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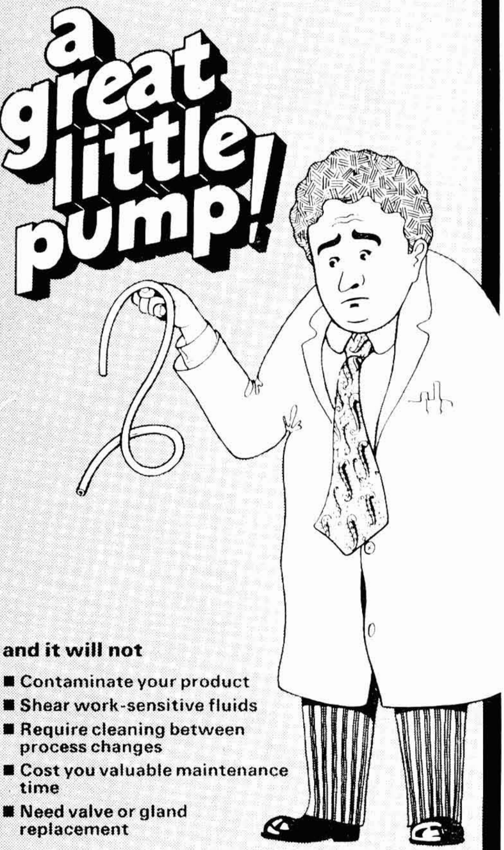
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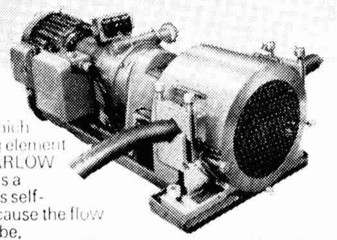

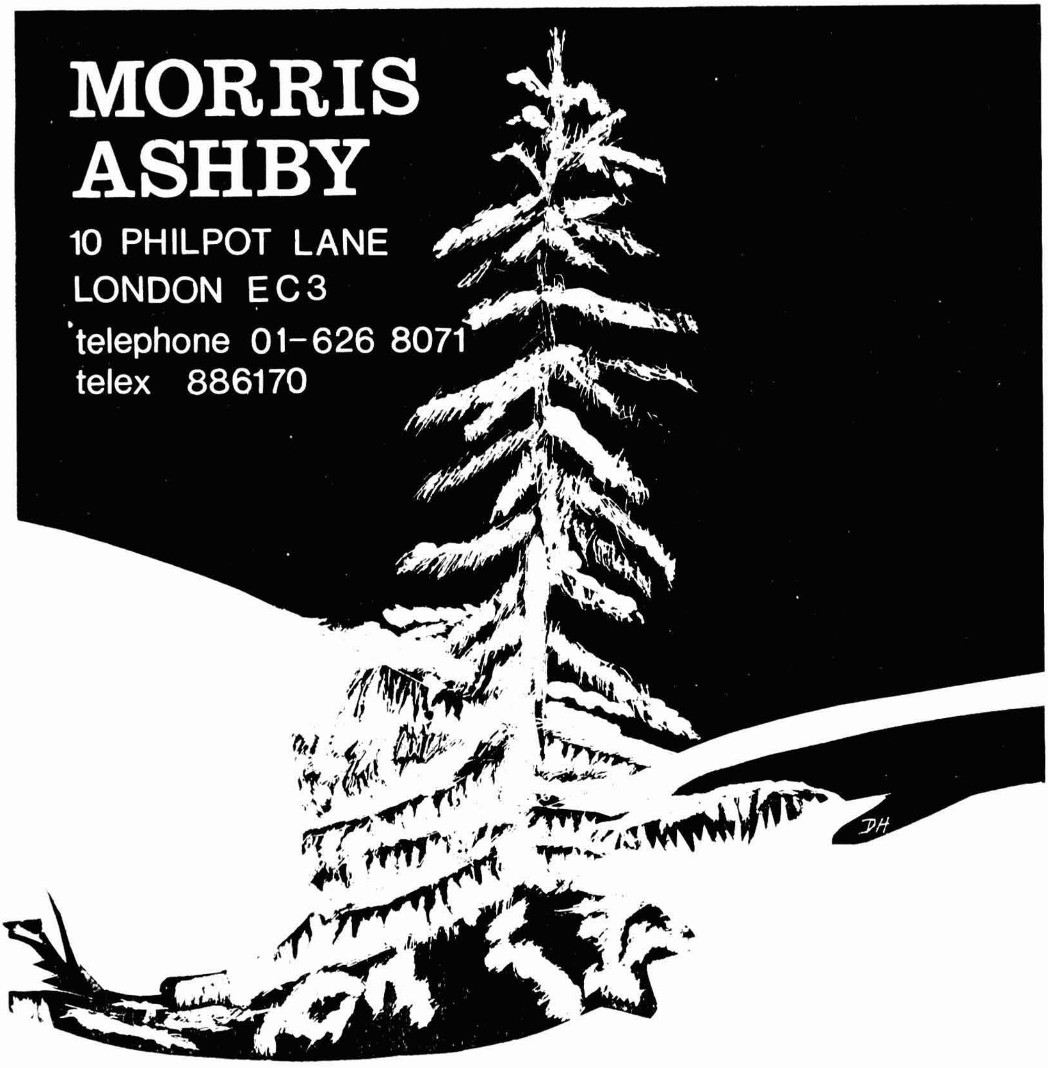
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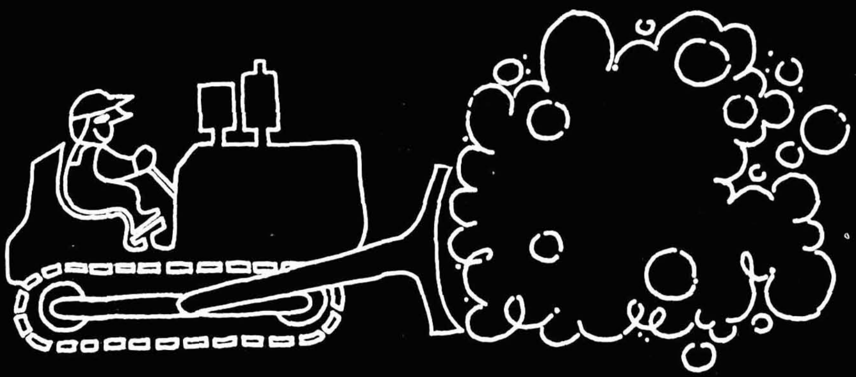

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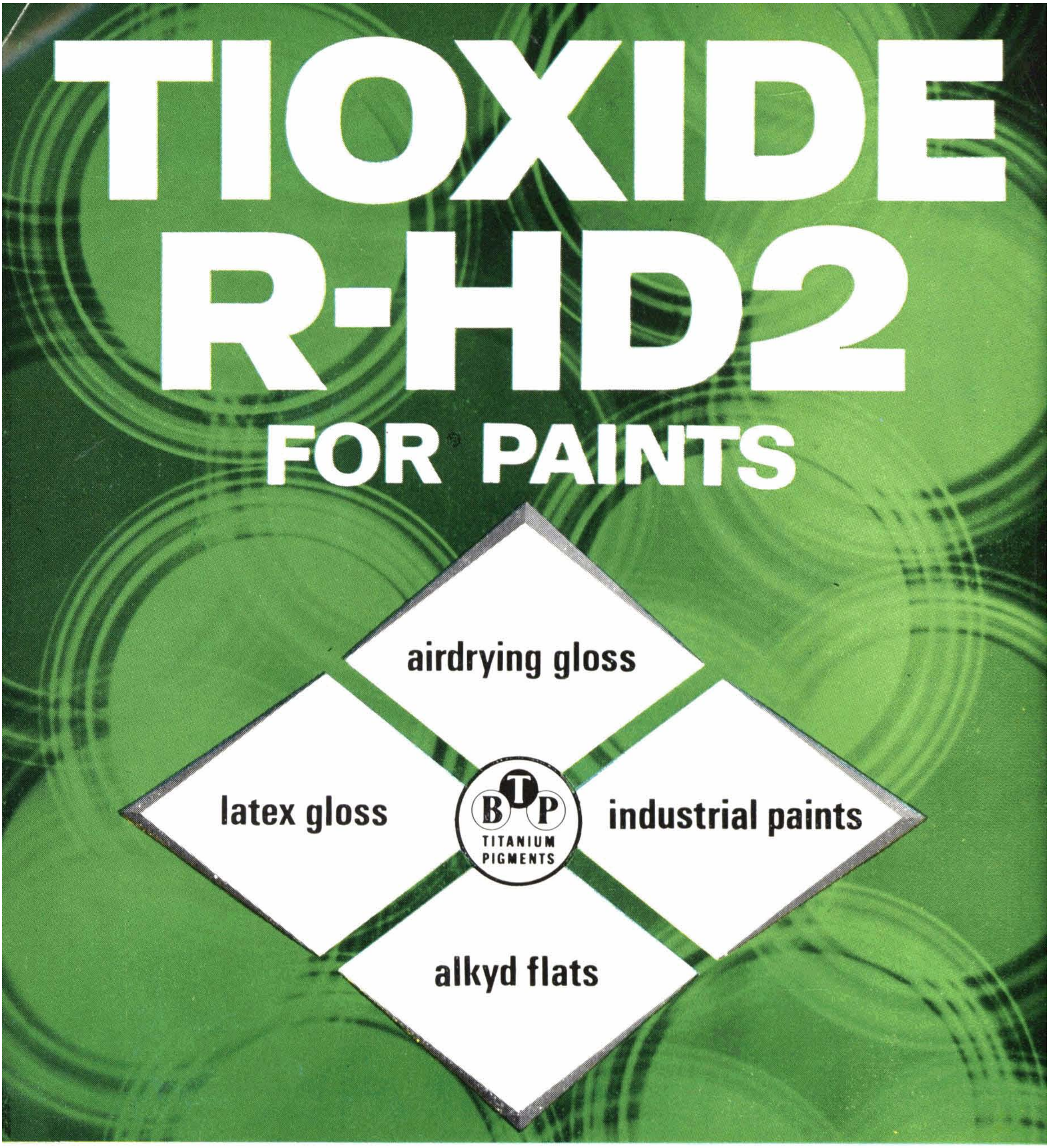
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Transactions and Communications

Water transport through paint films Part II: Water transport and cluster formation in non-pigmented films

By D. Y. Perera and P. M. Heertjes*

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Summary

Water diffusion coefficients of four non-pigmented paint films were calculated from permeation measurements. It was found that in some cases the diffusion coefficient was dependent on the water concentration. This phenomenon was satisfactorily explained by Zimm and Lundberg's cluster theory.

The clustering function and the mean cluster size were obtained from isothermal sorption measurements.

Keywords

Properties, characteristics and conditions primarily associated with dried or cured films

water permeation

Le transport de l'eau à travers des feuils de peintures. Deuxième partie: Le transport de l'eau et la formation de grappes en feuils non-pigmentés.

Résumé

On a calculé, à partir des mesures de pénétration, les coéfficients de diffusion d'eau pour quatre feuils non-pigmentés. En certains cas on a trouvé que les coéfficients de diffusion se dependait de la concentration de l'eau. Ce phénomène a été expliqué dans une manière satisfaisante par la théorie de la formation de grappes proposée par Zimm et Lundberg.

On a dérivé la fonction de la formation de grappes et la grandeur moyenne des grappes à partir des mesures de sorption isothermale.

Wassertransport durch Anstrich filmen II: Wassertransport und Schwarmbildung in Unpigmentierten Filmen

Zusammenfassung

Die Wasserdiffusionskoeffizienten von vier unpigmentierten Lackfilmen wurden aus Eindringungsmessungen errechnet. Dabei wurde festgestellt, dass der Diffusionskoeffizient in manchen Fällen von der Wasserkonzentration abhängt. Die Schwarmtheorie von Zimm und Lundberg erklärte dieses Phänomen ausreichend.

Die Funktion der Anhäufung und die durchschnittliche Grösse eines Schwarms wurden durch Messung der isothermalen Sorption berechnet.

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*University of Technology, Delft, Holland.

Перенос воды и образование пучков в непигментированных пленках

Резюме

Вычислялись коэффициенты диффузии воды для четырех непигментированных красочных пленок исходя из измерений проницаемости. Найдено что в некоторых случаях коэффициент рассеяния зависит от концентрации воды. Это явление удовлетворительно объясняется теорией пучков Цимма и Лундберга.

Получены функция пучкования и средняя величина пучков из измерений изотермической сорбции.

Introduction

In a previous paper[1], the water transport through four typical binders commonly used in paint manufacture was investigated. It was found that different permeation characteristics exist; the diffusion and solubility coefficients either increased, decreased or were constant with increase of the water concentration, depending on the affinity of the material for water.

This behaviour has already been reported in the literature on water transport processes through polymer films. For most hydrophilic materials (such as wool, cellulose, polyvinyl alcohol, nylon) the diffusion coefficient, D, increases with the water concentration, whilst for less hydrophilic materials (such as polyethylene[2], rubber hydrochloride[3, 4], ethylcellulose[5], polymethylmethacrylate[6], polyurethane elastomers[7]) D decreases with the water concentration. For hydrophobic materials (such as polyolefines) D is independent of the water concentration.

The clustering theory developed by Zimm[8] from statistical mechanics in 1953, and applied by Zimm and Lundberg[9] in 1956 to "sorption of vapours by high polymers", was subsequently used to explain the various aspects of the water transport mechanism through polymer films[3, 7, 10].

In the light of this theory, the water transport process through an air drying medium oil length alkyd, an epoxy resin, and a chlorinated rubber with and without plasticiser will be explained.

Materials and experimental

The materials investigated, their preparation, and the technique of water sorption measurements were described in an earlier paper[1].

Theoretical

Zimm arrived at the clustering function by defining a "molecular pair distribution function", $F_2(i, j)$ in such a way that $(1/V^2)F_2(i, j)\, d(i)\, d(j)$ is the probability that molecules i and j are each at the position specified by the co-ordinates (i, j) in the range $d(i)$ and $d(j)$. V represents the total volume of the system. Then the "cluster integral" G_{11} is defined as:

$$G_{11} = \frac{1}{V} \iint \{F_2(i, j) - 1\}\, d(i)\, d(j);$$

where i and j represent the molecules of component 1 of a binary mixture.

Further, using Mayer and McMillan's power series, Zimm found a relation between the penetrant activity (a_1), the volume fraction (Φ_1) and G_{11}:

$$\frac{G_{11}}{V_1} = -\Phi_2 \left[\frac{\partial (a_1/\Phi_1)}{\partial a_1}\right]_{P,T} - 1 = -(1-\Phi_1)\left[\frac{\partial (a_1/\Phi_1)}{\partial a_1}\right]_{P,T} - 1 \quad (1)$$

In Zimm's terms, V_1 represents the partial molecular volume of the penetrant, G_{11}/V_1 the tendency of the penetrant molecules to cluster, and $\Phi_1 G_{11}/V_1$ the excess of the penetrant molecules over the mean concentration found in the close vicinity of a given penetrant molecule.

The advantage of Zimm and Lundberg's theory over that of Flory-Huggins-Guggenheim lies in the fact that it can also be applied to systems where penetrant/polymer interaction takes place, because the "clustering function" contains no terms which are dependent on it. However, the theory is limited to systems of negligible compressibility, and does not show in what state water is present in the cluster if it is present in one or more phases[3].

It also assumes additivity of volumes in calculating volume fractions, which may cause errors in the clustering function calculation.

The three limiting cases of the clustering function

A detailed analysis of the clustering function shows that the magnitude of the function G_{11}/V_1 (see equation 1) can be:

(a) $G_{11}/V_1 = -1$
(b) $G_{11}/V_1 > -1$
(c) $G_{11}/V_1 < -1$

(a) When the activity coefficient $\gamma = a_1/\Phi_1$ does not vary with the activity (a_1), the function $G_{11}/V_1 = -1$, which is the ideal case. This means that a penetrant molecule can be replaced by another without disturbing their distribution.

(b) At high concentrations (high Φ_1), a_1/Φ_1 decreases with increase of the concentration, the tangent $\partial(a_1/\Phi_1)/\partial a$ has negative values, and G_{11}/V_1 becomes larger than -1 and very soon reaches positive values. This shows that the penetrant concentration in the close vicinity of a given penetrant molecule is higher than expected, in other words "cluster formation" takes place.

(c) At low penetrant concentrations, Langmuir type sorption is presumed to occur. The increasing negative values of G_{11}/V_1 with the water concentration indicate that an interaction penetrant-polymer exists.

The correspondence between the clustering function and the diffusivity

The three cases described above, which have still to be justified, must correspond to three cases for the variation of diffusion coefficient with water concentration.

(a) For the materials for which G_{11}/V_1 is constant and equal to -1 throughout the range of the concentration, the diffusion coefficient must also be independent of the concentration.

(b) High positive values for G_{11}/V_1 indicate strong cluster formation. Cluster formation may occur if the water/water interaction is stronger than the water/polymer interaction, and/or sufficient centres for initiating cluster formation or some form of capillary condensation are present in the material. As a consequence of the interaction of water molecules resulting in cluster formation, the amount of mobile single water molecules decreases when the total concentration increases, and *D* must decrease.

(c) Negative values for G_{11}/V_1 show that clusters are not formed in the film. This is the case for hydrophilic materials, where the interaction between water and polar groups is stronger than that of the water/water interaction. Therefore, no cluster formation will occur. In this case *D* increases with the increase of the water concentration.

In addition to these clearly defined cases, more complex ones may exist, when competitive processes of clustering and specific interactions occur. Then, *D* is the resultant of contrary processes, and unpredictable results are obtained. Another difficulty in the interpretation of the relation between the clustering function and the diffusivity may be caused by the enlargement of interstitial spaces, if swelling processes occur in the polymer network. The possibility might also exist that some type of cluster, such as a dimer or trimer, may contribute to the transport process. The clustering function does not give any information about the state of the water in a cluster.

Results and conclusions

The diffusion coefficients of the four binders, as determined in the earlier paper from the permeation measurements,[1] showed different dependencies

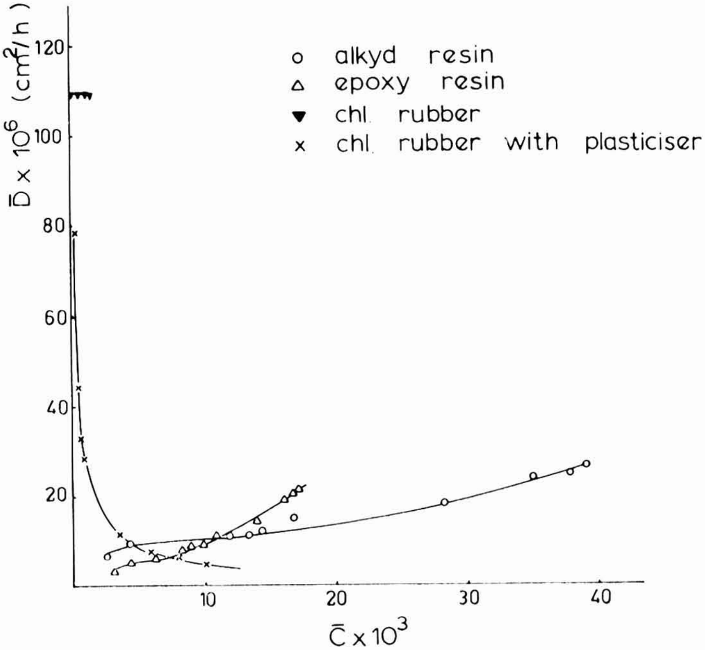

Fig. 1. Mean diffusion coefficient ($\overline{D}$) as a function of mean water concentration ($\overline{c}$)

on the water concentration (Fig. 1). An attempt has been made to explain the diffusion behaviour on the basis of Zimm's theory. The clustering function (G_{11}/V_1) and the mean cluster size ($1 + \Phi_1 G_{11}/V_1$) were calculated from equation 1, using the data from water sorption measurements (Fig. 2).

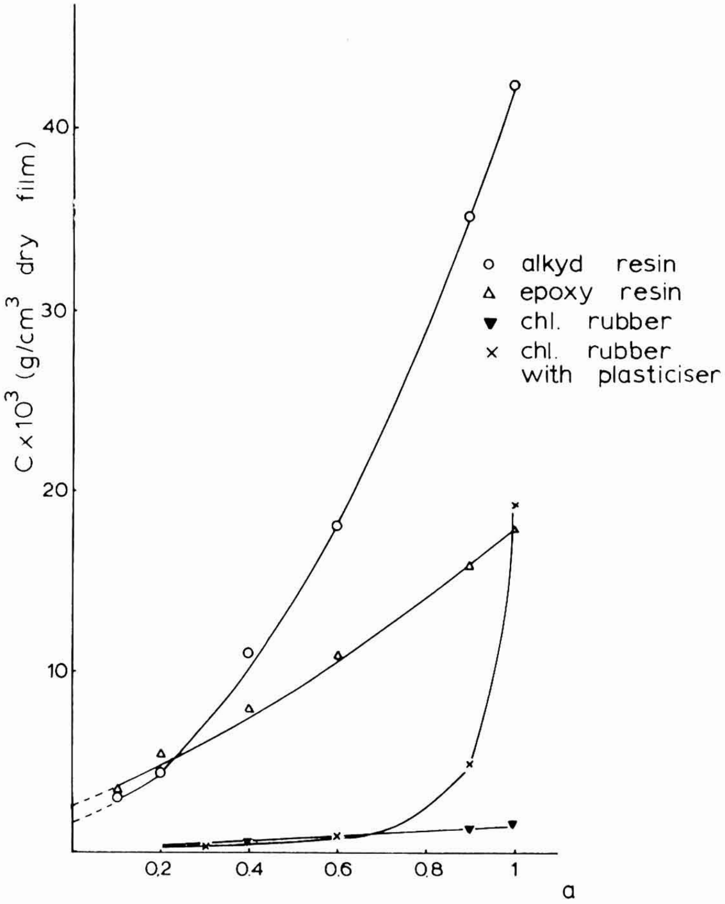

Fig. 2. Concentration (c) vs. activity (a)

Chlorinated rubber

The results obtained for G_{11}/V_1 are shown in Fig. 3. It can be seen that G_{11}/V_1 is -1 for almost the whole range of Φ_1 (which in this case is very small). The fact that $\overline{D}$ is independent of the concentration (Fig. 1) is in accordance with the interpretation given above. The system chlorinated rubber/water behaves as an ideal system.

Chlorinated rubber with chlorinated diphenyl as plasticiser

As the water concentration increases, the appearance of the film changes from clear to milky. This may be attributed to formation of clusters in the material. The effect can be seen visually, as well as with a phase contrast microscope.

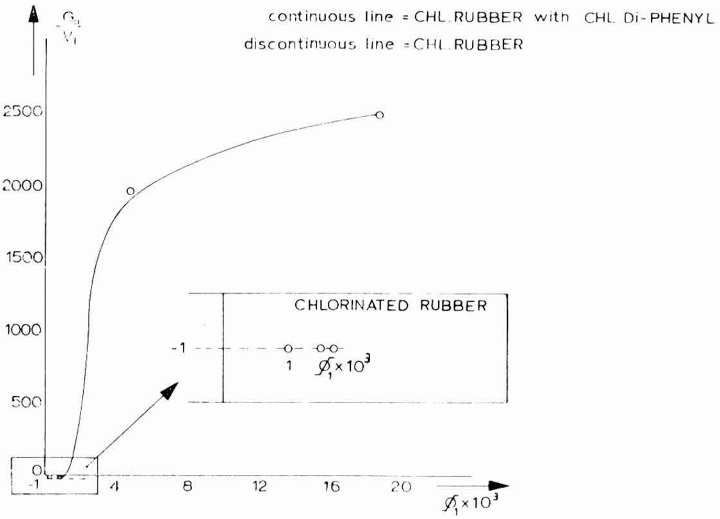

Fig. 3. Clustering function (G_{11}/V_1) vs. volume fraction (Φ_1)

The high positive values found for G_{11}/V_1 (Fig. 3) and the decrease of $\overline{D}$ with the concentration (Fig. 1) agree well with cluster formation in the film.

Although the exact reason for cluster formation in the film is not yet known, their existence cannot be doubted.

Epoxy resin

The hydrophilic epoxy resin represents an example of a material to which the clustering theory can be applied when interaction between water and polar groups in the film takes place. The clustering function (G_{11}/V_1) has negative values reaching -1 only at a high water concentration (Fig. 4). The strong interaction between water and the material prevents cluster formation, and explains the increase of $\overline{D}$ with concentration (Fig. 1).

Alkyd resin

The alkyd resin used is characterised by its dual behaviour, since both the interaction between the material and water and the water/water interaction may occur. The first interaction takes place at a low water concentration, and the latter at higher concentrations. The two effects influence both the diffusion coefficient (Fig. 1) and the clustering function (Fig. 4). The strong increase of $\overline{D}$ with concentration, characteristic of hydrophilic polymers, is counteracted by cluster formation. The values of the clustering function and the mean clustering size prove the presence of the clusters in the film (Table 1). This is confirmed by a microscopic examination of the alkyd film after soaking in water, a light turbidity being visible.

The importance of a complete series of measurements, including both sorption and permeation measurements must again be stressed.

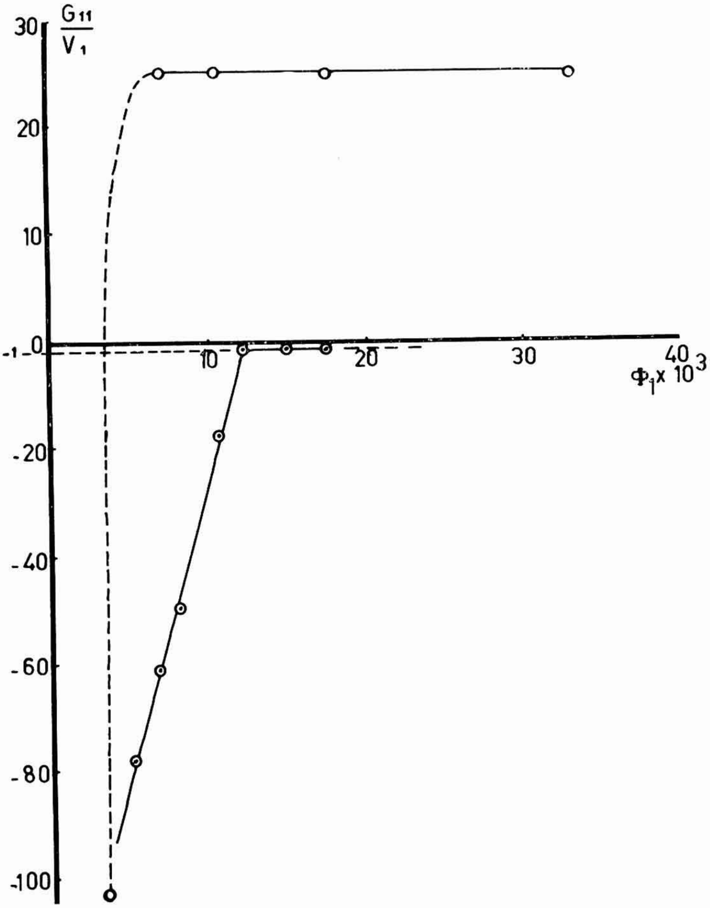

Fig. 4. Clustering function (G_{11}/V_1) vs. volume fraction (Φ_1) ○ Alkyd resin, ○ epoxy resin

Table 1

The clustering function (G_{11}/V_1) *and the mean cluster size* $\left(1 + \Phi_1 \frac{G_{11}}{V_1}\right)$ *calculated for* $a = 0.9$

Materials	G_{11}/V_1 (approximate values)	$1 + \Phi_1 \frac{G_{11}}{V_1}$ (approximate values)
Chlorinated rubber	1	0.998
Epoxy resin	1	1
Alkyd resin	25	1.8
Chlorinated rubber with plasticiser	1,989	10.8

From the permeation measurements, only the amount of water which actively participates in the transport process is determined, whereas in the sorption measurements, all the water molecules taken up by the film, independent of their mobility, are measured.

The recognition of the fact that the immobility of water is caused by specific interaction with the polar groups at low retentions, or by cluster formation at high retentions, gives a more comprehensive picture of the process of water transport.

[*Received 24 August 1970*

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The silicone treatment of titania

By B. V. Ashmead, M. Bowrey, P. M. Burrill, T. C. Kendrick and M. J. Owen

Midland Silicones Ltd, Barry, Glamorgan

Summary

The adsorption of various silicone polymers from solution on titania as substrate has been investigated. The adsorption of polydimethylsiloxanes increases with increasing molecular weight. The presence of functional groups, e.g. hydroxyl and amine groups, in the siloxane chain increases the adsorption, although there appears to be little difference between the adsorption of phenyl methyl fluids compared with similar molecular weight dimethyl fluids. The adsorption of palmitic acid and a typical paint resin on a treated pigment is less than that on the untreated pigment. The desorption of the dimethyl fluids is only possible with a solvent mixture of methyl cyanide and benzene, although this mixture will not desorb the hydroxy end-blocked fluid. Silicone treated pigments have been shown to disperse better in paint and plastic media than untreated pigments.

Keywords

Prime pigments and dyes
titanium dioxide

Properties, characteristics and conditions primarily associated with raw materials for coatings
surface treatment

Binders, resins, etc.
silicone resin

Processes and methods primarily associated with analysis measurement or testing
adsorption

Le traitement de l'oxyde de titane par silicones

Résumé

On a étudié l'adsorption sur l'oxyde de titane de divers polymères de silicones à partir de leur solutions. L'adsorption des polymethylsilicones s'augmente en accord avec l'augmentation du poids moléculaire. La présence des groupements fonctionnels, par exemple, des groupements hydroxylés ou aminés, dans la chaîne du siloxane augmente l'adsorption, bien qu'il paraisse à être une mince différence entre l'adsorption des fluides phénylméthyliques et celle des fluides diméthyliques de poids moléculaires semblables. L'adsorption de l'acide palmitique et également d'une résine classique pour peinture est plus faible dans le cas d'un pigment qui a été traité que d'un pigment exempt de tel traitement. On peult effectuer le désorption des fluides diméthyliques seulement à l'aide d'un mélange du cyanide de méthyle et du benzène, pourtant ce mélange ne peut pas enlever un fluide dont la chaîne se termine par un groupement hydroxylé. On a démontré que les pigments traités avec du silicone ont une facilité de dispersion supérieure dans les milieux pour peintures et pour plastiques que les pigments exempt du traitement.

Die Siliconebehandlung von Titania

Zusammenfassung

Die Adsorption verschiedener Siliconeopolymerer durch Titaniasubstrate aus Lösung wurde untersucht. Mit steigendem Molekulargewicht erhöht sich die Adsorption von Polydimethylsiloxan. Die Anwesenheit funktioneller, z.B. Hydroxyl- und Aminogruppen in der Siloxankette erhöht die Adsorption, obwohl nur geringe Unterschiede zwischen der Adsorption von Phenylmethylfluids im Vergleich mit der des-gleiches Molekulargewicht besitzenden-Dimethylfluids bestehen. Die Adsorption von Palmitinsäure und eines typischen Lackharzes auf einem vorbehandelten ist geringer, als die auf einem unbehandelten Pigment. Die

Desorption der Trimethylfluide is nur mit einer Lösungsmittelmischung von Methylzyanid und Benzol möglich, obwohl dieses Gemisch das durch Hydroxylgruppen endblockierte Fluid nicht desorbiert. Es erwies sich, dass mit Silicone behandelte Pigmente besser in Anstrichbindemitteln und plastischen Massen dispergierbar sind, als unbehandelte.

Силиконовая обработка двуокиси титана

Резюме

Изучалась адсорбция различных полисилоксанов из раствора на двуокиси титана в качестве субстрата. Адсорбция полиметиловых силоксанов увеличивается с повышением молекулярного веса. Наличие функциональных групп т. е. гидроксильных и аминовых групп в силоксановой цепи повышает адсорбцию, хотя повидимому и не наблюдается большой разницы между адсорбцией фенило метиловых жидкостей по сравнению с диметиловыми жидкостями одинакового молекулярного веса. Адсорбция пальмитиновой кислоты и типичной красочной смолы на обработанном пигменте меньше адсорбции на необработанном пигменте. Десорбция диметиловых жидкостей возможна только с растворной смесью цианистого метила и бензола, хотя эта смесь не десорбирует жидкость с молекулами блокированными на концах гидроксильными группами. Показано что пигменты обработанные силиконами рассеиваются в красках и пластических средах лучше чем необработанные пигменты.

Introduction

The study of the adsorption of various compounds on pigment surfaces has assumed increasing importance, and a large number of papers have appeared in the literature. Several reviews summarise the adsorption of polymers on a variety of hydroxylated substrates[1], and the adsorption of polymers and surfactants with titania as substrate has also received considerable attention[2].

The surface of a titania pigment, the principal commercial white pigment, needs to be modified for two reasons: to improve the durability of the media pigmented with the titania, and to improve the dispersibility of the titania pigments in paints and plastics. The durability and, to a certain extent, the dispersibility of both rutile and anatase pigments can be greatly improved by coating the pigment surfaces with various insoluble, polyvalent, hydrated metal oxides, the most common being oxides of zinc, aluminium, and silicon. Many of the commercially available pigments are coated with mixtures of these oxides to confer extra stability and durability. The current trend of the paint industry towards the use of low shear mixing equipment, e.g. the high speed dissolver, and the growing use of titania in plastics, with its associated mixing problems, has led to a real need for readily dispersible pigments. The dispersibility of titania pigments can be improved by treatment with silicones, and this technique is already increasingly used for plastics grade titanias, where maximum ease of dispersion of the pigment is the prime requirement. The fact that the silicone coating is inert and heat stable further recommends its use in thermoplastics. In paints, silicone treated titanias show improved ease and degree of dispersion, lower oil absorption, and higher initial gloss than conventional paint grade titanias. The siloxane coating can be chemically bound to the pigment surface, rendering it stable to desorption, and the future for these pigments in the paint industry is promising.

In this paper, the adsorption of several silicone polymers on two commercial grades of titania has been studied, together with a preliminary evaluation of some silicone treated pigments. The adsorption work has examined the effect of molecular weight and functional group on the adsorption isotherm. The effect of solvent has not been closely examined, since a full discussion of solvent effects on a typical hydroxylated surface has been given elsewhere[3]. The adsorption of a fatty acid and a typical paint resin on silicone treated pigments was investigated, as was the dispersion of these materials in paint media and PVC sheet.

Experimental

Titania

Two commercially available grades of titanium dioxide were used throughout the investigation; these were both pigmentary rutile grades which had been prepared by the sulphate process. The first, titania A, was an uncoated grade which is mainly used in floor coverings; the second, titania B, was a general purpose grade and has a surface modified with silica and alumina. These two grades were chosen as being representative, since it was desired to study the adsorption of various silicones on both an unmodified and a modified titania surface. A summary of the main properties of these two grades is given in Table 1.

Table 1

Grades of titania

Grade	Specific gravity	Oil absorption, g/100g pigment	TiO_2 content	Surface treatment
Titania A ..	4.1	18	$\nless$ 98%	Uncoated
Titania B ..	4.0	22	$\nless$ 93%	Al, Si

Silicone polymers

A summary of the silicone polymers used, with their molecular weights and composition, is given in Table 2. The dimethyl fluids, by the nature of their preparation, must contain some hydroxyl groups. These were removed in the case of 97–026 by refluxing the polymer with hexamethyldisilazane for about 24 hours, distilling off the excess hexamethyldisilazane, and re-precipitating the polymer with methanol from benzene solution. The polymer was dried before use, initially in a vacuum oven; subsequently, small samples were heated at 110°C under vacuum for over 24 hours.

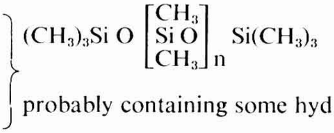
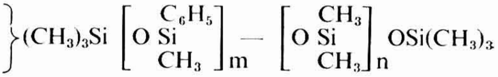
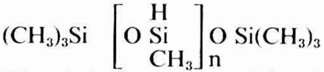
Gel permeation chromatography (GPC) was used in most cases to determine the molecular weights.

Other materials

A long oil linseed alkyd (Paralac 10W—ICI Ltd.) was chosen to study the adsorption of a typical alkyd resin on titania. This was supplied as a 70 per cent solution in white spirit, a figure which was confirmed by a solids determination. To investigate the dispersion of the treated titanias in paint media, two different

Table 2

Silicone polymers

Polymer	$\bar{M}n$	Chain length	Structure
97–024	2,800	37.8	 $(CH_3)_3Si\,O\left[\begin{array}{c}CH_3\\ Si\,O\\ CH_3\end{array}\right]_n Si(CH_3)_3$ probably containing some hydroxyl groups
97–025	6,100	82.4	
97–026	14,600	197	
97–027	28,000	379	
97–028	58,000	784	
Trimethyl-silylated 97–026 ..	14,600	197	Trimethylsilylated 97–026
97–029	3,000	38.1	 $(CH_3)_3Si\left[\begin{array}{c}C_6H_5\\ O\,Si\\ CH_3\end{array}\right]_m - \left[\begin{array}{c}CH_3\\ O\,Si\\ CH_3\end{array}\right]_n OSi(CH_3)_3$
97–030	2,000	18.6	
97–031	1,800	14.1	
97–019	950	12	α, ω hydroxy end-blocked dimethyl siloxane
97–032	2,100	35	 $(CH_3)_3Si\left[\begin{array}{c}H\\ O\,Si\\ CH_3\end{array}\right]_n O\,Si(CH_3)_3$
97–016	—	100	Dimethyl siloxane containing five amine functional side chain groups
97–033	—	—	Methyl silicone resin—35.1% solids

resins were used. The first was an air drying, linseed/glycerol, alkyd resin (BP Chemicals—Epok A1010/46), whilst the second was a thermosetting acrylic resin (BP Chemicals—Epok D1150).

The dispersion in plastics was investigated either by dispersing the titania in dioctylphthalate (Albright and Wilson) to study the characteristics in a liquid plasticiser or by dispersing the titania in pvc sheet formed by gelling a mixture of pvc powder (BP Chemicals—Breon S125/10) and dioctylphthalate.

AnalaR grade solvents were used for the adsorption experiments. They were allowed to stand over a molecular sieve (type 4A) for at least two weeks before use, and were only handled over argon in a dry-box.

Procedure

Adsorption experiments

The titania powder was dried in a force-draught oven for a period of 18 hours, generally at 200°C, some exceptions being noted in the text. A 4g sample of the titania powder was weighed into a screw-cap bottle and 10ml of a solution of the polymer of known concentration pipetted on to the powder in a dry-box in an argon atmosphere. The bottle was shaken for at least 14 hours at room temperature (20°C) and the supernatant liquid analysed by an infra-red technique, the peak at 1,261cm^{-1} being used to determine the polymer concentration remaining in solution. Sodium chloride cells of 1mm path length were used with a Perkin Elmer 237 infra-red spectrophotometer. Beer's Law plots of the polymers in the particular solvent were used in determining the polymer concentration after adsorption. The amount of polymer adsorbed, Γ, was determined from:

$$\Gamma = \frac{V}{M}(C_i - C_f)$$

where V = volume of polymer solution.
M = mass of titania powder.
C_i = initial polymer solution concentration.
C_f = equilibrium polymer solution concentration.

The specific adsorption value, Γ_o, is the amount of polymer adsorbed corresponding to saturation, i.e. the amount adsorbed on the plateau of the isotherm.

Dispersion studies

The dispersion of the various titanias in both the alkyd and in the acrylic resin was investigated, using a porcelain ball mill and a high speed dissolver (Kotthoff mixer—Model MS1 CAA). Both gave essentially the same results and only the studies conducted in the ball mill will be considered in detail. The constant charge used is given in Table 3, and 80 ceramic balls 18mm in diameter were used as the grinding media. The dispersion characteristics of the various titanias were measured by allowing the milling to proceed for various time intervals, when a sample of the mill base was withdrawn and the state of the dispersion assessed with the aid of a fineness of grind gauge (0.005in deep groove, 0-10 scale).

Table 3

Dispersion in alkyd and acrylic resins

Pigment	300g
Resin	30g
Xylene	95g

The dispersion in a liquid plasticiser was measured using the formulation in Table 4. This was dispersed with the high speed dissolver operating at 2,000rpm, using an 83mm diameter toothed impeller. The material to be dispersed was contained in a 16cm diameter beaker and the impeller was

Table 4

Dispersion in liquid plasticiser

Dioctylphthalate	217.5g
Pigment	112.5g
Epoxide plasticiser	6.0g
Caprylic acid	1.5g

centrally positioned 2cm above the bottom of the beaker. The state of dispersion was again measured by withdrawing samples after various time intervals and assessing them on the fineness of grind gauge. The epoxide plasticiser and the caprylic acid were added to achieve approximately equal viscosities for all the mixtures studied.

Samples of pvc sheet were prepared by gelling the mixture shown in Table 5 on a heated double-roll mill at 150°C. The resulting sheet was pigmented with 1 per cent by weight of titania and passed through the rolls for a further two minutes. A sheet 15cm × 15cm × 0.15cm was prepared by pressing the above sheet in a mould at 150°C under a pressure of 1,000psi.

Table 5

Dispersion in pvc sheet

Pvc powder	300g
Dioctylphthalate	150g
Ba/Cd stabiliser	6g

Results

Surface area

The method used to estimate the surface area of the adsorbents employed the adsorption of straight chain fatty acids from non-aqueous solution, and is based on studies with insoluble monolayers. Properly compressed films of these fatty acids on a water surface are monomolecular and occupy the same interfacial area per molecule, regardless of the number of carbon atoms in the molecule. Further, the molecules are orientated perpendicular to the interface, so that the area of the carboxylic acid group determines the interfacial area per molecule. In this study, the adsorption of palmitic acid from carbon tetrachloride solution was used. Fatty acid adsorption is probably a better choice than gas adsorption when investigating polymer adsorption because, by virtue of its size, the external surface accessible to the fatty acid molecule is roughly the same as that available to the polymer molecule.

The experiments were conducted in a similar manner to the polymer adsorption experiments in that an adsorption isotherm was constructed and the surface area estimated from the saturation value, assuming the cross-sectional area of one fatty acid molecule[4] to be 20.5Å^2. The values obtained are shown in Table 6.

Table 6

Surface areas of adsorbents

Sample	Surface area (fatty acid) m^2g^{-1}	Surface area (N_2 adsorption) m^2g^{-1}
A	5.21 ± 0.10	9.6 ± 0.2
B	5.93 ± 0.10	12.4 ± 0.2

Effect of surface hydroxyl concentration on adsorption

Other work has clearly shown that the adsorption of polydimethylsiloxanes is very sensitive to traces of water[5]. It seemed relevant to investigate the adsorption of a silicone fluid from *n*-hexane on titania as a function of the pretreatment. Samples of the pigment were heated for 18 hours at the stated temperatures before addition of the siloxane solution. Isotherms were constructed and the specific adsorption value, Γ_o, determined. The results are recorded in Table 7, together with the weight losses on heating.

Table 7

Effect of heat treatment on adsorption

Powder: B Polymer: 97–027 Solvent: *n*-hexane

Temperature	Γ_o mg m^{-2}	Weight loss mg g^{-1}
200°C	1.62	11.1 ± 0.5
120°C	1.39	8.2 ± 0.5
86°C	1.17	6.4 ± 0.5
As received	0.67	—

Powder: A Polymer: 97–027 Solvent: *n*-hexane

Temperature	Γ_o mg m^{-2}	Weight loss mg g^{-1}
200°C	1.55	6 ± 1
120°C	1.22	4 ± 1
86°C	1.09	3 ± 1
As received	0.79	—

There are definite differences between the weight losses for the two pigment samples, more reproducible values being obtained for B than for A. For B, a linear plot is achieved from a graph of amount adsorbed against weight loss, but the large spread in the weight loss values for A does not allow such an accurate plot to be constructed for this adsorbent. Since the weight loss is due to the removal of water, it follows that the amount of siloxane adsorbed is proportional to the surface hydroxyl concentration.

Adsorption of dimethyl and phenyl methyl fluids

The adsorption of five dimethyl fluids from *n*-hexane and benzene on pigments A and B was measured. Typical isotherms on both powders are included in Figs. 1 and 2. The results were expressed in the form:

$$\Gamma_o = KM^a$$

where Γ_o = specific adsorption in mg m^{-2}.

M = molecular weight of the polymer.

The values of constants K and a are shown in Table 8.

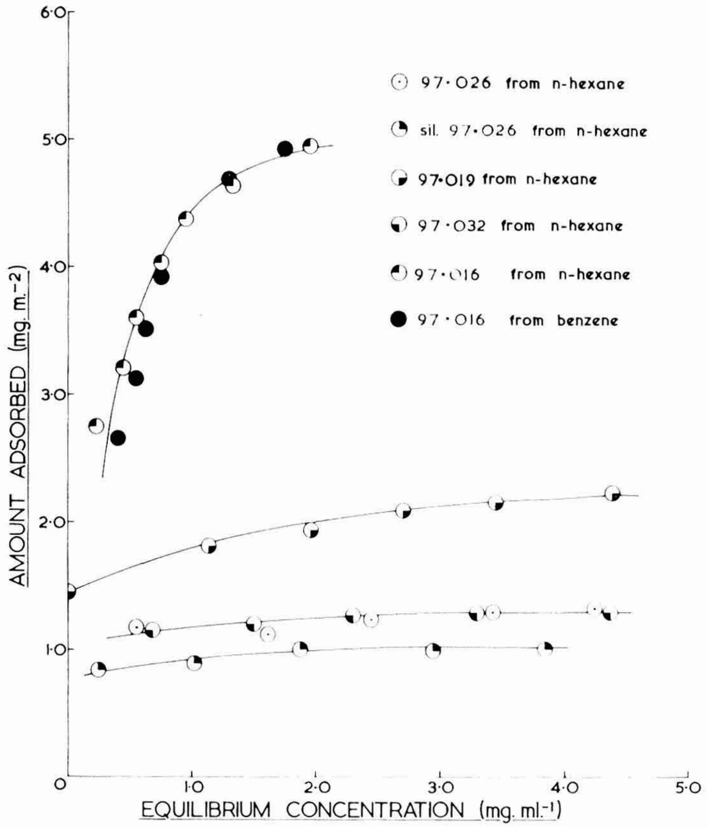


Fig. 1. Adsorption of siloxanes from n-hexane on titania A

Table 8

Adsorption of dimethyl fluids as a function of molecular weight

Powder	Solvent	*a*	*K*
B	*n*-hexane	0.21	0.196
A	*n*-hexane	0.26	0.108
B	benzene	0.39	1.22×10^{-2}
A	benzene	0.35	0.78×10^{-2}

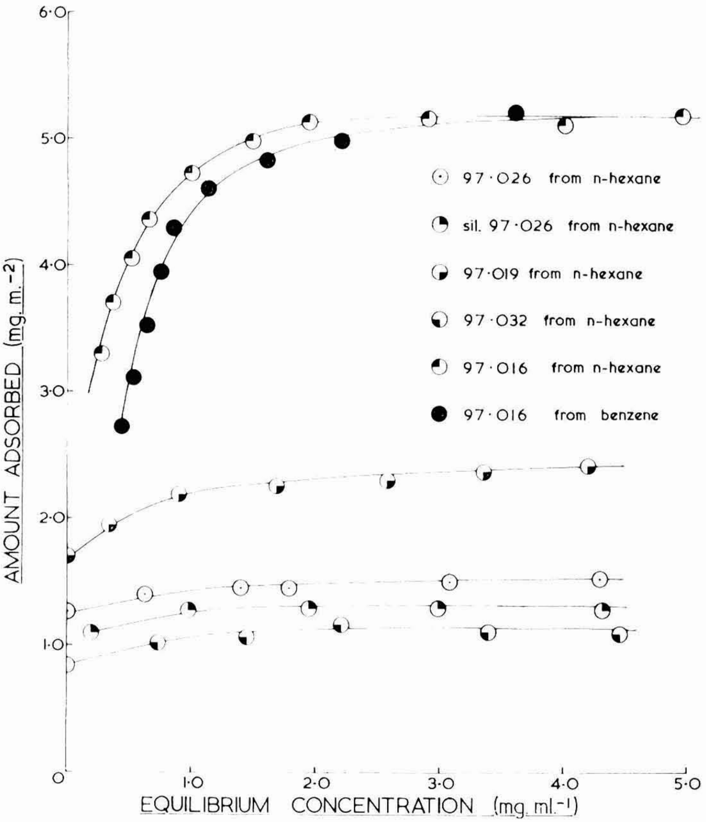


Fig. 2. Adsorption of siloxanes from n-hexane on titania B

It was not possible to measure the adsorption of two low molecular weight fluids from benzene on pigment A; the amounts adsorbed are very small or nothing. The amounts adsorbed from benzene are less than those from *n*-hexane, the values for the constants *K* and *a* being more dependent on the solvent than on the pigment.

The specific adsorption of the phenyl methyl fluids from benzene and *n*-hexane on pigments A and B is shown in Table 9, a more direct comparison between these fluids and the dimethyl fluids adsorbed from *n*-hexane being shown in Table 10. Figs. 3 and 4 show graphs of log (amount adsorbed in moles m^{-2}) against log (chain length) for both adsorbents. In this context, the chain length refers to the number of Si-O units.

Little difference is apparent in the adsorption behaviour of the two classes of fluid.

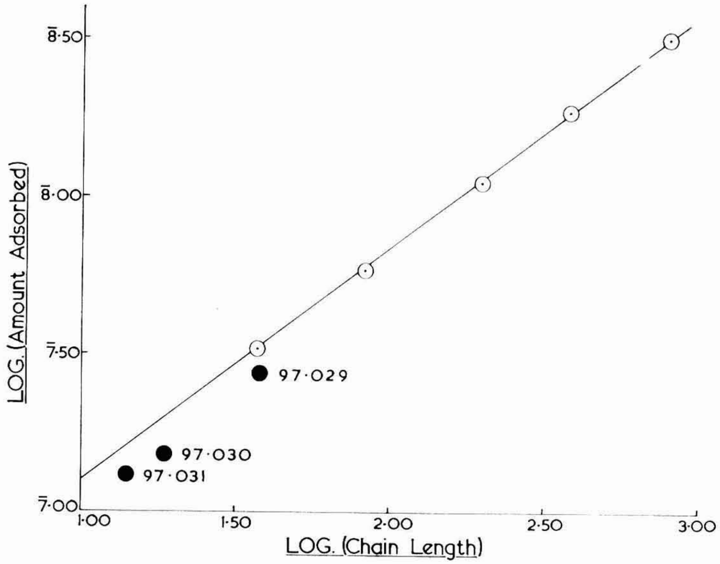


Fig. 3. The adsorption of dimethyl and phenyl methyl fluids from n-hexane on titania A

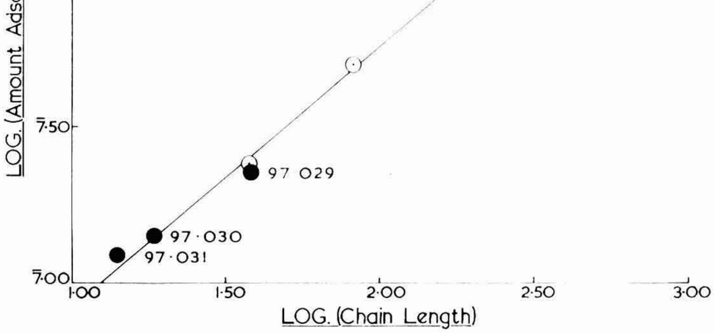


Fig. 4. The adsorption of dimethyl and phenyl methyl fluids from n-hexane on titania B

Table 9

Adsorption of phenyl methyl fluids

Fluid	% Ph	Amount adsorbed, mg m^{-2} (%)			
		A *n*-hexane	A benzene	B *n*-hexane	B benzene
97–029.. ..	4.1	1.09	Too low to measure	1.30	0.09
97–030.. ..	43	1.32		1.39	0.12
97–031.. ..	75	1.38		1.45	0.06

Table 10

Adsorption of dimethyl and phenyl methyl fluids from n-hexane

Fluid	M. wt.	% Ph	Amt. Ads., mg m^{-2}	Amt. Ads., moles m^{-2} $\times 10^{-7}$	Chain length
Powder A					
97–024 ..	2,800	—	0.845	3.02	37.8
97–025 ..	6,100	—	1.035	1.70	82.4
97–026 ..	14,600	—	1.303	0.89	197
97–027 ..	28,000	—	1.496	0.53	379
97–028 ..	58,000	—	1.775	0.31	784
97–029 ..	3,000	4.1	1.09	3.64	38.1
97–030 ..	2,000	43	1.32	6.60	18.6
97–031 ..	1,800	75	1.38	7.66	14.1
Powder B					
97–024 ..	2,800	—	1.163	4.15	37.8
97–025 ..	6,100	—	1.231	2.02	82.4
97–026 ..	14,600	—	1.413	0.97	197
97–027 ..	28,000	—	1.637	0.58	379
97–028 ..	58,000	—	2.004	0.35	784
97–029 ..	3,000	4.1	1.30	4.33	38.1
97–030 ..	2,000	43	1.39	6.95	18.6
97–031 ..	1,800	75	1.45	8.06	14.1

Effect of functional groups

Effect of hydroxyl groups: Previous work with glass as substrate[3] had indicated that hydroxyl groups in the polymer markedly influence the adsorption. This effect was also demonstrated with titania as substrate, using 97–026 which had been exhaustively trimethylsilylated, and the hydroxy end-blocked 97–019 (Figs. 1 and 2). The amount of the trimethylsilylated polymer adsorbed was reduced considerably compared to the original fluid. Polymer 97–019 is adsorbed in considerably larger amounts than the dimethylsiloxane polymers.

Adsorption of methyl hydrogen fluids: The adsorption of the methyl hydrogen fluid, 97–032, should be interesting in that a comparison between the adsorption of Si-H and Si-CH_3 groups to the surface hydroxyl groups may be made. The adsorption isotherms for 97–032 from *n*-hexane were determined and the amounts adsorbed compared with those for the dimethyl fluids (Table 11). Polymer 97–032 is adsorbed in greater amounts than a dimethyl fluid of comparable chain length.

Table 11

Adsorption of 97–032 from n-hexane

Fluid	Molecular weight	Amt. Ads., mg m^{-2}	Amt. Ads., moles m^{-2} $\times 10^{-7}$	Chain length
Powder A				
97–025	6,100	1.035	1.70	82.4
97–024	2,800	0.845	3.02	37.8
97–032	2,100	1.29	6.15	35
Powder B				
97–025	6,100	1.231	2.02	82.4
97–024	2,800	1.163	4.15	37.8
97–032	2,100	1.11	5.29	35

Adsorption of silicone resins: The adsorption of a methyl silicone resin was investigated. The resin, 97–033, was received as a solution in white spirit. All solution concentrations were calculated from the solids content, the initial solution being diluted with *n*-hexane. The results are shown in Table 12, where a comparison with some of the dimethyl fluids is made.

Table 12

Adsorption of silicone resins

Fluid	Amount adsorbed, mg m^{-2}	
	A	B
97–033	1.15	1.30
97–024	0.845	1.163
97–025	1.035	1.231
97–026	1.303	1.413

Adsorption of amine functional materials: A strong interaction would be expected between an amine grouping in the siloxane side-chain and a surface hydroxyl group. Isotherms for the adsorption of the fluid 97–016 were determined from both benzene and *n*-hexane (Figs. 1 and 2). The amount of material adsorbed is considerably greater than that of any other polymer investigated. Although benzene is adsorbed on a hydroxylated surface, the amine group is more strongly adsorbed, hence the expected non-dependence on solvent.

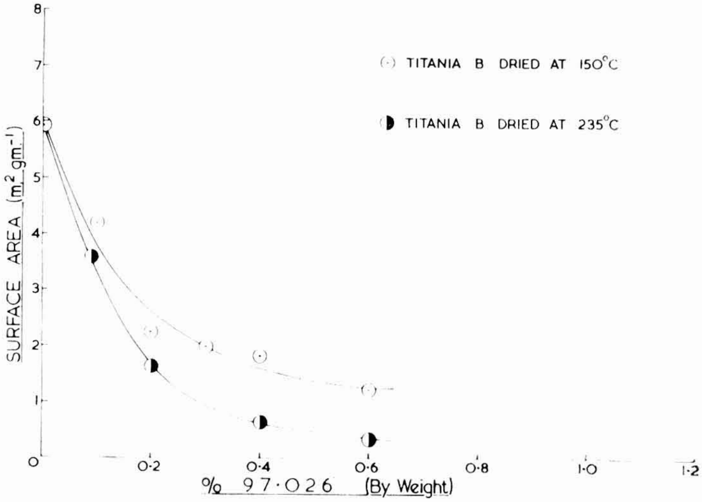


Fig. 5. The "apparent" surface area of silicone treated pigments

Adsorption on a silicone treated surface

The adsorption isotherms for both palmitic acid and an alkyd resin on a silicone treated titania were determined. The latter adsorbent was chosen because it represented a typical paint medium. Various samples of pigment B containing 0-0.6 per cent by weight of 97–026 were prepared. The pigment B was first dried at 150°C for 18 hours, the desired quantity of 97–026 applied as a solution in *n*-hexane and the titania subsequently washed with *n*-hexane prior to drying at 150°C.

Desorption

A number of experiments was conducted to investigate the stability of the siloxane coating on titania and to measure its resistance to various solvents. The method used was similar to that employed for the adsorption experiments; an adsorption isotherm for 97–026 pretreated at 150°C was constructed, and the resultant titania samples were washed with *n*-hexane, dried and then shaken with 10ml portions of various solvents to determine whether any of the adsorbed silicone coating had been extracted. A variety of solvents—benzene, toluene, xylene and white spirit—was used and, with all of these, it was found that no silicone could be desorbed. In order to determine the percentage of the coating desorbed under the most drastic conditions, experiments were carried out using a 10 per cent mixture of methyl cyanide in benzene as solvent. This mixture was chosen because of its polar nature and also because it has previously been shown to be a particularly effective solvent for extracting a silicone coating from a powder[5]. The adsorption and desorption isotherms for 97–026 on B are shown in Fig. 7. For desorption, the isotherm represents the amount of siloxane remaining on the surface and is determined from the difference between the initial amount adsorbed and the siloxane concentration in the desorbing solvent. In a further series of experiments, conducted using the hydroxyl end-blocked polymer 97–019 in place of 97–026, no desorption could be measured.

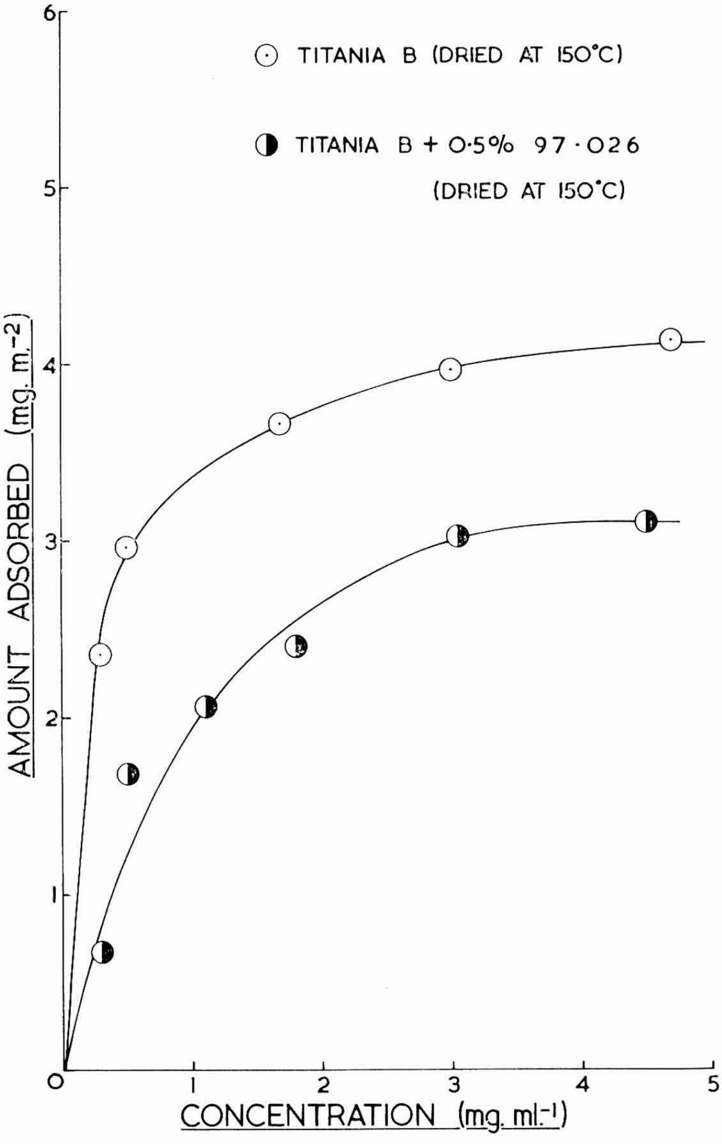


Fig. 6. The adsorption of Paralac 10W on treated and untreated titania pigments

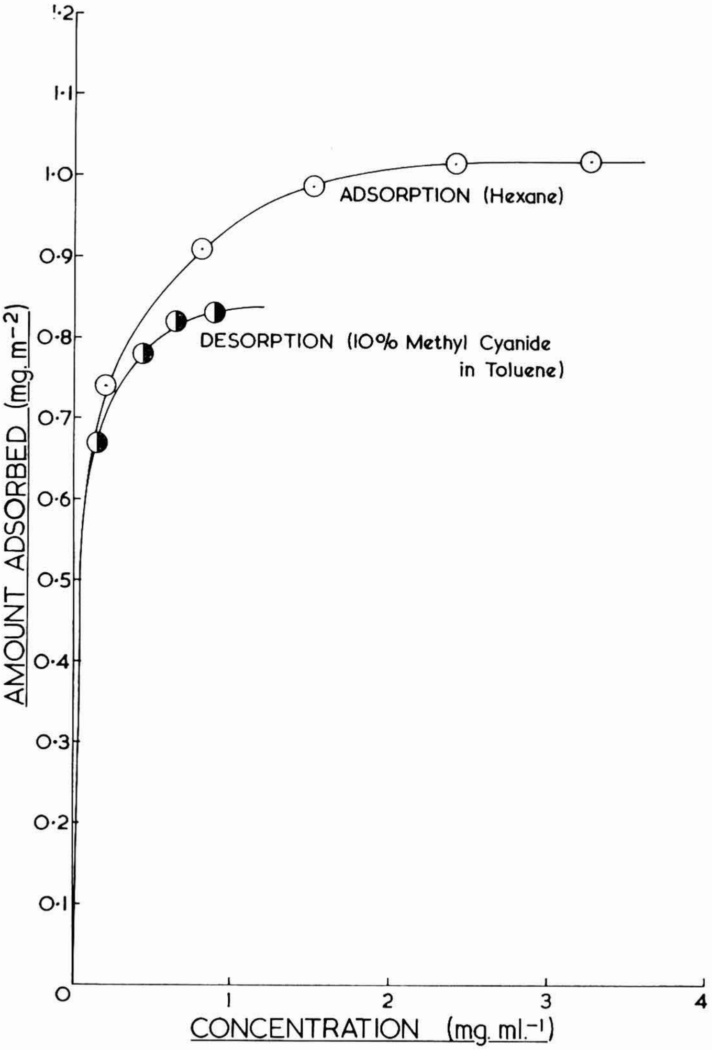


Fig. 7. Adsorption and desorption of a dimethyl fluid on titania B

Dispersion

The dispersion curves for various untreated and silicone treated titanias in the paint resins are shown in Fig. 8. The treated pigments were prepared by applying the silicone from *n*-hexane, although various other methods of treatment do exist. The effect of applying the treatment under different conditions was also investigated. The dispersion curves for pigment B that has been ball-milled with a solution of 97–026 in *n*-hexane, and for B treated with 97–026 and subsequently micronised, are also shown. The micronised pigment was prepared using a fluid energy mill (Apex Construction—Model 260).

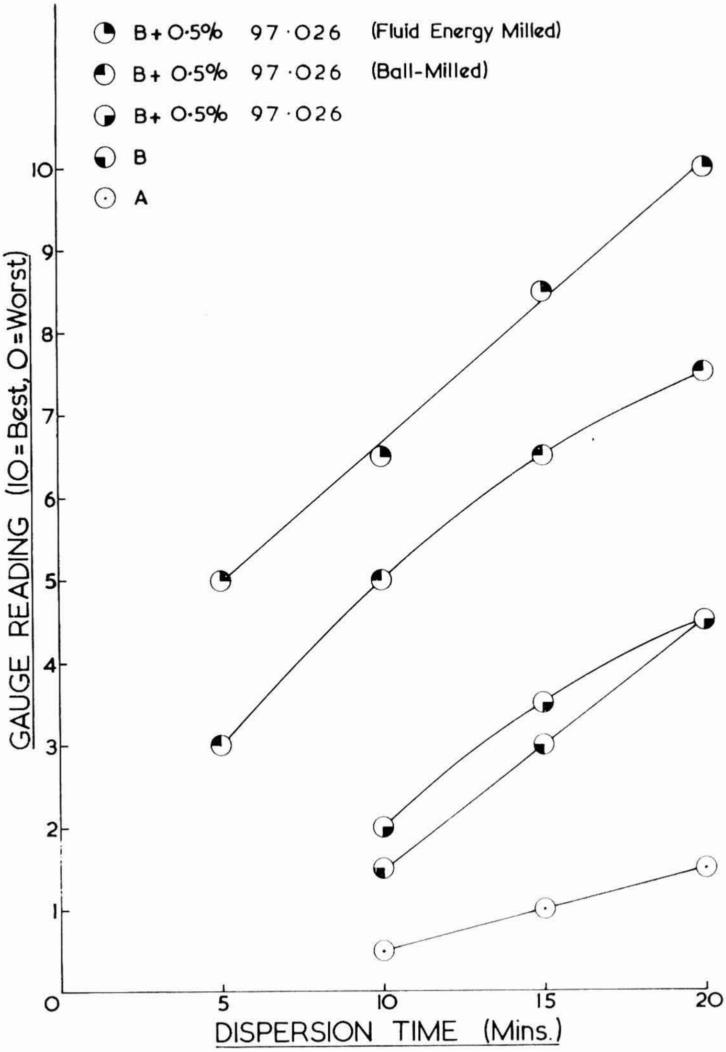


Fig. 8. Dispersion of treated and untreated titanias in paint resins

These results show that, in order to achieve optimum dispersibility in these resins, the pigment must be subjected to high shear either during or after treatment.

The dispersion of these pigments in the plasticiser paste is shown in Fig. 9, from which the superior dispersibility of the silicone treated pigments is obvious.

Although no quantitative measurements were made in the case of the pvc sheets, a visual assessment showed that a much better state of dispersion was achieved with the silicone treated pigments than with the corresponding untreated pigments. This better dispersion was exemplified by the higher opacity exhibited by the sheets pigmented with the silicone treated titania.

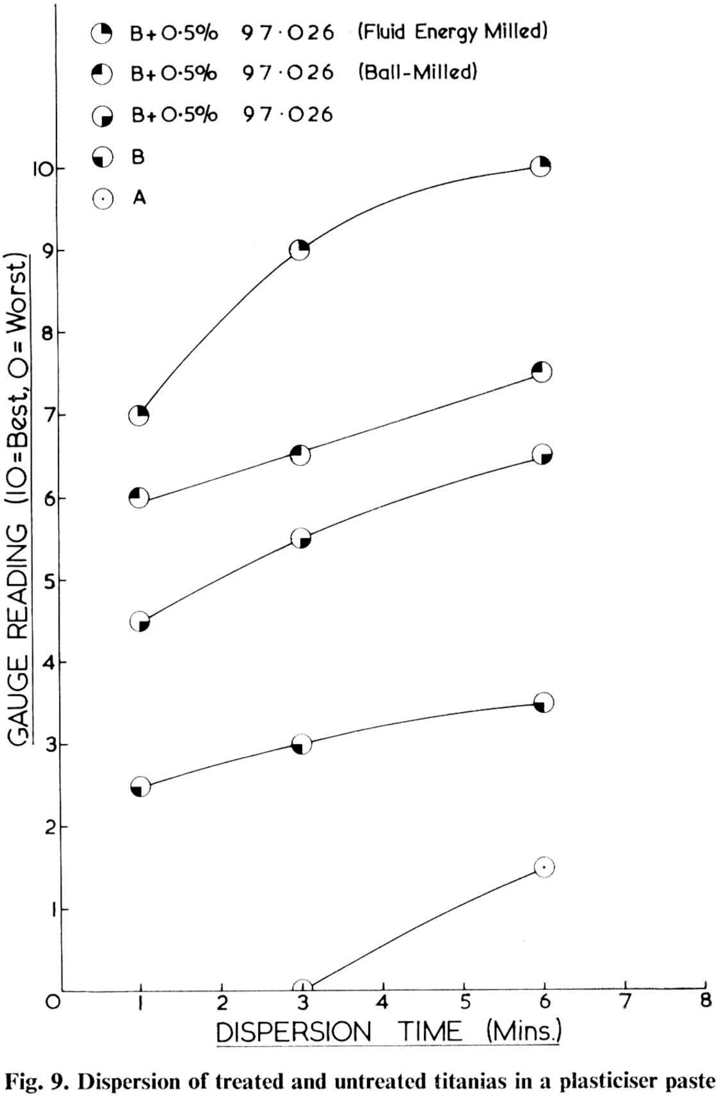


Fig. 9. Dispersion of treated and untreated titanias in a plasticiser paste

Discussion

The adsorption of polydimethylsiloxanes on glass and on iron has shown that water plays an important role in the amount of polymer taken up[5]. This marked inhibition by water has not been observed in any other polymer/adsorbent system. It seemed relevant therefore to investigate the possible effect of moisture on the adsorption on titania. This was done by examining the amount of polymer adsorbed as a function of the heat treatment of the powder. Heating the powder reduces the total number of hydroxyl groups which are present on the surface. In the case of silicas, physisorbed water can be removed from the surface by heating in air at 120°C [6], whereas ignition at temperatures about 200°C results in the loss of the geminal surface hydroxyl groups[7]. The surface of titania B, the modified rutile, contains a large proportion of silica, so that little modification of the surface, except for the loss of physisorbed water, should have occurred when heating the pigment to 200°C before adsorption. Outgassing of anatase TiO_2 at 150°C reduces the surface hydroxyl concentration to 4.9 per 100Å^2 from an estimated 12-14 per 100Å^2 on a fully hydroxylated surface[8]. It is clear from the results obtained that the amount adsorbed is a function of the pretreatment temperature. The amount of siloxane adsorbed therefore depends on the surface hydroxyl concentration and, for this reason, all transfers in the adsorption experiments were carried out under an argon atmosphere in a "dry-box".

No attempt was made to investigate the effect of solvent on adsorption, as a full discussion of this effect on siloxane adsorption on a hydroxylated surface has been given elsewhere[3]. Benzene has been shown to adsorb on a hydroxylated surface, whereas *n*-hexane interacts only very slightly, so that the amounts adsorbed from *n*-hexane give truer values for monolayer coverage. Both of these solvents are good solvents for polydimethylsiloxanes, so the adsorbed polymer must exist in an extended state rather than as random coils. Measurements under θ conditions in a solvent that does not interact with a hydroxylated surface would have been preferable, but all the so-called θ solvents for polydimethylsiloxanes at 20°C (methyl ethyl ketone, ethyl acetate, 2-butanone) interact with hydroxylated surfaces.

It is interesting to calculate how much polymer would be adsorbed in a monolayer spread flat on the pigment surface, and to compare this figure with the specific adsorption values. If it is assumed that the siloxane is adsorbed flat on the surface, with each $(CH_3)_2$ SiO unit occupying 22.7Å^2, as would be the case on a water surface[9], then the amount adsorbed on both pigments B and A would be 0.54mg m^{-2}. In every case studied, the specific adsorption figure is greater than this value. Many different pictures to explain this discrepancy could be presented for the adsorbed polymer molecule. To give a flat configuration, all the polymer segments would have to lie in the plane of the surface, and the entropy change resulting from a coiled polymer molecule in solution going to an adsorbed molecule lying flat on the surface must be excessively high.

The fact that the *a*-factor in the expression relating the amount adsorbed to the molecular weight is not zero further suggests that the polymer molecule is not adsorbed flat on the surface. Perkel and Ullman[5] describe the expected configurations of the adsorbed molecule with changing *a*-factor. When $a = 0$, the polymer is adsorbed flat on the surface, whilst when $a = 1$, the polymer is adsorbed at one point of attachment only. For intermediate values of *a*, it seems likely that the polymer molecule is adsorbed as a coil on the surface, although this coil is more compressed than the corresponding polymer coil that exists in bulk solution.

The adsorption of the phenyl methyl fluids is remarkably similar to the adsorption of the dimethyl fluids (Figs. 3 and 4). Comparing two polymers of similar chain length, it can be seen that slightly more 97–029 fluid is adsorbed than 97–024. Although benzene is strongly adsorbed on hydroxylated surfaces, the phenyl group attached to the siloxane chain is unlikely to behave similarly because of a delocalisation of the π electrons of the aromatic system into the *d*-orbitals of the silicon. It would appear that the phenyl methyl fluids are adsorbed in a similar manner to the dimethyl fluids.

The increased adsorption produced by the presence of hydroxyl groups in the polymer has been demonstrated in two ways. Trimethylsilation of 97–026 fluid reduces the amounts adsorbed on pigments A and B by 25 per cent and 15 per cent respectively, as compared with the adsorption of normal 97–026. The values obtained are, however, still well above the flat monolayer coverage figures, indicating that some surface coiling of the trimethylsilylated polymer is still occurring.

The adsorbed polymer film in the case of the trimethylsilylated fluid is thinner than the film resulting from the corresponding untreated fluid. More interesting are the results obtained with the hydroxyl end-blocked fluid, 97–019. A possible configuration for the adsorption of this molecule is a loose "hairpin" structure with both ends of the chain on the surface. Assuming that the area occupied by this molecule is determined by the cross-sectional area of the siloxane chain (32Å^2)[9], a simple calculation shows that the amount adsorbed would be 2.46mg m^{-2}. This value is in good agreement with the values of 2.40mg m^{-2} and 2.20mg m^{-2} obtained for B and A respectively.

The adsorption of the methyl hydrogen fluid 97–032 should be similar to that of a dimethyl fluid. Although the $\equiv$ Si-H group can be made to react chemically with the surface hydroxyl groups in the presence of a catalyst, the formation of a hydrogen bond between the $\equiv$ Si-H group in the polymer chain and the hydroxylated surface is unlikely. Table 7 shows that more of the methyl hydrogen fluid, 97–032, is adsorbed than a similar chain length dimethyl fluid. A material like 97–032 is readily hydrolysed by traces of moisture to give $\equiv$ Si-OH groups which, as was noted earlier, markedly increase the amount adsorbed.

The amount of the amine functional material 97–016 adsorbed is considerably greater than that of any of the other polymers studied. Benzene is adsorbed on a hydroxylated surface, but the amine group is more strongly adsorbed, which accounts for the fact that the adsorption of this polymer is independent of the solvent used.

By making a molecular model of the polymer molecule and estimating the possible areas which would be involved in bonding, it can be shown that only the five amine functional side chain groupings are involved in bonding with the surface. The value of 5.32mg m^{-2} which can be calculated agrees well with the experimentally determined value of 5.18mg m^{-2}. The majority of polymer adsorption isotherms reach the saturation value at very low solution concentrations, concentrations that generally cannot be accurately measured, and certainly not by infra-red spectroscopy. In the case of the amine functional fluid, however, the plateau is reached at a much higher concentration. This would indicate that, at low concentrations, the polymer is adsorbed in a relatively flat configuration, although still with all the amine functional groups being involved in the bonding. However, as the bulk solution concentration increases, the adsorbed state becomes more favoured and the adsorbed molecules are pushed tighter together until the above configuration is attained, with the amine groups just touching on the surface. Such a configuration would lead to a thick film being adsorbed.

The surface area determined by the adsorption of nitrogen gas at —196°C (using the classical BET method) always gives surface areas which are greater than those measured by the fatty acid adsorption method. Urwin[10] has shown that a proper analysis of a BET nitrogen surface area by the de Boer *t*-plot method can divide the surface area into two components—internal and external surface areas. The former part is caused by the samples being of a somewhat porous nature. His paper further shows that the area determined by fatty acid adsorption, assuming that the adsorbed acid molecule is orientated perpendicular to the surface, is equal to the external surface area component. It is very unlikely that the large siloxane molecule is able to diffuse into any of the porous parts of the substrate, and hence the external surface area would appear to be the better value to use in any interpretation of siloxane adsorption.

The surface areas of the samples of titania treated with 97–026 as measured by the adsorption of palmitic acid can be regarded as a measure of the untreated portion of the surface. The possibility of a different adsorption mechanism for palmitic acid on a silicone treated surface can be dismissed, since any interaction between the alkyl chain of the acid and the methyl groups in the fluid would result in the acid lying flat on the surface. In this configuration, the palmitic acid molecule would occupy[10] an area of 114Å^2, which would predict a surface area for pigment B some five and a half times the measured value. The fact that a small amount of palmitic acid is adsorbed even on a sample of titania which has been coated with the maximum quantity of silicone (corresponding to the maximum of the previously determined adsorption isotherm) implies either that the polar palmitic acid is displacing some of the physically adsorbed siloxane or, more probably, that a small number of unreacted hydroxyl groups are still present on the surface.

Two different modes of adsorption, depending on the functional groups attached to the siloxane chain, are possible. In the case of the dimethyl or the phenyl methyl fluids, the interaction between the surface hydroxyls and the alkyl or aryl groups on the siloxane can result in a weak adsorption, whilst the presence on the siloxane of various functional groups, such as amine or hydroxyl, can result in a much stronger adsorption. In this latter case, the formation of a chemical bond between the surface and the siloxane arises, a factor that is favoured either by the application of heat or by the use of certain catalysts. The difference in the nature of these two forms of adsorption is shown by the desorption experiments, since in the case of the weak adsorption the coating can be extracted, whilst this is not possible with the strongly adsorbed coating. The fact that the weakly adsorbed coating formed by the adsorption of 97–026 is only removed by a highly polar solvent implies that this coating is held much more strongly than a consideration of the forces involved would suggest. For desorption to occur, however, it is necessary for all portions of the molecule in contact with the surface to be removed. It is possible that fewer contacts exist after the desorption experiments, but that a sufficient number per molecule remain to keep the chain adsorbed.

The results obtained from the study of the dispersion of the treated titanias in the paint resins clearly demonstrate the superior dispersibility of the silicone treated samples, and also indicate that a certain amount of energy must be supplied to the system, either during or after treatment, to obtain maximum dispersibility. Energy is presumably necessary to break down any aggregates in the titania that have formed on standing. The amount of 97–026 adsorbed after simply shaking with a solution of the siloxane in hexane was compared with the amount adsorbed by milling the titania with the same siloxane solution. For pigment B dried at 120°C, $\Gamma_o = 1.19$mg m^{-2}, whilst milling increases this figure to 1.75mg m^{-2}. This would imply that the aggregates are being broken down and fresh surfaces made available for siloxane adsorption.

The dispersion of a powder in a liquid medium consists essentially of three consecutive stages; the wetting of the primary and secondary powder particles by the liquid and the removal of any moisture and gas adsorbed on their surface, the breaking down of the aggregates present and the wetting of the fresh surfaces exposed and, finally, the stabilisation of the dispersion. The high energy of the hydroxylated surface of titania gives rise to interparticulate associative forces which cause agglomeration to occur. The effect of silicone treatment is to reduce these forces, and therefore the particles separate more readily, more surface becoming available for wetting by the liquid phase. This mechanism appears to function when the treated titanias are dispersed in the plasticiser, since in this medium the unmilled treated pigments performed considerably better than they did in the paint resins.

The silicone treatment of titania will also reduce the aggregation that occurs on standing, by rendering the surface hydrophobic and preventing the adsorption of moisture, and also by lowering the initial high surface energy of the powder, since, in general, the adsorption of moisture and a high surface energy are the two factors promoting aggregation. The samples of titania used for this investigation already contain a large number of aggregates; the effect of silicone treatment alone, although facilitating the breakdown of these, was not sufficient to give a marked improvement in the dispersibility of the titania. For this reason milling was necessary to break down these initial aggregates. If, however, the silicone treatment were applied to an unaggregated sample (possibly during a stage in the manufacture), the need for this milling step might be removed.

Although silicone treated titania has been shown to disperse more readily in both paints and plastics than the untreated pigment, the durability of various media pigmented with the treated titania obviously needs further investigation before the full potential of this treatment can be assessed. In this investigation, a limited number of silicones has been evaluated and their adsorption characteristics measured. Various other functional silicones remain to be investigated but, of these, one class in particular is worthy of mention. A sample of B treated with N-β amino ethyl-γ-amino propyl trimethoxy silane was found to disperse well both in paints and plastics. An interesting possibility arises with this and related compounds, since this molecule is potentially able to bond chemically both to the pigment and to the organic medium.

Conclusions

To produce an effective silicone treatment for titania from non-aqueous solution, the pigment must initially be dried and the solvent used must be one that has the minimum interaction with the hydroxylated surface (*n*-hexane). The adsorption is governed by the molecular weight of the silicone, the amount adsorbed increasing with increasing dimethyl siloxane chain length. The presence of hydroxyl and amine functional groups on the siloxane side chain tends to increase the amount adsorbed, whilst the adsorption of the phenyl methyl fluids is essentially similar to the adsorption of the dimethyl fluids.

The effect of the silicone treatment of titania is greatly to improve its dispersion in both paints and plastics. A consideration of various methods of treatment has shown that the titania should be subjected to high shear either during or after treatment, in order to produce a pigment with optimum dispersing properties.

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The determination of sulphate and ammonium ions on rusted steel panels

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Summary

Methods for the determination of sulphate and ammonium ions at 0—100 ppm on rusted steel panels have been developed. The sulphate, after solution, is adsorbed on a column of alumina to remove iron, desorbed with ammonia and determined spectrophotometrically using barium chloranilate. The ammonia is distilled after reacting the steel with sodium hydroxide, and determined spectrophotometrically using sodium phenoxide/hypochlorite reagent.

Keywords

Types of surface	*Processes and methods primarily associated with analysis, measurement, and testing*
steel	ammonia determination colorimetry sulphate determination

Le dosage des ions sulfatés et des ions d'ammoniaque à partir des éprouvettes en acier rouillé

Résumé

On a mis au point des méthodes de dosage des ions sulfatés et des ions d'ammoniaque aux concentrations de 0 à 100ppm, à partir des éprouvettes en acier rouillé. Après sa dissolution, le sulfate est adsorbé sur une colonne d'alumine, afin d'enlever le fer, et ensuite désorbé par l'ammoniaque et dosé spectrophotométriquement au moyens du chloroanilate de baryum. L'ammoniaque est retirée par distillation, après le traitement de l'acier par l'hydroxyde de soude, et dosé spectrophotométriquement au moyens du réactif phénate/hypochlorite de soude.

Die Bestimmung von Sulfat- und Ammoniumionen auf Verrosteten Stahltafeln

Zusammenfassung

Methoden zur Bestimmung von Sulfat- und Ammoniumionen auf verrostetem Eisen im Bereich eines Gehaltes von 0-100 Teilen pro Mio. wurden ausgearbeitet. Das Sulfat wird zur Entfernung des Eisens nach Lösung in einer mit Aluminiumhydroxid gefüllten Kolonne adsorbiert, mit Ammoniak desorbiert und unter Benutzung von chloranilsaurem Barium spektrophotometrisch bestimmt. Nachdem die Reaktion zwischen Stahl und Natriumhydroxid beendet ist, wird der Ammoniak abdestilliert und unter Benutzung des Reagens Natriumphenolat-Hypochlorid spektrophotometrisch bestimmt.

Определение ионов сульфата и аммония на ржавых стальных панелях

Резюме

Разработаны методы определения ионов сульфата и аммония в 0-100 частях на миллион на ржавых стальных панелях. Сульфат, после растворения, адсорбируется на колонне окиси алюминия для удаления железа, десорбируется аммиаком и определяется спектрофотометрически применяя хлоранилат бария. Аммиак дистиллируется после реагирования стали с едким натрием и определяется спектрофотометрически применяя реагент из гипохлорита фенолята натрия.

Introduction

As part of a programme designed to establish a correlation between the corrosion of painted steel panels exposed to natural weathering and to simulated conditions in the laboratory, it became necessary to determine the concentration of chloride, sulphate and ammonium ions on rusted steel panels before painting. The chloride determination has already been described[1].

It is well known that small quantities of chloride, sulphate[2] and ammonium ions[3] markedly increase the rate of corrosion of steel surfaces and adversely affect the performance of applied paint systems. Although the concentrations of these ions necessary to accelerate corrosion are small, penetration into the metal, particularly if the surface is irregular, may be deep. Removal of an appreciable depth of metal is therefore often necessary to ensure complete recovery of the corroding ions. The problem, therefore, resolves itself into one of determining small quantities of specific ions in the presence of a large excess of iron.

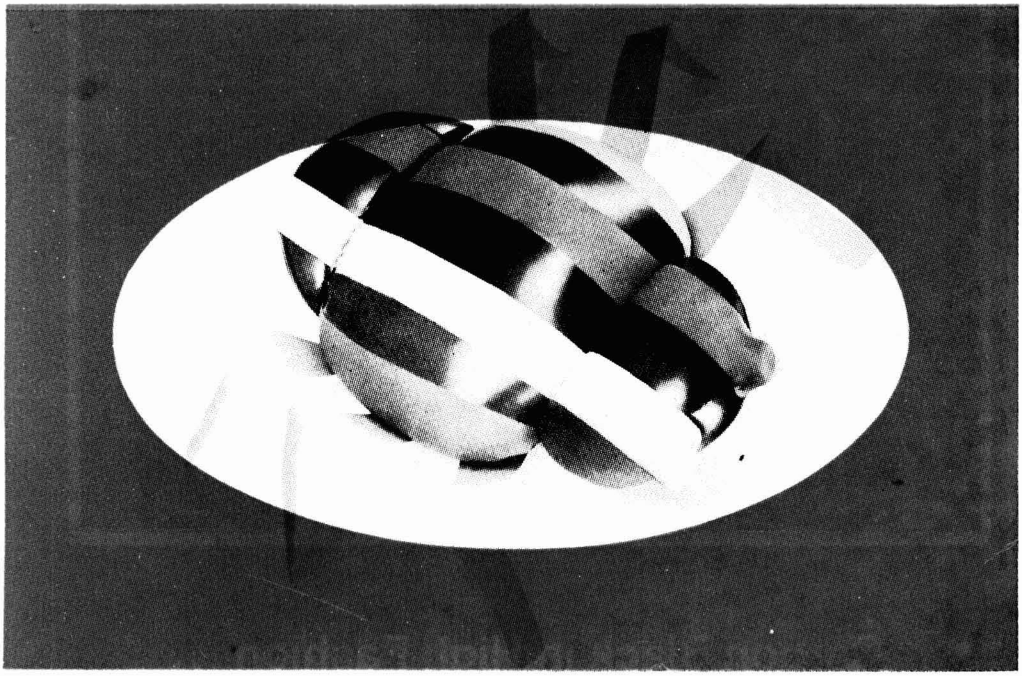
Experimental

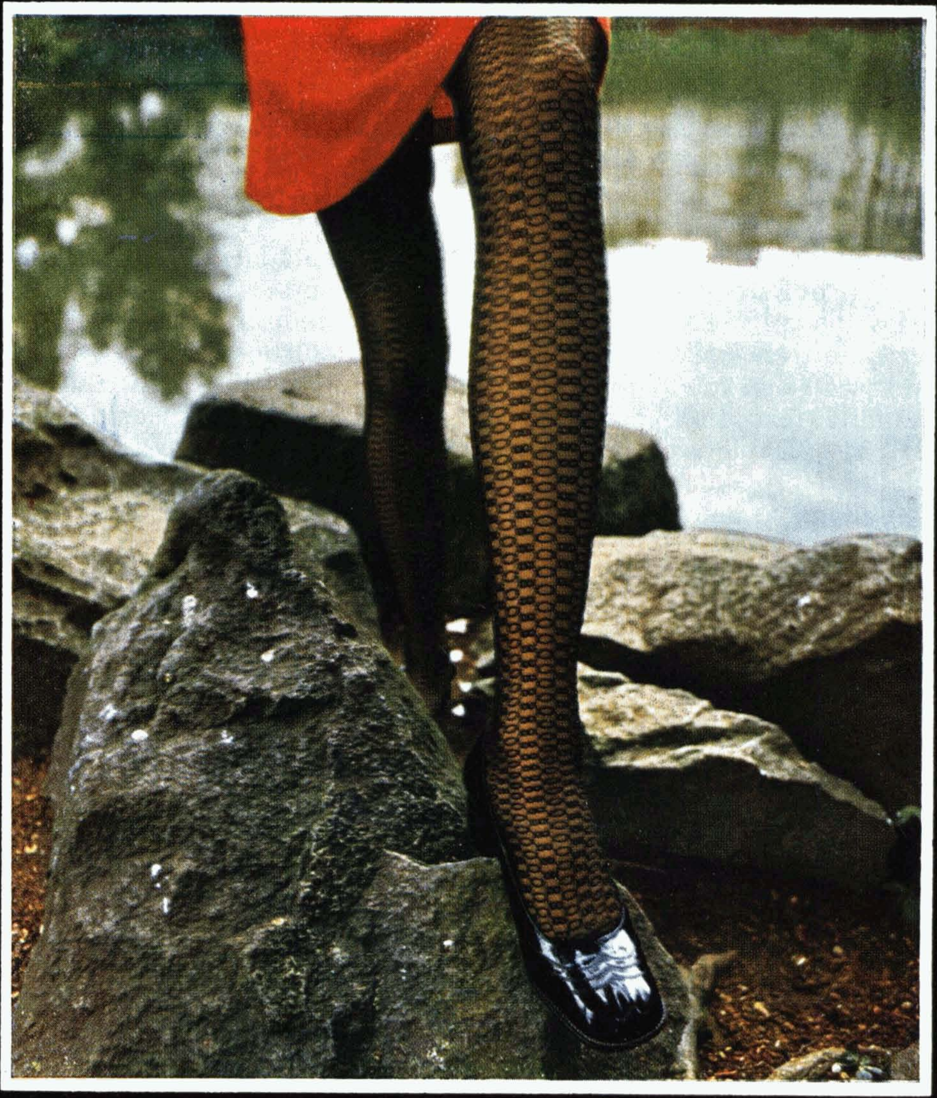
Determination of sulphate

In early attempts to determine sulphate, the surface layers of the steel plate were dissolved in dilute hydrochloric acid and the solution passed through a column of Dowex 50W-X8 cation exchange resin to remove iron. The sulphate in the effluent was then titrated with barium perchlorate using Sulphanazo III as indicator. Complete removal of the iron present was necessary to avoid interference with the titration, and to achieve this a high capacity column of 100-200 mesh resin was required, which needed regeneration after each determination. This procedure, involving a large sample volume, was too time consuming for a routine method.

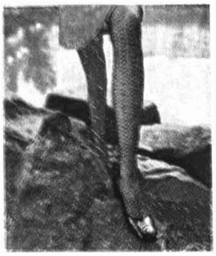
The alternative route of adsorbing the sulphate ion on an anion exchange resin was unsatisfactory because the sensitivity of the titration with barium perchlorate was much reduced by the presence of eluting agents (ammonium chloride or hydroxide), whether the solution was buffered or not. The possibility of using a second column of cation exchange resin to remove ammonia was considered but dismissed in view of the time factor involved.

F. Nydahl[4] has shown that an alumina column is particularly effective for adsorbing sulphate ion, which can subsequently be desorbed by hydroxide ions. This technique was used, the titration procedure being replaced by a method which was insensitive to the presence of ammonium ions and at the same time capable of covering the range of sulphate concentrations likely to





Carbon Black in High Fashion ...



Carbon Black in High Fashion

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S 170	71	0,98	650	17	200	for all types of black finishes
Special Black 5 *	75	0,83	430	20	240	for all types of black finishes
Special Black 15	84	0,96	250	25	100	for highest quality offset and letterpress inks
Special Black 4 *	80	0,86	300	25	180	in finishes applied by dipping or electrophoresis, high-grade flexo and special gravure inks and duplicating inks
Special Black 4 A	80	0,86	230	25	180	for high-grade printing inks, carbon paper and typewriter ribbons
Carbon Black LT	81	0,66	360	35	80	for paints, medium-priced printing inks, carbon paper and typewriter ribbons
Carbon Black LTD	81	0,66	360	35	80	
Printex® V **	83	0,95	400	25	110	for industrial and decorative paints, gravure, flexo and rotary news inks
Printex® 140 V *	84	0,91	360	29	96	for decorative paints, carbon paper, gravure, flexo and rotary new inks
Printex® 400	84	1,01	330	25	95	for letterpress and offset inks of good colour
Printex® 30 *	90	0,91	400	27	78	for rotary news inks
Printex® 300 ***	90	1,00	360	27	78	for gravure and inexpensive letterpress and offset inks
Printex® A*	94	0,73	300	41	46	for gravure inks
Printex® G *	98	0,64	250	51	31	for tinting paints, and in gravure inks and one-time carbon papers
Lamp Black 100	93	0,66	400	51	48	for tinting paints and in matt printing inks
Lamp Black 101 *	102	0,21	280	95	21	for tinting paints, with high resistance to flotation and pigment separation

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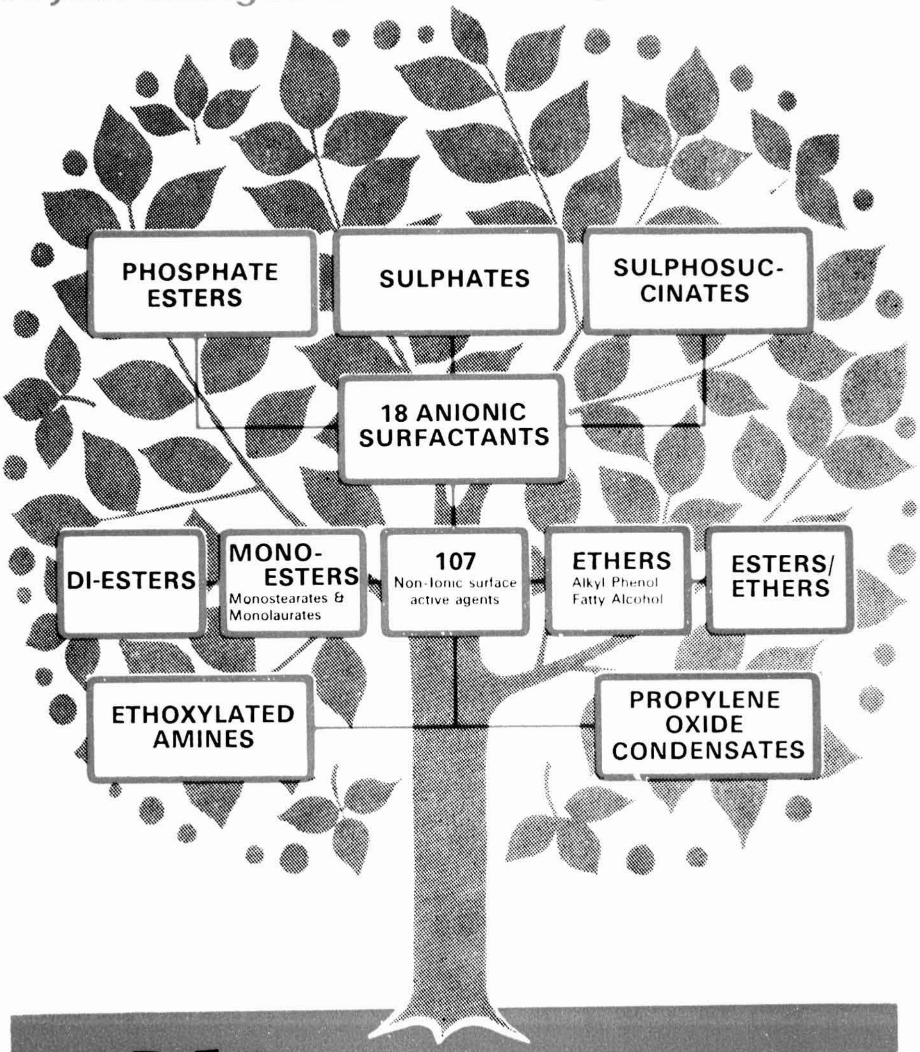

be met in practice. The gravimetric procedure will not meet this last condition as it is unsatisfactory at low levels of sulphate concentration. It was, however, used to check the reliability of a colorimetric procedure at the higher levels.

The colorimetric method selected[5] involves the reaction of solid barium chloranilate with sulphate ion in 50 per cent ethyl alcohol solution, liberating the coloured chloranilate ion, which absorbs at 530nm. The ethyl alcohol decreases the solubility of barium sulphate and barium chloranilate and so increases the sensitivity of the method:

$$BaC_6Cl_2O_4 \rightleftarrows Ba^{++} + C_6Cl_2O_4^{--}$$

$$SO_4^{--} + Ba^{++} + C_6Cl_2O_4^{--} \rightarrow C_6Cl_2O_4^{--} + BaSO_4$$

The amount of acid chloranilate liberated is proportional to the sulphate ion concentration.

Preparation of chromatographic column: A quantity of chromatographic grade alumina was digested in approximately normal hydrochloric acid at room temperature for about one hour, washed free from fines by decantation until the supernatant liquid was almost clear after standing for one minute, then dried in an oven at 110°C. The dried material was then sieved and that portion which passed a 200 BS sieve rejected.

Details of the column used are shown in Fig. 1. The column was filled with an aqueous slurry of alumina to a height of approximately 150mm. Normal hydrochloric acid (50ml) and water (30ml) were passed through the column before each determination.

Reagents: All solutions used were made up from AR grade reagents except where otherwise specified:

approximately N hydrochloric acid,
approximately 0.1N hydrochloric acid,
approximately 0.1N ammonium hydroxide,
approximately N ammonium hydroxide,
approximately 5N hydrochloric acid,
saturated solution of picric acid,
10 per cent (w/v) solution of barium chloride,
barium chloranilate,
potassium sulphate (previously dried at 105°C),
0.05M potassium hydrogen phthalate,
industrial methylated spirit.

Experiments with potassium sulphate solution: To confirm that quantitative recovery of sulphate ion from the alumina column was possible, preliminary experiments were conducted using a gravimetric procedure for the determination of sulphate adsorbed from potassium sulphate solutions.

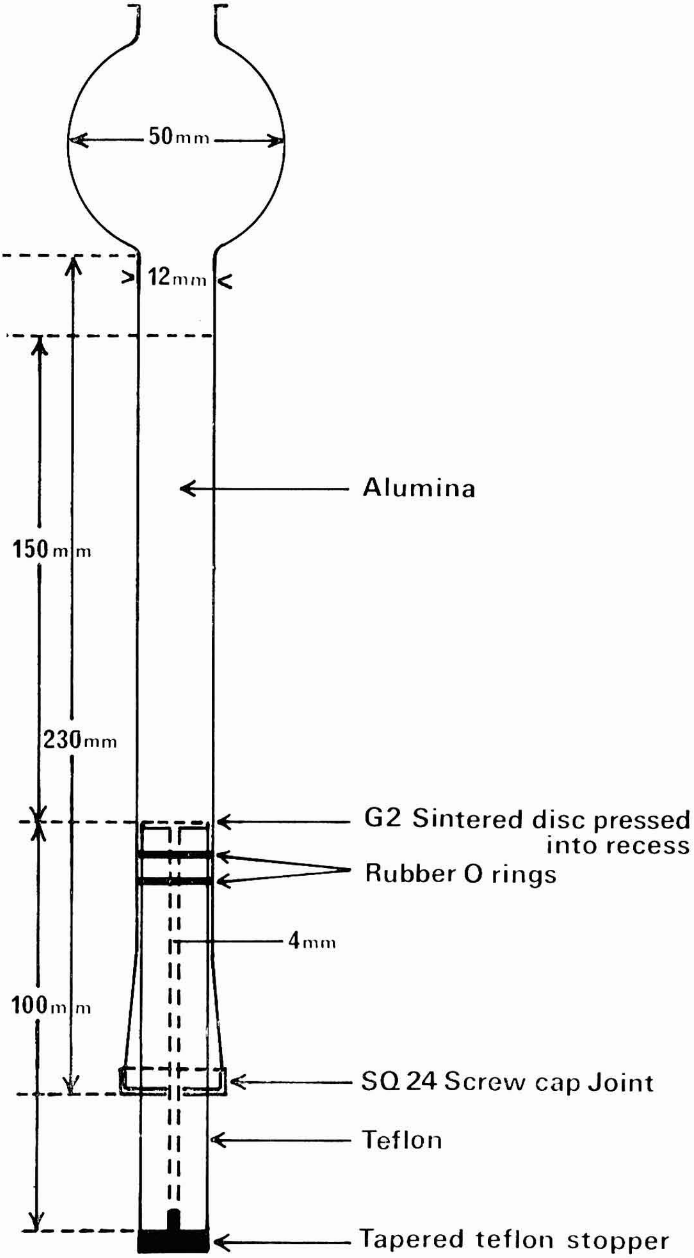

Fig. 1. Chromatographic column

A solution of potassium sulphate was prepared by dissolving 0.2530g of potassium sulphate in water and making the solution up to 100ml in a graduated flask. Normal hydrochloric acid (10.0ml) together with 10ml of this potassium sulphate solution were then passed through the column. The absence of sulphate in the column effluent was confirmed by tests with barium chloride solution.

The sulphate was desorbed by passing 10ml of normal NH_4OH followed by 30ml of 0.1N NH_4OH through the column, the effluent being collected in a 250ml beaker containing 3ml of 5N HCl. A saturated solution of picric acid (1.5ml) was added to the beaker, the solution boiled and the sulphate precipitated by adding 2ml of barium chloride solution to the boiling solution: the liquid was kept simmering for 5 minutes and then allowed to stand for 2 hours at room temperature. The precipitate of $BaSO_4$ was filtered on a G4 sintered glass crucible, dried and weighed.

Table 1

Results of experiments using potassium sulphate solution

SO_4^{--} Added (g)	SO_4^{--} Found (g)	% Recovery	Mean % Recovery
0.01394	0.01420	101.9	100.8
0.01394	0.01420	101.9	
0.01394	0.01376	98.7	

Experiments using steel plate: Sulphate determinations were carried out on metal plate (6in × 4in) treated as shown below.

(a) Original metal plate supplied to BS 1449 Part 1B, CR3/FF.18 BG.

(b) Metal plate as in (a), which had been subsequently grit blasted according to DEF 1053 Method No. 2.

(c) Metal plate prepared as in (b) and then dipped three times daily, at 10.00, 13.00, and 16.00 hrs for 5 days in the corrosive solution referred to below. Between dips, the panels were allowed to stand over distilled water in an enclosed atmosphere at 20°C.

Corrosive solution

Ammonium sulphate	1.86g
Sodium chloride	0.14g
Solution of sulphur dioxide (6g/100ml) (prepared as in BS 1391, clause 15)	17ml

Because of drainage of the corrosive solution, the top and bottom edges of the panel differed markedly in degree of corrosion. For this reason, 1in wide strips at the ends of the panel were not used for analytical purposes. To confirm that the alumina column gave reproducible results under working conditions a series of determinations was carried out using rusted steel panels.

Three 1in × 1in squares cut from an artificially rusted steel panel were refluxed with 100ml of 5N hydrochloric acid for 3 hours; after cooling, the solution was filtered through a glass-fibre paper and the filtrate halved. Sulphate was added to one half before passing it through the column but not to the other. The total sulphate concentration was then determined gravimetrically.

Table 2

Results of experiments using steel plate

Panel	SO_4^{--} added (g)	SO_4^{--} found (g)	
		Panel alone	Total
1	0.0070	0.0026	0.0096
2	0.0182	0.0021	0.0203
2	0.0182	0.0021	0.0203
3	0.0070	0.0018	0.0088
3	0.0070	0.0016	0.0086

Having established that an alumina column was capable of giving quantitative results for sulphate in the presence of a very large excess of iron, it was then necessary to determine the depth of penetration of sulphate into the steel plate. As the concentration of sulphate might vary from sample to sample, several acid extractions were carried out on the same sample and the sulphate determined on each. This was done by varying the strength of the hydrochloric acid (2N, 5N and 7N) used for refluxing. The 7N acid was found to dissolve the steel plate completely. The use of the strongest acid was considered undesirable, since reduction of sulphate might occur with too vigorous a reaction.

It was found that, when 100ml of 2N HCl was used, the thickness of the original panel decreased by the order of 0.015in, and sulphate, which was not present in the original HCl, was detectable in a second extract. With 5N HCl (100ml), some 0.030in of metal was dissolved and no sulphate was detectable in the second extract. It was therefore decided to use 100ml of 5N HCl in all subsequent determinations.

To prove that no reduction of sulphate occurred during dissolution of the metal, a sample of rusted steel was treated with 5N HCl (100ml) to remove sulphate and the remaining steel was washed several times with water to remove traces of sulphate. A further 100ml of 5N HCl, together with a known amount of potassium sulphate, was then added to the metal. After refluxing for 3 hours the sulphate in solution was determined.

Results

Sulphate added	0.01832g
Sulphate found	0.01824g
Percentage recovery	99.55

Experiments using barium chloranilate—Preparation of calibration curve: A calibration curve was constructed using 0.10-0.90ml aliquots, in 0.10ml steps, of a potassium sulphate solution containing 0.01g/ml SO_4^{--}. Successive aliquots of the sulphate solution were added to 30ml of water in a 250ml flask. Potassium hydrogen phthalate solution (10ml), industrial methylated spirit (50ml), and barium chloranilate (0.3g), were then added and the flasks shaken for 15 minutes. After filtering, the solution was transferred to a volumetric flask and made up to 100ml with water.

The absorbence of the solutions was determined at 530nm. A blank determination was carried out simultaneously, and this was used to adjust the instrument to zero absorbence before any sample readings were taken. The calibration curve is shown in Fig. 2. Beer's law is obeyed over the concentration range studied.

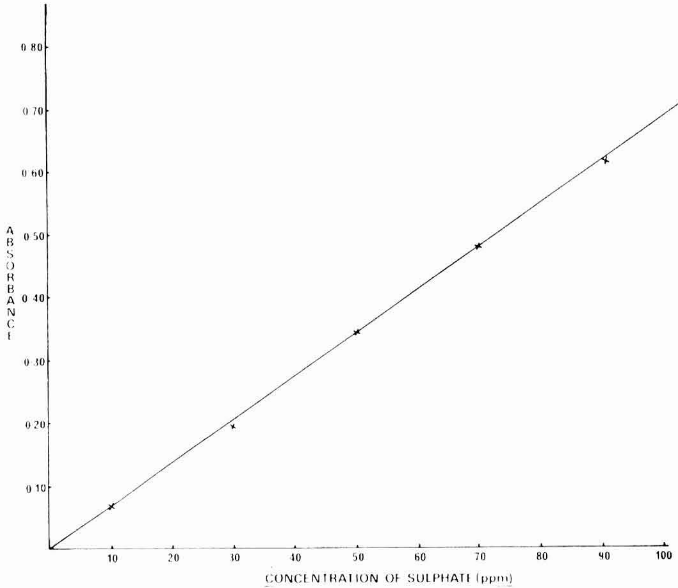

Fig. 2. Calibration curve for colorimetric determination of sulphate

Table 3

Results of experiments using barium chloranilate

Direct addition		After refluxing and passing through column	
Mls of K_2SO_4 solution	Absorbence	Mls of K_2SO_4 solution	Absorbence
0.10	0.071	0.10	0.0655
0.30	0.194	—	—
0.50	0.347	0.50	0.319
0.70	0.482	—	—
0.90	0.620	0.90	0.585

The procedure was repeated at the 10, 50, and 90ppm levels after refluxing the sulphate solutions with 5N HCl (100ml) and then passing the solution through the alumina column. Recoveries of 95, 93 and 94 per cent respectively were obtained using the calibration curve.

Comparison of gravimetric and colorimetric methods: Three 1in × 1in pieces of steel were digested with 5N HCl (100ml) for 3 hours, or until evolution of hydrogen ceased. The solution was cooled and the condenser washed down with 10ml of water. The solution was filtered and the remains of the steel plate washed with water (10ml). The filtrate was halved, and each half passed through the column, the sulphate then being determined gravimetrically and colorimetrically.

Table 4

Comparison of gravimetric and colorimetric methods

Panel number	Colorimetric		Gravimetric	
	SO_4^{--} found (g)	SO_4^{--}/sq ft steel (g)	SO_4^{--} found (g)	SO_4^{--}/sq ft steel (g)
1	0.0023	0.216	0.00214	0.205
1	0.0026	0.250	0.0025	0.240
4	0.0020	0.192	0.00182	0.174

The two methods agree to within 5 per cent, which is adequate for the level of sulphate involved.

Two separate determinations were carried out on three 1in × 1in pieces of virgin and grit blasted steel panel using the colorimetric method. In each case the whole of the 5N HCl extract (100ml) was used. With virgin metal both determinations gave a figure of 0.017g/sq ft of steel. The corresponding result for grit blasted metal was 0.024g/sq ft on both determinations. These results illustrate the importance of using blanks of original grit blasted steel in precise determinations.

The determination of ammonia

In early attempts to determine the ammonia present in rusted steel panels, the surface layers of the steel panels were dissolved in hydrochloric acid (2N); the resulting solution was transferred to a distillation assembly, made alkaline with sodium hydroxide (5N), and distilled in an attempt to separate the ammonia. The large excess of iron hydroxide made effective control of the distillation extremely difficult.

An alternative method was therefore sought. The direct action of sodium hydroxide (5N) on the steel was investigated and found to be satisfactory.

The ammonia was collected in dilute sulphuric acid (0.1N) and the determination was completed using Riley's method[6] as improved by Crowther and Large[7], which utilises the blue indophenol colour produced by sodium phenoxide/sodium hypochlorite with ammonia.

Preparation of reagents: All solutions used were made by using AR grade reagents. Nessler's reagent—potassium iodide (10g) was dissolved in 10ml of water and a saturated solution of mercuric chloride (60g l^{-1}) was added dropwise, with shaking, until a slight permanent precipitate formed. To this, 80ml of 9M potassium hydroxide was added and the solution diluted to 200ml. After standing overnight the clear solution was decanted and stored in a dark bottle.

Ammonia-free sodium hydroxide solution—A 100g portion of sodium hydroxide, together with 1.5g of potassium permanganate, was dissolved in 500ml of water and the solution was distilled until the distillate gave no reaction with Nessler's reagent.

Ammonia-free water—To a litre of water, 20g of sodium hydroxide was added and the solution distilled. The distillate was rejected until tests with Nessler's reagent showed that it was free of ammonia. The distillation was then continued until 500ml of distillate had been collected.

Sodium phenoxide solution—A solution of 62.5g of phenol in industrial methylated spirit was prepared, 18.5ml of acetone added and the solution diluted to 100ml with industrial methylated spirit and stored in a brown bottle. A 27g quantity of sodium hydroxide was dissolved in ammonia-free water, and the solution diluted to 100ml and stored in a polythene bottle. Both solutions were kept in a refrigerator at 0°C.

The solution of sodium phenoxide was prepared immediately before use by mixing 20ml portions of the two solutions and diluting to 50ml with ammonia-free water.

Sodium hypochlorite solution—A solution of sodium hypochlorite (10-14 per cent w/v) was diluted to give a solution containing 1.00 ± 0.05 per cent available chlorine when determined iodometrically. The solution was stored in a brown bottle in a refrigerator at 0°C and the available chlorine checked at frequent intervals.

Preparation of calibration curve: A solution of ammonium chloride was prepared by dissolving 0.2965g of AR ammonium chloride, previously dried over phosphorous pentoxide, in ammonia-free water and diluting to 100ml in a standard volumetric flask. Portions of 0.10 to 0.90ml, in steps of 0.20ml, were then transferred to distillation flasks containing 10ml of water. Each flask was connected to a splash head and a condenser fitted with a collecting tube which dipped into an absorbing solution consisting of 15ml of 0.01N sulphuric acid. Ammonia-free sodium hydroxide (150ml) was added to the flask and 70ml of distillate collected. The solution was then quantitatively transferred to a 100ml volumetric flask and the volume made up to the mark with water.

A 10.0ml portion of the distillate was transferred to a 25ml volumetric flask and 4.0ml of sodium phenoxide added. After mixing, 3.0ml of sodium hypochlorite solution were added and the solution was diluted to 25ml with ammonia-free water and allowed to stand for 10 minutes before measuring the absorbence at 625nm. A blank determination was carried out simultaneously, and this was used to adjust the instrument to zero absorbence before any sample readings were taken. The calibration curve (Fig. 3) was found to obey Beer's law.

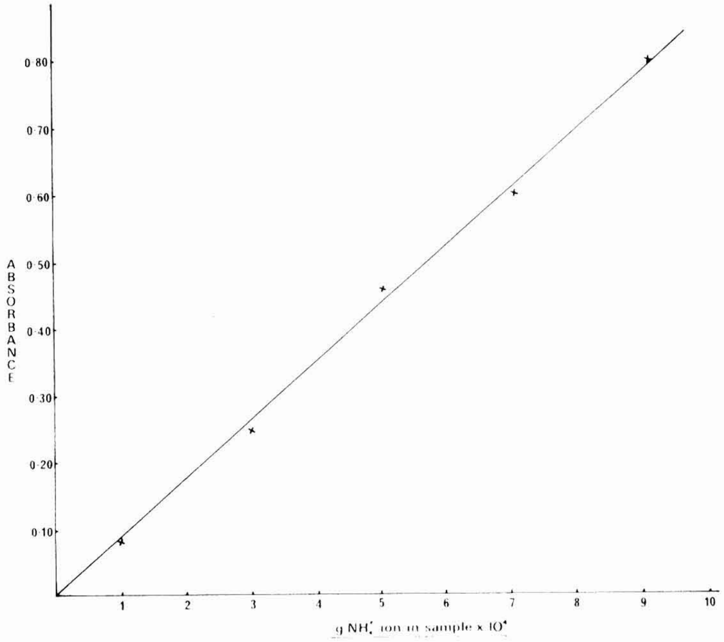

Fig. 3. Calibration curve for colorimetric determination of ammonia

Ammonia determinations on steel plate: Using the above procedure, ammonia determinations were carried out on virgin, grit blasted, and artificially corroded samples of steel plate. The corroded panels were prepared as described in the sulphate method.

In view of the small amount of ammonium ion expected, twelve 1in × 1in pieces of panel were taken, as opposed to three 1in × 1in for chloride[1] and sulphate. The results, shown in Table 5, are in all cases derived from different 6in × 4in panels of steel plate.

Table 5

Results of ammonia determinations

Sample	Absorbence	g NH_4/sq ft
Virgin metal (1)	0.0044	< 0.00001
Virgin metal (2)	0.0044	< 0.00001
Grit blasted panel (1)	0.0315	0.00042
Grit blasted panel (2)	0.0220	0.00036
Grit blasted panels after corrosive treatment:		
Panel 2	0.0862	0.0012
Panel 3	0.0862	0.0012
Panel 4	0.0915	0.0013

These results are of the order expected, and show that the reproducibility of the method is adequate.

Discussion

The results obtained above show that the methods developed for the determination of sulphate and ammonia in virgin and shot blasted steel panels have satisfactory accuracy and precision. The sulphate method is designed to measure the concentration in the corrosion products, but because metal has to be dissolved the results will include any sulphate in the original steel. If it is necessary to distinguish between these two sources of sulphate, corrections for the sulphate present in the virgin steel must be applied.

Similar corrections are required in the determination of ammonia, even though in this case there is no dissolution of the metal.

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On the adhesion of alkyd resin films to substrates other than glass

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Summary

It is shown that the theory developed for the peeling-off of a film from a substrate, expressed in four parameters for the viscoelastic properties of the resin film and two for the boundary layer between the resin and the substrate, can be used for other substrates as well as glass. The substrates used are polymethylmethacrylate, aluminium, stainless steel and brass.

Keywords

Types and classes of surface
aluminium
brass
polymethylmethacrylate
stainless steel

Types and classes of coating
alkyd coating

Properties, characteristics and conditions primarily associated with dried or cured films
adhesion

Sur l'adhérence des feuils de résines alkydes aux supports sauf de verre

Résumé

On démontre que la théorie mise au point pour la vitesse d'épluchement du feuil à partir du support, exprimée sous termes de quatre paramètres à l'égard des caractéristiques viscoélastiques du feuil de résine, et également de deux autres pour la zone interfaciale de la résine et du support, peut être appliquée aux autres supports sauf ceux de verre. Les supports utilisés ce sont polyméthylméthacrylate, aluminium, acier inoxydable et laiton.

Über die Haftung von Alkydharzfilmen auf Substraten ausser auf Glas

Zusammenfassung

Es wird gezeigt, dass die für die Abschälgeschwindigkeit eines Filmes vom Untergrund entwickelte Theorie, ausgedrückt in 4 Parametern für die viskoelastischen Eigenschaften des Harzfilms und in zwei Parametern für die Grenzschicht zwischen Harz und Substrat, auf andere Untergründe als Glas angewandt werden kann. Die benutzten Substrate sind Polymethylmethakrylat, Aluminium, nichtrostender Stahl und Messing.

Адгезия алкидно-смольных пленок к субстратам отличных от стекла

Резюме

Показано что теория разработанная для скорости шелушения пленки от субстрата, выраженная в четырех параметрах для вязкоупругих свойств смольной пленки и в двух параметрах для пограничного слоя между смолой и субстратом, может применяться для других субстратов кроме стекла. В качестве субстратов применяются полиметилметакрилат, алюминий, нержавеющая сталь и латунь.

Introduction

In a previous paper[1] a theory has been developed relating the peeling-off behaviour of an unpigmented alkyd resin film to the viscoelastic properties of the film, described with a four parameter model, and the adhesion of the film to a substrate, expressed in two boundary layer parameters. These parameters Δ and η_3 are considered to be characteristic of the binding of the film to the substrate. The viscoelastic properties of the film have been studied by performing creep experiments with free films and describing the measured deformation versus the time with the aid of the four parameter model. This model is shown in Fig. 1.

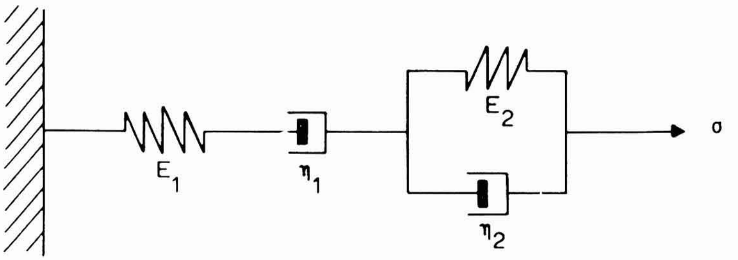

Fig. 1. The four element model for the description of the viscoelasticity of the resin films

The creep equation, resulting from this model is:

$$\varepsilon_t - \varepsilon_t^2 = \frac{\sigma(E_1 + E_2)}{E_1 E_2} + \frac{\sigma t}{\eta_1} - \frac{\sigma}{E_2} \exp - \frac{E_2}{\eta_2} t \quad \ldots\ldots\ldots\ldots(1)$$

in which ε_t = deformation at time t.
σ = load in g cm^{-2}.
t = time in seconds.

The values of E are then in g cm^{-2} and the values of η in g sec cm^{-2} (g = gram force). The changes in the width and the thickness of the film are negligibly small when the value of ε_t is smaller than 0.05-0.1; in these cases the correction ε_t^2 on ε_t due to the decrease in the film thickness and width is negligible.

Using this creep equation for the description of the deformation of the film when it peels off, and including the process in the boundary layer between the resin and the substrate in which the bond between film and substrate is broken, a relation between the peeling-off load σ and the time t_c needed for the peeling-off of a unit film length is obtained:

$$\frac{1}{\sigma} = \frac{E_1 + E_2}{\Delta E_1 E_2} + \frac{t_c}{\Delta(\eta_1 + \eta_3)} - \frac{1}{\Delta E_2} \exp - \frac{E_2}{\eta_2} t_c \quad \ldots\ldots\ldots(2)$$

In both equations (1) and (2) the exponential term approaches zero at high values of t or t_c and a semi-linear relationship between $1/\sigma$ and $t(t_c)$ should be observed under such conditions.

This theory has been verified[1] for a glass substrate, giving satisfactory results. In the present paper the applicability of the theory for substrates other than glass will be investigated.

Substrates other than glass

With glass as a reference substrate, the peeling-off behaviour of alkyd resin films (a long oil, pentaerythritol esterified, linseed oil modified alkyd resin, with a composition of about 25 per cent phthalic anhydride and about 62 per cent linseed oil) on various substrates has been studied. To eliminate the influence of ageing, all the experiments were carried out with films of nearly the same age (77-79 days).

The following substrates were used: polymethylmethacrylate (Perspex), aluminium, stainless steel and brass. The conditions chosen were: temperature 25°C, relative humidity 35.5 ± 0.5 and 70.5 ± 0.5 per cent. The cleaning of the surface of the panels of the various materials was carried out as shown below.

Polymethylmethacrylate (Perspex) was wiped with a piece of cloth wetted successively with alcohol, acetone and again with alcohol, was rinsed in distilled water, and finally dried in a desiccator at room temperature with an air stream of about 55 per cent relative humidity.

The metals were degreased either in the manner as described above for polymethylmethacrylate or etched for 15 minutes in a mixture of 10 per cent (by weight) concentrated hydrochloric acid and 10 per cent concentrated sulphuric acid in water. After this treatment, the panels were rinsed in running tap water and finally in distilled water. They were dried in an oven at 80°C and stored at room temperature at about 55 per cent RH under dust free conditions.

Glass was degreased and cleaned by leaving the panels overnight in a chromic acid solution. Finally, they were rinsed in running tap water, then in distilled water and dried at 80°C. The plates were stored at room temperature at about 55 per cent RH under dust free conditions.

A layer of the alkyd resin solution was applied to the cleaned panels with the aid of a doctor blade. The covered panels were then dried. The dry films had a thickness of approximately 50 microns.

Results

Peeling off

Glass: Because the results of the experiments are very sensitive to variables such as surface composition, surface cleaning, resin composition and the conditions during the application and drying of the resin, it is important to use a reference substrate for a given series of experiments. Glass has been chosen because of experience obtained with this substrate.

The following experiments have been carried out:

1. peeling off at 35.5 per cent relative humidity,
2. peeling off at 35.5 per cent relative humidity, but after extraction of the film substrate system for 3 hours with distilled water at 40°C, followed by a reconditioning for 14 hours at the experimental conditions,
3. as 1, but at 70.5 per cent relative humidity,
4. as 2, but at 70.5 per cent relative humidity.

The loads used in the experiment were chosen in such a way that the semi-linear relationship between $1/\sigma$ and t_c holds. The results obtained for glass are given in Fig. 2, showing the values of t_c versus $1/\sigma$. In Table 1, the values of $(E_1+E_2)/E_1E_2$ and $\Delta(\eta_1+\eta_3)$, as calculated from these lines, with those of the other substrates, are listed.

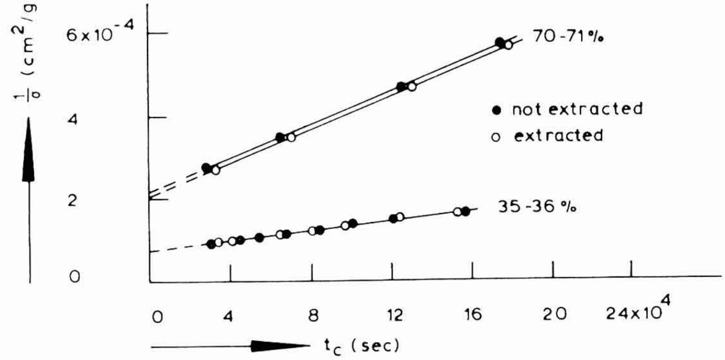

Fig. 2. The relation of t_c and $1/\sigma$ for the peeling off of an alkyd resin from glass

As can be seen from these results, there is a tendency towards a slower peeling off of the film when the substrate/film system has been extracted. Peeling off becomes more difficult when $(E_1+E_2)/\Delta E_1E_2$ and $1/\Delta(\eta_1+\eta_3)$ decrease. This tendency is in agreement with the observations of Walker[2] and Bullett[3] who, using a pull-off technique, both noticed a better adhesion of alkyd resin paints to stainless steel after leaching out the system with water. An explanation for this, in all probability, lies in changes in the boundary layer properties, because, in general, no changes have been found in the visco-elastic properties of an alkyd resin film after a short extraction with water (see below).

Polymethylmethacrylate (*Perspex*): The same peeling-off experiments as used for glass were carried out with polymethylmethacrylate, and the results are shown in Fig. 3 and the results of the calculations in Table 1.

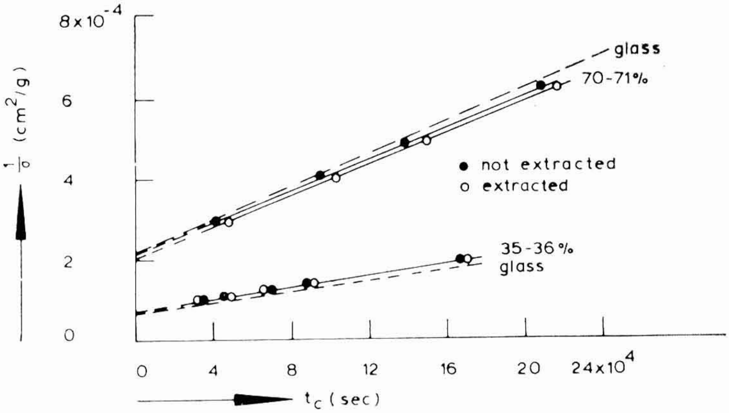

Fig. 3. The relation of t_c and $1/\sigma$ for the peeling off of an alkyd resin film from polymethylmethacrylate

It appears that with a low relative humidity the adhesion to Perspex is slightly less than the adhesion to glass, whilst at a high relative humidity the adhesion to Perspex is better than to glass. Probably the polarity of the substrate surface is of importance.

Aluminium. The metal panels were degreased either with an organic solvent or by etching with acid. The influence of the extraction with water has been investigated only on the etched metal surfaces. As can be seen from Fig. 4, a linear relation between $1/\sigma$ and t_c was again found, so equation (2) could be used. The increase in adhesion is remarkable with the etched substrate. Extraction of the film results in a sharp decrease in adhesion. Corresponding results have been reported by Tooke and Montalvo[4], who studied the adhesion of alkyd resin paints to aluminium. Probably a considerable hydrolysis of the resin occurs when the film is extracted with water. Bullett and Prosser[5] stress the fact that weak boundary layers may be formed on metal surfaces as a result of hydrolysis of the alkyd resin used, especially when the metal substrates contain zinc or magnesium. Aluminium alloys containing magnesium appear to have a surface rich in magnesium.

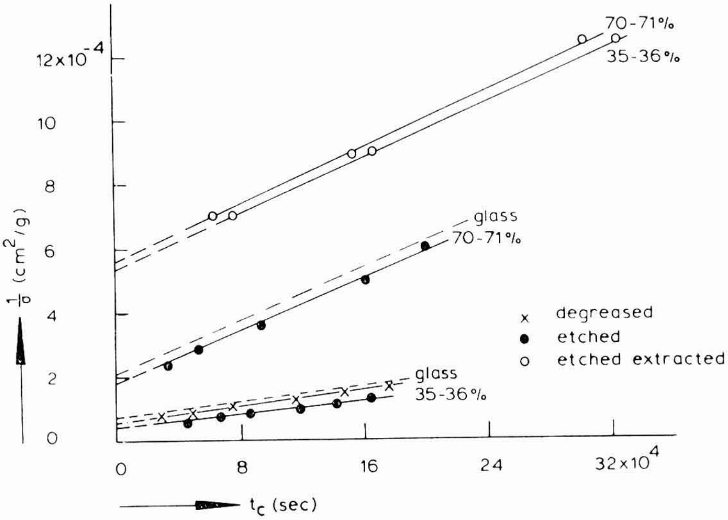

Fig. 4. The relation of t_c and $1/\sigma$ for the peeling off of an alkyd resin film from aluminium

Stainless steel and brass. The results of the peeling-off experiments with these substrates are shown in Figs. 5 and 6. The calculated values of $(E_1 + E_2)/\Delta E_1 E_2$ and $\Delta(\eta_1 + \eta_3)$ are again given in Table 1. As can be seen from Figs. 5 and 6, the adhesion to the degreased substrates is less than the adhesion to glass, whilst etching promotes adhesion. Extraction of the film/substrate system for a few hours, followed by drying of the system to the experimental low humidity conditions, results in a better adhesion. Corresponding results have been published by Bullett[3] for the pull-off adhesion of alkyd resin paints. From the results obtained, it follows that normal degreasing techniques can be insufficient to give good adhesion. On metal substrates, the adhesion of an alkyd resin is improved by etching the substrate surface. Extracting the film/substrate system for a short time with water followed by drying of the system improves adhesion, unless hydrolysis of the binder by alkaline metal soaps can occur, as with aluminium substrates.

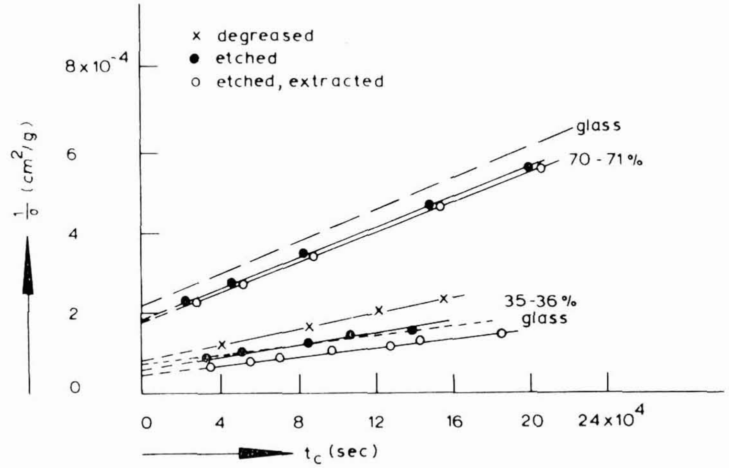

Fig. 5. The relation of t_c and $1/\sigma$ for the peeling off of an alkyd resin film from stainless steel

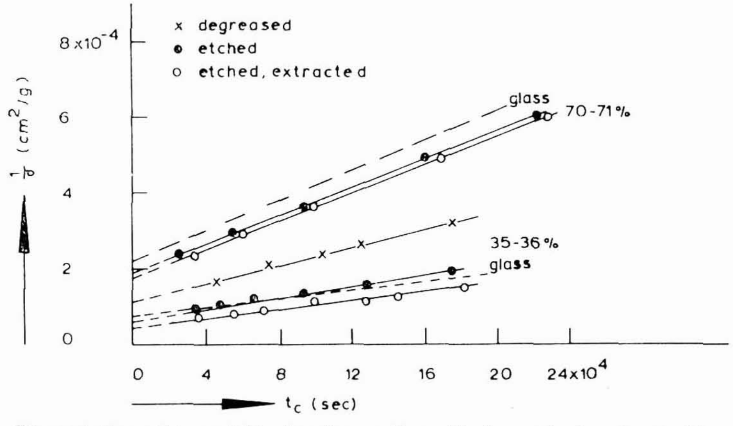

Fig. 6. The relation of t_c and $1/\sigma$ for the peeling off of an alkyd resin film from brass

Extraction of the film

Low molecular weight, highly polar fractions of the resin accumulate in the boundary layer between substrate and films, as has been shown by Crowl[6], Dintenfass[7], Doorgeest[8] and Sjollema and Radielovic[9].

When the alkyd resin film/substrate system is immersed in water, the film and the boundary layer will swell strongly, and their low molecular weight compounds will tend to dissolve. The dissolved resin fraction will tend to leave the boundary layer by diffusion and become distributed throughout the entire film matrix. Because of the short time of extraction used, the chance

Table 1

The results of the calculation of the constants $(E_1 + E_2)$ ΔE_1E_2 *and* $\Delta(\eta_1 + \eta_3)$ *of alkyd resin films on various substrates*

Substrate	Surface treatment	RH %	Extracted	$\frac{E_1 + E_2}{\Delta E_1E_2} \times 10^4$	$\Delta(\eta_1 + \eta_3) \times 10^{-9}$
Glass ..	Chromic acid	35.5	–	0.67	1.52
		35.5	+	0.66	1.54
		70.5	–	2.14	0.51
		70.5	+	2.10	0.52
Perspex ..	Alcohol/ acetone	35.5	–	0.71	1.37
		35.5	+	0.71	1.37
		70.5	–	2.10	0.51
		70.5	+	2.04	0.53
Aluminium ..	Alcohol/ acetone etched	35.5	–	0.57	1.60
		35.5	–	0.42	1.89
		35.5	+	5.33	0.49
		70.5	–	1.84	0.53
		70.5	+	5.59	0.46
Stainless steel	Alcohol/ acetone etched	35.5	–	0.81	0.98
		35.5	–	0.59	1.33
		35.5	+	0.44	1.86
		70.5	–	1.81	0.52
		70.5	+	1.71	0.52
Brass ..	Alcohol/ acetone etched	35.5	–	1.19	0.83
		35.5	–	0.62	1.45
		35.5	+	0.45	2.07
		70.5	–	1.84	0.53
		70.5	+	1.76	0.54

that very much of the dissolved fraction will leave the film is small and therefore no large influence on the viscoelastic properties of the films is to be expected. Extraction should have an influence, however, on the properties of the boundary layer, because the migration of the low molecular weight components to the bulk of the film enables a better orientation of the remaining bigger resin molecules towards the substrate, because there is less competition from smaller, more polar, molecules.

The result is a greater stiffness of the boundary layer. In other words, the components acting as a plasticiser in the boundary layer have been removed by extraction. When the film is dried after extraction, the transport of the dissolved components from the boundary layer to the bulk of the film is promoted by the fact that water can only leave the system at the film/air interface.

As a result of the extraction it may be expected that more bonds between film and substrate will be formed, so that Δ will be lower. When a metal substrate is used, a reaction of acid groups in the resin with the substrate is possible.

For low molecular weight components, this results in the formation of metal soaps that are more soluble than the acid itself. In addition, these soaps can, if they are alkaline enough, hydrolyse the binder. Because of the better solubility of the metal soaps, the effect of extraction of the film/substrate system will be more pronounced on the metal substrates than on glass or polymethylmethacrylate. If the acid group is a part of a large polymer molecule, the reaction with the substrate results in the formation of a strong bond between the polymer and its substrate[10]. Etching gives a good adsorption of the resin and hence an improved adhesion, on all metal substrates, because of the formation of a fresh clean surface. However, the increased roughness may also play a part in the better adhesion. The following effects of an extraction with water can thus be expected:

> because of the short extraction period used, no measurable influence on the viscoelastic properties of the free resin films after extraction is to be expected;
>
> the influence on the boundary layer between the film and the substrate is such that peeling off becomes more difficult after extraction; on metal substrates this effect is more pronounced than on substrates such as glass and polymethylmethacrylate;
>
> when hydrolysis of the alkyd resin by alkaline metal soaps can occur, peeling off will be strongly promoted by a breakdown of the boundary layer and the resin film by alkaline soaps;
>
> at high relative humidity conditions the film and boundary layer will contain so much water that the effect of extraction and reconditioning will be very small; also, the differences in behaviour between the alkyd resin films on the various substrates will become small while, under these conditions, all substrates will be covered with a (multi)layer of water between the resin layer and the substrate.

It has been stated above that, during the extraction period, metal ions from metal substrates might diffuse into the film matrix. To verify this, the authors extracted films applied to stainless steel and aluminium (300cm^2 film/substrate area has been treated with 150ml distilled water at 40°C for 3 hours) and the extraction liquid was analysed for metal ions by means of an emission spectrograph for the films and with atomic absorption for the liquid. The results obtained for the films are given in Table 2. Alkyd resin films formed on a glass substrate have been used as a reference.

Table 2

Ions present in films applied to stainless steel and aluminium after extraction. Amounts given as ppm of dry film weight. Glass as a reference substrate

Element	Stainless steel	Aluminium	Glass
Al	2	10	2
B	—	5	—
Ca	200	200	200
Co	40	20	20
Fe	110	20	0.4
Mg	2	200	1
Mn	2	8	0.1
Ni	5	1	2
Pb	200	200	200

It appears that, in addition to the metals Ca, Co and Pb, which are added as drying catalysts, ions from the substrates are also present. The high amount of magnesium in the film formed on the aluminium substrate after extraction with water is remarkable. Only in the extraction liquid for the system alkyd resin/stainless steel, were metal ions found: 1 ppm Fe, 0.1 ppm Ni and 1 ppm Cr.

Creep

It was noticed that the alkyd resin films on stainless steel and brass dried faster than the films on the other substrates. This is apparently the result of metal ions dissolving from the substrate into the film and acting as an additional drying catalyst.

It may be expected that the viscoelastic properties of the films formed on these substrates will differ from those of films formed on glass.

To verify this, the creep of the alkyd resin films formed on glass and stainless steel, prepared as described previously[1] and after storage during a night under the experimental conditions, was measured. The calculated values of $(E_1 + E_2)/E_1E_2$ and η_1 (equation 1) are given in Table 3. All films are of the same thickness (50μ) and of the same age (78 days).

Table 3

Effect of extraction of films on their viscoelastic properties

Substrate	Surface treatment	RH %	Extracted	$\frac{E_1 + E_2}{E_1E_2} \times 10^5$	$\eta_1 \times 10^{-9}$
Glass . .	Chromic acid	35.5	−	0.40	2.32
		35.5	+	0.42	2.32
		70.5	−	1.28	1.64
		70.5	+	1.26	1.66
Stainless steel	Alcohol/ acetone etched	35.5	−	0.33	4.58
		35.5	−	0.33	4.59
		35.5	+	0.31	4.58
		70.5		1.08	1.60
		70.5	+	1.05	1.61

From these results it follows that, for films on glass or stainless steel, the extraction as carried out has no significant influence on viscoelastic properties. On the metal substrate, the surface treatment also has no measurable influence on the rheological properties of the film. The conclusion from this is that the differences in peeling off behaviour on the same substrate may be regarded as resulting from different boundary layer properties.

Only with aluminium as a substrate are the rheological properties of the resin film changed following extraction of the film. The deformation under a given load is much greater than before the extraction. Hydrolysis of the resin by alkaline metal soaps in this case does not seem to be confined to the boundary layer alone, the film itself is also affected. For films that have not been extracted with water, the viscoelastic properties are equal to those of films dried on glass and independent of the surface treatment. The creep of extracted films measured at high relative humidity does not differ very much from that of non-extracted films under these conditions. Apparently the effect of hydrolysis is obscured by that of the high water adsorption in the resin film (Table 4.)

Table 4

The results of creep experiments with alkyd resin films dried on an aluminium substrate

Surface treatment	Extracted	RH %	$\frac{E_1 + E_2}{E_1 E_2} \times 10^5$	$\eta_1 \times 10^{-9}$
Alcohol/acetone etched		35.5	0.42	2.32
		35.5	0.44	2.31
	+	35.5	1.21	1.76
	−	70.5	1.28	1.63
	+	70.5	1.26	1.66

The period of water immersion involved in the preparation of free films is just a few minutes. In this period the hydrolysis of the film does not seem to be important, because no difference in the creep behaviour of alkyd resin films dried on glass and on aluminium is found. In order to obtain a stable system, the necessity of applying a layer that prevents the formation of the alkaline soaps on an aluminium surface, or of using unsaponifiable binders, is evident.

As has been indicated, the viscoelastic properties of alkyd resin films formed on glass or aluminium seem to be the same, with the exception of the films on aluminium after extraction with water. This is clearly demonstrated by considering the change of the strain—the relative elongation—divided by the load σ, with time. From equation (3) follows:

$$\frac{\varepsilon - \varepsilon^2}{\sigma} = \frac{E_1 + E_2}{E_1 E_2} + \frac{t}{\eta_1} - \frac{1}{E_2} \exp. - \frac{E_2}{\eta_2} t \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Graphs of $\frac{\varepsilon - \varepsilon^2}{\sigma}$ versus time, t, for films with the same viscoelastic properties in the experiments carried out under the same experimental conditions should coincide. Such graphs for films dried on the various substrates are represented in Figs. 6 and 7 (RH 35.5 and 70.5).

These figures prove that, within the limits of experimental error, the creep properties of films dried on polymethylmethacrylate and aluminium (with the exception of the extracted film on this substrate) are identical with the creep properties of the films dried on glass.

The creep behaviour of the films formed on stainless steel and brass is the same. These films are less easily deformed than the films on glass. As yet, no explanation has been found for the fact that, although the polymerisation of

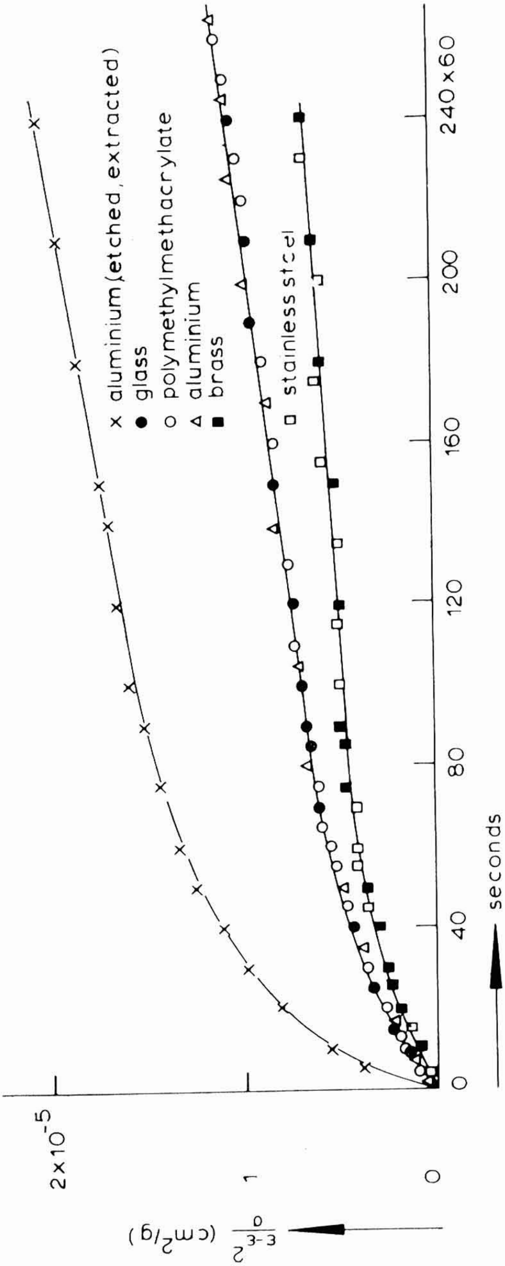

Fig. 7. Creep curves of alkyd resin films dried on various substrates at 35% RH

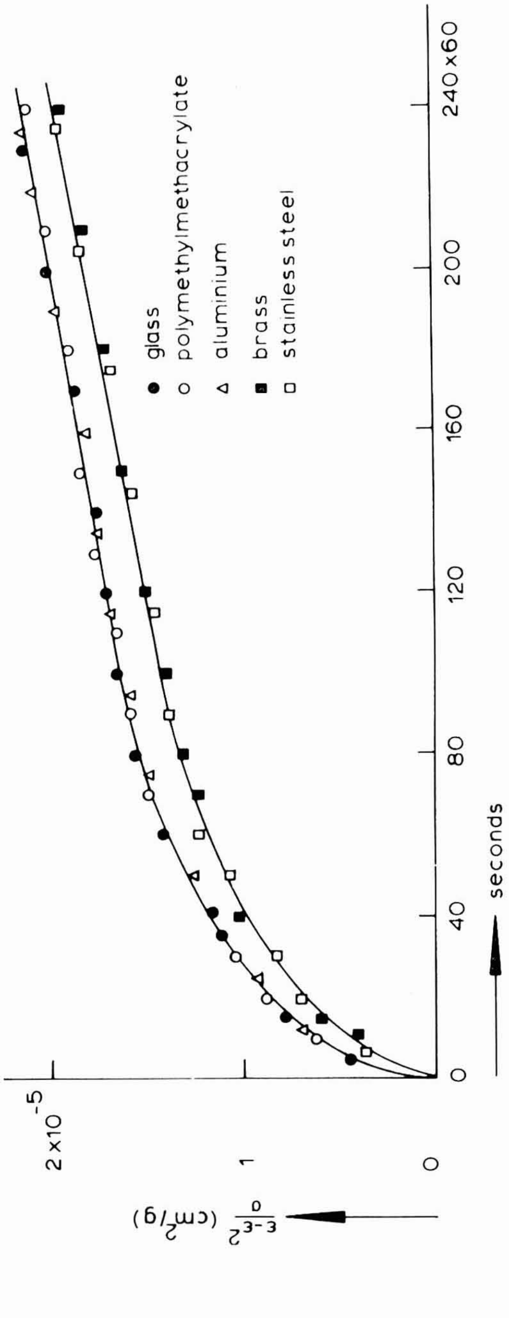

Fig. 8. Creep curves of alkyd resin films dried on various substrates at 70.5% RH

the films is accelerated by a dissolution of metal ions from the substrate, this effect for both films containing different ions is the same. As for the experiments with glass as a substrate, the reproducibility of the experimental results with the other substrates is good.

Calculation of Δ and η_3

It follows from the results of the creep experiments that the substrates can be divided into two groups. Within each group the viscoelastic properties of the films are the same and only dependent on the relative humidity. One group contains the substrates glass, polymethylmethacrylate and aluminium, the second group contains stainless steel and brass.

From the data given in Tables 1, 3 and 4, the values of Δ and η_3 can be calculated. Table 5 gives their values for the first group of substrates.

Table 5

Calculated values of the boundary layer parameters Δ and η_3

Substrate	Surface treatment	Extracted	RH %	$\Delta \times 10^2$	$\eta_3 \times 10^{-9}$
Glass	Chromic acid	—	35.5	6.3	21.9
		+	35.5	6.4	21.9
		—	70.5	6.0	6.8
		+	70.5	6.0	6.9
Polymethyl-methacrylate	Alcohol/acetone	—	35.5	5.9	20.8
		+	35.5	5.9	20.8
		—	70.5	6.1	6.7
		+	70.5	6.3	6.8
Aluminium ..	Alcohol/acetone etched	—	35.5	7.4	19.4
		—	35.5	10.0	16.6
		+	35.5	2.3	18.7
		—	70.5	7.0	6.6
		+	70.5	2.3	18.4

The influence of the extraction and reconditioning, as such, of alkyd resin films on glass or polymethylmethacrylate as a substrate is very small. The variations in the values of Δ and η_3 are not significant. The etching of the aluminium surface has a strong influence, the value of Δ increases. Now Δ is the relative elongation, the strain, between the binding groups—distance l_o—necessary for peeling off the films. When more bonds are formed with the substrate and the displacement of a binding point necessary to lose adhesion (δ) remains constant (the type of binding to the substrate does not change), increase in Δ means a decrease in l_o, because δ remains constant. Therefore, with the etched aluminium surface more bonds are formed. This increase of Δ is accompanied by a decrease of η_3 caused by hydrolysis starting in the boundary layer. Extraction promotes the hydrolysis of the film and the boundary layer, whilst soluble products are transported from the boundary layer into the bulk of the film. The number of bonds with the substrate will then decrease and so will Δ, whilst the viscosity of the boundary layer will not change much or increase only slightly, because products which may act as a plasticiser are transported to the bulk of the film.

The results calculated for the second group of substrates are given in Table 6. It appears that etching and extraction results in the formation of increasingly stronger boundary layers. The effect is more pronounced under conditions of low than at high relative humidity. The influence of etching again causes an increase of Δ. No hydrolysis of the boundary layer, as was the case with aluminium, is to be expected in these cases.

Extraction results in a further increase of Δ and also in an increase of η_3. The removal of the low molecular weight soluble fraction of the resin from the boundary layer causes an improved adsorption of the larger polymer molecules, by which Δ and the stiffness of the boundary layer η_3 are both increased.

Table 6

Calculated values of the boundary layer parameters Δ and η_3

Substrate	Surface treatment	Extracted	RH %	$\Delta \times 10^2$	$\eta_3 \times 10^{-9}$
Stainless steel	Alcohol/acetone	—	35.5	4.1	19.2
	etched	—	35.5	5.6	19.2
		+	35.5	7.5	20.2
		—	70.5	5.8	7.2
		+	70.5	6.0	7.4
Brass	Alcohol/acetone	—	35.5	3.0	23.0
	etched	—	35.5	5.3	22.7
		+	35.5	7.3	23.6
		—	70.5	5.7	7.7
		+	70.5	6.0	7.5

Conclusions

The model developed to describe the peeling off behaviour of alkyd resin films from a substrate is valid for substrates other than glass, for instance polymethylmethacrylate, aluminium, stainless steel and brass. The nature of the substrate used can influence the creep properties of the film, and surface treatment has a strong influence on the boundary layer properties. Variations in peeling-off behaviour can be explained in terms of these influences. Extraction of a film/substrate system results in the transport of a low molecular water soluble resin fraction from the boundary layer to the bulk of the film. For the extraction period used this has no detectable influence on the mechanical properties of the film itself. However, the properties of the boundary layer are changed in an appreciable manner—a stiffer layer with more bonds to the substrate is formed. This improves the adhesion of the films to the substrate. This result can be counteracted by hydrolysis of the boundary layer by alkaline metal soaps formed.

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Weathering of paint films III. Influence of wavelength of radiation and temperature on the chalking of latex paints

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Summary

Chalking induced in paint films by radiation of different wavelengths was studied in a xenon arc weatherometer. The experiments were carried out at two temperatures and at various humidities. Paints formulated with seven types of resin, zinc oxide, and anatase titanium dioxide were used in the experiments.

The rate of chalking of paint films was reduced to one fifth in some cases by lowering the temperature from 55°C to 37°C. The wavelength of radiation causing maximum chalking was found to lie in the range from 385nm to 415nm for paints formulated with zinc oxide, and from 355nm to 415nm for paints containing anatase titanium dioxide. Changes also took place in paint films that had not been irradiated, leading to a loss in weight without chalking, and this has been interpreted as cross-linking of the polymer molecules.

A possible reaction mechanism which could explain the observed phenomena is discussed.

Keywords

Types and classes of coating
latex coating

Equipment primarily associated with analysis, measurement and testing
weatherometer

Properties, characteristics, and conditions primarily associated with dried or cured films
chalking

Vieillissement des feuils de peintures

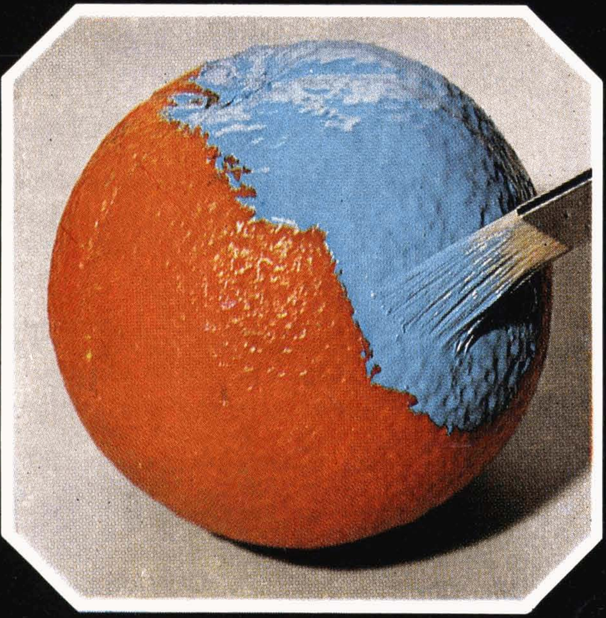
IIIème. Partie: L'influence de la longueur d'onde de la radiation et également de la température sur le farinage des peintures-émulsions

Résumé

On a étudié le farinage provoqué en feuils de peintures par la radiation de différentes longueurs d'onde au moyens d'un weathèrometre à arc de xénon. Les expériences ont été effectuées à deux températures et à diverses humidités. On a utilisé des peintures à base de 7 types de résine, de l'oxyde de zinc, et du dioxyde de titane du type anatase.

En certains cas le taux de farinage a été reduit à une cinquième par l'abaissement de la température de 55°C à 37°C. On a trouvé que la longueur d'onde de la radiation qui provoque le farinage maximal était dans la région de 385nm à 415nm pour les peintures à base de l'oxyde de zinc, et entre 355nm et 415nm ou il s'agit des peintures contenant du dioxyde de titane du type anatase. D'ailleurs, il y a eu des changements dans les feuils de peintures qui n'avaient pas été exposés à la radiation, de sorte qu'il y avait une perte de poids sans aucun farinage. On l'attribuée à la reticulation des molécules de polymère.

On discute un mécanisme de réaction qui pourrait expliquer les phénomènes observés.



Bewitterung von Anstrichfilmen

III. Einfluss von Bestrahlungswellenlänge und Temperatur auf Abkreiden von Latexfarben

Zusammenfassung

Das durch Bestrahlung mit verschiedenen Wellenlängen in Anstrichfilmen hervorgerufene Abkreiden wurde in einem Xenon-Bogenlampen Weather-o-Meter studiert. Die Versuche wurden bei zwei Temperatuten und bei verschiedener Luftbeuchtigkeiten vorgenommen. In diesen wurden Anstrichmittel, deren Rezepturen siebenerlei Harze, Zinkoxid und Anatas Titandioxid enthielten, verwandt.

In einigen Fällen wurde das Mass des Kreidens durch Herabsetzung der Temperatur von 55°C auf bis zu 37°C auf ein Fünftel reduziert. Es wurde beobachtet, dass die maximales Abkreiden verursachende Strahlungswellenlänge für mit Zinkoxid rezeptierte Farben zwischen 385nm und 415nm und für solche, die Anatas Dioxid enthalten, zwischen 355nm und 415nm liegt. Auch in Anstrichfilmen, welche nicht bestrahlt worden waren, stellten sich Veränderungen ein, die zu Gewichtsverlust ohne Abkreiden führten; dies wurde als Vernetzung des Polymermoleküls interpretiert.

Ein möglicher, die beobachteten Phänomene erklärender Reaktionsmechanismus, wird besprochen.

Выветривание красочных пленок

III. Влияние длины волны излучения и температуры на известкование латексоподобных красок

Резюме

Изучалось известкование в красочных пленках вызываемое излучением различной длины волны-на везерометре ксеноновой дуги. Опыты проводились при двух температурах и различных влажностях.

В опытах применялись краски формулированные с 7-ью типами смолы, окиси цинка и анатаза двуокиси титана.

Скорость мелования красочных пленок была понижена в некоторых случаях до одной пятой части путем понижения температуры от 55°C до 37°C. Найдено что длина волны излучения вызывающая максимальное мелование лежит в диапазоне от 385 нанометров до 415 нанометров для красок формулированных окисью цинка и от 355 нанометров до 415 нанометров для красок содержащих анатаз двуокиси титана. Наблюдались также изменения в красочных пленках которые не облучались, что вело к потере веса без известкования, и это объяснялось образованием поперечных связей полимерных молекул.

Обсуждается возможный реактивный механизм который мог бы объяснить наблюдаемое явление.

Introduction

One of the most important tasks in paint technology is to develop reliable accelerated testing methods, amongst which a procedure for determining the weatherability of paint films would probably rank as the most important. Progress in paint technology virtually stands or falls with the availability of such a method.

At present, the consensus of opinion on accelerated testing for weatherability appears to be that it is a rather unreliable guide for estimating the life of a paint on a given substrate and at a given location.

After trying many weatherometers and cycles, Novacki[1] came to the conclusion that, with sufficient experience and background information, one type of coating might be assessed as suitable or otherwise merely by selecting the appropriate condition for accelerated weathering. The reason for this very unsatisfactory state of affairs is that not enough is known about the mechanism of the changes, or at least the degree to which the variables making up the weather influence the process of deterioration in an exposed paint film.

One of the present authors[2] has emphasised the need for an advanced understanding of the reaction mechanism, or for a good grasp of the quantitative influence of the significant variables that play a role in the changes being studied.

The main reasons why nothing more reliable has been evolved appear to be as shown below.

The influence of factors responsible for the breakdown of a paint film on weathering has rarely been separated and quantitatively investigated. The most important variables that should be examined are the relative humidity, air temperature, and the intensity and wavelength of the incident radiation.

Too little attention has been given to the need for direct and quantitative measurements of changes in properties. The measurements that should be carried out are shown below.

Chalking should be determined by loss of weight of the paint film. The great majority of workers determine the tendency to chalk indirectly by measuring the loss of gloss, but this can give very misleading results[3].

Mechanical properties of the paint film should be determined by stress/strain measurements. The advantages of these are only now beginning to be more widely appreciated (for example, see Shur *et al*[4]).

Gloss measurements are usually made but, as has been pointed out, they do not provide a good basis for conclusions regarding the decomposition of resins leading to chalking.

Fading can be caused by chalking and also by changes in any dyestuff or pigment used. This is probably best determined by reflectometry.

The testing of finished paints is not considered by the authors to be the most important purpose of accelerated testing, which should preferably be used to study the way in which the various components of a paint influence its properties. For instance, anatase titanium dioxide is a pigment that causes strong chalking, but what happens if a part of this pigment is replaced by one which causes less chalking, such as rutile titanium dioxide or stainless steel? Questions of this kind need to be examined[5,6].

When sufficient data on the behaviour of the components of a paint under various conditions are available, it should be possible to formulate paints that are suitable for a given climate.

The project on the weathering of paint films carried out at the Division of Building Research has these two purposes in mind: the development of useful accelerated weathering tests for any climate, and determination of the interaction of the components of the paints on their properties.

This paper deals with the influence of the wavelength of radiation and of the ambient temperature on the chalking of latex paints.

Experimental

Materials

Pigments: Anatase titanium dioxide and zinc oxides A and C. The latter are made by the indirect process, A by oxidation of zinc metal waste, and C from pure ingot zinc. Both types were included because they exhibit differences in their mould-inhibiting properties. The zinc oxide pigments have a surface area (by nitrogen adsorption) of 4.6 m^2g^{-1}, a lead content of 0.05 per cent, and the largest particles present are about 1 μm but most are smaller.

Resins

1. Tetrapolymer of styrene, 2-ethylhexylacrylate, methylmethacrylate, and acrylonitrile.
2. Vinyl chloride/acrylate copolymer (60 per cent vinyl chloride).
3. Vinyl acetate/fumarate copolymer (18 per cent fumarate).
4. Vinyl acetate/acrylate copolymer (15 per cent acrylate) plus 5 per cent silicone resin.
5. Vinyl acetate/acrylate copolymer (15 per cent acrylate).
6. Pure acrylate copolymer.
7. Vinyl acetate polymer plasticised with dibutyl phthalate.

Filters: A set of Corning optical glass filters was used. The amount of radiation transmitted by these filters has been determined for ten wavelength bands and this information is given in Table 1[7].

Table 1

Relative energy distribution of radiation from a xenon-arc transmitted by filters for ten wavelength bands[7]

Filter used	Wavelength band (nm)										Total
	281 to 310	310 to 355	355 to 385	385 to 415	415 to 445	445 to 480	480 to 520	520 to 570	570 to 630	630 to 1900	
None	3.2	17.7	17.9	25.8	29.1	50.7	49.8	60.0	64.3	762.1	1100.4
A	0.5	14.8	16.1	23.3	26.5	46.5	45.8	55.7	59.8	722.9	1011.9
B	0.0	2.1	14.1	23.0	26.4	46.5	45.8	55.2	59.1	719.5	991.7
C	0.0	0.0	3.5	16.6	22.6	42.0	43.0	53.0	56.9	630.8	868.3
D	0.0	0.0	0.0	6.2	24.2	44.7	44.3	53.4	57.2	675.3	905.2
E	0.0	0.0	0.0	0.0	0.6	36.9	43.9	53.4	57.2	641.8	833.8
F	0.0	0.0	0.0	0.0	0.0	9.2	39.2	53.1	57.2	641.6	800.2
G	0.0	0.0	0.0	0.0	0.0	0.0	1.5	46.6	57.2	694.3	799.7
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.8	53.0	699.3	755.1
I	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	660.1	660.7

Total energy at the sample position was approximately 270 Btu ft^{-2} h^{-1} (3.07 MJ m^{-2} h^{-1})

Determination of chalking

The procedure used in this investigation was as follows. Weighed stainless steel panels 62.5 × 75mm (2.5 × 3in) were painted and dried to constant weight at 38°C. After exposure, the panels were kept at 38°C for 24h and then reweighed before and after removing the chalk with a dry cloth.

Procedure

Experiments were carried out in the xenon arc weatherometer at 30, 60, and 95 per cent relative humidity, air temperature 55°C, black body temperature 72°C, and at 60 per cent relative humidity, air temperature 37°C, and black body temperature 53°C. White paint film surface temperatures were 62°C and 41°C respectively.

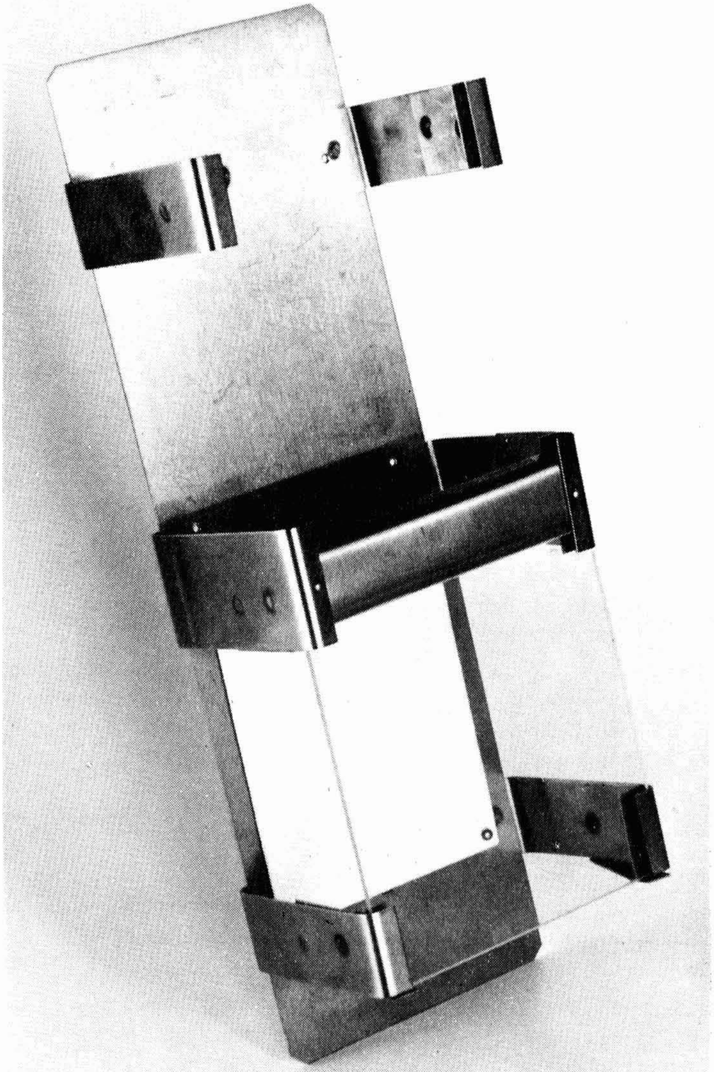


Fig. 1. Filter in position over stainless steel panel

The filters were positioned 50mm over the stainless steel panels, as shown in Fig. 1. They were open at the top and side to ensure that the air behind the filter had the same relative humidity as that over the panels without a filter. The temperature of a paint film behind a filter is somewhat lower than that of a film which has no filter over it, but the temperature difference is too small to influence the results to any significant extent. Note, for example, that the difference between the radiation intensity at a paint film behind filter D and at one without a filter is only about 20 per cent, with a consequent temperature difference probably not greater than 2°C. The difference in temperature would be correspondingly less for a pair of filters nearer together.

The results of these experiments are summarised in Figs. 2-7, and Tables 4 and 5.

Results and discussion

General

Chemical reactions are induced in a paint film when it is exposed to radiation, and these eventually lead to chalking and to changes in the elasticity of the coating. For chalking to occur, it is necessary for the binder to be decomposed to the extent that it ruptures and sets the pigment free. Changes in elasticity are probably brought about by cross-linking, further polymerisation, or both.

In the course of the experiments described in this paper, the paint films were also exposed behind a stainless steel shield so that no direct radiation fell on them. Under these conditions no chalking occurred, but a considerable loss of weight was observed. One feasible interpretation of this is that cross-linking of polymer molecules occurs by partial oxidation with the loss of some volatile products and recombination of the residue into the polymer network.

If a weight loss takes place in a coating shielded from radiation, a similar loss is also likely to occur in a paint film exposed to light, where it will simply be superimposed on the changes due to the radiation.

In an attempt to check the correctness of this view, the weight loss of the panels before removing the chalk, W_1 and the further weight loss, W_2, after removing the chalk, were determined. This can be achieved only if the conditions in the weatherometer are such that the chalk is not removed mechanically, as would be the case if the panels were sprayed, or if they were exposed outdoors. From the formulation of the paint, the amount of resin W_3 which was combined with the amount W_2 of pigment can be calculated, and the difference (W_1-W_3) ascertained. The following is an actual example. A paint pigmented with zinc oxide showed a weight loss of 159mg before removing the chalk, and of 615mg afterwards. The amount of chalk formed was therefore 456mg. The composition of the paint film was 24 per cent resin and 76 per cent pigment, or 31.6 per cent resin based on pigment weight. The amount of resin totally decomposed* is therefore 144mg, and there is an additional loss of 15mg resin which does not lead to the setting free of pigment but indicates that some change has taken place in the resin.

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*This expression means decomposition to volatile products.

In these calculations it has been assumed that the resin that originally held the pigment together was totally decomposed and that the chalk therefore consisted of pigment only, and that none has fallen off the vertically mounted panels. That the first assumption is reasonable has been shown by analysing for carbon in the chalk. The two samples analysed contained 0.24 and 0.38 per cent carbon respectively. The paint film contained 24 per cent by weight of a vinyl acetate/acrylate copolymer containing approximately 55 per cent carbon. This means that approximately 2-3 per cent of the resin previously combined with the pigment was still in the chalk.

The reasonableness of the second assumption can be seen from the results obtained with panels inclined to the horizontal. Under these conditions, too, the same phenomenon was observed, that is, the amount of resin W_3 which was originally connected with the pigment was smaller than the weight loss W_1 before taking off the chalk, as can be seen from Table 2.

Table 2

Weight losses of a paint film inclined at 19° to the horizontal

Paint formulation: Vinyl acetate/acrylate copolymer pigmented with anatase titanium dioxide at 40 per cent PVC

Exposure in xenon arc weatherometer at 40°C, 60 per cent RH, no filter

Exposure period (each approximately 133h)	Total loss of resin, i.e. weight loss before removal of chalk (mg)	Total decomposition of resin calculated from weight of chalk (mg)	Loss of resin ascribed for the time being to partial oxidation and cross-linking (mg)
1	35	0.5	34.5
2	35	10.8	24.2
3	17	6.3	10.7
4	18	7.2	10.8

The loss W_1-W_3 could have many causes. As the resin consists of polymers of different molecular weight and structure, various reactions could take place. Likely ones would appear to be the partial oxidation and consequent cross-linking of polymer molecules. These new compounds, which are probably of a higher molecular weight than the one they originated from, are likely to be less attacked by oxygen. From the experimental results it is, of course, impossible to deduce in detail what happens, but the reactions described would probably lead to a change in the mechanical properties of the paint film.

The following picture (one which certainly will need further modifications as work progresses) of what happens during the weathering of a paint film may be provisionally put forward. Part of the resin is totally decomposed and the pigment is set free, and part of the resin is changed in the manner described above, and very probably exhibits changes in its mechanical properties.

In this paper, therefore, a distinction will be made between the weight losses caused by the total decomposition of the resin, and those caused by the reactions described above. The latter loss will be called "weight loss caused by cross-linking," but this is only a convenient description of the result of the various changes occuring in the film and not a statement that this is actually happening. It is felt, however, that this is very probable.

A phenomenon similar to the one described here, namely, a weight loss in the absence of radiation, appears to have been observed for alkyd films[8]. The authors thought it likely that this loss was due to cross-linking between polymer molecules by oxidation reactions.

Influence of wavelength

It is recognised that only radiation between 300 and 400nm causes the total decomposition of the binder that eventually leads to chalking[9], but for a better understanding of the mechanism of the reaction, and in order to decide on the best source of radiation to be used in accelerated weathering experiments, it is desirable to specify the wavelength band responsible for this reaction somewhat more closely.

Neville[10] used optical filters mounted in front of the panels in an attempt to measure the influence of the wavelength of radiation on chalking. However, no safe conclusions on the wavelength responsible for the decomposition of the resin can be drawn from his results for the reasons shown below.

The panels and filters were mounted in such a way that only the average loss between the top part of the panel, which was exposed to unfiltered light, and that of the lower part of the panel behind a filter could be determined.

The filters were mounted only $\frac{1}{8}$in from the panels. This space is very small and almost certainly resulted in the relative humidity and temperature behind the panel being considerably different from the corresponding values for the part exposed directly.

No attempt was made to differentiate between the weight changes caused by radiation and those which occur in its absence. Similar objections have been raised in the discussion following the presentation of the paper by Bullett[11].

Vinyl acetate/acrylate copolymer (*resin 5*): The results at 60 per cent relative humidity with this resin using zinc oxides A and C and anatase titanium dioxide respectively as pigments are given in Fig. 2. To facilitate the discussion, the amount of radiation cut off by each filter, compared with the filter preceding it, has been tabulated in Table 3.

Table 3

*Reduction in radiation transmitted by each filter compared with that transmitted by the preceding filter**

Filter	Wavelength band (nm)				
	281 to 310	310 to 355	355 to 385	385 to 415	415 to 445
A	2.7	2.9	1.8	2.5	2.6
B	0.5	12.7	2.0	0.3	0.1
C	0.0	2.1	10.6	6.4	3.8
D	0.0	0.0	3.5	10.4	−1.6
E	0.0	0.0	0.0	6.2	23.6
F	0.0	0.0	0.0	0.0	0.6

*Derived from Table 1

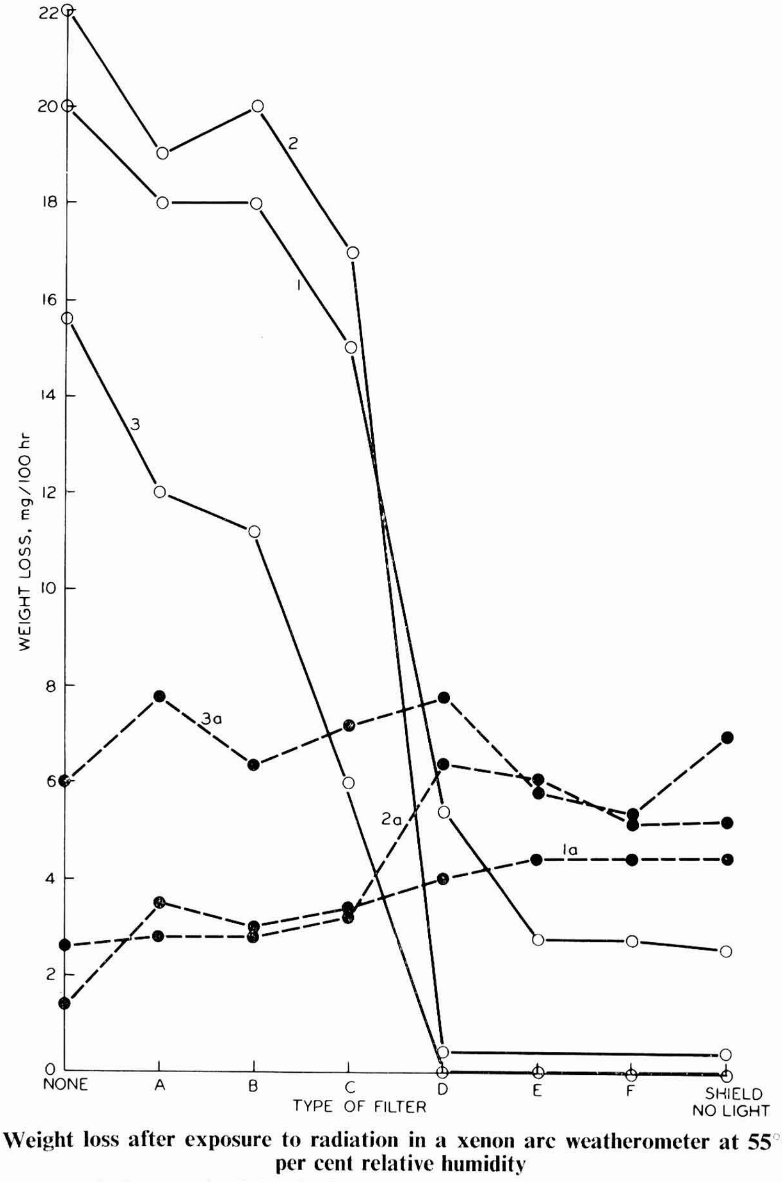


Fig. 2. Weight loss after exposure to radiation in a xenon arc weatherometer at 55°C and 60 per cent relative humidity

Paint formulation—resin 5, PVC 40 per cent
Pigments—1, 1a, zinc oxide C
2, 2a, zinc oxide A
3, 3a, anatase titanium dioxide

Full lines—totally decomposed resin
Broken lines—weight loss caused by cross-linking

Zinc oxide C: Introduction of filter A reduced the decomposition of the resin in a paint formulated with zinc oxide C by 10 per cent, and this may have been due to the reduction in energy of any of the wavelength bands given in Table 3.

Filter B did not reduce the decomposition of the resin, but there was a large reduction in energy in the range 310 to 355nm, indicating that this wavelength band is ineffective in causing decomposition. There was also a small reduction in the range 355 to 385nm, indicating that this band is probably also ineffective.

Behind filter C the decomposition decreased by 17 per cent compared with the decomposition behind filter B. This could be due to the reduction in radiation in any of the wavelength bands above 355nm.

Filter D caused a decrease of 63 per cent in the decomposition compared with that behind filter C, and this could be caused by reduction in radiation of the wavelength bands above 385nm. The assumption that radiation responsible for decomposition lies mainly in the range 355 to 385nm leads to the conclusion that, in the previous case, a reduction of 10.6 units caused a 17 per cent decrease in decomposition of the resin, but a further reduction by only 3.5 units led to a 53 per cent decrease. If, however, it is assumed that the wavelength band from 385 to 415nm is the one causing the changes in the paint film, the conclusion is that reductions in radiation of 6.4 and 10.6 units cause decreases of 17 and 53 per cent in decomposition respectively, which appears much more likely.

Behind filter E, radiation in the wavelength band 385 to 415nm is reduced by 6.2 units, and the decomposition of the resin falls to 50 per cent of that behind filter D.

A small amount of chalking still persists behind filter F and even behind the stainless steel shield, where no direct radiation reaches the paint film. This could be due to some reflected radiation reaching the film, but whatever the reason for the loss it does not alter the conclusion arrived at previously.

Zinc oxide A: The results for zinc oxide A (Fig. 2) are basically the same as for zinc oxide C, and the conclusions are similar. There is a slight increase in chalking from filter A to B, the causes of which are not clear, but this does not upset the previous inferences.

For the paints pigmented with either of the two zinc oxide pigments it is therefore the radiation from 385 to 415nm which causes the bulk of the decomposition.

Anatase titanium dioxide: As can be seen from Fig. 2 without detailed discussion, the two wavelength bands 355 to 385nm, and 385 to 415nm, cause about the same amount of decomposition of the resin.

Loss of weight which does not lead to chalking of a paint film has been interpreted as being due to partial oxidation and cross-linking. Curves 1a, 2a, and 3a show that the losses behind the filters and the stainless steel shield were quite considerable. Based on the values behind the shield they amount to 21, 24, and 43 per cent of the loss resulting from the total decomposition of the resin without filter.

For the zinc oxide pigments the decrease appeared to be smaller when radiation that could cause total decomposition of the resin was present. This is understandable, because this radiation probably also causes decomposition of cross-linked molecules.

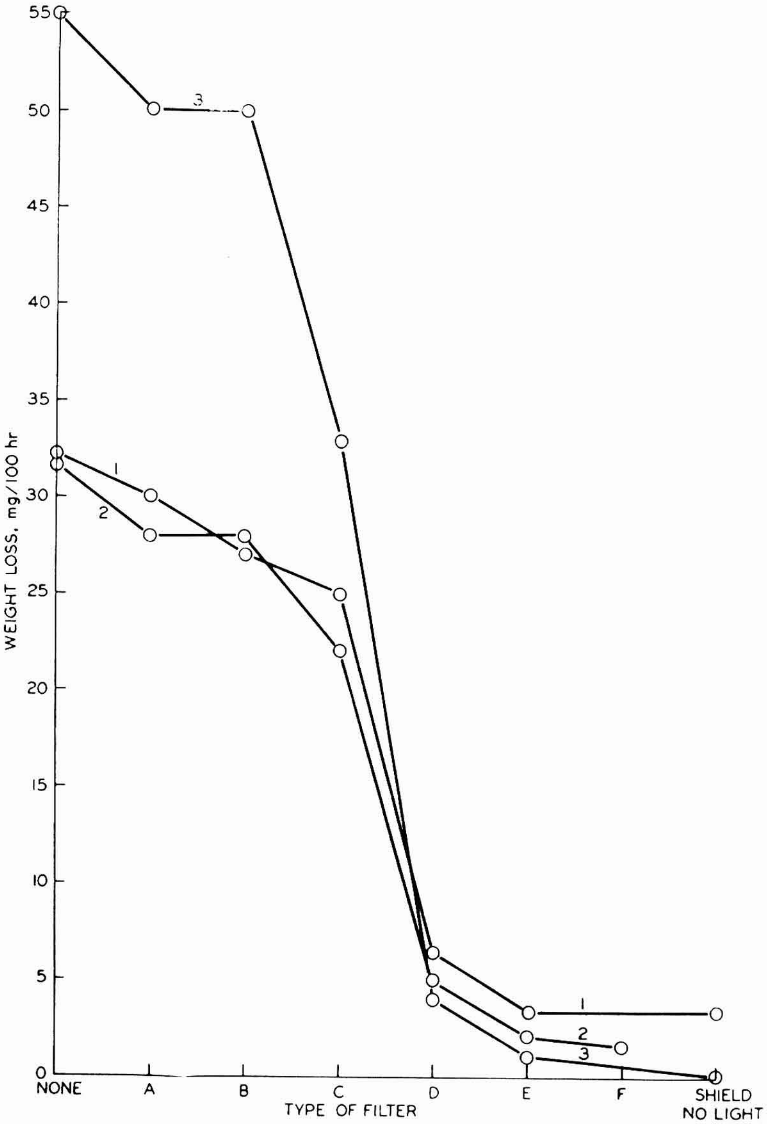


Fig. 3. Weight loss by total decomposition of resin after exposure in a xenon arc weatherometer at 55°C and 60 per cent relative humidity

Paint formulation—resin 7, PVC 40 per cent

Pigments—1, zinc oxide C
2, zinc oxide A
3, anatase titanium dioxide

The main conclusions are clear, that apart from the total decomposition of the binder which leads to chalking, other reactions also take place in the resin, and these can be measured by determining the loss of weight of a paint film before the chalk is removed.

Vinyl acetate polymer plasticised with dibutyl phthalate (*resin 7*): In this case, interpretation of the experimental data is complicated by the presence of the volatile plasticiser, and it is impossible to say how much resin is totally, and how much is only partially, decomposed.

The amount of plasticiser present is 17 per cent based on the resin in the paint, and assuming that the quantity of dibutyl phthalate lost is about the same in each case, an estimate of the amount of resin totally decomposed can still be made, but this is not possible for the cross-linked portion. Curves 1 and 2 of Fig. 3 show that, in the presence of zinc oxide, radiation from 385 to 415nm (see Table 1, filter D) causes most of the damage, and that, with anatase titanium dioxide, radiation from 355 to 415nm (filters C and D) causes chalking, as was the case with the paint based on the vinyl acetate/acrylate copolymer.

It is worthwhile pointing out that, whilst anatase titanium dioxide causes less degradation of the vinyl acetate/acrylate copolymer binder than the zinc oxides, the position is reversed with the vinyl acetate polymer binder. That is, it cannot be concluded that, if a pigment causes more or less chalking than another in a given binder, the same relationship will be found for other film formers.

Vinyl chloride/acrylate copolymer (*resin 2*): In this case, only anatase titanium dioxide caused total decomposition of the resin, the rate of decomposition being only about 10 per cent of that with vinyl acetate binder and 20 per cent of that with the vinyl acetate/acrylate copolymer (Fig. 4). The radiation responsible for the decomposition lies mainly in the range 355 to 385nm. The loss of resin by partial oxidation was in all cases only a fraction of that occurring in the vinyl acetate/acrylate copolymer binder.

Experiments at 30 and 95 per cent relative humidity

These experiments showed that the wavelength of the radiation that caused decomposition did not change with the relative humidity, but the rate of decomposition, both total and partial, increased sharply with the rising moisture content of the atmosphere. Fig. 5, 6, and 7 give the experimental results.

Vinyl acetate/acrylate copolymer: The increase in total decomposition of resin leading to chalking of paints pigmented with anatase titanium dioxide and the two zinc oxides is shown in Fig. 5. In all cases there was a sharp increase as the humidity rose, as has already been recorded[6] for anatase titanium dioxide. There was also an acceleration of the cross-linking reaction as the humidity rose. The values for this reaction are those found behind the shield.

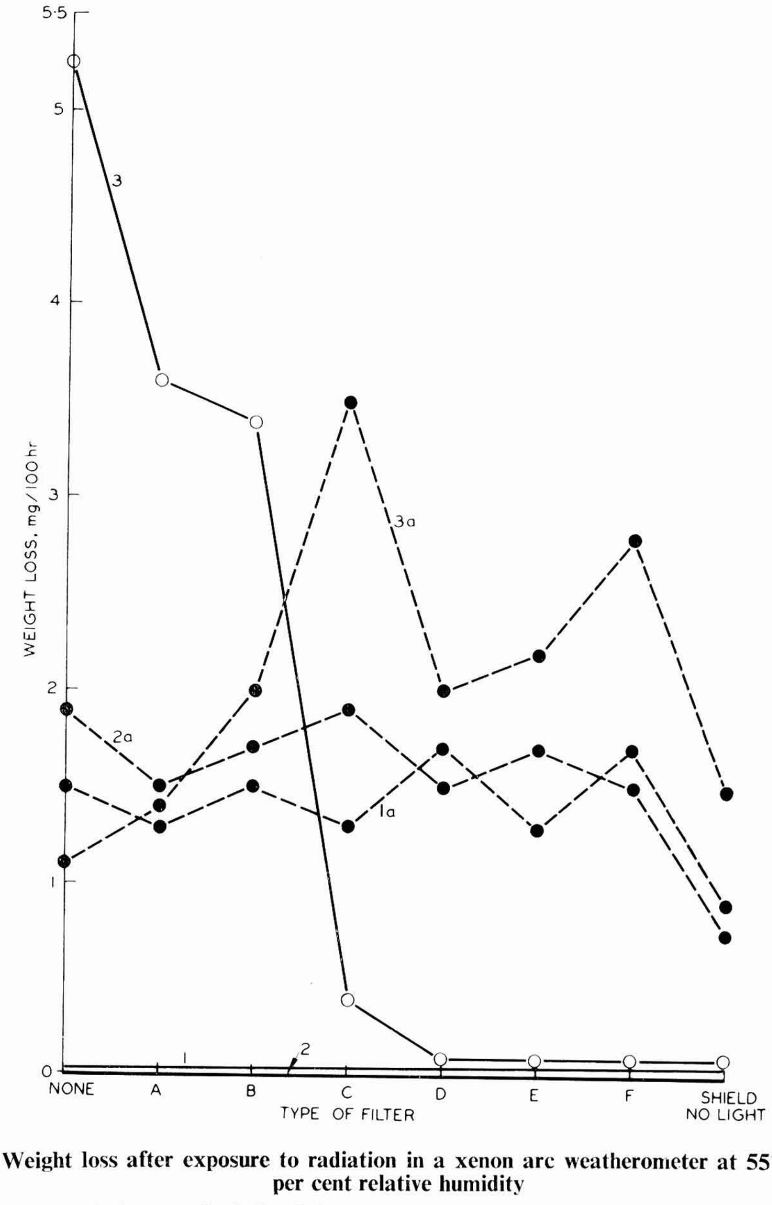


Fig. 4. Weight loss after exposure to radiation in a xenon arc weatherometer at 55°C and 60 per cent relative humidity

Paint formulation—resin 2, PVC 40 per cent,

Pigments—1, 1a, zinc oxide C
2, 2a, zinc oxide A
3, 3a, anatase titanium dioxide

Full lines—totally decomposed resin

Broken lines—weight loss caused by cross-linking

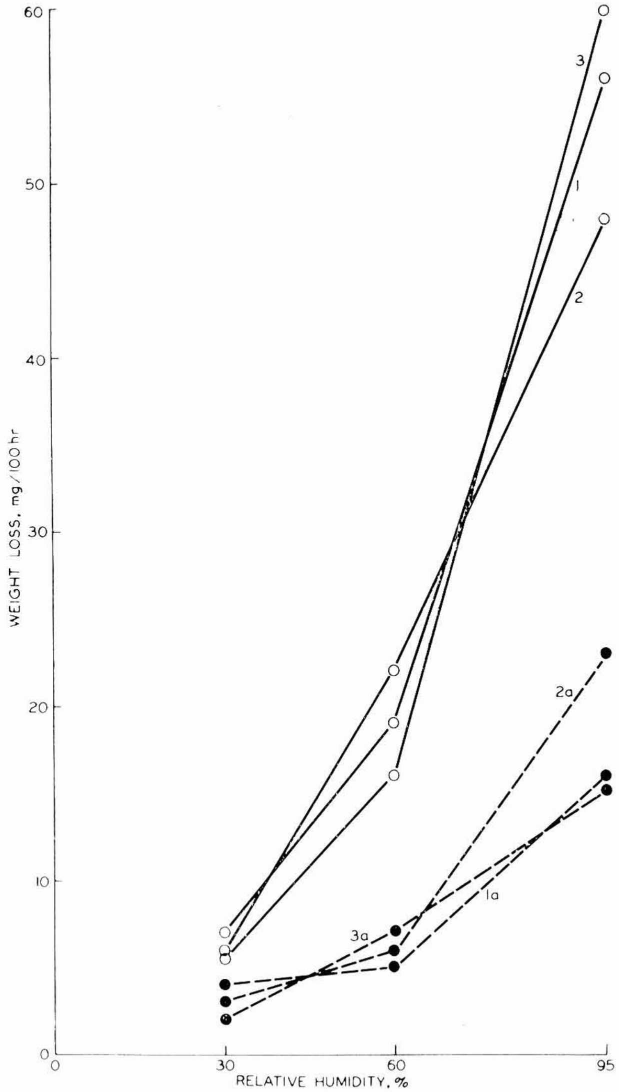


Fig. 5. Weight loss by total decomposition of resin after exposure to radiation in a xenon arc weatherometer at 55°C and various relative humidities

Paint formulation—resin 5, PVC 40 per cent

Pigments—1, 1a, zinc oxide C
2, 2a, zinc oxide A
3, 3a, anatase titanium dioxide

Full lines—totally decomposed resin

Broken lines—weight loss caused by cross-linking

Vinyl acetate polymer plasticised with dibutyl phthalate: Curves 1, 2, and 3 of Fig. 6 show the increase in total decomposition of the resin with humidity.

Vinyl chloride/acrylate copolymer: The zinc oxide pigments did not cause total decomposition of the resin, even at 95 per cent relative humidity, but the decomposition caused by anatase titanium dioxide and the cross-linking reaction caused by these pigments again increased with rising humidity (Fig. 7).

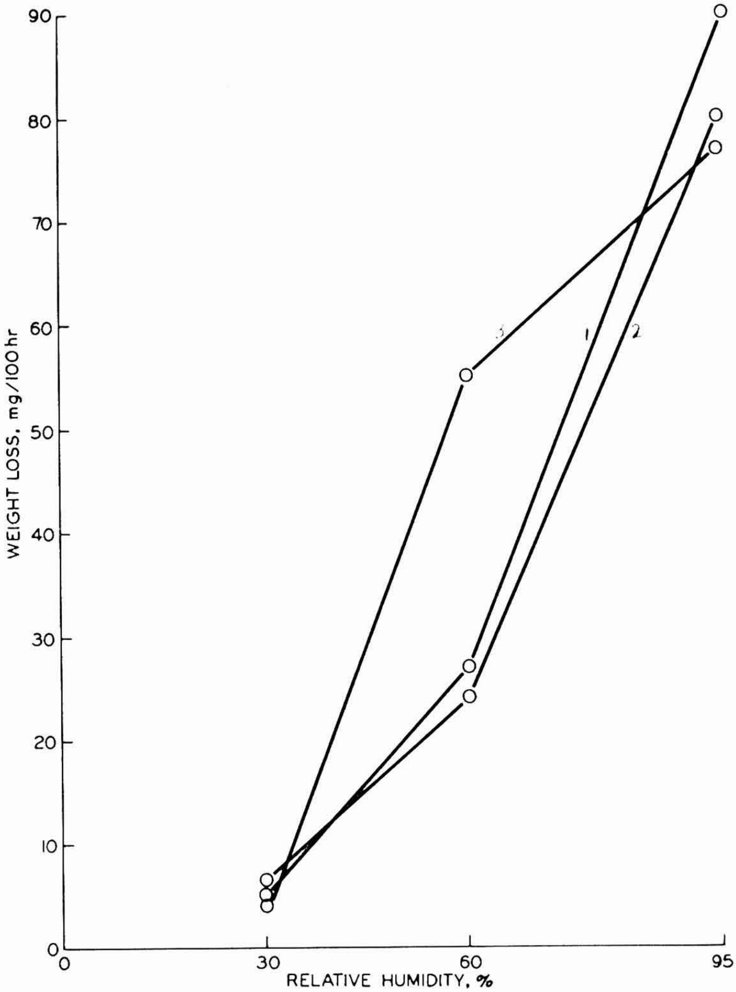


Fig. 6. Weight loss by total decomposition of resin after exposure to radiation in a xenon arc weatherometer at 55°C and various relative humidities

Paint formulation—resin 7, PVC 40 per cent

Pigments—1, zinc oxide C
2, zinc oxide A
3, anatase titanium dioxide

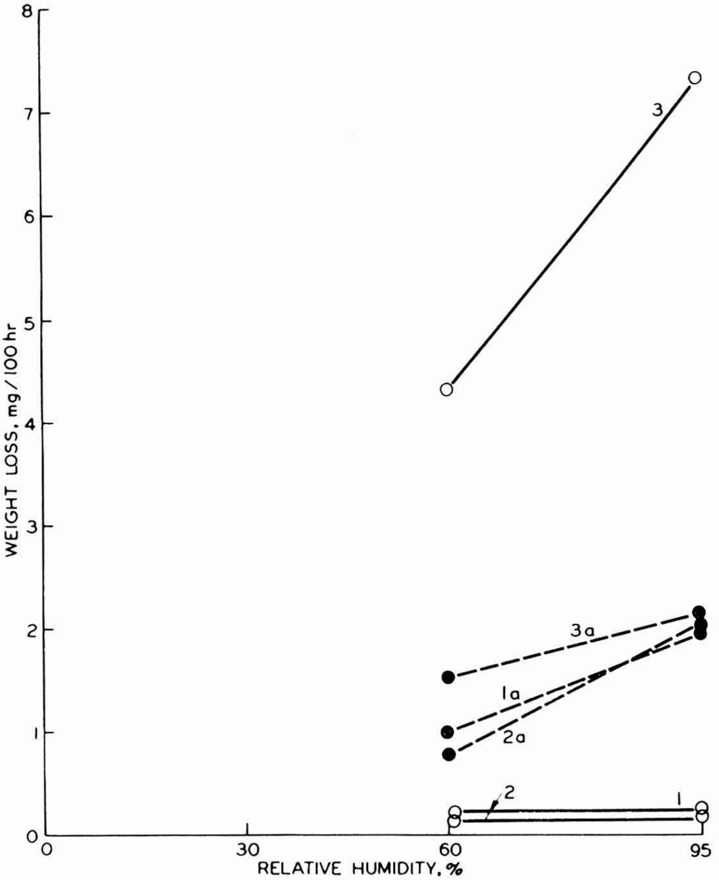


Fig. 7. Weight loss by total decomposition of resin after exposure to radiation in a xenon arc weatherometer at 55 C and various relative humidities

Paint formulation—resin 2, PVC 40 per cent

Pigments—1, 1a, zinc oxide C
2, 2a, zinc oxide A
3, 3a, anatase titanium dioxide

Full line—totally decomposed resin

Broken lines—weight loss caused by cross-linking

Influence of air temperature on chalking

All the experiments described so far were carried out at an air temperature of 55°C, although this temperature is rarely reached at any exposure site. Even at Lae, New Guinea, for example, the temperature rarely exceeds 30°C. It was therefore of importance to establish the influence of air temperature on decomposition of the resin.

To clarify this point, a set of experiments was carried out at an air temperature of 37°C (the lowest that could be obtained with the available equipment) and 60 per cent relative humidity. The results are given in Table 4. As can be seen, the chalking at 37°C is very much less than that at 55°C. The reduction is by no means constant, varying from 21 per cent (resin 6) to 54 per cent (resin 2).

The partial water vapour pressure at 37°C and 60 per cent relative humidity is 28mm Hg, and at 55°C at the same relative humidity it is 71mm Hg. In view of the great influence the partial water vapour pressure has on the rate of chalking it is thought that the observed difference at these two temperatures at the same relative humidity is to a large extent due to the different water vapour pressures under these conditions. This is borne out by the figures in Table 5.

In column C of Table 5 there is a combination of the effects of temperature and vapour pressure differences. If neither had any effect, the ratios shown should not differ from 1. In fact, the mean ratio is significantly lower than 1.

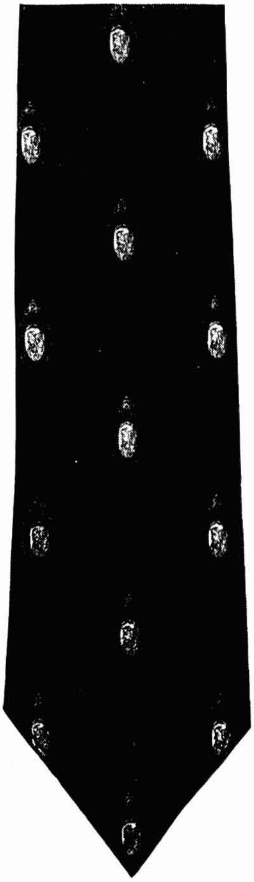
In column D there is only a temperature effect (vapour pressure constant) and the mean ratio cannot be shown to differ from 1, that is, there is therefore no significant temperature effect, in the range studied, at constant vapour pressure.

As the change in the rate of decomposition with temperature is not the same for all paint formulations, the ratings given to two resins will depend on the temperature at which the test is carried out. Ratings of the different formulations in the weatherometer at 37°C and at 55°C are compared (Table 4) with those found on outdoor exposure at Highett, Victoria. With the exception of resin 1, the ratings as found from the weatherometer experiments at 37°C are nearer to those at Highett than those found at 55°C.

More reliable conclusions could be drawn from accelerated weathering experiments if they were carried out at 30°C instead of at 55°C. This reduction in temperature would decrease the rate of acceleration, but this could probably be corrected by increasing the intensity of radiation between 355 and 415nm, the range which has been shown to be responsible for total decomposition of the resin. However, it cannot be taken for granted that such an increase in intensity would not distort the relative rating of the various formulations. It is therefore most important to direct further work towards establishing the connection between the intensity of radiation and chalking.

Reaction mechanism

The following reaction mechanism is suggested by two observations. First, the fact that chalking occurs at all means that, for the decomposition of the binder to occur, contact between the polymer molecule and the pigment is not necessary. If such contact were indispensable the reaction would stop after a layer of molecules sufficiently close to the surface of the pigment had reacted, but this is clearly not the case. Secondly, the decomposition reaction is highly dependent on the partial water vapour concentration in the atmosphere. This makes it likely that water plays some direct role in the reaction, rather than an indirect role such as facilitating the diffusion of oxygen to the reaction site. The reaction $2H_2O + O_2 + 49{,}846$ cal $2H_2O_2$ is one that might occur on



The tie is blue terylene, with the Association's insignia woven in red and gold silk.

The blazer badge has the insignia embroidered in silver and gold wire on a red and blue ground.

The plaque has the insignia hand-painted in red and gold on a blue ground.

The car badge has the insignia embossed in red and gold on a blue ground, the whole being covered in transparent polypropylene, with a thick chrome surround. Bar and grille fittings are available.

Council has authorised the production of a tie, blazer badge, wall plaque and car badge bearing the Association's insignia. These items are available only from:—

THRESHER & GLENNY

Lancaster Place, Strand,
London, W.C.2.

To: Thresher & Glenny Ltd., Lancaster Place, Strand, London, W.C.2.
As a member of the Association, please accept my order for the following:

......OCCA tie	£1.33	....	
......OCCA blazer badge	£3.75	....	
......OCCA wall plaque	£2.20	....	
......OCCA car badge (state bar or grille)	£2.20	....	
(All prices include postage and packing)		______	
If tie is required airmail add 33p		______	
Total Remitted		______	

Name ....

Section/No. ....

Address ....

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The ties will be supplied from stock; all other items are made to order. Only the tie can be supplied by airmail at an extra cost of 33p.

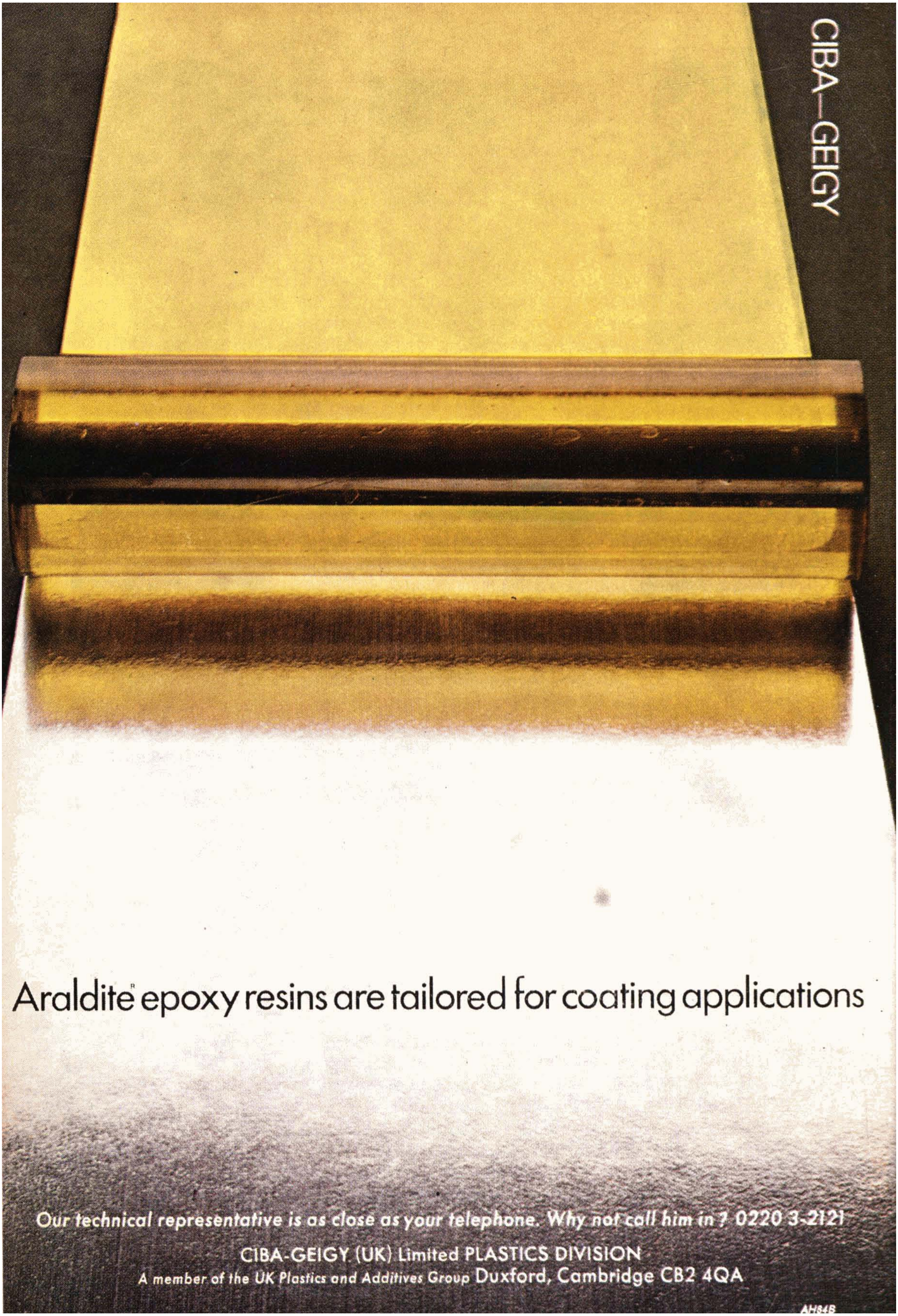

Table 4

Chalking caused by anatase titanium dioxide

Pigment volume concentration 40 per cent. Exposure in xenon arc weatherometer at 37°C and 55°C at 60 per cent RH, and outdoors at Highett, Victoria

Resin used	Rate of chalking at 37°C (Weight loss mg/133h)	Rate of chalking at 55°C (Weight loss mg/133 h*)	Relative rate of chalking at 37°C referred to resin 7	Relative rate of chalking outdoors at Highett, Victoria† referred to resin 7	Relative rate of chalking at 55°C referred to resin 7
1. Tetrapolymer	21	49	0.32	0.24	0.29
2. Vinyl chloride/acrylate copolymer	20	37	0.32	0.34	0.22
3. Vinyl acetate fumurate copolymer	38	130	0.58	0.52	0.77
4. Vinyl acetate/acrylate copolymer with silicone	30	78	0.46	0.43	0.46
5. Vinyl acetate/acrylate copolymer	32	141	0.49	0.61	0.83
6. Acrylate copolymer	26	118	0.40	0.53	0.70
7. Vinyl acetate polymer with dibutyl phthalate	65	169	1	1	1

*From Fig. 1 of Reference 6

†From Table 3 of Reference 6

Table 5

Comparison of the weight losses at 37°C and 55°C of a paint film at 28mm Hg partial water vapour pressure

Film pigmented with anatase titanium dioxide at 40 per cent PVC

Exposure in xenon arc weatherometer without filters

Resin used	(A) Weight loss at 37°C and 60 per cent RH* (mg/133 h)	(B) Weight loss at 55°C and 24 per cent RH† (mg/133 h)	(C) Ratio of weight losses at 37°C and 55°C, at 60 per cent RH‡	(D) Ratio of weight losses at 37°C and 55°C, at 28mm Hg water vapour pressure ((A)/(B))
1. Tetrapolymer	21	10	0.43	2.1
2. Vinyl chloride/acrylate copolymer	20	18	0.54	1.1
3. Vinyl acetate/fumurate copolymer	38	40	0.29	0.95
4. Vinyl acetate/acrylate copolymer with silicone	30	44	0.38	0.68
5. Vinyl acetate/acrylate copolymer	32	42	0.23	0.76
6. Acrylate copolymer	26	46	0.22	0.57
7. Vinyl acetate polymer with dibutyl phthalate	65	48	0.38	1.35

*From Table 4

†Derived from Fig. 1, Reference 6

‡Derived from Table 4

the surface of the pigment, the energy necessary for this being supplied by the radiation. The upper limit of the wavelength of light which causes decomposition is 4150 Å, and N quanta (N = Avogadro's number) of this radiation is equivalent to 67,600 calories, which is sufficient for the reaction to proceed. With the above equation, it might be expected that the rate of decomposition would rise with increase in water vapour pressure, and this is what is observed.

It has been claimed that evidence of decomposition of the binder at a certain distance from the pigment particles has been seen in electron microscope photographs of weathered paint films[8], and this has been ascribed to an unknown, fast moving, molecular species.

The cross-linking reaction also increases as the water vapour concentration rises, and a similar mechanism could operate here. However, in this case, the process also occurs in the dark, and the necessary energy for the formation of hydrogen peroxide could not arise from radiation. In postulating the following mechanism, it is stressed that it is a speculation which is, nevertheless, worthy of consideration.

A thermally excited binder molecule can react with oxygen, and the reaction proceeds with evolution of heat. Direct attack by oxygen on the polymer molecule may occur in only a comparatively few cases when a special excitation exists. If water molecules are also present, part of the heat of reaction could be used for supplying the energy to the reaction $2H_2O + O_2 = 2H_2O_2$. The hydrogen peroxide would then be able to react with a greater range of binder molecules than would oxygen.

Conclusions

The wavelength band of radiation causing total decomposition leading to chalking in a paint film depends on the pigment used. With zinc oxide the band responsible is between 385 and 415nm, and with anatase titanium dioxide the band is between 355 and 415nm.

The three types of resin used as binders in this investigation did not have any influence on the wavelengths of radiation causing decomposition.

Paint films lose weight if they are shielded from radiation, and this has been interpreted as partial oxidation leading to cross-linking. If this view is correct, the loss of weight may correlate with decrease in elasticity, and strain/stress measurements could be replaced, under appropriate circumstances, by a simple determination of weight loss.

Total decomposition and cross-linking of the resin both increase sharply with humidity.

The rate of chalking of paint films in the weatherometer at 60 per cent relative humidity is much lower at 37°C than at 55°C.

A reaction mechanism in which formation of hydrogen peroxide plays an important role has been postulated to explain the observed phenomena.

[*Received 15 October 1970*

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Next month's issue

The Honorary Editor has accepted the following papers for publication, and these are expected to appear in the June issue:

"On the adhesion of laminated films to substrates" *by P. M. Heertjes and J. de Jong.*

"The adsorption of alkyd resins by titanium dioxide pigments and its relation to the hiding power of alkyd systems" *by K. Goldsbrough and J. Peacock.*

"Water transport through paint films. Part III Correlation of data obtained by differences in water vapour pressure and osmotic pressure" *by D. Y. Perera and P. M. Heertjes.*

"Rheology and printing properties" *by C. O. Rosted.*

Reviews

VISCOELASTIC PROPERTIES OF POLYMERS

By J. D. FERRY. New York: John Wiley & Sons, Inc. 2nd Edition, 1970. pp. xxi + 671. Price £14.05

The first edition of this book became a standard work nearly ten years ago. With the developments that have taken place since then and Professor Ferry's deep understanding and facile presentation of them, the second edition can hardly fail to succeed it worthily.

Chapters have been added on dilute solutions and on cross-linked polymers, both topics which, as the author says, are now much more susceptible to treatment in terms of molecular theories. The general approach is still mathematical rather than descriptive but, whilst the profusion of equations and bald presentations in the shorthand of mathematical physics may strike terror in the hearts of mere chemists, a careful reading indicates that little is needed for understanding beyond a good working knowledge of calculus and some familiarity with matrix notation. If chemists and technologists allow their appreciation of such matters to be deficient, Heaven help them these days, for modern science will not wait upon their idleness or their inertia.

Chapters 1 and 2 deal adequately with the general features of viscoelastic properties, and the next two treat the phenomenological theory of linear behaviour in both the exact and approximate (or practical) sense. Useful approximations, with examples of the relevant calculations, appear in Chapter 4, whilst Chapters 5-8 deal with the experimental methods applicable to the different classes of materials.

Chapters 9 and 10, on dilute and concentrated solutions, with particular reference to molecular theories, are models of excellence, having regard to the deficiencies of knowledge in the present state of the art.

There follow discussions of the effect of temperature and pressure on viscoelastic properties, the rubber/glass transition, the behaviour of cross-linked and filled polymers, the glassy state, crystalline polymers, concentrated solutions, plasticised polymers and gels. Finally the author presents an appreciation of bulk deformation and an outline of the applications of the whole theory of viscoelastic behaviour to practical problems. For our readers, unfortunately, this contains little of direct relevance, but he will be short-sighted who cannot extrapolate the conclusions to the coatings industry.

As an indication of the complexity of the subject, it may be noted that, in terms of sheer symbolism alone, a has six meanings, D has nine, G has 10, M has 11, and τ_i has 12. Such is one of the problems facing those determined to follow the march of scientific progress.

The index had either to be short, as it is at $4\frac{1}{2}$ pages, or to occupy some 40 pages. We would not presume to contest the author's choice.

Altogether an admirable volume and a "must" for the bookshelves of all concerned with the practical behaviour of polymer systems despite its ruinously high price.

A. R. H. TAWN

CHEMISTRY AND PHYSICS OF CARBON, VOLUME 5

Edited by P. L. WALKER, JR. New York: Marcel Dekker, Inc., 1969. pages xii + 388. Price £10.80

This book is the fifth in a series concerned with recent advances in carbon research and development, and contains four comprehensive reviews by leading workers in the field. The first is on pyrolytic carbon, while the remainder are concerned with graphite.

J. C. Bokros (Gulf General Atomic Inc., San Diego) in his chapter entitled "Deposition, structure and properties of pyrolytic carbon" (118 pages) gives a balanced and well illustrated account of the structure and properties of carbon coatings for nuclear fuel particles, and includes, for reference purposes, results for carbons deposited on large formers and dispersed carbons. The emphasis is placed on the relation between the structure and the process conditions, and between structure and properties (mechanical, thermal, irradiation induced and impurity diffusion) of pyrolytic carbon. This is not a comprehensive review of all facets of these widely used carbons.

In the second chapter, B. T. Kelly (UKAEA, Culcheth) reviews the "Thermal conductivity of graphite" (96 pages), and considers the highly oriented graphites including natural graphites, pyrolytic graphites, and whiskers or filaments, and measurements on commercial polycrystalline materials. An excellent account is given of the theory of the conductivity of a perfect graphite crystal and the effects of crystal boundary scattering, isotope scattering, phonon-phonon scattering and electron-phonon scattering. The imperfect graphite crystal is discussed, and detailed comparisons between theory and experiment are presented. It seems that the theory of thermal conductivity of graphite is well established although there still remains much work to be done.

The third chapter, on the "Study of defects in graphite by transmission electron microscopy" (98 pages), is by P. A. Thrower, of UKAEA Harwell, and demonstrates the potential of the electron microscope in the study of defects in solids. An enormous amount of such work has been done, and the recent studies of two point defects—vacancy and interstitial—in graphite and their interaction, is reviewed. The emphasis is on defects caused by neutron damage, and also by intercalation with halogens, by the introduction of boron and by quenching from high temperatures. The chapter is adequately illustrated with electron micrographs.

In the final chapter, J. C. Hooley (University of British Columbia) discusses the "Intercalation isotherms on natural and pyrolytic graphite" (49 pages). Many substances readily penetrate interstitially between the basal planes of graphite, and this property may be used as a measure of crystallinity. Data for the halogens (bromine in particular), chromyl and other metal chlorides, various metals, and nitric acid, are discussed, together with some thoughts on the theoretical aspects.

The high standard set in the previous volumes in this series is maintained in the present book, and it is a worthwhile addition to the literature on carbon.

G. D. PARFITT

Hull Section

Some aspects of paint formulation

A students' evening was held at the Queens Hotel, Hull on 21 January with Mr F. D. Robinson in the chair. Mr B. J. Howells, who was to have given a talk on the above subject, was indisposed and his place was taken by his colleague, Mr T. W. Wilkinson of Laporte Industries Limited.

In the first part of his lecture Mr Wilkinson summarised early formulations in which pigment loadings were described in oz or lb per gallon of paint, developing to pigment/binder by weight descriptions. The value of formulation description by pigment volume concentration was illustrated by means of slides depicting the variation of film properties, e.g. hiding power, gloss, blistering, permeability, with PVC, and the concept of critical volume concentration was introduced.

In the second part of his lecture, Mr Wilkinson illustrated the systematic approach to paint formulation, taking as his example an exercise in the selection of extender for an emulsion paint. Slides recording the influence of various synthetic and naturally occurring extenders on significant properties, e.g. cost, colour and opacity, were shown.

A short discussion period followed, after which Mr Robinson thanked the speaker for his interesting and informative talk.

This lecture had been given previously to another section and a fuller account of it is given in an earlier issue of this *Journal* (1970, **54,** 106).

J.A.H.

Choosing coloured pigments

The second student evening of the present session was held at the Queens Hotel, Hull on 18 March and took the form of a talk entitled "Choosing coloured pigments." This was given by Mr P. Adamson of Reckitts Colours, who described test methods used in his own laboratory for the evaluation of pigment properties, relating these to the requirements of the paint or plastic in which the pigment would be used.

Mr Adamson stressed that light fastness was very dependent on the depth of shade and indicated that it was important to assess this property at a number of colour strengths, for example, mass tone and 1/3rd, 1/25th, and 1/200th standard depth. Standard cloths were exposed simultaneously with the test specimens to daylight or to ultra-violet light in a fadeometer. These cloths faded at rates in the ratio 1:2:4 . . . etc and the test was discontinued when the colour change on cloth no. 7 corresponded to four on the grey scale; the latter comprised a series of grey chips whose upper and lower halves defined a standard difference in luminous or reflectance value. The light fastness of the test specimen was then described in terms of the appropriate numbered cloth.

In the evaluation of the weather resistance of coloured pigments in paint films, the internal cloth reference scale was not employed. Colour differences were reported on the grey scale after exposure for 6, 12 and 24 months.

The heat resistance of pigments was assessed from the behaviour of paint films under a variety of stoving conditions ranging from 45 minutes at 80°C to ten minutes at 180°C. A non-yellowing alkyd amino binder was commonly employed and differences in shade between panels stoved at 80°C and at other temperatures were referred to the grey scale.

Test methods for the measurement of resistance to bleed on overspraying, and to solvents, plasticisers and reagents were also briefly described, and Mr Adamson concluded his talk with an account of the preparation and properties of ultramarine blue.

A discussion followed in which many of the students took part and a vote of thanks to the speaker was proposed by Mr F. D. Robinson.

J.A.H.

Manchester Section

The use of carbon black in paints, plastics and printing inks

The third meeting for student members of the section was held in the Manchester Literary and Philosophical Society's rooms on Wednesday 13 January 1971. The meeting was attended by 40 students and guests, with Mr F. Redman (who deputised for Mr Mitchell) in the chair. Mr B. E. Thomas of Columbian International spoke on "The use of carbon black in paints, plastics and printing inks."

Mr Thomas began by saying that the main use of carbon black was in the rubber industry, but that this talk would be mainly about its use as a colour. He pointed out that about 260 different shades of black could be observed, starting with high intensity blacks, going through medium to the coarse blue grade blacks mainly used for tinting.

Carrying on from here he said that the oldest reference to carbon black was believed to have been found in China, and the first modern impingement or channel black was produced in the United States of America, a patent being granted for the production of carbon black by the Rhoda process in 1878. The 1920s saw the first furnace blacks and in the 1940s the first oil blacks were produced by the furnace process.

Starting with the channel process, Mr Thomas outlined the various methods of producing carbon blacks, and indicated how the characteristic properties of the various blacks could be related to their method of manufacture.

He explained, for instance, that in the channel process an electrostatic charge was produced on the particles of carbon formed inside the flame, and therefore these particles repelled each other. Thus the carbon black produced had a high surface area with chemically absorbed oxygen on its surface. This gave easy wetting properties to the black, but the high surface area limited the possible pigmentation levels.

Passing on to the lamp black process, he described how the particles were formed outside the flame. These particles were coarse with very little chemically absorbed oxygen and no charge. Blacks produced by the furnace process had been improve by modernisation of the process, thus, by controlling temperature, electrical charge, oxygen, and using atomised oil sprays and horizontal or vertical furnaces, the properties of the furnace blacks could be carefully controlled.

Mr Thomas developed his lecture by explaining the importance of different properties of the various carbon blacks in relation to their end use. How tinting strength was mainly dependent on particle size, surface chemistry on the absorbed chemicals, and structure on the degree of agglomeration which directly affected viscosity. He pointed out that in many cases the property requirements conflicted with each other, making the preparation and selection of a satisfactory product difficult.

Outlining various outlets for carbon black, Mr Thomas started with news-inks. For these he said cheap, good wetting blacks with rapid dispersion were required, problems encountered and overcome being rub-off and strike-through.

In web offset, where good intense black images were essential, and good flow, excellent dispersion, and a high pigment loading were also required, post-treated furnace blacks were used.

In the gravure field, where a black with good cover was required because of the low viscosity of these inks which limited the level of pigmentation, post-treated furnace blacks were used.

In paint, fine channel blacks were used for automobile finishes, low cost furnace blacks for chassis blacks, marine paints, and drum finishes. For thermoplastic and thermosetting acrylic finishes, specially surface treated channel blacks had been developed. He did mention that there was as yet no answer to the age old problem of flotation in carbon blacks.

Carbon black was important in plastics because of its high UV absorption, its incorporation giving a tremendous improvement in the stability of plastics. He also pointed out that carbon black gave a different colour in different plastics due to variations in dispersibility and also that its use for colouring cold water piping was controlled in the British Specification due to the presence of benzyprene in the carbon black.

Mr Thomas rounded off the lecture by commenting on the future of channel black production in the USA.

After a lively question time a vote of thanks was proposed by Mr Davies and carried with acclamation.

R.W.

Information Received

(In case of difficulty regarding addresses, members and subscribers to the JOURNAL *should apply for details to Director & Secretary of the Association at the address shown on the front cover.)*

Tintometer Sales Limited has recently announced that it has been appointed sole distributor of the products of **Munsell Color Company Inc.** As well as the "Munsell book of color," Tintometer is handling the other *Munsell* products, including colour charts and sample clips, and has available a catalogue and price list.

It has recently been announced that **Cabot Carbon Limited** has moved its sales office from Croydon to the plant facilities at Stanlow, Cheshire. The object of this move is stated to be to achieve the closest possible integration of all functions of the company.

A new company, **Russell pH Limited,** has recently been formed to manufacture pH electrodes designed to operate with all the well known pH meters of British, Continental or American design. On receipt of the make, design, and model number of pH meter, Russell pH will supply electrodes with the appropriate E point and terminations, thus eliminating the need for major adjustments to the meter or special adaptors. A catalogue, showing the wide range of applications catered for, and price list are available from Russell pH.

An agreement has been reached between **British Oxygen Chemicals Limited** and **Vinyl Products Limited** by which Vinyl Products will manufacture and market BOC's *Vandike* and *Vanweld* polymer emulsions. Marketing of the emulsions by Vinyl Products commenced from 1 March, and the manufacture will be transferred by the end of 1971. BOC says that the discontinuation of the *Vandike* and *Vanweld* range is in order that more effort can be devoted to the highly specialised range of *Vantac* pressure-sensitive emulsions, polyvinyl pyrolidone and other high pressure acetylene chemicals, melamine, dicyandiamide, and tall oil products.

The Organics and Pigments Division of **Laporte Industries Limited** has recently appointed **Aceto Chemical Co. Inc.,** of New York, as exclusive distributors in the eastern US for the marketing of Laporte chloride process titanium dioxide pigments.

A new range of lead-free masonry finishes has been launched by **Goodlass Wall.** It is claimed that *GW masonry coating* is the best on the market by virtue of its high dirt resistance and low dirt retentions, its colour fastness, alkali resistance, and mould retardence. Based on Shell *VeoVa* resin, *GW masonry coating* is available in 11 colours.

Molteni Off Mech., the Milan-based machinery manufacturer, has recently announced the availability of a 150hp disperser with hydraulic drive. Designed for manufacturers faced with the necessity of larger production units, these machines are installed on overhead concrete platforms, and operate simultaneously on two vessels of up to 2,000 litre total capacity, mounted at 120° to each other. The vessels are mounted on wheeled tracks so that they can rotate, and the rotary motion is imparted by a hydraulic drive on one of the supporting wheels. The machine head is fitted with shafts with two impellers, one at the container bottom and one midway up, and with a nylon-bladed scraper for the vessel walls, and is raised hydraulically by means of a gear pump with a 5½hp motor. The hydraulic motor on the machine head is driven by a power pack, with a pump of suitable capacity; overall control is accomplished with a central console.

Full details are available from Molteni's UK, Commonwealth and Eire agents, **G. J. Erlich Limited.**

A new product from **Harmon Colours Inc.,** *Indofast Brilliant Scarlet R-6335*, a perylene red to Pigment Red 123, is now available from **Allied Chemical International.**

Adcola Products Ltd. has recently introduced a new portable pyrometer for measuring the temperature of liquids. Measuring 7.5in in length and weighing 6.5oz, models are available with ranges from 100-500°C or 100-800°C.

A booklet supplying abstracts of over 60 patents dealing with electron beam curing has been published by **R. H. Chandler Ltd.** Copies can be supplied by the publishers at a price of £1.00 post free.

Thiokol Chemicals Limited has recently issued a "Technical Service Report" on the use of chlorinated paraffins as plasticisers in polysulphide sealants. From a preliminary investigation using the compatibility of the plasticisers with polysulphide liquid polymers and volatility characteristics as criteria, the majority of commercial chlorinated paraffins were found suitable for further evaluation. The lower chlorine content plasticisers were found to have limited compatibility, and hence were unsuitable. The others were fully evaluated in a typical sealant compound, and several grades were found to impart properties which can be valuable for good sealant performance. Copies of the report are available from Thiokol.

The availability of *Nordel* hydrocarbon rubber in the UK has been announced by the **Du Pont Company (UK) Ltd.** A terpolymer of ethylene, propylene and a non-conjugated diene, *Nordel's* processing characteristics can be varied widely by varying the ratios of monomers. Seven types are currently available, and details can be obtained from Du Pont.

"Bakelite resins for surface coatings: types and uses" is the title of a leaflet issued by **Bakelite Xylonite Limited** giving suggested formulations for various types of coating. Copies of the leaflet are available from BXL.

A new publication on *Snowcal* whiting, a naturally produced ground calcium carbonate filler and extender, is now available from the **Cement Marketing Company Ltd.** The booklet is entitled the "Blue Circle *Snowcal* whiting manual."

Berger, Jenson and Nicholson Limited has recently announced the formation of **British Paints and Chemicals,** a sister division of **Berger-Hall Paints,** the division formed earlier this year.

The new division will be the headquarters of the marine, special coatings and elastomers business of the company, and of the **Resinous Chemicals** division.

A new range of *Universal Stainers* has been introduced by **Hadfields (Merton) Ltd.** Sold in transparent plastic tubes, the stainers can be mixed with most decorative paints to produce a lasting effect in many shades.

Of the 12 colours available, seven are prefixed "permanent," and can be used to obtain clear pastel shades free from any muddy tone. The remaining five shades can be used to mute subtly the cleaner shades, or to produce neutral shades.

The **Tin Research Institute** has issued a new booklet entitled "In every sphere." A 36-page booklet in full colour, the publication gives full details of the Institute and its activities.

A range of resins for integral skin polyurethene foams has been introduced by **Cray Valley Products Limited.** A series of polyester polyols, the new systems produce in one operation polyurethene foams with a sandwich-like structure, having a hard, smooth, skin and a rigid foam interior. Initially, two systems are being marketed, based on *Synolac 300* and *Synolac 3001* with *Synocure 3009*.

CVP has also issued the "CVP resin finder for 1971," giving full details of all its resins.

Manchester

The present and future trends in motor car finishing

Sixty-seven members and guests met on Friday 12 February under the chairmanship of Mr S. Duckworth, to hear Mr H. L. Quick of Chrysler (UK) Ltd. discuss "The present and future trends in motor car finishing."

The production capacity of the UK motor industry was about 2,000,000 cars per annum, and the painting process consumed about five gallons per vehicle. The finishing process was in three stages: pretreatment and priming, surface preparation, and colour coat application. Mr Quick traced historical development of pretreatment and priming from phosphating in about 1910, through rotodipping in the fifties, to electrocoating in the last three years. The development of finishing coats was traced from the original nitrocellulose, through baking alkyds, to acrylics. Metallics were now widespread, but Mr Quick considered that early failures, caused when the styling demanding them was ahead of the technology formulating them, had considerably delayed their eventual introduction.

Future finishing methods would be influenced by legislation, particularly concerned with safety and with the environment, e.g. solvents evaporated during application were both effluent and pollutant. It would be necessary to increase the corrosion protection offered by the finish; winter usage of salt on roads had increased (1.6M tons in 1970) to a similar level to that of Detroit, when expressed in terms of weight/mile. This extra protection would require better primers and finishes of improved adhesion. Constructional methods were unlikely to change in five years and fillers would still be needed, but re-flow would probably improve ease of application.

Colour coats were likely to become predominantly metallic, with extremely bright colours, and there were possibilities that coloured base coats would be used with clear top coats, combining high opacity and very high gloss together with extra protection. Presently there was a durability gap between factory finish and refinish systems, and this would have to be bridged.

Mr Quick found difficulty in predicting the longer term future but guessed that plastic bodies, now just around the corner, would still be there in ten years' time.

Following a lengthy and interesting discussion, the vote of thanks was proposed by Mr N. Seymour.

D.A.P.

Midlands

Pigment/vehicle interactions

A meeting of the Midlands Section was held on Friday 15 January 1971, when 54 members and guests were present, under the chairmanship of Mr H. J. Griffiths, the Section Chairman, to hear lectures by Dr Apel and Dr Jettmar of BASF. The venue was the Winston Restaurant, Birmingham, and the talks were preceded by a dinner which was an excellent sample of traditional English fare.

Both lecturers opened their addresses with amusing anecdotes and made what proved to be quite unnecessary apologies for their command of the English language. The meeting was pleased, on behalf of OCCA, to receive compliments on the organisation, particularly with respect to the *Journal* and the Exhibition.

Dr Apel spoke first on the subject of the nature of the surfaces of phthalocyanine pigments. He discussed the relevance of various physical measurements used to characterise the nature and area of pigment surfaces and considered that adsorptive power was the most singularly useful. To test the practical situation, the relevant resin/solvent system was used, but gas adsorption provided basic data. Specific adsorptions were measured for each pigment with respect to gaseous nitrogen, water, methanol, acetone and pentane. It was noted that the non-flocculating types of phthalocyanine blues tended to be distinguished by giving similar results with both nitrogen and water. The property of non-flocculation was thus related to a polar, hydrophilic surface.

It was postulated that polar pigments selectively adsorbed polar or low molecular weight fractions of the binder. Non-polar species tended to adsorb high molecular weight polymer in relatively high quantities, leading to viscous, immobile areas in the matrix.

Photographic evidence on this subject was provided by Dr Jettmar. Optical microscopes detected flocculation but magnification was too low to study individual particles. Electron microscopes were only useful on solid samples, and dried paints and inks had undergone compaction and did not reveal the processes leading to final structure.

Dr Jettmar and his colleagues had developed a system whereby the dried films were swollen in a mixture of butyl and methyl methacrylates, the swollen sample was ultramicrotomed to below 1,000A thickness and the sections were examined under the electron microscope. The optical microscope indicated that such sections were representative of the wet films from which the dry films were obtained. The methacrylates depolymerised in the electron beam, leaving light areas where swelling was greatest, believed to indicate areas of low molecular weight polar polymer.

It was observed that titanium dioxide particles were well dispersed and surrounded by heavily swollen areas. Alpha copper phthalocyanine appeared in lightly swollen diffuse areas, indicating combination with part of the binder to form flocculates of high viscosity; this process immobilised quite high proportions of binder. The more polar beta copper phthalocyanine tended to locate in or at the periphery of the more swollen areas, which were believed to be the paths of escaping solvent.

Excellent photographs and a magnificent short cine film of Benard cells were shown. It was indicated that polar pigments tended to follow the flow paths emerging from cell centres and flowing across the surface. Non-polar pigment in viscous pigment-binder flocculates located in the calm non-mobile zones and eventually disappeared from the surface altogether. Daniel's method of preventing this separation by co-flocculation was referred to.

A summary of the desirable factors was stated to be narrow binder molecular weight distribution, high pigment/binder interactions, sufficient energy input and time for maximum wetting and design for co-flocculation. A longer and well-illustrated account of the microscopic examination was published in *J. Pt. Tech.*, October 1969, pp. 559-566.

A lively discussion took place and the meeting closed with a vote of thanks proposed by Mr H. J. Clarke who referred to a feast of information but admitted to an attack of technical indigestion, a problem shared by many of the audience.

R.J.K.

Developments in automobile finishing

A meeting of the Midlands Section was held at the Birmingham Chamber of Commerce on Friday 19 February 1971 with Mr F. Cooper, the Association Hon. Treasurer, in the chair and in the presence of 37 members and guests. Mr H. L. Quick of Chrysler

(UK) gave a talk entitled "Developments in automobile finishing." His lecture was basically the same as delivered to the Manchester Section earlier in February which is reported elsewhere in this *Journal*.

R.J.K.

Trent Valley Branch

The future of water-thinnable coatings

A meeting of the Trent Valley Branch was held on Thursday 21 January, at the British Rail School of Transport, Derby, with 35 members and guests present. Mr P. D. Hare, in the chair, introduced Mr A. J. Becalick of Lennig Chemicals Ltd., who gave a talk on the above-mentioned topic.

Mr Becalick indicated that quite a considerable amount of time had already been spent on experimenting with the use of water as a reducing solvent, and it was apparent that the use of water based finishes was very much on the increase. The main reasons could be summarised quite briefly as: no toxicity and no fire hazards.

On the other hand, due to somewhat complicated chemistry, the production cost was relatively high (resin costs, for instance, would be increased). The end user must, therefore, be prepared to pay more for a water-based paint, but in return would obtain very marked advantages such as ease of application, quick drying, good storage properties (no skinning, etc.). In the UK, however, it had been found that on occasions the drying time had been impaired because of water vapour present in the atmosphere.

Mr Becalick then referred to the development work in the field of water thinnables that had taken place in the USA. For instance, a coarse particle size acrylic emulsion had been developed for exterior use. This gave good adhesion on previously painted surfaces. Propylene glycol was preferred to ethylene glycol as the coalescing agent.

The present market for water-based emulsions in the States was approximately 25,000 tons per annum. This covered both interior and exterior use, and it was obvious that alkyds were being replaced by emulsion finishes.

Similar types to those mentioned above had been available in the UK for the past three years, but so far had not proved very popular. The main reasons for this were probably that a very high gloss and quick drying finish were demanded in this country and the humidity level was generally higher than in the USA. It was mentioned that the American product incorporated a wet edge retention aid, therefore poorer drying characteristics could be expected.

The future of water-based paints in the decorative field appeared to be very good, and it was expected that 30-40 per cent more of this type than the conventional alkyd paint would be manufactured in the future.

One particular property of a water-based finish was of outstanding importance, namely: that of ease of application over conventional paints. The higher cost of the finish was adequately compensated for by quick application. There was also a lack of "paint" odour. Generally speaking, it was expected that this type would give a better performance than a normal alkyd.

Mr Becalick went on to mention briefly the use of water-based paints in industrial finishes, where such factors as air pollution and fire hazard were more important.

There seemed to be little doubt that industry would ultimately settle for this type of finish for such uses as coil coating paints, wood coatings (primers for window frames, etc.), metal coating, etc. The acrylic emulsion primers, for instance, gave good weathering properties, and would thus be particularly suitable for outside work, whilst thermoplastic acrylic emulsions, already very popular in the USA, were eminently suitable for coil coating, etc.

Mr Becalick was firmly convinced that there was a very definite future for water-thinnable coatings in this country, but it was now up to the marketing organisations to sell the idea to both the public and industry.

The lecture was illustrated by a series of slides and a very lively discussion period wound up the evening.

A vote of thanks was proposed by Mr J. Burns for a very interesting and informative talk.

D.F.G.

Newcastle

Flooring compositions

The fifth meeting of the Newcastle Section in the current Session was held in the Royal Turks Head Hotel, Newcastle upon Tyne, on Thursday 4 February 1971, when Mr A. Jolly and Mr Rooney of Synthetic Resins Ltd. presented a paper entitled "Flooring compositions."

Mr Jolly began by discussing the use of polyester systems in seamless flooring. Polyesters were easy to apply, possessed excellent wear resistance, had good acid resistance, low viscosity, good workability and could be internally flexibilised. The disadvantages were the odour of styrene and their poor performance under damp conditions, particularly rising damp. These systems were ideally suited for applications where a rapid turn-round was required and where there was no rising damp.

He then turned to polyurethane systems for flooring. One-pack moisture cured polyurethanes were usually employed. They had the advantages of good hardness, flexibility and chemical resistance and could be used over a wide range of application temperatures. They also had the advantage over polyesters in that they adhered well to slightly damp substrates. They had the disadvantage of poor odour and bubbling due to the evolution of the CO_2 during the moisture cure reaction.

Mr Rooney then discussed the preparation and use of epoxy resin based systems. He discussed the various epoxy flooring compositions, including floor paints, self-levelling compositions, trowelling compositions and terrazzo flooring, outlining the epoxy and curing agent systems used for the varying compositions together with their properties and performance.

Mr Jolly then concluded by summarising the various products available and their comparative performance, pointing out that no one system was suitable for all requirements and that the correct product needed to be selected for the particular performance required.

The Section Chairman opened the discussion and the lecturers ably answered questions put to them by Messrs Blenkinsop, Gilkes, Du Rieu, Alexander and Tate. Mr Tate ended the meeting by thanking the lecturers for a very interesting lecture.

A.L.

Scottish

Eastern Branch

The application of computational methods to pigment technology

The first ordinary meeting of the session was held in the Carlton Hotel, Edinburgh, on Wednesday 21 October 1970, with Mr P. A. Gower in the chair. Dr D. A. Plant of ICI Ltd. spoke on "The application of computational methods to pigment technology."

In his talk Dr Plant discussed the application of computational methods to four different problems encountered in the surface coating industry.

Mill base formulation using a Red Devil shaker

The object was to determine the optimum conditions for efficient dispersion using a Red Devil shaker.

The computer was first fed with the fixed data; for example, the optimum single mill base formulation (the ideal formulation for dispersing a single pigment). Then the input data for the dispersion to be considered was fed in, for example, the ball volume and the charge to voids ratio. The computer then calculated the optimum formulation.

Hiding power

The paint to be examined was laid down at a set of fixed film thicknesses over a white and black background. Reflectance measurements were taken and the contrast ratio for each film thickness calculated by the computer, which could also compound the contrast ratios for any film thickness.

Colour matching

Spectrophotometric measurements of the specimen to be matched were taken at 16 different wavelengths covering the visible band of the spectrum, and the data fed into the computer. In the calculations the scattering of light was assumed to be trivial against the background.

A first estimate colour match was made. The computer then compared the data from the specimens to be matched with that of the first colour match. The differences could be shown by an oscilloscope. The ratios of the different pigments in the first colour match were then adjusted until a straight line was obtained on the oscilloscope. An experienced operator can usually obtain a satisfactory colour match in three attempts.

Rheology of printing inks

A "Laray" viscometer was used to measure the rheology of the printing ink under examination. The time of fall of the rod was noted under a series of weights from 0 to 1,000g. The results were fed into the computer which calculated the viscosity and apparent yield value of the ink. It was claimed that the use of a computer was more accurate than the normal graphical method, as it overcame the problem of where to draw the tangent to the curve.

J.H.S.

Metrication

The second ordinary meeting of the session was held in the Carlton Hotel, Edinburgh, on Wednesday 4 November, when Mr F. Munday of PIRA and Mr S. Grant of Wiggins Teape Ltd. spoke on "Metrication." This was a joint meeting with the BPBMA.

Mr Munday dealt with the theoretical aspects; discussing the advantages and disadvantages of metrication and tracing the history of the subject from the CGS system of 1872 to the full System International of 1960.

The advantages of metrication would mainly be in the field of education, though there would be savings in the time taken for calculations and it would help in standardisation; for example, "A" paper sizes. Disadvantages would include the large amount of re-education and the recalibration of instruments. Unanimity of units would be another problem; for example, the gas industry was changing to the joule as the unit of power whilst the Electricity Board were continuing with the kilowatt-hour.

Mr Grant gave the second part of the lecture and dealt with the practical implementation of metrication. To allow for a smooth transition, it was important for a company to nominate one person as that company's metric co-ordinator. Mr Grant went on to say that as far as Wiggins Teape was concerned, it was decided that only necessary changes to allow the company to trade as a metric concern would be considered. A list of all instruments and gauges was therefore prepared and these were classified as follows: essential ones to be metricated; desirable ones to be metricated; the rest.

The cost of changes one and two was calculated and, owing to the high cost, only instruments and gauges in the first classification were metricated.

A programme of training was also undertaken, in which one person from each department underwent a training course and everyone in the firm received a training manual. Mr Grant felt it was very important for a smooth transition that everyone should feel involved.

J.H.S.

Thames Valley

Special problems of paints and mastics in building techniques

Mr E. L. French of Taylor Woodrow Construction Ltd. was introduced as the guest speaker by the Section Chairman, Mr B. Jacob, at the fourth meeting of the 1970-71 session, held on Thursday 21 January at the Beech Tree, Beaconsfield. Under the title, "Special problems of paints and mastics in building techniques," Mr French said he wished to dwell largely on some problems that had faced him personally as a coatings user. He added that in his remarks his aim was to stimulate the coatings industry into better solutions to some current problems.

He quoted the latest figures for usage of building and decorative paints as 70 million gallons, divided up into 30 per cent oil based, 30 per cent emulsion and 30-40 per cent varnish, bitumen, and a host of miscellaneous products. A recent survey on methods of use showed that 50 per cent by volume was accounted for by brush, 10 per cent by roller, 10 per cent by airless spray and 10 per cent by normal spray. He felt that paint manufacturers should harmonise more with equipment manufacturers to devise new, and to improve existing, methods of application. A case for improved durability could also be made out on the basis of reduced maintenance. Coatings of exceptional longevity were already available, such as silicone/alkyds, polyester/isocyanates, and it was up to the coatings industry to persuade potential users of the benefits to be derived from these more expensive products.

An insight into the manufacture and painting of precoated building components was gained from a series of colour slides, during which the effectiveness of moisture vapour barriers in sandwich construction was discussed without any firm solution being put forward. Another challenging problem not yet fully resolved was how to give fast drying/stacking performance and yet maintain good flexibility for the protection of wood.

The role of preservatives in timber construction was touched on, the need being for maximum repellence and fungus resistance without the necessity for aesthetic appeal. Pentachlorophenol had given trouble by upsetting the adhesion of the following paint coatings. The need for different sorts of wooden joints requiring different types of protection was often overlooked. Some slides showed the inadvisability of applying surface coatings, rather than absorbent protectives, to cedar cladding.

Aluminium was among the front rank of the "newer" materials now coming to the fore. Very little was protected by anodising and strippable coatings were employed extensively. Often they were not satisfactory as they refused to peel uniformly at the appropriate time.

Next he turned to concrete surfaces; notable among problems were excessive dirt retention and a variation in absorbency which gave unsightly patchwork exteriors. At present there seemed no solution. Absorbency was affected by quality of the mix, the source of the aggregates and again by the nature of the environment and it was impossible to control these to a sufficient extent. A new line of thought from polymer chemists was required to solve these problems.

Mastics, it was said, presented few real problems provided that the joint design was sound in the first place. However, it would be of considerable benefit if the mastic would accept wet surfaces without fear of bond failure.

Mr French ended by showing a colour movie that gave an insight into the manufacture and on-site erection of prefabricated building products. Question time reflected the keen interest in the subject generally among the 28 members and 10 visitors present.

Mr Bishop, in giving the closing vote of thanks, made a plea for much more prior consultation and discussion between the contractors, architects and the paint suppliers before building commenced.

R.E.G.

Notes and News

Technical Exhibition

21-25 June 1971

The Exhibition Committee is pleased to announce that it has accepted the late applications of two companies at OCCA 23. These are Crystal Tack Cloth Co. Ltd—Stand 62a, and Dyeing Services Ltd.—Stand 71d.

An amendment has to be made to the list of exhibitors published in the January issue of the *Journal*, since we have been notified that Synres International NV previously exhibited in 1965 under a different company name. Consequently the number of companies who have not previously shown at an OCCA Exhibition is 17 and 32 did not show at OCCA 22.

The *Official Guide* has now been published and is available, without charge, from the address on the front cover of this *Journal*, or by telephoning 01-606 1439 Ext. 3 or telex 883711.

Report of Meeting of Council

A Meeting of Council was held on Thursday 25 February at Wax Chandlers' Hall, London. There were 16 members present, under the chairmanship of the President, Mr A. S. Fraser.

It was reported that Mr A. B. Lock had accepted Council's invitation to represent the Association on BSI Committee PVC/14—"Colours for paints," and that Mr J. H. Sparrow would represent the Association on Committee PVC/24—"Water thinned priming paints," to replace the late Mr J. E. Pooley.

The Council was informed that, despite the postal strike, many applications for the Association's Conference, to be held at Torquay from 4-8 May, had either been delivered or telephoned to the office. A notice had been prepared for inclusion in the February issue of the *Journal* (which would be despatched as soon as the strike ended) stating that applications received after 1 March (the original closing date) would still be considered. It was hoped that preprints and the other information would be sent in the first half of April to those who had registered, but, if the postal strike were to continue, their despatch might be delayed until later in that month.

The postal strike had also impeded the collection of editorial and advertising matter for the *Official Guide* to the Exhibition (21-25 June) with the result that the final date of despatch might be delayed on this occasion. It was planned to send these to members about two months before the exhibition. However, Council was told that all other arrangements for the Exhibition were well in hand.

Copies of the provisional accounts for 1970, together with notes and estimates for 1971, had been circulated after approval by the Finance Committee. They were adopted (subject to final audit) for presentation to the members in the Annual Report which would be circulated (if postal conditions allowed) well before the Annual General Meeting on 7 May, a notice for which was sent to members in December.

The Finance Committee at its meeting on 10 February had also discussed the position arising from the 825 Rolls-Royce £1 shares held by the Association but it had been decided that it was not considered advisable to sell them at the time of the meeting and the market value had been assessed for the 1970 Balance Sheet at 40p each.

Council decided that, in view of the delay in forwarding membership subscriptions caused by the postal strike, the period of grace allowed to members for the payment of their 1971 membership subscriptions should be extended from March to April. Consequently, any member whose subscription is four months in arrears will not receive any issues of the *Journal* after 1 May until payment of all subscriptions due, but will receive three issues (February, March and April) as well as that for January, which had already been circulated.

It was reported that the Jordan Award Committee had met on 28 January and that the award of £100 would be presented to Mr J. R. Groom for his paper entitled "Milling—a printing ink variable," which appeared in the March issue of the *Journal*. Mr Groom is an Ordinary Member attached to the West Riding Section and he presented the paper to that Section in December 1970.

Council agreed upon the list of names of those members, in addition to the President and the President Designate (or immediate Past President) who will be *ex officio* members, to be approached to serve on the Professional Grade Committee. It was further agreed that the President Designate (Mr A. W. Blenkinsop) would be the first chairman and that the Professional Grade Committee should report to Council on 3 June with full details of the scheme for an optional Professional Grade for Ordinary Members. If this document is accepted by Council, it will then be published in the *Journal* before the next session.

As this was the last meeting of Council that Mr Fraser would chair as President, he took leave to thank the members for their support during his term of office, and felt sure that they would continue to give their support to Mr Blenkinsop during his term of office, which will start at the Annual General Meeting on 7 May.

Hull Section

Ladies Evening: Home made wines

A meeting was held at the Queens Hotel, Hull, on 1 March, and attended by 25 members and guests. Mr G. D. McWilliam, of the Hull and District Winemakers Club, gave a short talk during which he discussed the principles of wine making, the choice of ingredients and methods of preparation. Several especially favoured recipes were given, and on this occasion the customary discussion period was replaced by a wine tasting and coffee and biscuits. A vote of thanks for an enjoyable and successful evening was proposed by Mr F. D. Robinson.

J.A.H.

News of Members

Dr R. J. Ceresa, an Ordinary Member attached to the London Section, has been appointed as director of divisional research of the European division of W. R. Grace & Company. Dr Ceresa will be based at Grace's St. Neots technical centre.

Mr H. Jones, an Ordinary Member attached to the Manchester Section, has recently relinquished his directorship of

Geigy (UK) Limited and his special responsibilities for corporate planning. Mr Jones, who joined Geigy in 1932, has been a Member of the Association since 1955.

Following the formation of CIBA-GEIGY (UK) Limited, as already reported in this *Journal*, details of the marketing department have been announced, and several members are involved.

Mr D. G. Addenbrooke, an Ordinary Member attached to the Manchester Section, is sales manager, paint industry group.

Mr C. A. Carey, an Associate Member attached to the London Section, is representative for the paint industry group, South of England.

Mr K. C. D. Bruce, an Ordinary Member attached to the London Section, is sales manager, ink industry group.

Mr R. Turnbull, an Ordinary Member attached to the London Section, is representative for the ink industry group, South of England.

Mr C. Musgrave, an Ordinary Member attached to the Manchester Section, is sales manager, plastics industry group.

Mr M. B. Jarvis, an Ordinary Member attached to the Manchester Section, is representative for the plastics industry group, North of England.

Mr R. C. Sykes, an Ordinary Member attached to the Midlands Section, is a representative for the synthetic fibres group.

In the regional section of the marketing department, which will service all industries:

Mr D. M. Varley, an Ordinary Member attached to the Manchester Section, is sales manager;

Mr W. H. Bradburn, an Ordinary Member attached to the Manchester Section, and Mr J. N. McKean, an Ordinary Member attached to the West Riding Section and that Section's Vice-Chairman, will act as representative in the North and Scotland;

Mr E. H. Hall, an Associate Member attached to the Bristol Section, and Mr E. J. Hurst, an Associate Member attached to the Bristol Section, will act as representatives in the South West and Wales;

Mr D. D. Kimber, an Ordinary Member attached to the Midlands Section, will act as representative in the Midlands;

Mr A. Morris, an Ordinary Member attached to the London Section, will act as representative in the South East;

Mr F. D. H. Sharp, an Associate Member attached to the Irish Section, and Chairman of that Section, will act as representative in Ireland.

Mr T. J. Bickerton, an Ordinary Member attached to the London Section, is joint head of the division's marketing services section, and Mr D. F. Grimmer, an Associate Member attached to the Midlands Section, will carry out customer liaison in the Midlands.

Mr K. A. Leach, an Ordinary Member attached to the London Section, has been appointed technical sales manager of Columbian International (GB) Limited, following reorganisation of the company's sales structure.

Dr W. Funke, an Ordinary Member attached to the General Overseas Section, is to be managing editor of "Progress in Organic Coatings," the new review journal launched by the Swiss publisher Elsevier Sequoia SA.

Mr A. R. H. Tawn, an Ordinary Member attached to the London Section, and the Association's Hon. Research and Development Officer, and Mr P. Fink-Jensen, an Ordinary Member attached to the General Overseas Section, are to be consulting editors of "Progress in Organic Coatings."

Following the formation of British Paints and Chemicals Division of Berger, Jensen and Nicholson Ltd:

Mr V. C. Thompson, an Ordinary Member attached to the Bristol Section, has been appointed managing director, having been managing director of John Hall & Sons (Bristol and London) Limited;

Mr R. Wilson, an Ordinary Member attached to the Newcastle Section, has been appointed technical director, and director of Resinous Chemicals, Mr A. A. Duell, an Ordinary Member attached to the Newcastle Section and Section Vice-chairman, is director of the elastomers operations;

Mr J. N. Bailey, an Ordinary Member attached to the Newcastle Section is appointed general manager, protection special coatings division.

XI FATIPEC Congress

The theme of the XI FATIPEC Congress, to be held in the Palazzo dei Congressi, Florence, from 11-16 June 1972, will be "Developments and evolution in the production, evaluation and application of paints and printing inks."

The Congress is to be organised by AITIVA, the Italian association, under the chairmanship of Mr A. Levi. As well as the usual plenary sessions and shorter, more specialised papers, a feature of this Congress is to be a science symposium, running concurrently with other sessions, entitled "Pigment/vehicle interaction in the fluid state." This will comprise a limited number of papers invited by AITIVA.

Papers for the congress are now required, the official congress languages being English, French, and German. Authors wishing to present a paper should send their script to:

Segreteria del Congresso FATIPEC,
Via S. Giovanni di Dio 7,
20123 Milano, Italy.

The closing date for receipt of papers is 31 October 1971.

Resfilm '71

The annual research film conference organised by the British Industrial and Scientific Film Association will take place at Keele University on 7-9 September 1971. Entitled Resfilm '71, it will cover research film on the natural sciences.

This will be the first time that the conference has moved from its traditional venue at the National Physical Laboratory, and it will be a residential conference, with delegates accommodated at the University.

Professor Moore Memorial Lecture

The second Professor Moore Memorial Lecture is to be held on Thursday 21 October 1971, when Sir Harry Melville will speak on "Elastomers." Full details are available from the Registrar, University of Bradford, Bradford, Yorkshire BD7 1DP.

PMA report on polyurethene hazards

The Paint Industry Technical Committee of the Paintmakers Association of Great Britain Limited, together with its Health and Safety sub-committee, has produced a report entitled "The hazards arising from the manufacture and use of polyurethene paints and varnishes: precautions to be adopted." Copies are available on request to the PMA.

New international review journal

A new journal entitled "Progress in organic coatings" is to be published by Elsevier Sequoia SA, a member of Associated Scientific Publishers.

The editorial policy of the new journal is stated to be to summarise and analyse the progress and current state of knowledge in the field of organic coatings and related subjects. The reviews will concentrate on subjects which have undergone significant development in recent years, and will be compiled by specialists having an intimate knowledge of the literature in their field.

The aim of this policy is to provide a critical assessment of the published literature and at the same time a definition of the state of the art, thus easing the burden for scientists and technologists by providing them with concise information without the need to study either the original literature or the abstract journals.

The journal is to be published at irregular intervals initially, but an eventual frequency of four issues a year is planned. The subscription price is 131.75 Swiss Francs for the first volume; further details and sample copies are available from the publisher, PO Box 851, 1001-Lausanne, Switzerland.

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

ATKINSON, RICHARD CLYDE, 29 Bantam Drive, Blairgowrie, Randburg, South Africa. (*South Africa*)

BAILEY, JOHN NOEL, c/o British Paints Ltd., Portland Road, Newcastle upon Tyne. (*Newcastle*)

BRUCE, DAVID BRECKINRIDGE, 204 Queens Drive, Liverpool L15 6XX. (*Manchester*)

BUCHERT, GERHARD HANS, Plascon Paints PO Box 10, Luipaardsvlei, Transvaal, South Africa. (*South Africa*)

COCKETT, MICHAEL A., BSc, MSc, PO Box 1057, Cape Town, South Africa. (*South Africa*)

COETZEE, THOMAS ANDRIES, Plascon Paints & Chemical Ind., PO Box 10, Luipaardsvlei, Transvaal, South Africa. (*South Africa*)

EVANS, DAVID WILFRED SHAWYER, BSc, PhD, FRIC, SAPRI University of Natal, PO Box 16, Congella, Durban, Natal. (*South Africa*)

FOLKARD, EDME FRANCOIS, 3 Height Street, Doornfontein, Johannesburg. (*South Africa*)

FOSTER, GEOFFREY LAMBSIN, BSc, PhD, FRIC, "Bryher," Newlands Drive, Maidenhead, Berks. (*Thames Valley*)

GEEVE, H. PO Box 2203, Bloemfontein, South Africa. (*South Africa*)

HATTON, THOMAS FREDERICK, HND, LRIC, 17 Berkeley Close, Offerton, Stockport, Cheshire. (*Manchester*)

HORSFIELD, KENNETH WILLIAM, LRIC, AMICorr.T., 22 Brecks Lane, Kippax, Leeds. (*West Riding*)

HULATT, MICHAEL JOHN, BSc, PhD, Dulux Ltd., PO Box 2099, Port Elizabeth, Cape Province. (*South Africa*)

KUBETZKO, HEINZ, Plascon Paint Ltd., PO Box 10, Luipaardsvlei, Transvaal, South Africa. (*South Africa*)

LEE, JOHN TREVOR, 11 Main Street, Skidby, Cottingham, East Yorks Hu16 5TZ. (*Hull*)

MILLS, THOMAS NELSON, LIRI, "Chessington," 41 Russell Street, Durban, Natal. (*South Africa*)

NORBURY-LEA, ANTHONY, 7 Waverley Drive, Cheadle Hulme, Cheshire. (*Manchester*)

PERRINS, LESLIE, 148 Whalley Road, Wilpshire, Nr. Blackburn, Lancs BB1 9LJ. (*Manchester*)

RILEY, DENIS VINE, 146 De Wet Street, Krubersdorp North, Krugersdorp, Transvaal. (*South Africa*)

ROTTER, A. EDUARD, Plascon Paint & Chemicals, PO Box 10, Luipaardsvlei, Transvaal. *(South Africa)*

RUKIN, MICHAEL, PO Box 663, Durban, Natal, South Africa. *(South Africa)*

STEPHENS, BENJAMIN JOHN, PO Box 10, Luipaardsvlei, Transvaal, South Africa. *(South Africa)*

WEBER, FRITZ, Plascon Paint, Box 10, Luipaarsdsvlei, Transvaal. *(South Africa)*

WILKINSON, ROY ROWLEY, 32 Malmesbury Road, Cheadle Hulme, Cheadle, Cheshire. *(Manchester)*

Associate Members

BLECHSCHMIDT, ERNST, 6373 Weisskirchen, Taünüsblick 11, Germany. *(Overseas)*

FOYN, JOHN NEVILLE, Plascon Paints & Chemical Industry, PO Box 10, Luipaardsvlei, Transvaal. *(South Africa)*

LIEBE, HUBERT SIEGFRIED, Hoechst SA Pty. Ltd., Box 8692, 3 Caxton Street, Industria-West, Johannesburg. *(South Africa)*

Student Members

CURRIN, JOHN BARRY, 2 Lorraine Avenue, Umbilo, Durban. *(South Africa)*

EDWARDS, PHILIP WILLIAM, 41 Chaucer Avenue, Hayes, Middx. *(Thames Valley)*

HILTON, GEOFFREY, 3 Devon Drive, Silksworth, Sunderland, Co. Durham. *(Newcastle)*

SOUTHALL, GARFIELD JEFFEREY, 41 Pickering Road, Hull, HU5 6TA. *(Hull)*

YATES, ALAN FREDERICK JAMES, 10 Austwick House, Heysham Drive, Holme Wood, Bradford BD4 04R Yorks. *(West Riding)*

Forthcoming Events

Details are given of meetings in the United Kingdom up to the end of the month following publication, and in South Africa and the Commonwealth up to the end of the second month.

Friday 4 May

West Riding Section: Luncheon Lecture, "High-risk insurance" by Mr A. Tiley, to be held at the Astoria Restaurant, Roundhay, Leeds, at 1.00 p.m.

Tuesday 4 to Saturday 8 May

Oil and Colour Chemists' Association Torquay Conference: To be held at the Palace Hotel, Torquay.

Friday 7 May

Oil and Colour Chemists' Association Annual General Meeting: To be held at the Palace Hotel, Torquay, at 2.15 p.m.

Friday 11 June

Irish Section: Golf outing.

Monday 21 to Friday 25 June

Oil and Colour Chemists' Association 23rd Technical Exhibition, OCCA 23 To be held at the Empire Hall, Olympia.

Oil and Colour Chemists' Association

President: A. S. FRASER

The Oil and Colour Chemists' Association was formed in 1918, to cover paint, printing inks, pigments, varnishes, drying and essential oils, resins, lacquers, soaps, linoleum and treated fabrics, and the plant, apparatus and raw materials useful in their manufacture. In 1924 it absorbed the Paint and Varnish Society. The stated purpose of the Association is to promote by discussion and scientific investigation the technology of the industries concerned with the above-mentioned products, and to afford members opportunity for the interchange of ideas. This is achieved by the regular holding of ordinary meetings at which papers are presented, and the organisation of annual technical exhibitions, biennial conferences, educational activities and practical co-operative experimental work. Details of these activities are given in the *Journal of the Oil and Colour Chemists' Association*, which is published monthly, and whose pages are open to receive communications and other pronouncements on scientific and technical matters affecting the members of the Association and the industries concerned. The Association's meetings also afford opportunities for members to meet informally and socially.

There are Sections of OCCA in Auckland, Bristol, Hull, Ireland, London (with a Southern Branch), Manchester, the Midlands (with a Trent Valley Branch), Newcastle upon Tyne, Scotland (with an Eastern Branch), South Africa (with Branches in the Cape, Transvaal and Natal), Thames Valley, Wellington, and the West Riding, and these are responsible for the conduct of their own local affairs. There is also a General Overseas Section. There is also a close alliance between the Association, the Federation of Societies for Paint Technology in the United States, and the Fédération d'Associations des Techniciens de l'Industrie des Peintures, Vernis, Emaux et Encres d'Imprimerie de l'Europe Continentale (FATIPEC). The Association also maintains cordial relations with the Scandinavian Federation of Paint and Varnish Technicians (SLF).

The five Sections previously maintained by the Association in Australia formed (1.1.68) the Oil and Colour Chemists' Association Australia, having the same aims and activities as, and working in close liaison with, the parent body.

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. Student Membership, which is intended primarily for students, is open without restriction to persons under the age of 21 and to those up to 25 who are following a course of technical study. The annual subscription in each case is £5.25, except for Student Members whose subscription is £1.05. An entrance fee of 50p is payable by all members. Applications for membership are invited from suitably qualified persons who are engaged or otherwise interested in the industries noted above. Applications, which should be supported by two members of the Association (one of whom must be an Ordinary Member), should be forwarded to the Director & Secretary at the address given below. Application forms and full details of membership may be obtained from the offices of the Association.

PUBLICATIONS

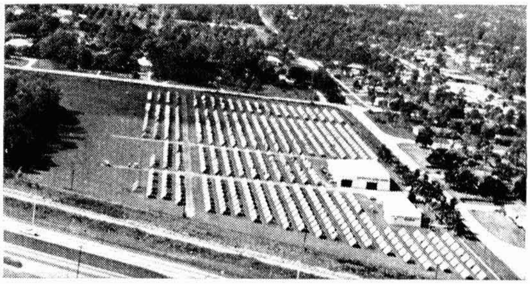
Journal of the Oil and Colour Chemists' Association. Published monthly. Subscription rate to non-members in UK and abroad; £10.00 p.a. post free; payable in advance.

An Introduction to Paint Technology (Second Edition with additional chapter). Pp. 187, illustrated, with index, £1.00 (including postage).

Paint Technology Manuals

Part 1: "Non-convertible Coatings," Second Edition, Pp. 343, £1.80.
Part 2: "Solvents, Oils, Resins and Driers." Second Edition, Pp. 268, £1.80.
Part 3: "Convertible Coatings," Pp. 318, £1.75.
Part 4: "The Application of Surface Coatings," Pp. 345, £1.75.
Part 5: "The Testing of Paints," Pp. 196, £1.75.
Part 6: "Pigments, Dyestuffs and Lakes," Pp. 340, £1.75.

Director & Secretary: R. H. Hamblin, M.A., F.C.C.S., Wax Chandlers' Hall, Gresham Street, London EC2V 7AB.




FLORIDA
*Sub-Tropical Miami

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introduction to paint technology

second edition with additional chapter

The sales of this Association publication now exceed 13,000, and because of continuing high sales of the second edition, and the need for a work of reference to be constantly abreast of the latest developments in its field, the Council of the Oil and Colour Chemists' Association has authorised the addition of an eleventh chapter to the "Introduction to Paint Technology." Entitled "Recent Developments," the Chapter incorporates up-to-date information on the latest advances in the technology of the paint and allied industries.

This addition will help the "Introduction to Paint Technology" to maintain its position as an invaluable aid to young entrants into the industries and to marketing and other personnel requiring a basic knowledge of the principles and techniques of surface coating production and application.

new chapter

The new chapter is subdivided into three sections

resins and media

Including polyester, epoxy, polyurethane resins and developments in water based paints, vinylics, etc.

application techniques

Including electrodeposition, powder coatings, strip-coating, aerosol spraying.

instrumental testing and control methods

Including colour measurement, viscometers, brushability, hardness, film thickness, weatherometers, and use of computers.

The book contains 204 pages including 11 line diagrams, 8 photographs of common paint defects, and comprehensive index. Copies can be obtained from the Oil and Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London E.C.2, price £1 (post free).

CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of 50p per line. Advertisements for Situations Wanted are charged at 12½p per line. A box number is charged at 5p. They should be sent to the Director & Secretary, Oil & Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2. Telephone: 01-606 1439.

SITUATIONS VACANT

TECHNICAL SALES REPRESENTATIVE

COATING RESINS

BIP Chemicals Ltd., Oldbury, have a vacancy in the Midlands for a Technical Sales Representative with experience of the paint industry and in particular the field of industrial stoving finishes, to promote the sale of "Beetle" surface coating resins. A good standard of education is essential and provided that the applicant's background is suitable, previous selling experience is not absolutely necessary. Commercial and technical training will be given.

The preferred age is 23-28.

The Company offers good conditions of employment including a contributory Pension and Life Assurance Scheme. The salary paid will be in accordance with the Company's Salary Administration Scheme.

A Company car will be provided.

Application in writing should be made to the Personnel Manager,

BIP

TURNER & NEWALL LIMITED

TN

BIP Chemicals Ltd

Popes Lane, Oldbury, P.O. Box No. 6., Warley, Worcs.

SITUATIONS VACANT

We require several responsible Chemists/Physicists with experience in the surface coating industry for development work in our newly built and equipped laboratory.

Please apply in the strictest of confidence to the Managing Director, Shuck Maclean & Co. Ltd. (Printing Inks), Albion Close, Petersfield Avenue, Slough, Bucks.

TECHNICAL EXHIBITION

21-25 June 1971

SITUATIONS WANTED

PAPER TECHNOLOGIST with experience of modern practices in paper making, coating adhesives, pigments and auxiliaries, seeks technical or customer liaison position in paper making, printing, or allied trades serving the paper and other industries. Box No. 331.

B.Sc., A.R.I.C., Over 20 years experience, research, development and production, Paints and Pigment manufacture, seeks suitable position salary negotiable. London, S.E. area preferred. Apply Box No. 332.

SITUATION VACANT

CSIRO

AUSTRALIA

POLYMER CHEMIST

DIVISION OF PROTEIN CHEMISTRY

GENERAL Applications are invited from polymer chemists for a Postdoctoral Fellowship tenable at this Division of the Commonwealth Scientific and Industrial Research Organization, located at Parkville, Melbourne, Victoria.

The Leather Research Section is an integral part of the Division of Protein Chemistry, and is primarily concerned with the structure and properties of hides and skins and with the leather obtained from them. The Division has a research staff of some 60 organic and physical chemists, biochemists and biophysicists. Research within the Division also includes projects on the structure and chemistry of the wool fibre and its constituent and related proteins and on synthetic peptides.

DUTIES A project has been initiated in the Leather Research Section to investigate the incorporation of polymers into leather. The long term objective of this work is to improve the uniformity of the properties over the whole area of the tanned hide without detracting from the favourable properties of the natural leather.

The appointee will be expected to develop a research program involving synthesis of polymers and co-polymers with different types of backbones and side-chains, and to investigate the relation between the properties of these polymers and of the leather into which they have been incorporated.

QUALIFICATIONS Applicants should have a Ph.D degree in chemistry or equivalent qualifications supported by satisfactory evidence of research ability. Some postgraduate research experience in synthetic polymer chemistry is desirable and industrial experience relating to the synthetic polymer field would be an added advantage.

SALARY Depending upon qualifications and experience, the appointment will be made within the salary range of Research Scientist, $A7,484—$A9,494 p.a., or Senior Research Scientist, $A9,880—$A11,517 p.a. Salary rates for women are $A428 p.a. less than the corresponding rates for men but equal pay will be attained in January 1972. Promotion within CSIRO to a higher classification is determined by merit.

CONDITIONS The Fellowship is offered initially for a period of three years and will be conditional upon passing a medical examination. An initial probationary period of twelve months may be specified.

Applications, (quoting Appointment No. 462/358), and stating full name, place, date and year of birth, nationality, marital status, present employment, details of qualifications and experience, together with the names of three or four persons acquainted with the applicant's academic and professional standing, should reach:—

The Deputy Chief Scientific Liaison Officer,
Australian Scientific Liaison Office, 64-78, Kingsway, LONDON, WC2B 6BD
by the 15th May, 1971.

Applications in U.S.A. and Canada should be sent to Professor H. C. Webster, C.M.G., Counsellor (Scientific), Australian Embassy, 1601 Massachusetts Avenue, N.W., WASHINGTON, D.C. 20036, U.S.A.

SITUATIONS VACANT

INK TECHNICIANS

SUN CHEMICAL CORPORATION USA

Ink technicians previously recruited in this country are having very successful and rewarding careers with the General Printing Ink Division of Sun. Why not join them? University graduates aged between 28 and 40 with several years experience in the ink industry are preferred. A number of positions are available, including a senior post, in raw material evaluation, as well as situations for those skilled in the manufacture of offset and letter press inks and secondly in flexo gravure inks.

Apply in the first instance to J. G. EVANS, European Consultant, Sun Chemical Corporation, Fieldhead, St. John's Park, Menston, Ilkley, Yorkshire LS29 6ES.

INSTITUTE FOR INDUSTRIAL RESEARCH AND STANDARDS

PAINT TECHNICIAN

(Chemistry Department)

Applications are invited for the above post in the Surface Coatings Section of the Chemistry Department.

This post is intended for a technician with at least two years' laboratory experience in the field of paint technology.

Appointment will be made at Technician Grade I level; minimum academic qualifications:—

> Science Laboratory Technicians' Certificate of the City and Guilds of London Institute, or two approved science subjects at G.C.E. Advanced Level, or an approved equivalent.

SALARY: within the range £1,167—£1,690 per annum.

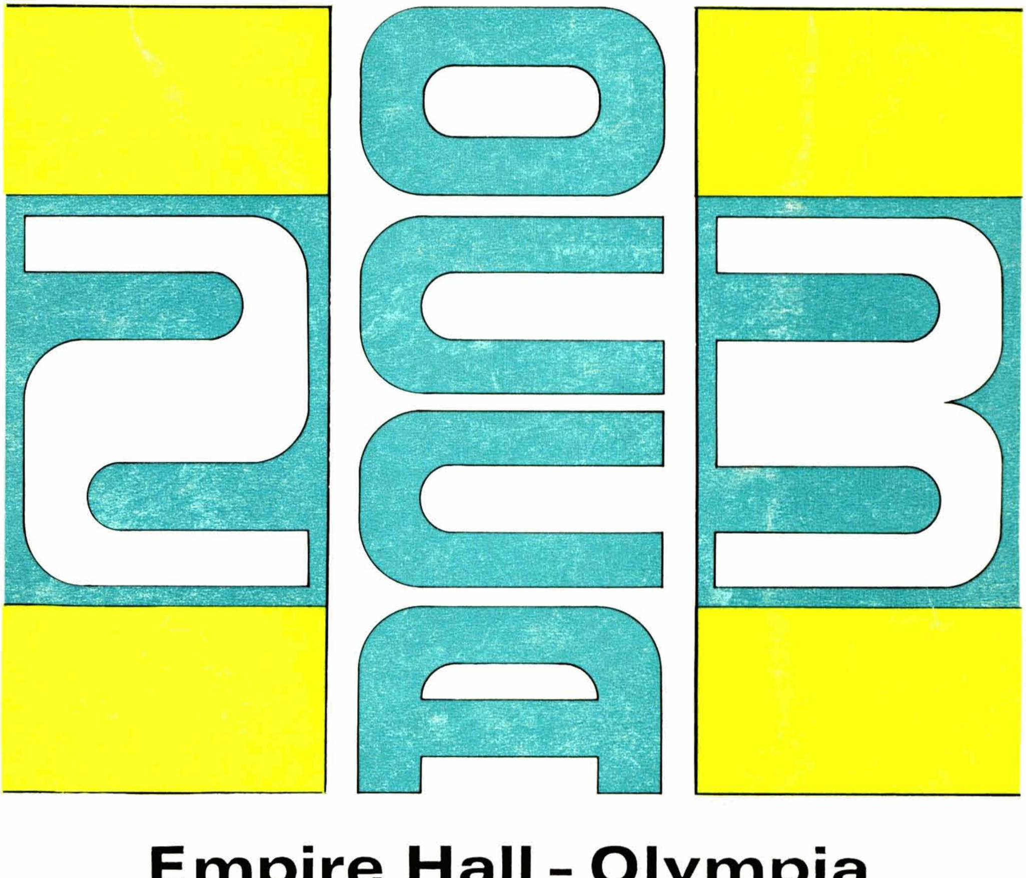
CONDITIONS: five-day week; non-contributory Superannuation Scheme, contributory Widows' and Children's Pension Scheme.

Application forms are available from THE PERSONNEL MANAGER, INSTITUTE FOR INDUSTRIAL RESEARCH AND STANDARDS, BALLYMUN ROAD, DUBLIN 9, IRELAND, who should receive completed forms not later than 31 May 1971.


MARKETING DEPARTMENT
Paints Division

Oil and Colour Chemists' Association

Technical Exhibition



Empire Hall - Olympia
London - 21-25 June 1971

Copies of the Official Guide have now been sent to all members. Further copies are available on application to the Association's Offices

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Printed in England by Metchim & Son Ltd., 8 Storey's Gate, Westminster, London, S.W.1.