 are the only two fungicides which increase the fungal resistance of the three media. The effect is noticeable with the alkyd medium but only marginally so with the other two media.

No intregity failures were observed. A number of panels were still glossy, especially those of the chlorinated rubber paints. In general, apart from the rot, the panels were in good condition. The fungicides did not affect the durability, except that Orthocide 83 did cause an increase in the chalking.

Discussion

Comparison between panels painted at Maribyrnong and at Lae

Analysis of the results after 7 and 15 months' exposure did not reveal a significant overall difference between panels painted in the two localities.

The ledge on the panels

The ledge was placed on the panels to furnish a shaded area which would simulate eaves or a window sill on the wall of a house and facilitate mould growth. This expectation was fully borne out in the trials; even some of the best paints showed mould growth under the ledge, and the fungus often spread downwards from this area. However, there were complicating features about the ledge. Wood fungi entered some of the panels through the mortise joint by which the ledge was attached, and spread upwards and downwards under the paint films and this could have induced the rot observed on about one-third of the panels. The ledge fell

Table 5
Effect of fungicides and media on mould growth

Fungicide	Control			Mystox LPL						p-Toluene sulfonamide						Cadmium dehydroacetate					
Concentration				2%			4%			2%			4%			2%			4%		
Months of exposure	7	15	24	7	15	24	7	15	24	7	15	24	7	15	24	7	15	24	7	15	24
Linseed oil	0	0	0						All reading zero												
Long oil alkyd	6	5	5	8	8	8	8	8	8	9	5	5	8	6	5	—	4	4	7	4	5
Polyvinyl acetate	7	6	6	6	8	7	8	7	8	8	6	5	8	6	5	7	6	7	8	6	5
Chlorinated rubber	9	7	7	9	9	8	9	9	9	8	8	8	10	9	8	9	8	8	9	8	4

out of 20 per cent of the panels, leaving an unprotected surface on which fungi could become established. In view of these drawbacks, the use of the ledge is not recommended in future trials.

Frequency of assessments

The assessment of fungal growth after a period of seven months' exposure did not enable any differentiation between panels having poor resistance to fungal growth and, in particular, did not show whether fungal attack occurred prior to the commencement of chalking of the chalking type zinc oxide paints. Frequent assessments in the early stages of the exposure might have assisted in elucidating the mechanism by which fungal growth is resisted.

Future programmes should be planned with frequent assessments, preferably every four weeks, during the first six months, and it is desirable that the same operators make the observations.

Fungi identified in the Lae area

Ref. 3

Specimens of fungi have been collected from panels and other painted surfaces in New Guinea on three different occasions and identified at Defence Standards Laboratories.

(a) *Aureoboisidium pullulans* was present on panels that had been exposed at Lae by the Commonwealth Department of Works from December 1957 to May 1959 but there was no sign of *Cladosporium herbarum*.

(b) Samples of fungal growth collected from painted surfaces at Lae in April/May 1960, at the time this trial was commenced, showed that *Cladosporium* was the commonest organism.

(c) At the seven months' inspection twenty specimens of fungi were taken from the panels on the racks and from a painted wooden building in the area; eight of these were *Pullularia* but none were *Cladosporium*, and of a total of fifty specimens collected at random from the panels, other painted surfaces and vegetation in the vicinity, and which are detailed in Appendix E, only one was *Cladosporium*.

Whiteley in a personal communication in 1961 cites 38 occurrences of *Cladosporium* to 13 of *Pullularia* on paint sampled in the Far East. At this stage, therefore, the evidence as to which of *Cladosporium* or *Pullularia* is the more common fungus on paint in the tropics is not conclusive but it is possible that the incidence of any particular species of fungi

may vary with the season and even from year to year. A seasonal or yearly variation is not inconsistent with the findings of other workers[3].

Occurrence of algae and lichens in the Lae area

Disfiguration of paint surfaces in the tropics is usually attributed to moulds, but algae and lichens were also prevalent on painted houses. On the test panels, algae were commonest at the sides where the water ran down at the ends of the ledges and on the tops of the ledges where a pool of rainwater collected.

Conclusions

Linseed oil was markedly inferior in fungal resistance to the other media. Alkyd vehicles prepared from a variety of vegetable oils and using pentaerythritol or glycerol as the polyol were similar in fungal resistance to the polyvinyl acetate vehicle examined. Best resistance was shown by the chlorinated rubber vehicle.

Most of the fungicides tested were ineffectual at the concentrations used. Orthocide 83, however, markedly improved the fungal resistance of the linseed oil medium. Mystox and possibly Orthocide 83 improved the fungal resistance of the other three media tested.

An important objective of the trial was to elucidate the mode of action of zinc compounds, particularly zinc oxide, as anti-fungal agents. It was found that the fungal resistance of linseed oil paints is markedly improved if either chalking or chalk-resistant zinc oxide is present in the pigment in a significant proportion e.g. 15 per cent or more; chalking zinc oxide is more effective than the chalk-resistant type in this regard. On the other hand, varnish based paints in which chalk-resistant zinc oxide comprised 45 per cent of the pigment were no better in fungal resistance than corresponding paints containing no zinc oxide; the effect of chalking type zinc oxide in varnish media was not examined.

There is evidence to suggest that chalking does not intrinsically inhibit fungal growth. It appears, however, that for a zinc containing material to be effective the zinc must become available in a water soluble form at or near the surface of the film and this state may be promoted by chalking. Alternatively, zinc oxide may be effective because it is intrinsically fungistatic. If this view be accepted, chalking of a paint containing zinc oxide will increase the exposed surface area of the fungistatic material and so inhibit mould growth.

It seems that the improvement in fungal resistance brought about by the better fungicides becomes less, even marginal,

| Orthocide 83 | | | | | |
| 2% | | | 4% | | |
7	15	24	7	15	24
4	0	0	9	1	0
7	7	6	10	5	7
8	9	8	8	8	7
10	9	7	10	7	8

as the inherent resistance of the medium in which they are incorporated increases. Also it appears that the beneficial effect of zinc oxide in promoting mould resistance may become less with more resistant vehicles. It seems, therefore, that the solution to the problem of preventing fungus growth on paint films may be in the direction of improving the inherent resistance of the paint medium.

Acknowledgments

References

1. Rischbieth, J. R., DSL Circular 10, 1947.
2. Arnold, M. H. M., and Clarke, H. J., *JOCCA*, 1956, **39**, 900.
3. Reynolds, E. S., *Mycologia*, 1950, **42**, 432.

Appendix A

Formulation of DSL paints

	Parts by weight

No. 1—*Linseed oil*

Rutile titanium dioxide (Rutiox CR)	22.33
Blanc fixe	35.10
Asbestine	9.57
Raw linseed oil	22.28
Linseed stand oil, 130-140 poises	7.92
Mineral turpentine	12.55
Cobalt naphthenate driers (6 per cent Co) (equivalent to 0.05 per cent Co on oil)	0.25
	110.0

Five other paints were made by replacing the linseed oil/mineral turpentine medium at the same pigment volume concentration by the following:

	Per cent

No. 2—*Linseed alkyd* (Beckosol P-381)

Non-volatile containing 65 per cent linseed oil	70
Mineral turpentine	30
Acid value 5	

No. 3—*Safflower alkyd* (Rhodene L42/70)

Non-volatile containing 64 per cent safflower oil	70
Mineral turpentine	30
Acid value 6	

No. 4—*Pentaerythritol linseed alkyd* (Rhodene P2/70)

Non-volatile—pentaerythritol alkyd resin containing 70 per cent linseed oil	70
Mineral turpentine	30
Acid value 7	

No. 5—*Pentaerythritol safflower alkyd* (Rhodene M82/70)

Non-volatile—pentaerythritol alkyd resin containing 74 per cent safflower oil	70
Mineral turpentine	30
Acid value 3	

No. 6—*Linseed/tung phenolic*

Non-volatile—Phenolic resin	30%	
Linseed oil	35%	62
Tung oil	35%	
Volatile		38
Acid value 14		

Five other paints were made by replacing the linseed oil/mineral turpentine medium of Paint No. 19 at the same pigment volume concentration by the following:

No. 7—*Linseed alkyd* (Beckosol P381)

Non-volatile containing 65 per cent linseed oil	70
Mineral turpentine	30
Acid value 5	

No. 8—*Safflower alkyd* (Rhodene L42/70)

Non-volatile containing 64 per cent safflower oil	70
Mineral turpentine	30
Acid value 6	

No. 9—*Pentaerythritol linseed alkyd* (Rhodene P2/70)

Non-volatile—pentaerythritol alkyd resin containing 70 per cent linseed oil	70
Mineral turpentine	30
Acid value 7	

No. 10—*Pentaerythritol safflower alkyd* (Rhodene M82/70)

Non-volatile—pentacrythritol alkyd resin containing 74 per cent safflower oil	70
Mineral turpentine	30
Acid value 3	

No. 11—*Linseed/tung phenolic*

Non-volatile—Phenolic resin	30%	
Linseed oil	35%	62
Tung oil	35%	
Volatile		38
Acid value 14		

Nos. 12-16

Correspond exactly with paints No. 7-11 but where the acid value of each varnish media has been reduced to zero by reacting the free acids with diazo-methane.

No. 17—*Linseed oil media*

Replace 15 per cent of the pigment volume of paint No. 1 with chalk-resistant zinc oxide.

No. 18—*Linseed oil media*

As above but with 30 per cent replacement with chalk-resistant zinc oxide.

No. 19—*Linseed oil media*

Rutile titanium dioxide (Rutiox CR)	12.33
Blance fixe	19.25
Asbestine	5.28
Chalk-resistant zinc oxide	30.14
Raw linseed oil	22.28
Linseed stand oil (130-140 poises)	7.92
Mineral turpentine	12.55
Cobalt-naphthenate driers (6 per cent Co) (equivalent to 0.05 per cent Co on oil)	0.25
	110.00

No. 20—*Linseed oil media*

As above but with 60 per cent replacement with chalk-resistant zinc oxide.

Nos. 21-4—*Linseed oil media*

Corresponds with paints numbers 17-20 but replacing the chalk-resistant zinc oxide with chalking zinc oxide.

No. 25—*Linseed oil media*

Formulation as paint No. 19 but using chalk-resistant acicular zinc oxide in place of chalk-resistant zinc oxide.

No. 26—*Linseed oil media*

Formulation as paint No. 19 but replacing the chalk-resistant zinc oxide with chalking colloidal zinc oxide.

No. 27 and 29—*Linseed oil media*

Sufficient of the pigment in paint No. 1 was replaced by zinc tetroxy chromate to give a zinc content equivalent to 45 per cent by volume of zinc oxide.

Rutile titanium dioxide (Rutiox CR)	6.97
Blanc fixe	11.05
Asbestine	3.01
Zinc tetroxy chromate	43.66
Raw linseed oil	22.28
Linseed stand oil (130-140 poises)	7.92
Mineral turpentine	12.55
Cobalt naphthenate driers (6.0 per cent Co)	0.25
	107.69

No. 28

Basic zinc chromate is introduced in like manner as zinc tetroxy chromate into a paint based on the formulation of paint No. 1 i.e. sufficient of the pigment was replaced by the basic zinc chromate to give a zinc content equivalent to 45 per cent by volume of zinc oxide.

No. 30

Replaces 70 per cent of the rutile titanium dioxide in paint No. 1 by anatase titanium dioxide.

No. 31

The rutile titanium dioxide and blanc fixe in paint No. 1 was replaced by lithopone to give a zinc content equivalent to 26 per cent of zinc oxide by volume which is the maximum which can be introduced without altering the pigment/vehicle ratio.

No. 32

As paint No. 19 but replacing the rutile titanium dioxide by anatase titanium dioxide.

Nos. 33-50

In order of type and concentration of fungicides as below:

				Percentages		
Copper 8 quinolinolate	..	..	..	0.15	0.3	0.6
Phenyl mercury acetate	..	..	..	0.03	0.09	0.3
Phenyl mercury oxime	..	..	..	0.03	0.09	0.3
Pentachlorophenol	..	..	..	0.3	0.6	1.5
Tributyltin naphthenate	..	..	..	0.03	0.09	0.3
Nuodex 321	..	..	..	0.3	0.6	1.5

No. 51

Zinc naphthenate added to the reference paint to give a zinc content of 2.0 per cent.

Appendix B

Formulation of Chemical Inspectorate paints

(a) *Linseed oil based paints*

	Parts by weight
No. 1016	
Rutile titanium dioxide (Rutiox CR)	22.33
Blanc fixe	35.10
Asbestine	9.57
Raw linseed oil	22.28
Linseed stand oil, 130-140 poises	7.92
White spirit	12.55
Cobalt naphthenate driers (6 per cent Co) (equivalent to 0.05 per cent Co on oil)	0.25
	110.0

Fungicidal versions of the untreated control were made by adding 2 per cent or 4 per cent of fungicide on the non-volatile content of the paint; i.e. 1.77g or 3.54g of fungicide per 100g of wet paint:

No. 1017—Standard paint + 2% Mystox (Lauryl pentachlorphenol)

No. 1018	,,	,,	+ 4% ,, ,, ,,
No. 1019	,,	,,	+ 2% *p*-toluene sulfonamide
No. 1020	,,	,,	+ 4% ,, ,,
No. 1021	,,	,,	+ 2% Cadmium dehydroacetate
No. 1022	,,	,,	+ 4% ,, ,,
No. 1023	,,	,,	+ 2% Orthocide 83 (N-trichloro-methylmercapto-4-cyclohexene-1:2-diocarboximide)
No. 1024	,,	,,	+ 4% ,,

(b) *Chlorinated rubber based paints*

No. 1026—Untreated control without addition of fungicide. The formulation of this paint was:

	Parts by weight
Alloprene B	23.35
Cerechlor IS	10.0
Xylol	37.3
Cyclohexanone	8.0
White spirit	8.0
Rutile titanium dioxide (Rutiox CR)	13.35
	100.0

Fungicidal versions of the untreated control were made by adding 2 per cent or 4 per cent of fungicide on the non-volatile content of the paint, i.e. 0.93g or 1.86g of fungicide per 100g of wet paint:

No. 1027—Chlorinated rubber + 2% Mystox LPL

No. 1028	,,	,,	+ 4% ,,
No. 1029	,,	,,	+ 2% Paratoluene sulfonamide
No. 1030	,,	,,	+ 4% ,, ,,
No. 1031	,,	,,	+ 2% Cadmium dehydroacetate
No. 1032	,,	,,	+ 4% ,, ,,
No. 1033	,,	,,	+ 2% Orthocide 83
No. 1034	,,	,,	+ 4% ,, ,,

(c) *Long oil alkyd gloss paints*

No. 1035—Untreated control without addition of fungicide. The formation of this paint was:

	Parts by weight
Alkyd resin, Paralac 9HW (75 per cent soln. in white spirit)	51.6
Rutile titanium dioxide, Rutiox CR	31.3
White Spirit	15.0
Dipentene	2.1
Cobalt naphthenate driers (6 per cent metal)	0.16
Calcium naphthenate driers (4 per cent metal)	2.42
Lead naphthenate driers (24 per cent metal)	0.4
	102.98

(Driers equivalent to 0.025 per cent Co, 0.25 per cent Ca and 0.25 per cent Pb on solid resin)

Fungicidal versions of the untreated control were made by adding 2 per cent or 4 per cent of fungicide on the non-volatile content of the paint, i.e. 1.4g or 2.8g fungicide per 103g of wet paint:

No. 1036—Lond oil alkyd + 2% Mystox LPL

No. 1037	,, ,,	,,	+ 4% ,,
No. 1038	,, ,,	,,	+ 2% Paratoluene sulfonamide
No. 1039	,, ,,	,,	+ 4% ,,
No. 1040	,, ,,	,,	+ 2% Cadmium dehydroacetate
No. 1041	,, ,,	,,	+ 4% ,, ,,
No. 1042	,, ,,	,,	+ 2% Orthocide 83
No. 1043	,, ,,	,,	+ 4% ,,

(d) *Polyvinyl acetate emulsion paints*

No. 1044—Untreated control without addition of fungicide.
The formation of this paint was:

	Parts by weight
Pigment paste	
Rutile titanium dioxide (Rutiox CR)	100.0
Wet ground mica (micafine P)	20.0
Lithopone	30.0
China clay (Stockalite)	10.0
Sodium benzoate	4.0
Sodium nitrate	0.6
Lissapol N	0.4
5 per cent solution Cellofas A	30.0
5 per cent solution Calgon	3.0
Water	105.0
	303.0
Plasticised emulsion	
Polyvinyl acetate emulsion, Vinamul N9700 (55.6 per cent solids)	180.0
Butyl cellosolve phthalate	15.0
	195.0

Paint	
Pigment paste	303.0
Plasticised emulsion	169.5
	472.5

Fungicidal versions of the untreated control were made by adding 2 per cent or 4 per cent of fungicide on the non-volatile content of the paint, i.e. 1.13g or 2.26g of fungicide per 100g of wet paint:

No. 1045—Pva emulsion + 2% Mystox LPL

No. 1046	,,	,,	+ 4%	,,
No. 1047	,,	,,	+	Paratoluene sulfonamide
No. 1048	,,	,,	+ 4%	,, ,,
No. 1049	,,	,,	+ 2% Cadmium dehydroacetate	
No. 1050	,,	,,	+ 4%	,, ,,
No. 1051	,,	,,	+ 2% Orthocide 83	
No. 1053	,,	,,	+ 4%	,,

Appendix C

Ratings of DSL paints after 24 months

Panel no.	Description of paint	Chalking	Erosion	Checking	Cracking	Flaking	Mould	Dry rot
M 1	Standard-linseed oil control	Not exposed for 2 years						
M 2	Linseed alkyd Beckasol P381	5	10	10	10	10	7	·ǀ·
M 3	Safflower penta alkyd Rhodene L42/70	6	10	10	10	10	7	
M 4	Linseed penta alkyd Rhodene P2/70	4	10	10	10	10	7	
M 5	Safflower alkyd Rhodene M82/70	3	10	10	10	10	6	
M 6	Tung phenolic EF2329	2	10	4	6	9	5	
M 7	45% pigment in 1 replaced by chalk resistant* zinc oxide Beckasol P381	2	10	10	10	10	8	
M 8	Pigment as in 7 Rhodene L42/70	2	10	10	10	10	7	
9	Pigment as in 7 Rhodene P2/70	2	10	10	10	10	6	·ǀ·
10	Pigment as in 7 Rhodene M82/70	2	10	10	10	9	7	
11	Pigment as in 7 EF2329	2	10	4	7	10	4	·ǀ·
12	Pigment as in 7 P381 Acid value 0	2	10	10	10	10	7	
13	Pigment as in 7 L42/70 Acid value 0	5	10	10	10	10	7	
14	Pigment as in 7 P2/70 Acid value 0	2	10	10	9	9	6	·ǀ·
15	Pigment as in 7 M82/70 Acid value 0	2	10	10	10	10	9	
16	Pigment as in 7 EF2329 Acid value 0	Film flaked off						
17	15% of pigment in 1 replaced by zinc oxide Linseed oil vehicle	9	10	10	8	10	3	·ǀ·
18	30% of pigment 1 replaced by chalk resistant zinc oxide Linseed oil vehicle	3	10	10	10	5	4	·ǀ·
19	45% of pigment 1 replaced by chalk resistant ZnO Linseed oil vehicle	2	10	10	10	10	5	
20	60% of pigment in 1 replaced by chalk resistant ZnO Linseed oil vehicle	Panel lost						
21	15% of pigment 1 replaced by chalking ZnO Linseed oil vehicle	2	10	4	8	10	5	
22	30% of pigment 1 replaced by chalking ZnO Linseed oil vehicle	2	10	4	10	10	6	
23	45% of pigment 1 replaced by chalking ZnO Linseed oil vehicle	2	10	5	9	9	7	
24	60% of pigment 1 replaced by chalking ZnO Linseed oil vehicle	2	10	7	4	10	7	
25	45% of pigment 1 replaced by acicular ZnO Linseed oil vehicle	4	10	2	5	10	3	
26	45% of pigment 1 replaced by colloidal ZnO Linseed oil vehicle	2	10	2	10	10	9	
27	Pigment 1 replaced by Zinc tetroxy chromate to give 45% ZnO Linseed oil vehicle	6	10	10	8*	10	4	+
28	Pigment in 1 replaced by basic $ZnCrO_4$ to give 45% Zn Linseed oil vehicle	9	10	10	10	10	5	
29	Pigment in 1 replaced by zinc tetroxy chromate to give 45% Zn Linseed oil vehicle	6	10	10	7*	10	4	·ǀ·
32	45% of TiO_2 in 1 replaced by ZnO anatase E Linseed oil vehicle	2	10	5	8	10	6	

* Denotes wood cracking

Appendix D

Ratings of Chemical Inspectorate paints after 24 months

Panel no.	Description of paint	Chalking	Erosion	Checking	Cracking	Flaking	Mould	Dry rot
1026	Chlorinated rubber (CR) paint untreated control	8	10	10	10	10	7	+
1027	CR control + 2% Mystox LPL	7	10	10	10	10	8	
1028	CR control + 4% Mystox LPL	8	10	10	10	10	9	
1029	CR control + 2% toluene sulfonamide	9	10	10	10	10	8	+
1030	CR control + 4% toluene sulfonamide	9	10	10	10	10	8	+
1031	CR control + 2% cadmium dehydroacetate	6	10	10	10	10	8	
1032	CR control + 4% cadmium dehydroacetate	6	10	10	10	10	4	+
1033	CR control + 2% Orthocide 83	4	10	10	10	10	7	+
1034	CR control + 4% Orthocide 83	6	10	10	10	10	8	
1035	Long oil alkyd gloss paint untreated control	7	10	10	10	10	5	
1036	Alkyd control + 2% Mystox LPL	5	10	10	10	9	8	
1037	Alkyd control + 4% Mystox LPL	5	10	10	10	10	8	
1038	Alkyd control + 2% toluene sulfonamide	7	10	10	10	10	5	
1039	Alkyd control + 4% toluene sulfonamide	7	10	10	10	10	5	+
1040	Alkyd control + 2% cadmium dehydroacetate	6	10	10	10	10	4	
1041	Alkyd control + 4% cadmium dehydroacetate	6	10	10	10	10	5	
1042	Alkyd control + 2% Orthocide 83	5	10	10	10	10	6	
1043	Alkyd control + 4% Orthocide 83	5	10	10	10	10	7	
1044	Polyvinyl acetate emulsion untreated control	6	10	10	10	10	6	
1045	Pva emulsion + 2% Mystox LPL	8	10	10	10	10	7	+
1046	Pva emulsion + 4% Mystox LPL	7	10	10	10	10	8	
1047	Pva emulsion + 2% toluene sulfonamide	8	10	10	10	10	5	+
1048	Pva emulsion + 4% toluene sulfonamide	6	10	10	10	10	5	+
1049	Pva emulsion + 2% cadmium dehydroacetate	7	10	10	10	10	7	
1050	Pva emulsion + 4% cadmium dehydroacetate	6	10	10	10	10	5	+
1051	Pva emulsion + 2% Orthocide 83	5	10	10	10	10	8	
1053	Pva emulsion + 4% Orthocide 83	4	10	10	10	10	7	+

Next month's issue

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

Radiochemical investigation of ionic penetration into paint films *by A. Fialkiewicz and M. Szandorowski*

The influence of various parameters on the dispersibility of organic pigments in paints *by O. Hafner*

Convenience in wallcoverings *by B. J. Sauntson*

Appendix E

Fungi collected in New Guinea

Number	Fungus	Location where found and substrate
1	*Trichoderma viride*	On painted wall at TAA Mess at Lae
2	*Pullularia pullulans*	Panel 45, Rack 8
3	*Stemphylium sp. Neutospora Sitophila*	On painted wall at airport, Coreka
4	*Helminthosporium sp.*	On painted barn at Mt. Hagen
5	*Pullulans*	Painted wall, Head Office of Department of Works, Lae
6	*Aspergillus niger Pullulans*	Small painted hut at Depot, Muming
7	*Torula sp.*	On painted wall at TAA Mess at Lae
8	*Curvularia sp. Trichoderma viride*	On dead leaf of tree closest to paint racks
9	*Torula sp.*	On painted shed at Muming
10	*Pullulans Pleospora sp.*	Panel M.1020, Rack 6
11	Unidentified	Painted wood at Oompsie
12	*Trichoderma viride*	Panel 34X, Rack 7
13	Unidentified	Panel 33, Rack 8
14	*Pullularia pullulans*	Panel 45, Rack 8
15	*Pullularia pullulans*	Panel 95-156, Rack 6
16	*Pullularis pullulans*	Paint strip, Head Office of Department of Works, Lae
17	Unidentified	Paint on DCA Control Building, Airport, Coroka
18	*Fusarium sp.*	On painted oil drum, Mt. Hagen
19	*Trichoderma viride*	Panel M108-286, Rack 2
20	*Fusarium sp.*	From paint on railing, Markham River bridge
21	*Fusarium sp.*	From bark of tree near racks 2 and 3
22	*Pullularia pullulans Fusarium sp*	From branch of tree near racks
23	Unidentified	From paint on bridge at Cabensis
24	Unidentified	From paint at TAA Mess at Lae
25	*Trichoderma viride*	From cobweb under ledge on rack 1
26	*Trichoderma viride*	From cobweb on Rack 3 near to tree
27	*Trichoderma viride*	Panel M1019, Rack 5
28	*Pullularia pullulans*	Paint on exterior wall—office at TAA Mess, Lae
29	*Pullularia pullulans Trichoderma viride*	From tree near Racks 2 and 3
30	*Pestalotia sp.*	From dead leaf on tree near Racks
31	*Trichoderma viride*	From paint at Muming
32	*Cladosporium sp.*	Paint on barn at Mt. Hagen
33	*Pullularia pullulans Fusuarium sp.*	From cobwebs on Panel, Rack 4.
34	*Fusarium sp.*	From cobwebs on panel near tree, Rack 2
35	*Trichoderma viride*	Mushroom, Panel 120-377, Rack 6
36	*Trichoderma viride*	From painted trolley, airfield Mt. Hagen
37	*Torula sp.*	From tree near racks
38	*Pullularia pullulans*	From bark of tree near racks
39	*Fusarium sp.*	From leather at TAA Mess
40	*Trichoderma viride*	Panel 47X, Rack 7
41	*Pullularia pullans Trichoderma viride*	Paint on QEA shed at Minj
42	*Fusarium sp.*	Paint on wall, Head Office, Lae
43	Unidentified	Mould on leaf of Paw Paw behind racks
44	*Pullularia pullulans*	From leaf on tree near Racks 2 and 3
45	*Trichoderma viride*	From tree near racks
46	*Helminthosporium Neurospora sit*	Paint on iron at TAA Mess
47	*Nucor sp.*	Cottony material on wall at TAA Mess
48	*Torula*	Panel M1023, Rack 5
49	*Trichoderma viride*	Cobwebs under ledge on a panel from Rack 4
50	*Pullularia pullulans*	Paint on wall of Head Office at Lae

Appendix F

*Average climatic data for Lae, New Guinea**

	Jan.	Feb.	Mar.	Apl.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Year
Rainfall, (a) mm	292	251	330	429	335	338	533	516	498	302	351	285	4460
Days of rain (a)	22	19	23	20	23	22	25	24	24	20	21	22	265
Maximum temperature °C (b)	30	30	30	29	29	28	27	27	28	29	30	31	29
Minimum temperature °C (b)	23	23	23	24	24	23	22	21	22	23	24	24	23
Relative humidity (%) at hours:													
0300 (c)	91	91	91	96	96	91	95	95	95	95	94	93	94
0900	81	81	81	83	87	86	89	89	83	79	79	79	83
1500	73	73	73	73	76	73	75	79	75	73	76	73	74
2100	87	87	87	87	87	87	87	87	87	83	87	87	87
Sunshine, h/month (d)	172	140	176	175	184	136	126	124	153	199	195	192	1972
Sunshine, h/day (d)	$5\frac{1}{2}$	5	$5\frac{3}{4}$	$5\frac{3}{4}$	6	$4\frac{1}{2}$	4	4	5	$6\frac{1}{2}$	$6\frac{1}{2}$	$6\frac{1}{4}$	$5\frac{1}{2}$

* Figures supplied by the Commonwealth Bureau of Meteorology

(a) Average for 25 years (b) Average for 20 years (c) Average for 10 years (d) Average for 7 years

Short Communication

The adhesion of multicoat systems after nine years' exposure

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Summary

The exposure programme designed to examine the effect of long term ageing and environmental conditions on the adhesion of a range of surface coating systems described in this *Journal* in June 1969 has been terminated after nine years. Adhesion measurements have indicated that no major loss of adhesion has occurred, and in several cases the final adhesion values are greater than those obtained before exposure.

L'adherence des systèmes de peintures en multicouche après une période de neuf ans d'exposition au intempéries

Résumé

Le programme des essais destinés à l'investigation des effets du vieillissement à longue terme et de l'environnement sur l'adhérence d'une gamme de systèmes de peintures décrit dans ce Journal en juin 1969 a été terminé après neuf ans. Les mesures de l'adhérence ont démontré qu'aucune perte importante d'adhérence ne s'est produite et en plusieurs cas les valeurs de l'adhérence ultime sont supérieurs à ceux qui se rendaient avant l'exposition.

Die Haftung mehrschichtiger Filmsysteme nach neunjähriger Bewitterung

Zusammenfassung

Das im Juni 1969 in dieser Zeitschrift beschriebene Bewitterungsprogramm zur Prüfung der Auswirkungen auf lange Sicht von Alterung und Umweltbedingungen auf die Haftung von einer Reihe von Anstrichsystemen wurde nach neun Jahren beendet. Aus Haftungsmessungen ergab sich, dass keine wesentliche Verminderung eintrat, und dass in einigen Fällen die endgültigen Haftungswerte grösser wurden als sie vor der Exponierung festgestellt worden waren.

Introduction

Ref. 1, 2

In June 1969 the author reported the results of an investigation into the effect of natural weathering on the adhesion of multicoat paint systems exposed for four years[1]. The programme was designed to examine the effect of exposure time and climatic conditions on paint adhesion under the climatic conditions prevailing at the time of measurement. For this reason, tests were conducted outdoors without previous conditioning of the films before test. All adhesion measurements were carried out by the torque spanner technique[2]. It was concluded from the accumulated data that the adhesion of the systems tested and, by inference, of many other conventional coatings, varied considerably during the period of exposure. Further, the adhesion may fall to a small fraction of the original value without major failure occurring, and this loss of adhesion may be recovered at a later date. The picture presented was of the property of adhesion to the substrate fluctuating rapidly and reversibly within very wide limits. All the coating systems tested showed this variation, many of them to the same extent. There was also strong evidence that this variation was directly related to the water content of the ambient air. It was concluded that, under normal conditions, typical surface coating systems are unlikely to fail by loss of adhesion, although some permanent loss of adhesion must be anticipated on ageing. It was also suggested that this cyclic loss of adhesion could occur without allowing corrosion of the substrate to take place.

The panels described in the original paper have now been exposed for nine years, and several are showing signs of advanced breakdown, although it is only fair to say that some of this breakdown is attributable to failures occurring from the points of damage in the panels caused by the multiplicity of adhesion determinations carried out, and these points being subsequently patch primed. A final adhesion determination has now been carried out, and the visual appearance of the panels assessed. It may be of interest to readers of the original paper to see to what extent the conclusions drawn in that paper remain valid after the more prolonged exposure period.

Experimental

Ref. 1, 2

The experimental plan, panel preparation, exposure conditions, systems tested and test schedule have been described in the earlier paper[1], but it is perhaps not out of place briefly to restate the salient features.

Twelve paint systems, representing three of the major mechanisms of film formation, were exposed to natural weathering at an angle of 45° facing due south at Aldermaston, Berkshire. Aldermaston is a rural site substantially free from atmospheric pollution. The systems and substrates exposed are shown below.

System	Substrates	Coatings
1	Steel and aluminium	Etch primer to DEF1408 Cream chlorinated rubber undercoat to *H*R852 Cream chlorinated rubber finish to HR852
2	Steel and aluminium	Red oxide/zinc chromate primer to DEF1035 Light grey undercoat to DEF1156 Cream finish to DEF1156
3	Steel and aluminium	Red oxide/zinc chromate primer to CS8072 Light grey undercoat to CS8072 Service brown styrenated epoxide finish to CS8072
4	Steel and aluminium	Red oxide/zinc chromate polyamide cured epoxide primer White adduct cured epoxide finish
5	Steel and aluminium	Red oxide/zinc chromate polyamide cured epoxide primer White polyamide cured epoxide finish
6	Steel and aluminium	Red oxide/zinc chromate polyamide cured epoxide primer White aliphatic polyurethane to DTD5580
7	Steel and aluminium	Red oxide/zinc chromate polyamide cured epoxide primer White aromatic polyurethane
8	Steel and aluminium	Zinc rich primer to DEF1217 Cream chlorinated rubber undercoat to HR852 Cream chlorinated rubber finish to HR852
9	Wood	Red and white lead primer Light grey undercoat to DEF1156 Cream finish to DEF1156
10	Wood	Red and white lead primer Grey styrenated epoxide ester undercoat to CS8072 Service brown styrenated epoxide ester finish to CS8072
11	Wood	Linseed oil/TDI urethane oil
12	Wood	Red and white lead primer Proprietary white alkyd undercoat Proprietary white alkyd finish

All panels were tested by the torque spanner technique[2] after being allowed to condition for 72 hours under laboratory conditions (40 per cent RH, 60-65°F).

Results

The visual assessment ratings of the panels after 9 years' natural exposure are shown in Table 1. Reference to this Table will show that all the systems tested were chalking freely, although the aliphatic cured polyurethane was measurably superior in this respect. In many cases no major film defect was apparent and the systems retained their basic integrity, certainly all but one system showed complete protection of the substrate. The single case of lack of protection

occurred with the polyamide cured epoxide system on mild steel, which showed scattered corrosion patches over the entire panel area. These corroded areas were distinct from those points damaged by the adhesion determinations and subsequently patch primed to repair the damage.

The styrenated epoxide ester system showed incipient checking on both steel and aluminium which had not progressed to the cracking stage. This same system on wood was free from checking, but showed advanced cracking and flaking. This behaviour seems somewhat anomalous but it is probable that the cracking and flaking arose from defects in the wooden substrate (which was badly cracked) rather than from defects in the paint system. The polyamide and adduct cured epoxide systems both showed advanced checking and cracking, which had progressed to the flaking stage on both steel and aluminium. The two alkyd systems on wood also showed checking, cracking and flaking.

Reference to Table 2 will show the original measured adhesion and site of failure for every system, together with the final values measured after nine years' exposure. Twelve paint and substrate combinations showed an increased failing load (and, therefore, film strength) and nine of these were positively identifiable as systems with increased adhesion, as the site of failure remained at the substrate/paint interface. The remaining eight systems showed some loss of adhesion, although in two cases, at least, the loss was minor. In only three cases—the styrenated epoxide ester on mild steel, the aliphatic polyurethane on aluminium and the aromatic polyurethane on aluminium—was the loss in adhesion substantial. In the latter two cases the primer was common to both. None of these systems showed corrosion of the substrate.

Discussion

From a practical point of view it is apparent that the experimental assessment would have been improved if panels had been exposed in duplicate such that the assessment of film deterioration could have been carried out on a panel which had not been used for adhesion determinations. It is possible that some of the defects noted, particularly cracking and flaking, could have arisen from points of damage to the film caused by removal of the paint locally, but this is not considered to be too serious a defect since it can only result in a pessimistic rather than an optimistic assessment.

In general, all the systems under test performed as well as might be expected; only the two epoxide systems showed atypical breakdown although the author has observed cracking defects on adduct cured epoxide systems in other exposure series. The adhesion determinations showed clearly that loss of adhesion to the substrate is not a major problem in normal service life and there was certainly no evidence of widespread loss of or deterioration in adhesion in the long term.

It has also been demonstrated that the major variations in adhesion caused by environment and described in the previous paper do not necessarily lead to a progressive deterioration in the recovered adhesion, nor do these variations cause a deterioration in the protective properties of the paint systems. Only one system, the polyamide cured epoxide on mild steel, showed corrosion after nine years, and the final measured adhesion was greater than the original. Further, there was no evidence that this particular system showed any greater variation in adhesion over the period of exposure than any other system which was free from corrosion.

Table 1

Final observations on panels after nine years' natural weathering

Paint system	Substrate	Appearance	Chalking	Checking	Cracking	Flaking	Corrosion coated*	Corrosion stripped*	Comments
1 Etch primer/chlorinated rubber	Steel	2	0	5	5	5	Re 0	Re 0	Some minor cratering of film, brittle
1 Etch primer/chlorinated rubber	Aluminium	2	0	5	5	5	Re 0	Re 0	Isolated small blisters, some minor cratering
2 Oleoresinous primer/alkyd	Steel	2	0	5	5	5	Re 0	Re 0	Film in very good condition
2 Oleoresinous primer/alkyd	Aluminium	2	0	5	5	5	Re 0	Re 0	Isolated small blisters
3 Styrenated epoxide ester primer/undercoat/finish	Steel	1	0	4	5	5	Re 0	Re 0	Dense very small blisters, faded
3 Styrenated epoxide ester primer/undercoat/finish	Aluminium	2	0	4	5	5	Re 0	Re 0	Badly faded
4 Polyamide epoxide primer/ adduct epoxide finish	Steel	0	0	2	2	1	Re 0	Re 0	Flaking at points of repair
4 Polyamide epoxide primer/ adduct epoxide finish	Aluminium	0	0	0	2	2	Re 0	Re 0	Flaking general over entire area
5 Polyamide epoxide primer/ polyamide epoxide finish	Steel	0	0	0	0	1	Re 0	Re 5	Badly discoloured. Scattered small blisters
5 Polyamide epoxide primer/ polyamide epoxide finish	Aluminium			Panel lost					
6 Polyamide epoxide primer/ aliphatic polyurethane finish	Steel	2	2	5	5	5	Re 0	Re 0	—
6 Polyamide epoxide primer/ aliphatic polyurethane finish	Aluminium	2	2	5	5	5	Re 0	Re 0	Scattered collapsed small blisters
7 Polyamide epoxide primer/ aromatic polyurethane finish	Steel	1	0	2	3	5	Re 0	Re 0	Badly yellowed. Area of small pits
7 Polyamide epoxide primer/ aromatic polyurethane finish	Aluminium	1	0	3	3	5	Re 0	Re 0	Badly yellowed
8 Zinc rich primer/ chlorinated rubber	Steel	2	0	5	5	5	Re 0	Re 0	Film in very good condition
8 Zinc rich primer/ chlorinated rubber	Aluminium	2	0	5	5	5	Re 0	Re 0	Film in very good condition
9 Red and white lead primer/ alkyd undercoat and finish	Wood	0	0	1	2	3	—	—	—
10 Red and white lead primer/ styrenated epoxide undercoat and finish	Wood	0	0	5	0	0	—	—	Cracking due to substrate cracks
11 Linseed urethane oil	Wood			Panel failed completely within 4 years					
12 Red and white lead primer/ alkyd undercoat and finish	Wood	0	0	3	3	4	—	—	Scattered small blisters

5—No breakdown.   0—Complete failure

* European Corrosion Scale

Table 2

Effect of natural weathering on the adhesion of multicoat systems

Paint system	Substrate	Initial adhesion				Final adhesion after 9 years		
		MPa ± SD	psi ± SD	Site of failure		MPa ± SD	psi ± SD	Site of failure
1	Mild steel	15.20 ± 0.96	2,200 ± 139	100% adhesion from etch primer finish		20.19 ± 2.13	2,930 ± 309	0-5% adhesion from metal 80-90% adhesion from etch primer
1	Aluminium	9.71 ± 1.03	1,570 ± 162	100% adhesion from etch primer		13.23 ± 1.72	1,920 + 250	60-80% adhesion from etch primer
2	Mild steel	12.54 ± 1.06	1,820 + 155	60% adhesion from metal 40% cohesion of finish		13.37 ± 1.34	2,940 + 195	20-60% adhesion from metal 0-40% cohesion of undercoat
2	Aluminium	10.70 ± 1.45	1,500 ± 211	20-60% adhesion from metal 40-80% cohesion of primer		13.50 ± 1.81	1,960 ± 262	80-90% adhesion from metal 10-20% cohesion of undercoat
3	Mild steel	24.94 ± 2.18	3,620 ± 317	50% adhesion from primer 50% cohesion of undercoat		16.05 ± 2.54	2,330 ± 368	0-30% adhesion from metal 10-30% cohesion of undercoat
3	Aluminium	23.43 ± 1.81	3,400 + 271	40-60% adhesion from primer 40-60% cohesion of undercoat		38.58 ± 2.20	5,600 ± 319	30-100% adhesion from metal 0-10% cohesion of undercoat
4	Mild steel	11.30 ± 0.63	1,640 + 92	100% adhesion from metal		28.87 ± 1.36	4,190 + 198	30-60% adhesion from metal 0-40% adhesion from primer
4	Aluminium	11.44 ± 0.81	1,660 ± 118	100% adhesion from metal		13.37 ± 0.57	1,940 ± 83	70-100% adhesion from metal
5	Mild steel	20.67 ± 1.01	3,000 + 147	100% adhesion from metal		18.12 ± 0.81	2,630 ± 117	30-100% adhesion from metal
5	Aluminium	23.01 ± 1.58	3,340 ± 230	100% adhesion from metal		Panel lost		
6	Mild steel	33.07 +	4,800 +	No failure		31.14 ± 1.42	4,520 ± 206	10-90% adhesion from metal
6	Aluminium	33.07 +	4,800 +	No failure		13.92 ± 1.06	2,020 ± 154	70-100% adhesion from metal
7	Mild steel	31.00 ± 1.98	4,500 ± 287	60% adhesion from metal 40% adhesion from primer		25.29 ± 2.12	3,670 + 308	10-90% adhesion from metal
7	Aluminium	27.91 ± 2.49	4,050 + 362	60% adhesion from metal 40% adhesion from primer		14.88 ± 1.03	2,160 ± 149	80-100% adhesion from metal
8	Mild steel	2.13 ± 0.30	310 ± 43	100% adhesion from metal		18.00 ± 1.05	2,610 ± 152	0-30% adhesion from metal, 70-100% cohesion of finish
8	Aluminium	1.99 ± 0.12	290 ± 17	100% adhesion from metal		18.19 ± 0.48	2,640 ± 70	40-100% adhesion from metal
9	Wood	3.65 ± 0.63	530 ± 91	100% adhesion from wood		10.37 ± 0.61	1,650 ± 88	100% adhesion from wood*
10	Wood	4.96 ± 0.16	720 ± 24	100% adhesion from wood		9.99 + 0.77	1,450 ± 112	20-100% adhesion from wood*
11	Wood	15.06 ± 0.77	2,200 ± 112	100% adhesion from wood		Panel failed within 4 years		
12	Wood	3.17 ± 0.20	460 ± 29	100% adhesion from wood		14.26 ± 1.09	2,070 + 159	10-30% adhesion from wood*

* Some removal of fibres from the wood surface

Conclusions

The work has indicated that of the paint systems examined (which may be considered to be a typical selection), few show any marked loss of adhesion after nine years' exterior exposure. Further, the cyclic loss and recovery of adhesion due to environmental conditions does not cause progressive loss of adhesion or lessen the protective properties of the paints examined.

In this respect the conclusions drawn in the original paper remain valid.

References

1. Walker, P., JOCCA, 1969, 52, 516.
2. Holloway, M. W., and Walker, P., JOCCA, 1964, 47, 812.

Information Received

Anchor factice to be manufactured in Australia

Anchor Chemical's range of factices—already manufactured in England, Italy and Africa—is to be produced by the Harrison Manufacturing Company of Sydney, Australia.

Anchor Australia, a subsidiary of the Anchor Chemical Company which already supplies speciality rubber chemicals, curing agents for epoxide resins and plastics raw materials, will market both the Anchor and Harrison factices on the domestic market and in nearby countries.

Janke & Kunkel equipment available in UK

As a result of successful negotiations between Janke & Kunkel and Sartorius Instruments Limited, the former company's range of laboratory apparatus for homogenising, stirring and analysing is once again available in the United Kingdom.

New research laboratories

A new £70,000 suite of laboratories has been opened at Leeds University and will mean increased research into dyes, pigments and pharmaceutical powders with a grant of £86,000 from the Wolfson Foundation. The new facilities are to be used by the Wolfson Organic Powders Research Unit, which will be using the latest X-ray, laser, electron microscope and thermal analysis techniques for its research.

Reliance acquisition

Reliance Universal Inc, with corporate headquarters in Louisville, Kentucky, USA, through a newly-formed subsidiary has acquired the outstanding stock of Van Galen-Van der Sande SA, Mechelen, Belgium.

Van Galen-Van der Sande is an established manufacturer of industrial chemical coatings with annual sales of $3 million. Its products are sold mainly to the furniture industry of Belgium which is one of the largest in Europe.

RTZ reorganisation

RTZ Chemicals Limited, a wholly owned subsidiary of RTZ Borax, has now completed the reorganisation of the chemical companies announced late last year.

The present businesses of Hardman & Holden Limited, Manchester, and Barium Chemicals Limited, Widnes, will in future be conducted by three companies—Vine Chemicals Limited, Manox Limited and Manchem Limited.

Vine Chemicals Limited, based at Widnes, will be responsible for the group's interests in zinc oxide, barium products, sodium sulfide produced at the Widnes and Burry Port works and certain other products from the Hardman & Holden range, such as sodium hydrosulfite.

Manox Limited, based at Manchester, will be responsible for the coloured pigments manufactured by the group at its Miles Platting and Biddulph works, together with sodium ferrocyanide.

Manchem Limited, also at Manchester, will be responsible for the remaining products of the Hardman & Holden range, including speciality chemicals for the surface coating and rubber and plastics industries. Manchem will also take over Hardman & Holden's sole distributorship for the sale of DuPont pigments in the UK and for the distribution of Byk Mallinckrodt products and Wyrough and Loser polydispersions.

Solvay/Laporte plan new organic peroxide plant in Brazil

Solvay et Cie, Brussels, and Laporte Industries Limited, of London, England, have announced their decision to manufacture organic peroxides in Brazil through a new company now being formed—Interox do Brazil. The manufacturing plant is to be located adjacent to the Industrias Quimicas Electro Cloro SA chemical complex at Elclor, Brazil.

Substantial metrication in the engineering industries

The Metrication Board has announced that a recent survey involving over 600 companies in the engineering industries reveals that production has now reached an average of 44 per cent (by value) in metric or metric-compatible units. It is expected that a figure of 60 or 70 per cent will be achieved by the end of 1975.

Readers intending to submit items for publication in this *Journal* are reminded that only SI units will be acceptable from the January 1975 issue onwards.

Tennants to distribute BP Chemicals drum solvents

BP Chemicals International Limited has agreed in principle to the appointment of Tennants Consolidated Limited as exclusive distributors in the United Kingdom of BP Chemicals range of methylated spirits and oxygenated solvents sold in drums and cans.

The association between the two companies is of long standing. Tennants are sales agents for a number of BP Chemicals products, including the chlor-alkali range; BP Chemicals holds a 49 per cent interest in Synthite Limited (a member of the Tennant Group).

New products

Drostholm solvent cleaner

A new solvent recovery unit manufactured by Drostholm Products, of Denmark, has been introduced to the UK by C. & A. Simms (Engineers) Limited, of Chester. The machine is capable of cleaning acetone, benzole, ethanol, methanol, methylene chloride, xylene, iso-propyl alcohol, toluene and trichloroethylene, at the rate of 7 gallons per hour. It has a recovery rate of approximately 95 per cent, dependent upon the level of contamination in the solvent. Using a 440 volt 3-phase power supply the machine has an automatic switch-off.

New cab products from Eastman

Eastman Chemical International AG has announced two new products. EAB-551-0.01 is a new cellulose acetate butyrate (cab) ester which exhibits a tenfold viscosity advantage (0.01 seconds versus 0.10 seconds) over the previous low viscosity cab ester. EAB-555-0.2 is intended for water reducible coatings. The product is not soluble in water but is soluble in mixtures of organic solvents and water. The high hydroxyl content of EAB-555-0.2 enables it to improve levelling and hardness characteristics of water based enamels.

In addition, new data is available on the durability of gel coats and back-up resin systems based on TMPD glycol.

Literature

CIL release agents

A new comprehensive brochure is available from Compounding Ingredients Limited on the company's complete range of release agents. The 31-page booklet covers release agents for rubbers, thermoplastics, urethanes, resins, foams, and includes new materials such as the belt coating release agent and semi-permanent coatings for a variety of rigid and flexible surfaces.

Safety in electrostatic spraying of powder coatings

A new booklet giving recommendations for safe electrostatic spraying of powder coatings has been issued by the Paintmakers Association of Great Britain. Copies are available at 10p each from Paintmakers Association, Prudential House, Wellesley Road, Croydon CR9 2ET.

Techniques of assessing air pollution damage to paints

A lecture entitled "A study to evaluate techniques of assessing air pollution damage to paints" was presented recently at a meeting of the American Chemical Society. A number of copies of Atlas "Sunspots" in which the paper was published are now freely available from Wentworth Instruments Limited, North Green, Datchet, Slough SL3 9JH, England.

Courses, symposia etc.

Particle size analysis and environmental pollution

A colloquium on the applications of particle size analysis to environmental pollution, organised by the Particle Size Analysis Group of the Analytical Division of the Society for Analytical Chemistry, Chemical Society, will be held at Cavendish Hall, Nottingham University, on 18 and 19 September.

The principal theme will be the application of particle characterisation methods to environmental pollution by particulate matter. There will be two plenary and 10 to 12 other papers, and the proceedings will be published.

Registration forms are available from Mr M. W. G. Burt, Building B9C5, AWRE Aldermaston, Reading RG7 4PR and the registration fee, which will include accommodation for the nights 17 and 18 September, the colloquium dinner and all other meals and a copy of the Proceedings, is expected to be about £15.00.

Midlands

We need paint

At the meeting held on 15 February, the Chairman introduced Mr R. J. King (the Section's Hon. Student Liaison Officer), who spoke on the subject of "We need paint"; "we" in this context referring to the audience, who need paint as a means of earning a living.

The lecturer commenced by stating definitions of the various terms he would be using. A paint chemist was identified as a formulator, one of whose major tasks was cost control, and the importance of a well-balanced, soundly trained team of chemists was stressed.

Mention was briefly made of a whole list of problems which were currently affecting the industry, all of which stemmed at least partly from its dependence on other industries. Even growth rate was virtually impossible to control from within the industry. The lecturer went on to discuss the economics of the industry, with emphasis on the vital part played by the paint chemist in profitability and also in the wider aspects of his company's activities. Following this, a detailed assessment was made of those aspects of recruitment, training and job satisfaction where improvements could profitably be made by many paint manufacturers. Mention was made of the potential usefulness of OCCA membership in this context.

The final part of the lecture was concerned with the problem areas currently affecting the industry, notably alternative materials, environmental considerations, price and availability of raw materials, and the flammability regulations.

After a prolonged discussion period, which had to be finally terminated by the Chairman, the vote of thanks was given by Mr D. J. Silsby.

F.W.C.

Scottish

Eastern Branch

Marketing in Europe

The third meeting of the session was held in the Carlton Hotel, Edinburgh, on Wednesday 16 January, when Sir James Marjoribanks gave a talk on the above subject. Sir James, a member of the British negotiating team, began by surveying the various markets available in Europe. These were exemplified by reference to several products, including a few rather unlikely items which have proved extremely popular in European markets. No products should be classed as "non-runners" in the EEC, even if they failed in Britain.

The second part of the talk was devoted to an explanation of the correct method and best steps to take in order to promote a product in the EEC. Sir James also gave advice on the best advance preparations to make prior to paying a promotion or sales visit to a European company.

During question time, the speaker was of the opinion that a common European currency was unlikely in the near future. It was also mentioned that the full benefits of membership of the Common Market would not be felt in Britain for another year or two. The meeting closed with a hearty vote of thanks for a very informative talk.

P.S.N.

Computers in general

The fourth meeting of the session was held in the Carlton Hotel, Edinburgh, on Wednesday 20 February, when Mr F. Lawry of Croda Polymers Ltd., gave a very interesting talk on the use of computers in industry.

The speaker began by listing the commercial applications such as invoicing, and stock control, and everyday uses, such as traffic control, and Glasgow Fire Brigade's information store on buildings, exits, hydrants, etc. It was pointed out that the public were apprehensive about computers, mainly due to the bad coverage they had received in the press. Any mistakes made, however, were due to human error and not the machine itself. As in many other walks of life, it was only the mistakes and misuses which were publicised.

The speaker warned that the reasons for purchasing a computer must be good and valid. If management policies were wrong, then the purchase of a computer would only amplify the mistakes made at electronic speed.

The programming process was described, commencing with the request and terminating with the print-out result.

The talk was very humorous and enjoyable, and the meeting ended with a very hearty vote of thanks.

P.S.N.

OCCA—XXVII Exhibition

The international forum for technical display and discussion in the surface coating industries

Olympia, London. 22-25 April 1975

Motif of the Exhibition

The motif for 1975, designed by Robert Hamblin, continues the theme of OCCA-26, in which attention was drawn to the European Economic Community, by extending it to show the world-wide interest aroused by the Association's annual Exhibitions in London, which in recent years have attracted visitors from more than 50 overseas countries.

The colours of the motif this year are predominately light blue and green, symbolising the world, surrounded by dark blue. These colours will be carried throughout the publicity leading up to the Exhibition and will also be incorporated on the fascias of the stands; the green colour running from north to south and the light blue colour running from east to west. This gives the Exhibition both an entity in design and pleasing differences in colour as visitors move from corridor to corridor.

Venue

As in 1974, the Exhibition will be of four days' duration and will open on the **Tuesday morning at 09.30 and will close on the Friday at 16.00.** The Exhibition of raw materials, plant and equipment used in the paint, printing ink, colour, and allied industries will take place at the Empire Hall, Olympia, London.

Invitation to exhibit

Copies of the Invitation to Exhibit are being despatched to those companies and organisations, in the United Kingdom and overseas, which have shown at past Exhibitions or have already requested information on the 1975 Exhibition. Completed application forms for stand space must be returned to the Director & Secretary of the Association not later than **1 October 1974.**

At the twenty-sixth Exhibition, in April 1974, there were direct overseas exhibitors from 13 countries, besides many overseas companies which showed through British associates. A full review of this Exhibition, showing the countries from which visitors came and the products on display, appeared in the June issue of this Journal.

International forum

The Exhibition affords a splendid opportunity for the technical display of information and a unique forum for the informal interchange of technical advice and experience between those employed in the supplying and manufacturing industries. Any organisation which has not previously received an Invitation to Exhibit and wishes to do so should contact the Association's offices as soon as possible.

Association Dinner and Dance 1974

The Association's biennial Dinner and Dance took place at the Savoy Hotel, London, on Friday 31 May 1974 when 270 members and guests were received by the President, Mr L. H. Silver, and Mrs Silver.

The President stated in his address of welcome to the guests and ladies that this occasion, in particular, was a social one and there would be only two short speeches, allowing the company to take full advantage of the entertainment to be provided by the Jerome orchestra. The arrangement met with approval and the dance floor was crowded until the end of the evening.

It was Mr Silver's pleasant duty to ask the Guest of Honour, Mr M. Malaga, President of the Federation of Societies for Paint Technology, to accept a scroll to be presented at a suitable function to Mr R. W. Matlack, retiring executive vice-president of the FSPT, conferring upon him Honorary Membership of this Association in recognition of his work in promoting co-operation between OCCA, the FSPT and kindred organisations throughout the world. Replying to the President's address of welcome, Mr Malaga said he was delighted to accept the scroll to present to Mr Matlack. He also commented on the wonderful hospitality shown to him, and wished everyone a very enjoyable evening.

The Association's other guests were:

Mr T. L. Houghton, President of the Institute of Metal Finishing; Mr H. G. Cole, President of the Institution of Corrosion Technology, and Mrs Cole; Mr P. A. Sturge, President of the Paint Research Association, and Mrs Sturge.

The President, Mr L. H. Silver (right), Mrs Malaga, Mrs Silver, and the Association's Guest of Honour, Mr M. W. Malaga (President of the Federation of Societies for Paint Technology)

Admissions to Professional Grade

The following admissions have been approved by the Professional Grade Committee:

Fellows

Joseph Stephen Boroky (*General Overseas—Australia*)
William Alan Grainger (*Irish*)
Robert Stanley Yorath (*Wellington*)

Associates

Martin William Booth (*Wellington*)
Ian Clifford James Dury (*Thames Valley*)
Robert John Goodman (*General Overseas—Spain*)
David Basil Harty (*General Overseas—Australia*)
Erik Naess (*General Overseas—Norway*)
Peter Samuel Nisbet (*Scottish—Eastern Branch*)

Licentiate

Anthony Chambers (*London*)

London Section

Thirty-sixth Annual General Meeting

The thirty-sixth AGM was held on 19 April 1974 at the Polytechnic of the South Bank, under the chairmanship of Mr R. H. E. Munn. In proposing the adoption of the Committee's Report, Mr H. C. Worsdall, the Section Honorary Secretary, said that the Committee had suffered a loss during the session due to the sudden death of Dr V. Crowl, the Hon. Publications Officer. Mr Worsdall paid tribute to his work for both the Section and the Association. A varied selection of meetings had brought attendance similar to other sessions. The Committee were especially pleased with the response to the Hastings symposium. This was the first time the section had organised a weekend symposium for members, their wives and children, and it is hoped to arrange similar events in the future. The Committee's report was seconded by Mr B. H. Ducker and adopted unanimously.

Dr H. R. Hamburg presented the financial report which was also adopted unanimously. Officers were elected for the coming session.

Mr J. T. Tooke-Kirby presented a report on the Southern Branch. Following the meeting the ladies and guests joined the main body for a talk by Mr E. V. Elwes of the British Epicure Society on "Wine and its enjoyment." Mr Elwes talked of various types of wine and their history. The talk was concluded by members being invited to sample some of the wines mentioned.

Obituary

Colin Galbraith Cochrane, BSc, AH-WC, FRIC

By the passing of Mr C. G. Cochrane, Technical Director of Craig & Rose Ltd, Edinburgh, on 1 May, the Scottish paint trade and OCCA have lost a prominent and well-loved member.

Mr Cochrane, who spent all his working life with Craig & Rose, would have completed 50 years' service next November when he intended to retire. During a large part of that time he was an enthusiastic member of the Scottish Section and latterly of the Eastern Branch, which he served for some years on Committee.

His warm friendly nature and great sense of humour endeared him to all who were privileged to know him, and we extend our sympathy to his widow Margaret, to his son and daughter-in-law in Canada, and to his daughter and son-in-law in London.

He will be sadly missed.

Register of Members

The following elections to Membership have been approved by Council. The Section to which new Members are attached is given in italics.

Ordinary Members

ACKROYD, JOHN RODERIC, BSc, 21 Greenbanks, Wilmington, Dartford, Kent DA1 1NU.   (*London*)

BATES, EDWARD ALBERT, 13A Singleton Road, Patcham, Brighton, Sussex.   (*London*)

BINGHAM, MICHAEL HENRY, 18 Ladywell Gate, Welton, Brough, East Yorkshire.   (*Hull*)

CLAPSHOE, COLIN GEORGE, Unalco Ltd, Bowater House East, 68 Knightsbridge, London SW1X 7LP.   (*London*)

FRASER, IAN EVENDON, 20 Harptree Drive, Walderslade, near Chatham, Kent ME5 0TH.   (*London*)

HOLTBY, TERENCE GEORGE, 23 Maytree Close, Guildford GU1 1PJ.   (*London*)

HOOPER, DAVID EDWARD, LIMF, 15 Rectory Lane, Byfleet, Surrey.   (*London*)

HOWELL, DENIS, BSc, LRIC, 10 Ulster Gardens, Edinburgh EH8 7JZ.   (*Scottish*)

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Optional Professional Grade for Ordinary Members

The innovation of the Professional Grade has proved to be most successful, as evidenced by the impressive list of names in the December issue of the *Journal*. For the convenience of potential applicants, the full regulations for admission and a chart indicating different routes to the various grades are shown below. **Members are reminded of the recent amendments to the regulations, which are shown here in red.**

Routes to the Professional Grades
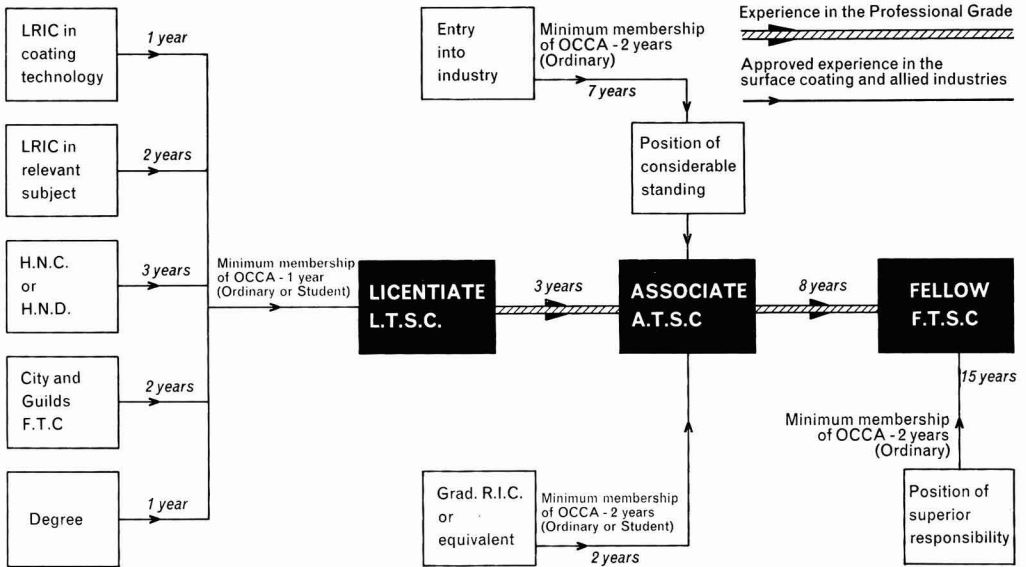
Note: At present there is no restriction on Students up to 21; between 21 and 25 a certificate from the employer or college confirming the course being taken is required.

Regulations for admission to the Professional Grade

Note: For the sake of simplicity, reference is made only to UK examinations etc., but equivalent qualifications overseas will naturally be accepted.

A. Licentiate

1. Shall be an Ordinary Member of the Association and have been an Ordinary Member or Student of the Association for not less than one year.

2. Shall have attained the age of 22.

3. (a) Shall be a Licentiate of the Royal Institute of Chemistry in Coatings Technology (*viz*. Higher National Certificate + Endorsement in coatings technology + 1 year approved experience in the science or technology of coatings after passing the endorsement examination).

OR (b) Shall be a Licentiate of the Royal Institute of Chemistry in another relevant subject such as advanced analytical chemistry, colour chemistry or polymer science, and shall have two years' approved experience of coatings since so qualifying.

OR (c) Shall hold the Full Technological Certificate of the City and Guilds of London Institute in a relevant subject as approved by the Professional Grade Committee and shall have two years' approved experience in the science or technology of coatings since gaining the FTC.

OR (d) Shall have passed Higher National Certificate or Higher National Diploma with three years' approved experience in the science or technology of coatings since qualifying, but two years' approved pre-qualification experience shall be deemed equivalent to the third post-qualification year.

OR (e) Shall be graduate in relevant subject with not less than 1 year's approved experience.

OR (f) Shall have passed such other qualifications as approved by the Professional Grade Committee from time to time.

4. Shall be required to satisfy the Professional Grade Committee, or some other body approved by the Professional Grade Committee in a *viva voce* examination and submit a dissertation on a topic previously approved by the Professional Grade Committee.

5. Shall normally be sponsored by three Ordinary Members of the Association in the professional grade (either Associate or Fellow) at least one of whom must be a Fellow.

6. Shall have paid the fee stipulated by the Council and have paid the current subscription payable by an Ordinary Member.

B. Associate, being already a Licentiate

1. Shall, since his election to the Licentiateship, have practised the science or technology of coatings for not less than three years.

2. Shall provide evidence acceptable to the Professional Grade Committee of his superior professional skill and maturity.

3. Shall hold the City & Guilds of London Institute Insignia Award OR shall submit a thesis or dissertation of comparable level on a topic previously approved by the Professional Grade Committee OR shall have published work which, in the opinion of the Professional Grade Committee, is of comparable merit.

4. MAY be required to satisfy the Professional Grade Committee or some other body as approved by the Professional Grade Committee in a *viva voce* examination.

5. Shall normally be sponsored by three Ordinary Members of the Association in the professional grade (either Associate or Fellow) at least one of whom must be a Fellow.

6. Shall have paid the fee stipulated by the Council and have paid the current subscription payable by an Ordinary Member.

C. Associate, not already a Licentiate

EITHER

1. Shall be not less than 24 years of age.

2. Shall be an Ordinary Member of the Association and have been an Ordinary Member or Student of the Association for not less than two years.

3. Shall hold the Graduateship of the Royal Institute of Chemistry or Institute of Physics or a University or Council of National Academic Awards degree recognised by the Royal Institute of Chemistry or Institute of Physics as giving full exemption from the Graduateship examination.

4. Shall have not less than two years' approved post-graduate experience in the science or technology of coatings.

5. Shall normally be required to satisfy the Professional Grade Committee or some other body approved by the Professional Grade Committee, at a *viva voce* examination.

6. Shall normally be sponsored by three Ordinary Members of the Association in the professional grade (either Associate or Fellow) at least one of whom must be a Fellow.

7. Shall have paid the fee stipulated by the Council and have paid the current subscription payable by an Ordinary Member.

OR

8. Shall be not less than 30 years of age.

9. Shall be an Ordinary Member of the Association and have been an Ordinary Member of the Association for not less than two years.

10. Shall have been engaged in practising the science or technology of coatings for not less than seven years and shall have attained a position of considerable standing in the industry.

11. Shall normally be required to satisfy the Professional Grade Committee in *viva voce* examination of his professional competence.

12. Shall normally be sponsored by three Ordinary Members of the Association in the professional grade (either Associate or Fellow) at least one of whom must be a Fellow.

13. Shall have paid the fee stipulated by the Council and have paid the current subscription payable by an Ordinary Member.

D. Fellow

Note: This is the senior award of the professional grade and signifies that the holder has made outstanding contributions to the science or technology of coatings or has reached a position of eminence in the industry through the practice thereof. The Professional Grade Committee will require substantial evidence of professional maturity in the science or technology of coatings although commercial experience will be taken into account in assessing the merits of candidates.

1. Shall be not less than 33 years of age.

2. Shall have been an Ordinary Member of the Association for not less than two years.

3. Shall be engaged in a position of superior responsibility in the coatings industry.

4. EITHER (a) shall have been an Associate of the professional grade for at least eight years;

   OR   (b) shall have not less than fifteen years' experience of the science or technology of coatings in a position of superior responsibility.

5. Shall submit, with his application, an account of his experience, with due reference to scientific and technological interests, achievements and publications.

6. Shall normally be sponsored by three Ordinary Members of the Association in the professional grade, all of whom must be Fellows.

7. Shall have paid the fee stipulated by the Council and have paid the current subscription payable by an Ordinary Member.

The fees payable with applications are as follows:

Fellow—£10.00   Associate—£6.00
Licentiate—£3.00
(Plus VAT at standard rate)

Application

Completed application forms should be returned, together with the appropriate remittance, to the Director & Secretary at the Association's offices (except in the case of those Members attached to the Auckland, South African and Wellington Sections who should address their forms to their Section Hon. Secretaries).

The Committee wishes it to be known that Members rejoining the Association after a period in other industries may include length of service as an Ordinary Member before their resignation as part of the qualifying periods for entry into the Grade.

Students wishing to apply for entry into the Professional Grade must first make application in writing for upgrading to Ordinary Membership, giving the reasons for their eligibility for such regrading. Applications, together with the appropriate remittance, should be addressed as for application for admission to the Professional Grade.

Potential applicants are recommended to give the fullest possible details of their appointments, including the number and type of staff under their control, and indicating to whom the applicant is responsible, as this aids the committee considerably in its deliberations.

It is felt that applicants for admission to the Licentiate grade might wish to have further information on the pattern which it is suggested should be followed for dissertations, the subjects of which have first to be approved by the Professional Grade Committee.

The dissertation should be preceded by a short summary and commence with a brief introduction and some account of the current state of knowledge. Where practicable it should follow the general format of a paper in *JOCCA*.

The dissertation may be a review of a subject, a theoretical treatment, descriptive of practical work or a combination of these. It must indicate that the candidate has a reasonably wide and up-to-date knowledge of his chosen subject and understands the basic scientific principles underlying it, and that he is able to think critically and constructively.

Where practical work is described, some attempt should be made to draw theoretical conclusions or to form some provisional hypothesis, together with an outline of what further work would be required to confirm the views put forward or further to advance the knowledge of the subject.

Where the dissertation is a review or a theoretical treatment, there should be an attempt to contrast and compare any opposing views expressed in earlier works, to examine the views critically, to suggest any compromise interpretation, to account for all the known facts and to outline any further work by which the opposing views could be tested.

Where applicable, references should be given to published work, graphs, diagrams etc. to be appended.

Length: Text should be approximately 5,000 words.

Applicants should refer to the paper by Moss which appeared in the January 1973 issue; the Professional Grade Committee feels that candidates for the Licentiate grade could with advantage use this paper as a model for their dissertations.

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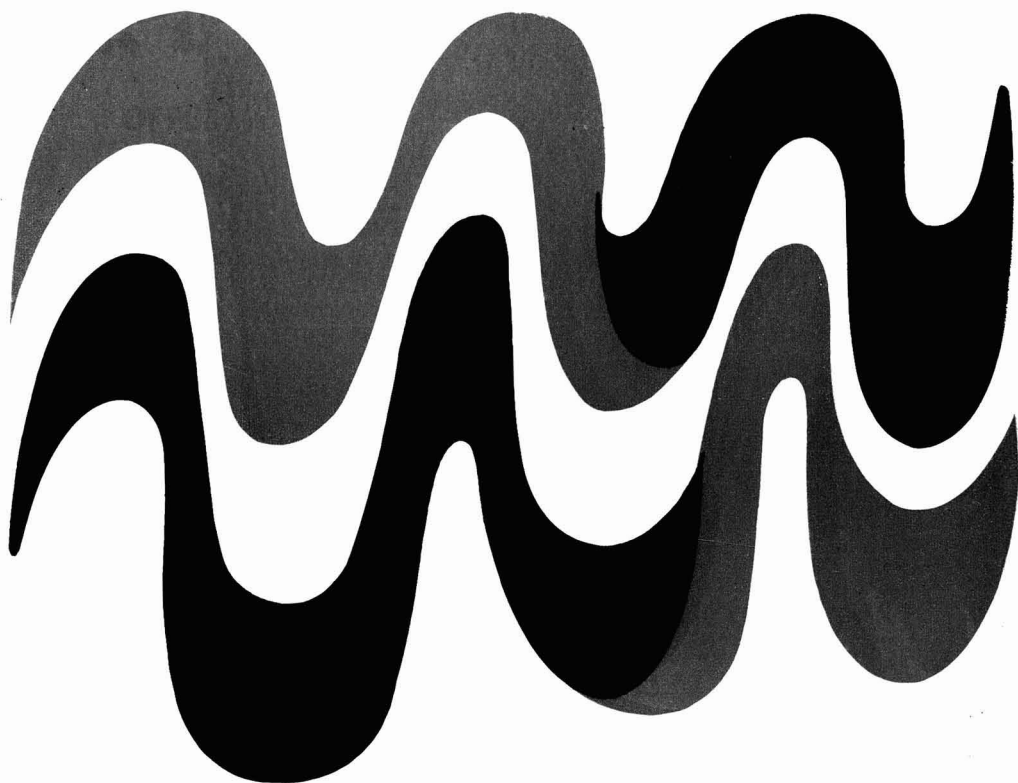
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