

JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION



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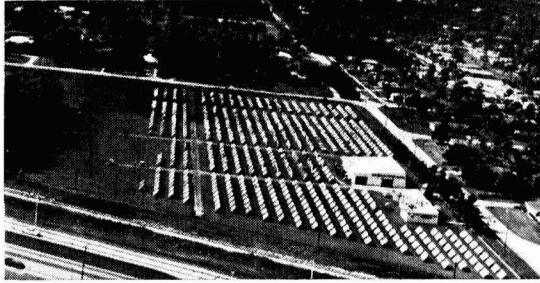
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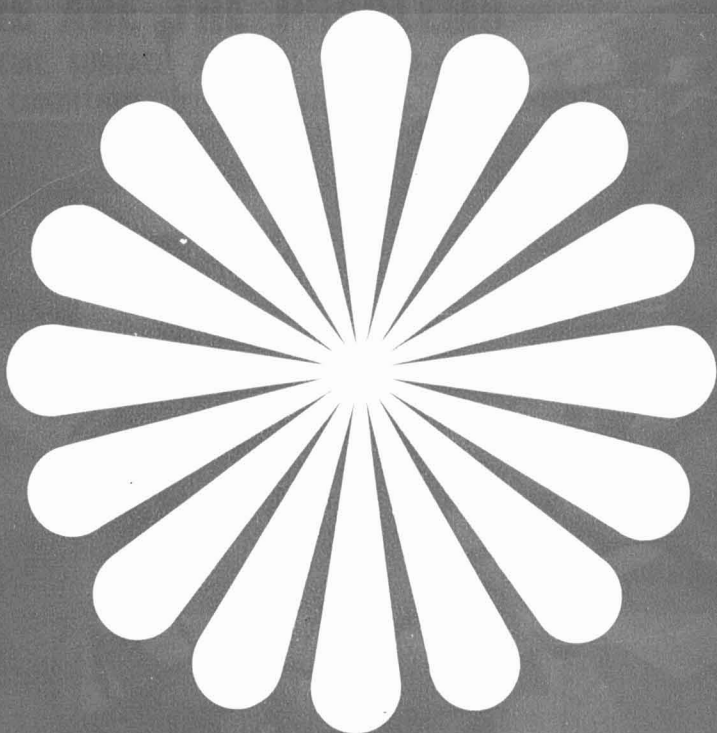
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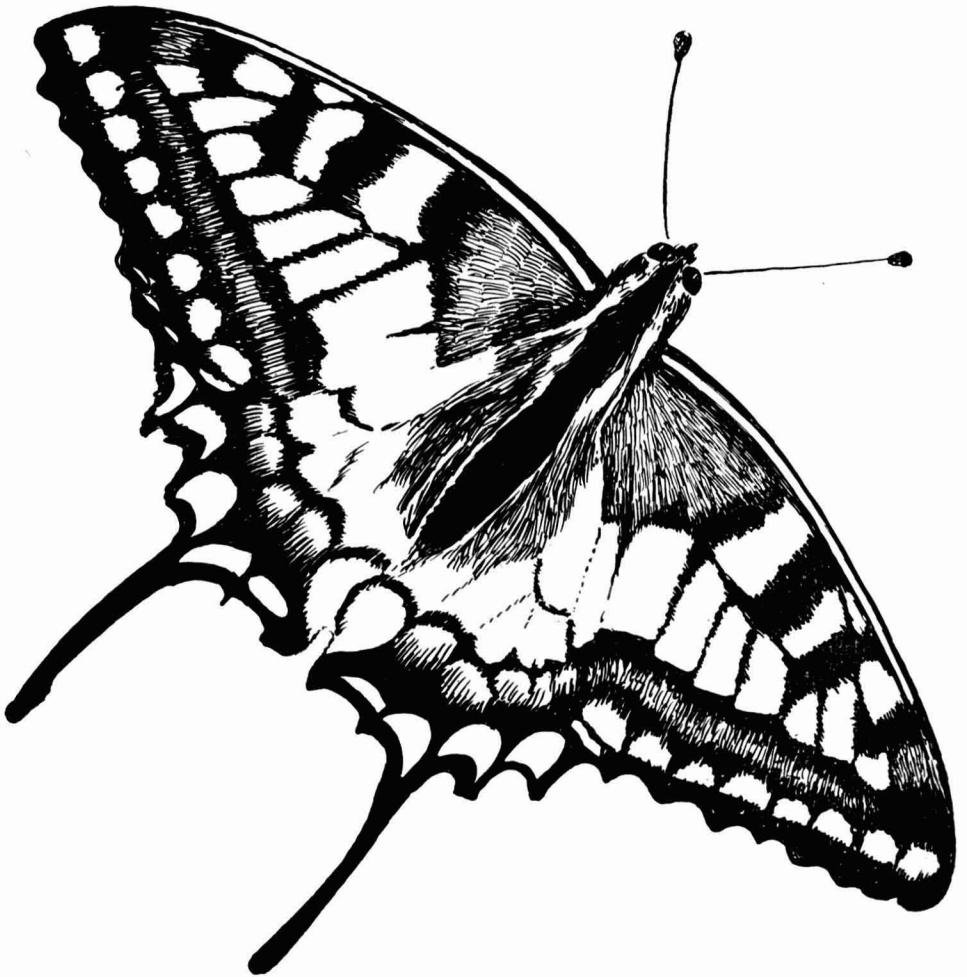
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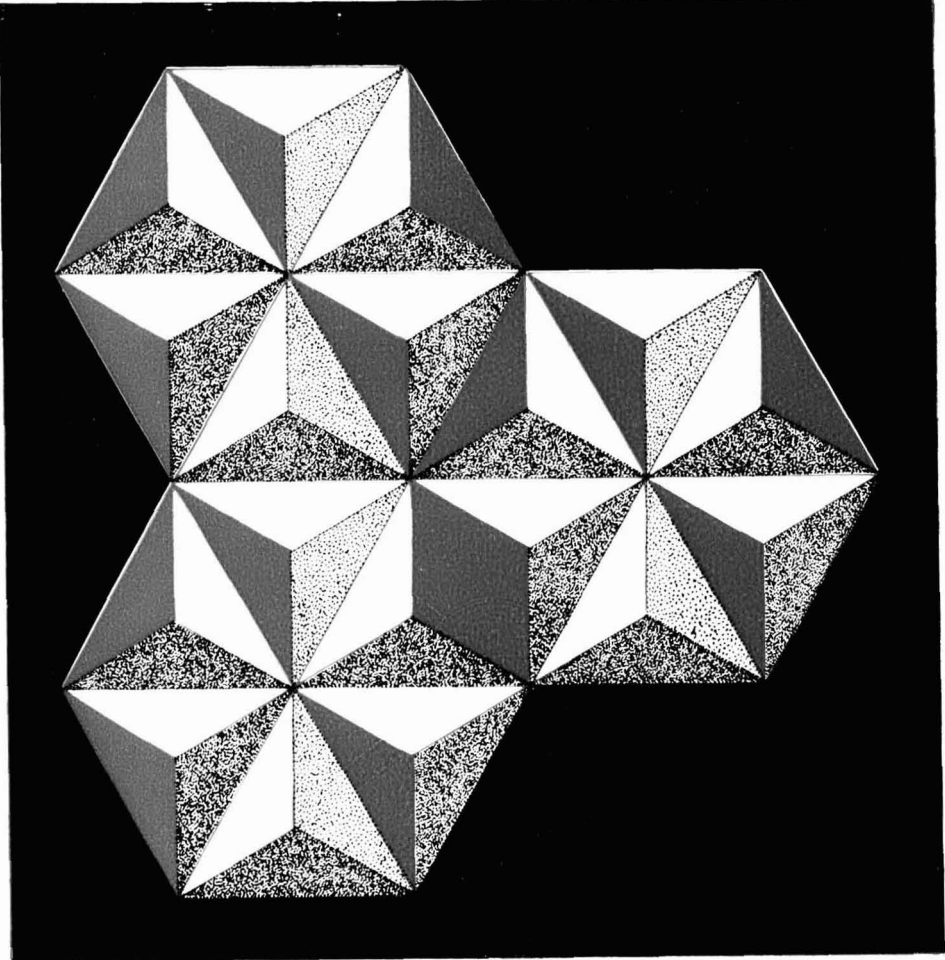
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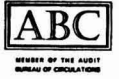
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Transactions and Communications

Water transport through paint films Part IV: Correlation of data obtained by differences in water vapour pressure and in osmotic pressure

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

Paint Research Institute TNO, Delft, Holland

Summary

The mean water diffusion coefficients calculated from the water vapour permeation measurements in Part I of this series are compared with the mean water diffusion coefficients calculated from the osmotic experiments in Part III.

The dependence of diffusion on the concentration ($D=f(c)$) and on the concentration profiles ($c=f(x)$), in the steady state have been determined. According to the nature of the material, D may be constant, or may increase or decrease with the increase of the water concentration. Consequently, the concentration/distance curve may be linear, concave or convex towards the distance axis.

For the epoxy resin, the very high water transport rates found in a few osmotic measurements have been explained in terms of $D=f(c)$, and $c=f(x)$.

The osmotic measurements can be considered for all the materials investigated as an extension of the permeation measurements to the experimental conditions of high water concentration on both sides of the films.

Keywords

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

osmosis
water permeation
water vapour transmission

Transport de l'eau à travers des feuil de peintures

IV^{ème}. Partie: La corrélation des données dérivées des différences de la pression de vapeur d'eau et de la pression osmotique

Résumé

Les coefficients moyens de diffusion d'eau, calculés à partir des mesures de la pénétration d'eau mentionnées dans la I^{ère}. Partie de cette série, sont comparés avec les coefficients moyens de la diffusion d'eau calculés à partir des expériences osmatiques citées dans la III^{ème}. Partie.

On a déterminé, sous le régime stable, le rapport entre la diffusion et la concentration, $D=f(c)$, et les profiles de concentration, $c=f(x)$. Selon la nature de la matière, D peut

*University of Technology, Delft.

être constant ou peut s'augmenter ou se diminuer en fonction de l'augmentation de la concentration d'eau. Par conséquent, la courbe de concentration/distance peut être linéaire, concave, ou convexe par référence à l'axe de distance.

A l'égard de la résine époxyde, les taux de transport d'eau très élevés mis en évidence par des mesures osmotiques peu nombreuses ont été expliqués sous termes de $D = f(c)$ et $c = f(x)$.

En ce qui concerne tous les matériaux examinés, on peut considérer les mesures osmotiques en tant qu'une extension des mesures de pénétration aux conditions expérimentales où existe une concentration d'eau élevée à tous les deux côtés des feuillets.

Wassertransport durch Lackfilme

Teil IV: Korrelation von Konstanten, aus den Unterschieden im Wasser-Dampfdruck und osmotischen Druck

Zusammenfassung

Die aus den Wasserdampfdurchdringungsmessungen im Teil I dieser Serie berechneten durchschnittlichen Diffusionskoeffizienten werden mit dem aus osmotischen Experimenten im Teil III berechneten durchschnittlichen Wasserdiffusionskoeffizienten verglichen.

Die Abhängigkeit der Diffusion von der Konzentration ($D = f(c)$) und den Konzentrationsprofilen ($c = f(x)$) im Dauerzustande wurde bestimmt. Je nach der Natur des Materials könnte D konstant sein oder sich mit grösserer Wasserkonzentration vergrössern oder verkleinern. Infolgedessen kann die Konzentrationswegstreckenkurve linear, konkav oder konvex gegen die Entfernungsmittellinie sein.

Für Epoxidharze wurden die hohen in einigen osmotischen Messungen gefundenen Wassertransportgeschwindigkeiten, ausgedrückt als $D = f(c)$ und $c = f(x)$, erklärt.

Die osmotischen Messungen kann man für alle untersuchten Materialien als eine Erweiterung der Durchdringungsmessungen unter den experimentellen Bedingungen hoher Wasserkonzentration auf beiden Seiten des Films ansehen.

Перенос воды в красочных пленках. Часть IV.

Соотношение данных полученных на основании разницы между давлением водяного пара и осмотическим давлением

Резюме

Средние коэффициенты диффузии воды, рассчитанные из измерений проницаемости водяного пара в части I настоящей серии, сравниваются со средними коэффициентами диффузии воды, рассчитанными на основе осмотических опытов в части III.

Определяется зависимость диффузии от концентрации ($D=f(c)$) и от профилей концентрации ($c=f(x)$) в установившемся состоянии. Согласно с природой материала, D может быть постоянным или может увеличиваться или уменьшаться с увеличением концентрации воды. Поэтому кривая концентрации может быть линейной, вогнутой или выпуклой по отношению к оси.

Для эпоксидных смол, чрезвычайно высокие скорости переноса воды обнаруженные при некоторых осмотических давлениях, объясняются на основе $D=f(c)$ и $c=f(x)$.

Осмотические измерения могут рассматриваться для всех испытанных материалов как обобщение измерений проницаемости до экспериментальных условий для высокой концентрации воды на обеих сторонах пленки.

Introduction

In the preceding papers, the transport of water through four binders, determined by means of differences in vapour pressure¹ and osmotic pressure² has been reported. Thermodynamic considerations indicate that the transport of a penetrant through a membrane is dependent only on the driving forces

acting on the film, and not on the way in which they were attained. This principle remains valid so long as the film characteristics are not changed by the environmental conditions producing the driving forces.

As has already been shown for all the materials investigated, such changes do not occur. It follows therefore that it might be possible to correlate the results obtained by means of vapour pressure differences with those obtained by means of osmotic pressure differences.

The results expressed in terms of the mean diffusion coefficients (\bar{D}) and plotted as a function of the mean water concentration (\bar{c}), are summarised in Figs. 1, 4 and 7, for epoxy resin, alkyd resin, and chlorinated rubber with plasticiser, respectively.

At first sight it would appear that in some of the osmotic measurements unexpectedly high \bar{D} -values (\bar{D}_{osm1} and \bar{D}_{osm2}) were obtained for epoxy resin.

These are the cases in which the experimental conditions were such that a very high water concentration was present on both sides of the films, but there was only a small driving force.

Similar results were reported in the literature for the permeation of organic solvents through a number of different polymer membranes under analogous experimental conditions^{3, 4}. To the authors' knowledge, only a few workers have investigated the permeation of water through paint films under comparable experimental conditions⁵.

These authors limited the interpretation of the results to qualitative considerations, on the basis of theories already advanced in the literature³.

The aim of the present paper is to elucidate, as quantitatively as possible, the factors which might determine the very high diffusion coefficients of water through epoxy resin films under certain experimental conditions. For the other materials investigated, results obtained with the two methods mentioned above will also be compared and discussed.

Theoretical

As previously shown^{1, 2}, an amended form of Fick's relation describing the transport process of a penetrant through a membrane was deduced on thermodynamical grounds, viz.:

$$q = - Dc \frac{d \ln a}{dx} = - D \frac{c}{a} \frac{da}{dx} \dots \dots \dots (1)$$

The diffusion coefficient, D , is dependent on the temperature, and may also be dependent on the concentration, c , and therefore on position, x .

For the sake of simplicity, the treatment has been restricted to the isothermal and steady state conditions, for which the flux, q , is the same through each section of the membrane. Then q is independent of the temperature, position and time, and equation (1) can be transformed to:

$$q \int_0^L dx = qL = \int_{a_2}^{a_1} D \frac{c}{a} da \dots \dots \dots (2)$$

If D is concentration-independent, the diffusion coefficient can be calculated from the rearranged equation (2):

$$qL = D \int_{a_2}^{a_1} \frac{c}{a} da \text{ or } D = \frac{qL}{\int_{a_2}^{a_1} \frac{c}{a} da} \dots\dots\dots(3)$$

For materials where diffusion is dependent on concentration, equation (3) gives a mean diffusion coefficient, \bar{D} , known in the literature as the “integral diffusion coefficient”⁷.

Equation (3) may then be written:

$$\bar{D} = \frac{qL}{\int_{a_2}^{a_1} \frac{c}{a} da} \dots\dots\dots(4)$$

In the preceding papers^{1, 2}, \bar{D} -values of the materials investigated at different mean concentrations have been calculated.

It was concluded that, for the hydrophilic materials, the mean diffusion coefficient depends markedly on the concentration. It follows that, for a better evaluation of equation (1), the concentration dependence of diffusion has to be taken into consideration.

Derivation of concentration dependence of the diffusion coefficient

Using a procedure analogous to that of Crank⁶, the dependence of the diffusion coefficient on the concentration could be obtained as follows:

Equation (2) may be written

$$qL = \bar{D} \int_{a_2}^{a_1} \frac{c}{a} da = \int_{a_2}^{a_1} D \frac{c}{a} da \dots\dots\dots(5)$$

Introducing for the sake of simplicity

$$\frac{c}{a} = m \text{ and } \int_{a_2}^{a_1} \frac{c}{a} da = M$$

equation (5) can be rewritten as follows:

$$qL = \bar{D}M = \int_{a_2}^{a_1} D m da \dots\dots\dots(6)$$

Now, D can be determined by two different sets of experiments, as shown below.

By a series of experiments in which the lower activity a_2 (at the downstream boundary of the film) is maintained constant, while the higher activity a_1 (at the upstream boundary of the film) is varied. By differentiation of equation (6) with respect to a_1 , it follows that:

$$\frac{d(\bar{D}M)}{da_1} = \bar{D}m + M \frac{d\bar{D}}{da_1} = D_{a_1} m \dots\dots\dots(7)$$

or

$$D_{a_1} = \frac{d(DM)}{da_1} \cdot \frac{1}{m} = \bar{D} + \frac{M}{m} \cdot \frac{d\bar{D}}{da_1} \dots\dots\dots(8)$$

By a similar series of experiments, in which the activity at the upstream boundary a_1 is maintained constant, and the activity at the downstream boundary a_2 is varied.

The same mathematical treatment may then be applied, resulting in equation (9):

$$D_{a_2} = \bar{D} - \frac{M}{m} \cdot \frac{d\bar{D}}{da_2} \dots\dots\dots(9)$$

As has already been shown¹, m and M can be calculated from the sorption measurements. By graphical differentiation of the curve \bar{D} versus a_1 or \bar{D} versus a_2 with respect to a_1 and a_2 respectively, the tangents $d\bar{D}/da_1$ or $d\bar{D}/da_2$ can be obtained. Introduction of these values in equations (8) or (9) gives the values of the differential diffusion coefficient, D . The calculated D -values can be represented either as a function of the activity or of the concentration, since the dependence of the concentration on activity is known from the sorption measurements.

The two methods must, of course, give the same results. However, some small differences can be expected as a result of the errors introduced in the calculations by the inaccuracy of the graphical differentiation and integration in the determination of $d\bar{D}/da$ and M respectively.

The conditions of the experiments described in Part I for system I (viz. $a_1 = \text{variable}$, $a_2 = 0$) and system II (viz. $a_1 = 1$, $a_2 = \text{variable}$) are in agreement with the boundary limits required respectively by equations (8) and (9) above. Consequently, the values of \bar{D} already reported (see Part I) could be used in the calculations of D .

Concentration profiles

If the concentration dependence of diffusion is known, the concentration distribution through a film can be determined graphically or analytically.

The graphical method may be by trial and error, and is laborious because it necessitates the examination of a large number of curves, until the tangent on the curve describing $a = f(x)$ corresponds with da/dx as calculated from equation (1).

Analytically, the concentration profiles can be obtained from equation (2) if mathematical expressions for $D = f(a)$ and $c = f(a)$ are known. By keeping one limit of the integrals (i.e. a_1 and L , respectively) constant, and then introducing various values of a_2 into the resulting relationship from the integration, the distance x in the film corresponding with a_2 is obtained. As a result, $a = f(x)$ is determined. Because $c = f(a)$ is known, $c = f(x)$ can also be obtained.

The equation describing the curve D versus a , as obtained by "curve-fitting", for both the alkyd resin and the epoxy resin takes the form of:

$$D = K_1 - \frac{K_2}{\ln a} - \frac{K_3}{\ln^2 a} - \frac{K_4}{\ln^3 a} - \dots$$

Unfortunately this relationship, when multiplied by $c/a = f(a)$, gives mathematical expressions that are difficult to integrate. Consequently, in the present paper the concentration profiles were determined by the graphical method only.

Results and discussion

Since the materials investigated show different behaviour with respect to water, each will be discussed separately.

Epoxy resin

The mean water diffusion coefficients of the epoxy resin have been calculated from water vapour (\bar{D}_v) and osmotic permeation measurements (\bar{D}_{osm}) by applying the equation (4). They are shown in Fig. 1 as a function of mean water concentration (\bar{c}). The results derived from the two permeation methods agree satisfactorily for moderate \bar{c} -values. However, as mentioned before, very high mean diffusion coefficients have been obtained for two cases of the osmotic measurements (\bar{D}_{osm1} and \bar{D}_{osm2}).

The two cases correspond to situations in which very high water concentrations on both sides of the film are present.

It can be seen from Fig. 2, in which the diffusion coefficient calculated from equations (8) and (9) is plotted as a function of the concentration, that, at very high water concentrations, D increases very rapidly with the concentration.

Such a dependence predicts very high mean diffusion coefficients for situations in which, on both sides of the film, very high water concentrations are present.

This is confirmed by the very high \bar{D}_{osm} values (\bar{D}_{osm1} and \bar{D}_{osm2}) obtained for the cases of the two osmotic measurements described above, for which the water concentration is high but the difference in concentration is small.

Because the dependence of the diffusion coefficient on the concentration directly affects the concentration profile through the film, the above results can also be interpreted in terms of the concentration distribution across the film, as suggested by Long³. For this purpose, the concentration profile through the film for one case has been calculated, viz. when at the upstream boundary of the film $c = 17.8 \times 10^{-3} \text{g cm}^{-3}$ ($a = 1$), and at the downstream boundary of the film $c = 0$ ($a = 0$) (see Fig. 3). As expected, the concentration does not change linearly with the distance (x). From the upstream side, it decreases slowly over nearly the whole distance x , and falls sharply when it approaches the downstream boundary. The main resistance to diffusion occurs in the vicinity of the downstream boundary of the film. This effect was called by Long³, the "effect at downstream concentration".

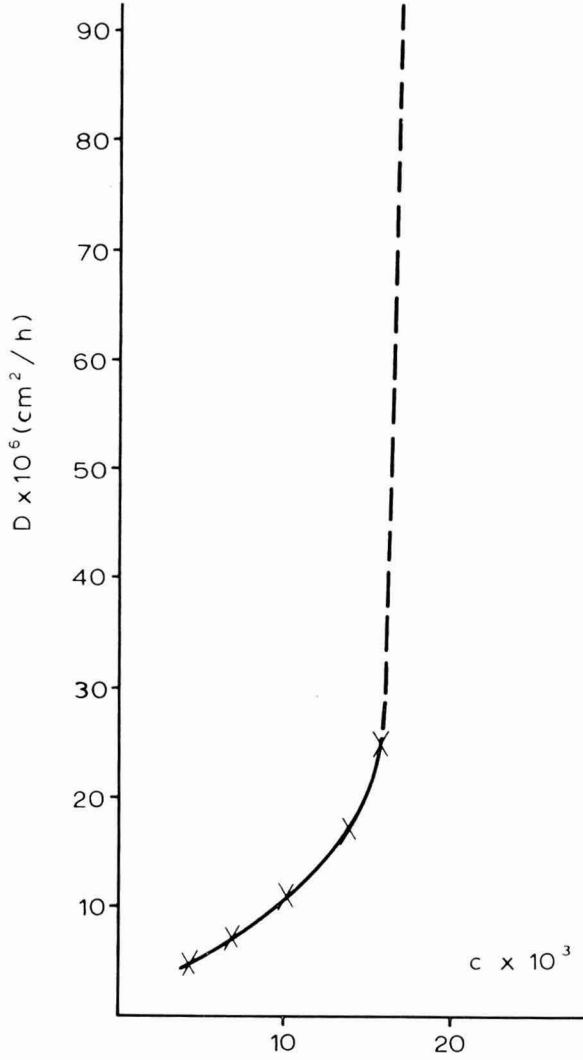


Fig. 2. Epoxy resin. Diffusion coefficient as a function of concentration

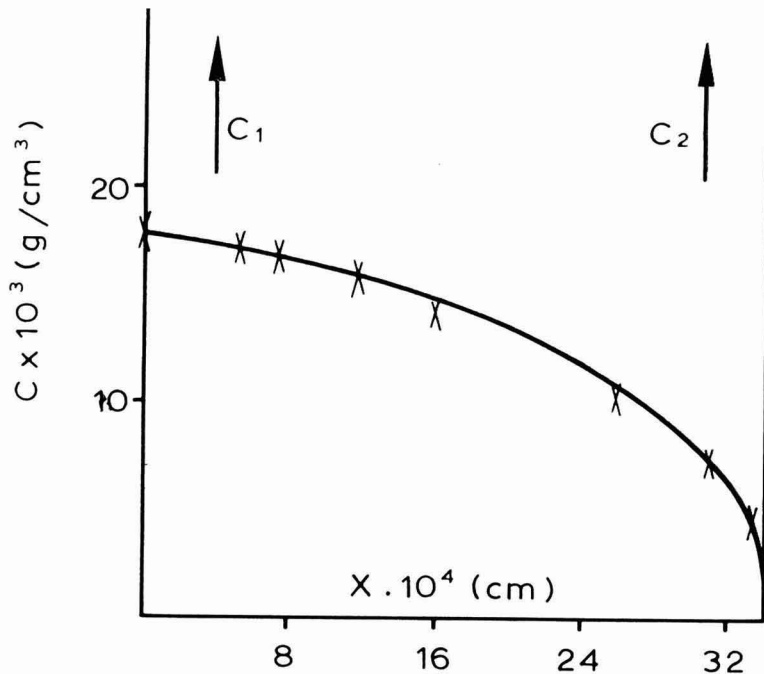


Fig. 3. Epoxy resin. Concentration distribution across the film, when at the upstream boundary $c_1 = 17.8 \times 10^{-3} \text{ (g cm}^{-3}\text{)}$ and at the downstream boundary $c_2 = 0$

Alkyd resin

The mean diffusion coefficients as calculated from the osmotic and the water vapour permeation experiments are summarised in Fig. 4.

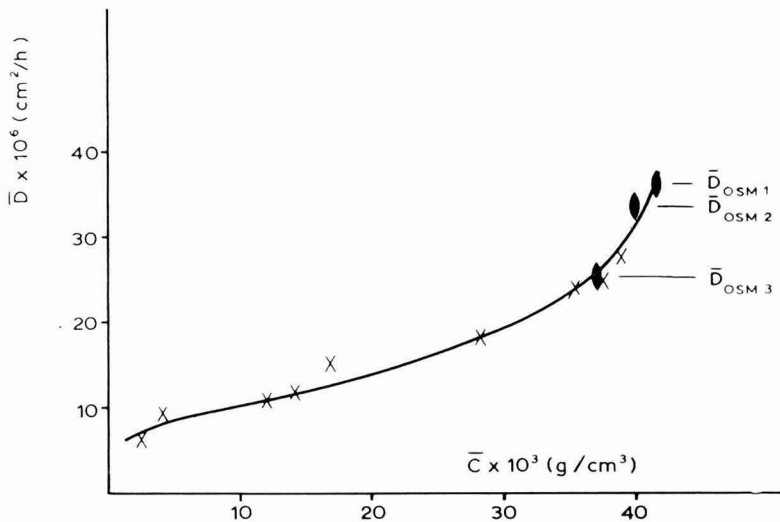


Fig. 4. Alkyd resin. Mean diffusion coefficients determined from water vapour (X) and osmotic (O) measurements as a function of the mean water concentration \bar{c}

For the hydrophilic alkyd resin, a behaviour similar to that of the epoxy resin is to be expected. However, in contrast with the epoxy resin (see Fig. 1), no jump in diffusion coefficient at very high water concentrations was found. This result seems to be a direct consequence of the formation of clusters of water in the alkyd resin films at higher concentrations (see also the results obtained with the plasticised chlorinated rubber).

The presence of the clusters of water in the alkyd resin film, as already shown in a previous paper⁸, may strongly decrease the mobility of the water molecules. As a result, the diffusion process is slowed down and lower diffusion coefficients than expected at higher concentration are obtained. In the literature⁹, similar cases of competitive processes of specific site and cluster interactions affecting the diffusion process have already been reported.

The dependence on concentration of the diffusion coefficient (Fig. 5) as well as the concentration profiles (one example is shown in Fig. 6), reflect this situation. The increase of D with c is moderate, and consequently the concentration profile is less concave towards the abscissa, when compared with that of the epoxy resin.

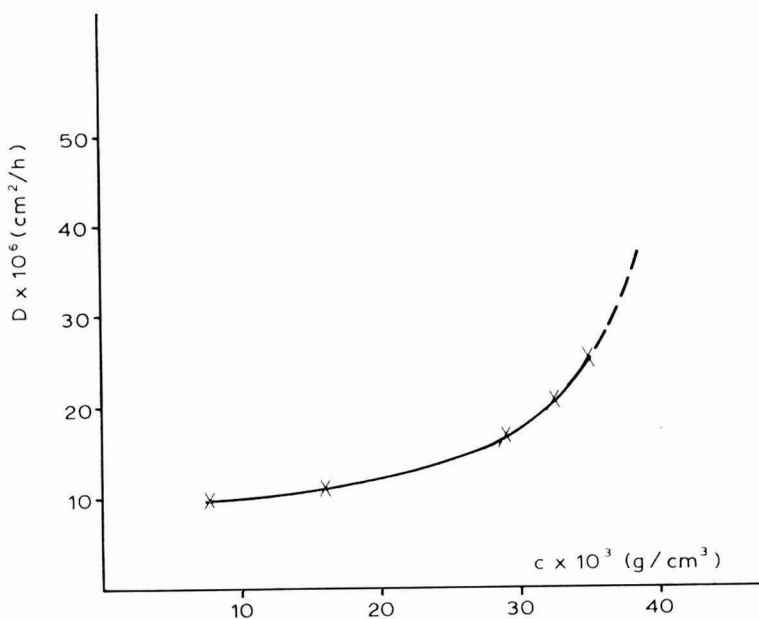


Fig. 5. Alkyd resin. Diffusion coefficient as a function of concentration

Chlorinated rubber

The results obtained with hydrophobic chlorinated rubber have previously been described^{1, 2}. The experiments with water vapour under various conditions have led to the conclusion that the diffusion coefficient is independent of concentration ($D = \bar{D} = \{110 \pm 10\} \times 10^{-6} \text{cm}^2 \text{h}^{-1}$). For water permeation under the osmotic conditions used, a somewhat higher diffusion coefficient value was obtained ($D_{osm} = \{120 \pm 10\} \times 10^{-6}$).

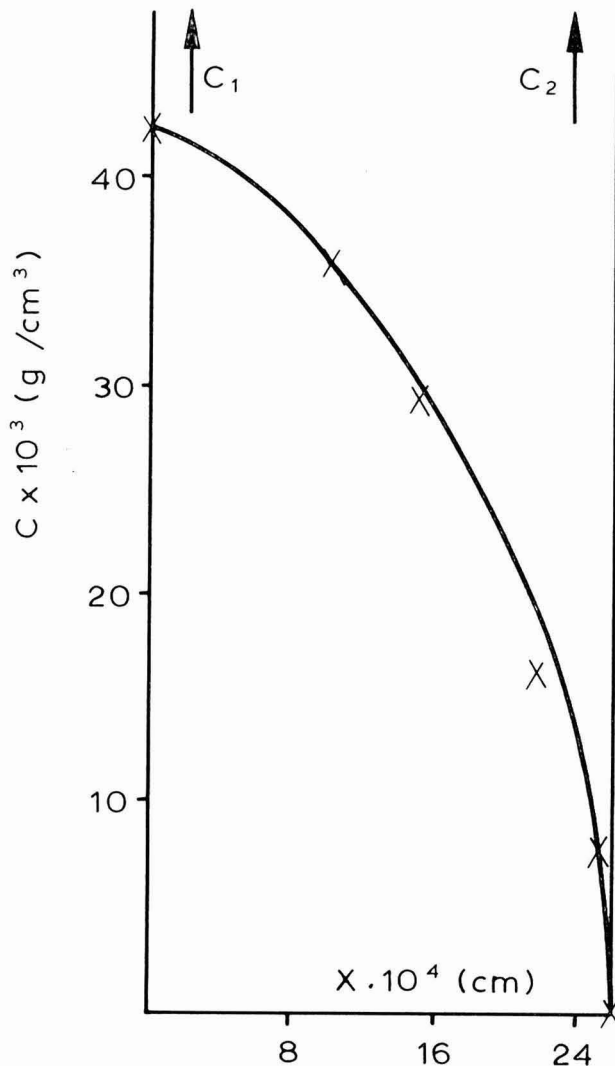


Fig. 6. Alkyd resin. Concentration distribution across the film, when at the upstream boundary $c_1 = 42.4 \times 10^{-3}$ (g cm⁻³) and at the downstream boundary $c_2 = 0$

It is probable that the inaccuracy of the sorption method at very low water uptake¹ is the cause of this difference. A constant D means that the concentration profile is linear.

Chlorinated rubber with chlorinated paraffin

Comparing the results obtained from the osmotic measurements (\bar{D}_{osm}) with those of water vapour measurements (\bar{D}_v), it can be concluded that a good agreement exists (see Fig. 7). As has already been reported⁸, the strong decrease of \bar{D} with c is a direct result of the immobilisation of the water molecules by the formation of clusters of water in the film.

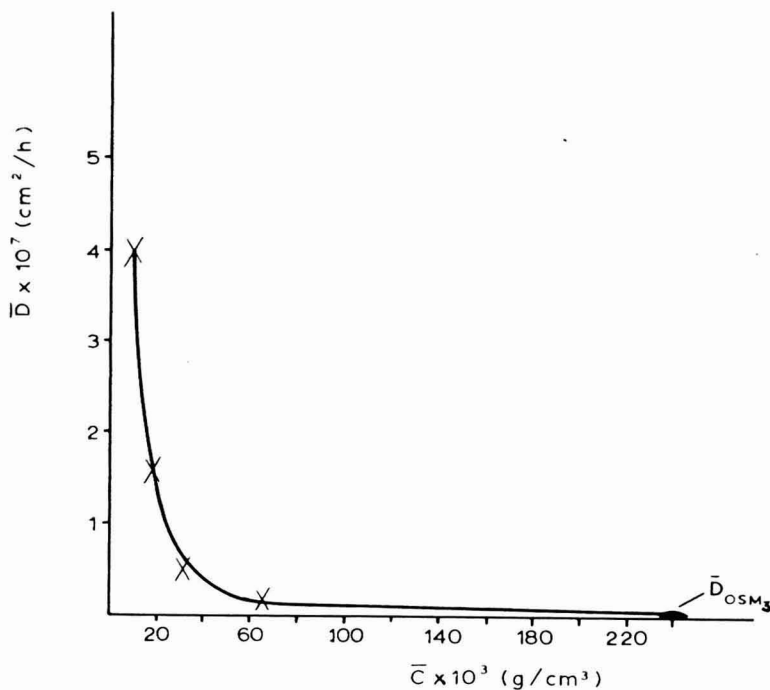


Fig. 7. Chlorinated rubber with chlorinated paraffin. Mean diffusion coefficients determined from water vapour (X) and osmotic (●) measurements as a function of the mean water concentration \bar{c}

A concentration profile, from the calculated dependence of D on c (see Fig. 8) was determined. Such a concentration profile (see Fig. 9) shows that, in this case, the resistance lies on the side of the high water concentration.

Conclusions

The mean water diffusion coefficients (\bar{D}) calculated from the osmotic and water vapour permeation measurements under steady state conditions, can be interpreted very satisfactorily in terms of the dependence of the diffusion coefficient, (D), on the concentration.

The good agreement between the results obtained from the two permeation methods shows that the osmotic measurements can be considered as an extension of the water vapour measurements, for the experimental condition of high water concentration on both sides of film.

For the hydrophilic materials, the diffusion coefficient increases with increasing concentration. Consequently, the concentration profiles are concave towards the distance axis. For the epoxy resin at very high water concentration, D increases almost asymptotically with the water concentration. It follows that, for cases in which very high water concentrations are present on both sides of the film, very high \bar{D} -values are found, because they approach the values of D . For the alkyd resin, the presence of clusters of water at high water concentrations decreases the mobility of the molecules of water. As a result, the diffusion coefficient increases only moderately with concentration.

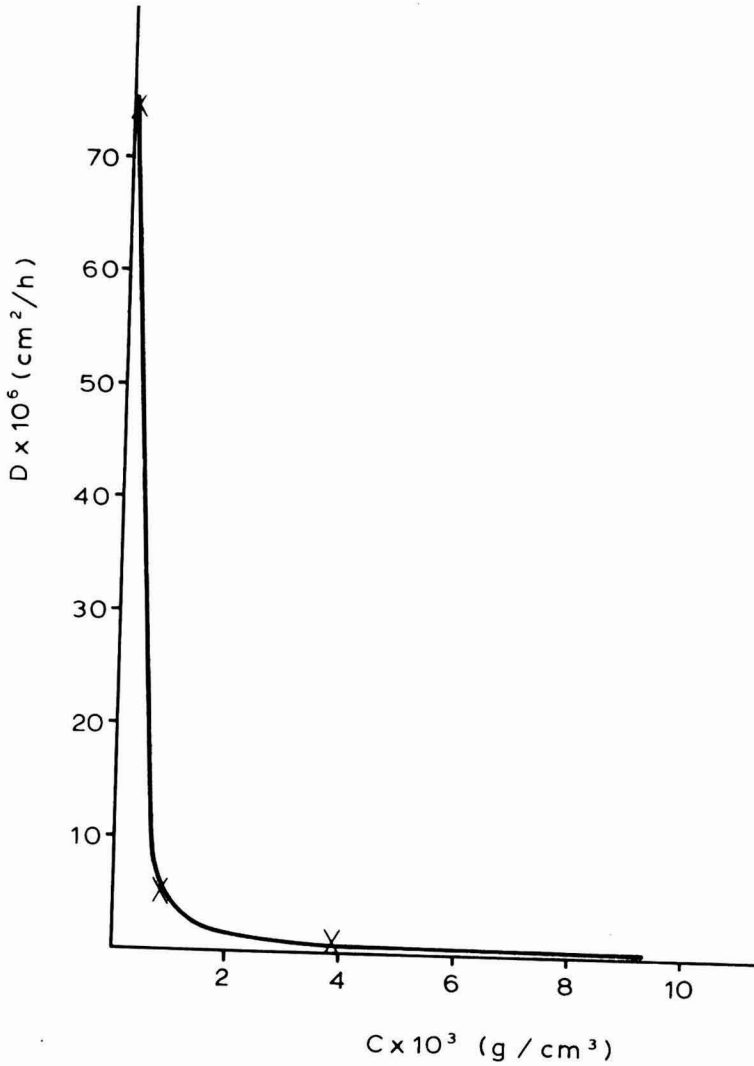


Fig. 8. Chlorinated rubber with chlorinated paraffin. Diffusion coefficient as function of concentration

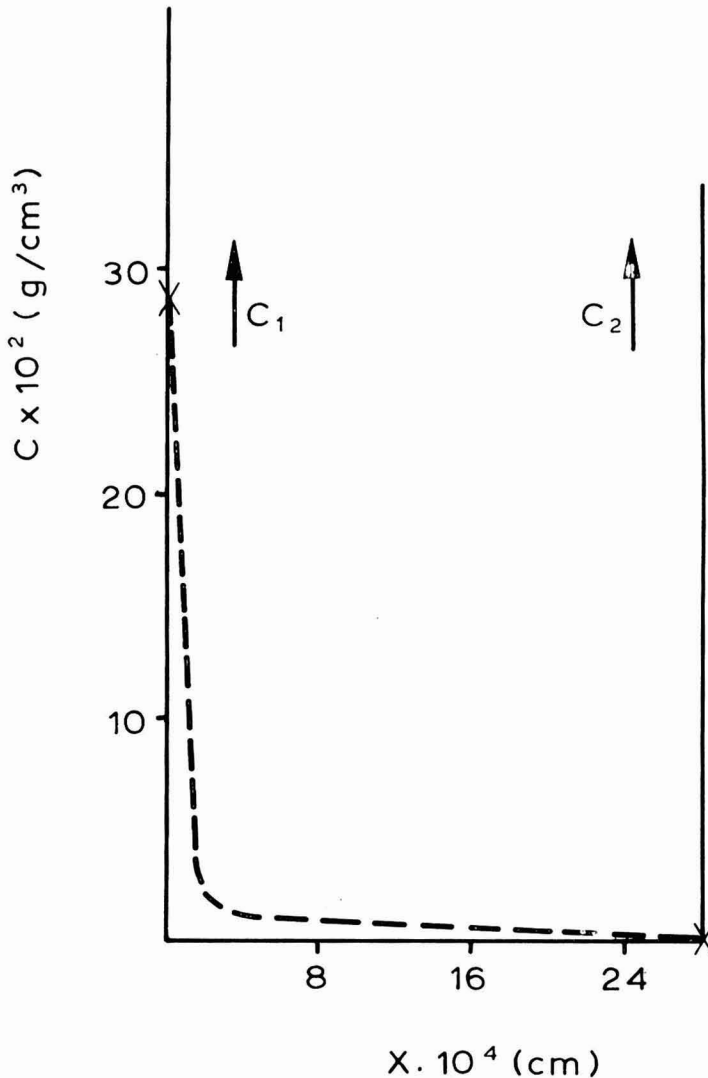


Fig. 9. Chlorinated rubber with chlorinated paraffin. Schematic description of the concentration distribution across the film, when at the upstream boundary $C_1 = 29.7 \times 10^{-2} \text{ (g cm}^{-3}\text{)}$ and at the downstream boundary $C_2 = 0$

The diffusion coefficient of the hydrophobic chlorinated rubber is independent of concentration. Consequently, the curve describing the concentration profile is linear.

For the plasticised chlorinated rubber, the diffusion coefficient decreases steeply with the water concentration. As a consequence the concentration distance curves are convex towards the distance axis. This behaviour is attributed to the strong tendency of the water molecules to form clusters.

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The relationship between the ion exchange capacity and the corrosion protection efficiency of alkyd based anti-corrosive paints

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Summary

The ion exchange capacity of a number of lacquers consisting of pigmented alkyds has been measured and compared with the anti-corrosive efficiency of the lacquers. The anti-corrosive properties were tested by applying the lacquers in thin films on cold-rolled steel panels and exposing the panels in outdoor exposure or in a salt fog chamber. It was found that the ion exchange capacity is a modifying factor in the corrosion protective property of pigmented alkyds. This applies to lacquers pigmented both with so-called active pigments such as red lead or zinc chromate and inactive pigments such as titanium dioxide. Measurement of the ion exchange capacity is suggested as a method of characterising anti-corrosive paints of this kind. Measurement of the ion exchange capacity at certain intervals during exposure of anti-corrosive paints or anti-corrosive paint systems may be developed to be a useful tool for following the progressive deterioration.

Keywords

Types and classes of coating
alkyd coating

Process and methods primarily associated with service or utility
ion exchange

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

Le rapport entre les caractéristiques des peintures alkydes anti-corrosives en tant qu'échangeurs d'ions et leur rendement de protection contre la corrosion

Résumé

On a déterminé les caractéristiques d'échange d'ions pour une gamme de résines alkydes pigmentées et l'on les a comparées avec le rendement anti-corrosif des vernis. Les propriétés anti-corrosives ont été appréciées en appliquant des feuillets minces des vernis aux panneaux d'acier laminé à froid, et ensuite en les exposant aux intempéries ou à un brouillard salin. On a trouvé que la caractéristique de l'échange exerce un effet modificateur sur la propriété anti-corrosive des alkydes pigmentées. Cela s'applique aux vernis pigmentées soit par des pigments soi-disant réactifs, tels que minium ou chromate de zinc, soit par les pigments inertes tels que dioxyde de titane. On propose le dosage de la caractéristique de l'échange en tant qu'une méthode pour caractériser les peintures anti-corrosives de cette sorte. Le dosage de la caractéristique de l'échange après de diverses périodes d'exposition des peintures anti-corrosives ou des systèmes de peintures anti-corrosives peut devenir un outil avantageux pour suivre leur détérioration progressive.

Die Beziehungen Zwischen der Fähigkeit Ionen Auszutauschen und der Antikorrosiven Schutzwirkung von Rostschutzfarben auf Basis von Alkydharzen

Zusammenfassung

Die Ionenaustauschfähigkeit einer Anzahl von aus pigmentierten Alkydharzlösungen bestehenden Lacken wurde gemessen und mit ihren antikorrosiven Eigenschaften verglichen. Letztere wurden nach Auftragen dünner Filme auf walzblanken Eisenblechtafeln durch deren Bewitterung oder Exponierung in der Salznebelkammer geprüft. Es wurde festgestellt, dass die Fähigkeit Ionen auszutauschen ein modifizierender Faktor in den Korrosionsschutzeigenschaften pigmentierter Alkydharze ist. Dieses ist sowohl der Fall bei Lacken enthaltend sogenannte aktive Pigmente, wie z.B. Bleimennige oder Zinkchromat, oder auch inaktive Pigmente, wie z.B. Titandioxid.

Das Messen der Ionenaustauschfähigkeit von Rostschutzfarben bzw. deren Filmsystemen in gewissen Intervallen während ihrer Exponierung könnte zu einem nützlichen Werkzeug entwickelt werden, um deren fortschreitenden Abbau zu verfolgen.

Соотношение между ионообменной способностью и эффективностью предохранения от коррозии в алкидных противокоррозийных красках

Резюме

Измерялась ионообменная способность ряда лаков, состоящих из пигментированных алкидов, и сравнивалась с эффективностью предохранения этих лаков от коррозии. Противокоррозийные свойства испытывались путем нанесения лаков, в виде тонких пленок, на хладнокатанные стальные панели и подвергая их выветриванию на открытом воздухе или в соляной камере. Найдено что ионообменная способность является модифицирующим фактором в противокоррозийных предохранительных свойствах пигментированных алкидов. Это относится как к лакам пигментированным так называемыми активными пигментами, как например свинцовый сурик или хромат цинка, так и к неактивным пигментам, как например двуокись титана. Измерение ионообменной способности рекомендуется как метод характеризующий противокоррозийные краски этого типа. Измерение ионообменной способности в определенные интервалы времени в течение выветривания противокоррозийных красок или красочных систем, может, при усовершенствовании, стать полезным пособием для изучения прогрессивного износа.

Introduction

Steel structures can be protected from the corrosive environments of the atmosphere either by inhibiting the anodic or cathodic electrode reaction or by interposing a barrier of high resistance in the path of the ionic flow in the electrolyte solution (Mayne¹). By anti-corrosive painting, several of these effects can be achieved.

The anodic or cathodic reactions can be inhibited by certain types of pigments in the paint formulation, for example, by the addition of zinc-containing pigments to the paint, the potential of the steel substrate can be lowered to an extent at which it becomes impossible for the positively charged ferrous ions to leave the metal surface. This process is also known as cathodic protection. Similarly, by the addition of oxidising pigments such as chromates the potential of the steel substrate is raised to such a value that a stable oxide film is formed over the entire surface. This process is also known as anodic protection. Finally, by the use of a binder with very low ionic permeability, the anodic and the cathodic areas can be isolated from one another; this system functions as a barrier layer in the electrolyte, provided that the adhesion of the paint to the substrate is perfect.

Maitland² investigated the conductivities of unpigmented free paint films immersed in electrolyte. The conductivity of the film changed quickly for the first five minutes at 25°C, and continued to change slowly over about three

weeks at room temperature. The quick change was dependent upon the water uptake of the film and the ionisation of ionogenic groups of the film, such as carboxyl groups in the case of alkyd films, caused by the presence of water.

Mayne and co-workers have continued their investigations of the change in the electrical conductivities of paint films immersed in electrolytes. The results of their studies have been summarised in a recent publication by Mayne¹. The slow change was attributed by Cherry and Mayne³ to a continuous ion exchange process. For example, in the case of alkyd films the more firmly attached hydrogen ions of the carboxyl groups are exchanged with the more mobile metallic ions of the surrounding electrolyte solution. Khullar, Ulfvarson and Wåhlin⁴ found that the acid groups that take part in the ion exchange process are to a large extent formed during the drying of the alkyd films. Indications have also been found that the bivalent ions such as Ca^{++} and Mg^{++} take part in this ion exchange process as monovalent ions. On the other hand, it has been impossible to decide whether the acid groups formed have different dissociation constants (pK_s), or whether all the groups have approximately the same dissociation constants, as there were indications for both postulates.

As has been pointed out by Maitland and Mayne⁵ the ability of the paint film to protect the substrate is dependent upon the electrical resistance of the film in the absence of inhibitive pigments. Khullar and Ulfvarson⁶ have investigated the ion exchange capacities of free films of 26 different binders at pH 5.6—6.0. The same binders were also applied on cleaned cold-rolled steel panels at a controlled film thickness of 40 μm and these panels were exposed to corrosive environments according to three different methods: outdoor exposure tests for one year, immersion tests, and salt spray chamber tests according to a modification of the SIS method 18, 41, 90. The results of these tests showed that there was a negative correlation between the ion exchange capacity and the corrosion protection efficiency of a paint film at a high level of significance. Hence, the higher the ion exchange capacity, the lesser the corrosion protection efficiency of the unpigmented paint film. It was further shown that, in the case of films with high ion exchange capacity, the conductivity increased more

Table 1

Rank correlation coefficients¹⁰ (r_a and r_b) showing the relationship between the ion exchange capacity and corrosion protection efficiency of unpigmented paint films. The coefficients are different from zero at the level of significance shown by the footnotes

Test	Salt spray	Immersion	Outdoor exposure	ion exchange capacity
Salt spray	1	0.718* 0.727	0.903— 0.916	— 0.797* — 0.803
Immersion	—	1	0.693* 0.704	0.611† — 0.616
Outdoor exposure ..	—	—	1	— 0.790* — 0.797
Ion exchange capacity ..	—	—	—	1

*99.9% level of significance.

†98.0% level of significance.

rapidly compared with films of low ion exchange capacity. The results of the above investigations are summarised in Table I and Fig. 1. These investigations have been extended to study what rôle the ion exchange capacity of a pigmented alkyd paint film plays in the corrosion protection of the steel substrate, even though other variables also influence this property of the pigmented paint film.

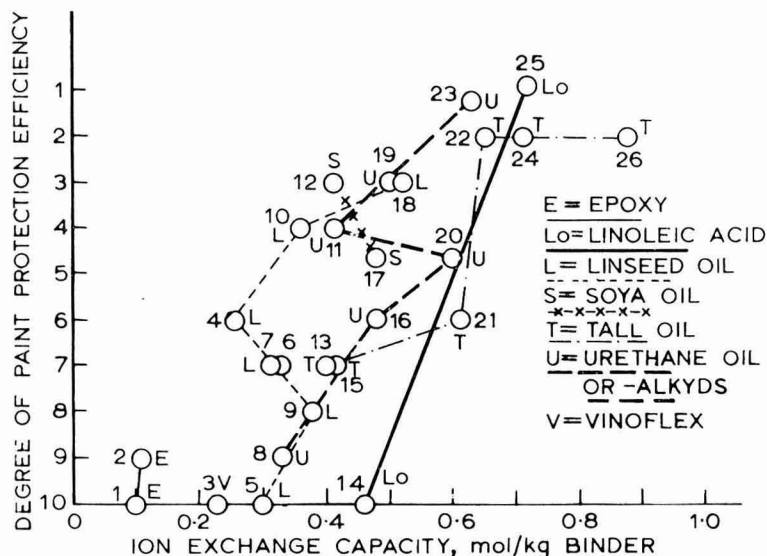


Fig. 1. Relationship between the ion exchange capacity of various binders and the degree of paint protection efficiency (according to SIS 18 51 11) of these binders when applied to steel panels and exposed for 500 hours in salt spray chamber according to SIS 18 41 90, but with intermittent spray 3 minutes every hour. The figures refer to Table 7 in reference 6.

Experimental

Ion exchange capacities of pigmented paint films

Three oil modified alkyds, A, B, C with high, medium and low ion exchange capacities respectively, were selected for pigmentation. The alkyds A and C were previously investigated by the authors, numbers 26 and 7 respectively in Fig. 1. (Khullar and Ulfvarson⁶). The pigments used in this study included red lead, zinc chromate, Oncor M 50 (basic lead silico-chromate), zinc oxide (all active pigments), iron oxide and titanium dioxide. Three levels of pigment volume concentration (PVC), 9, 18 and 35 per cent, were selected. The weights used in the various paint formulations were calculated from the pigment densities and the densities of the binders based upon the total solids in the binders, the values used being obtained from the raw material manufacturers. All pigments used were of commercial grade and no extenders were added to the systems. Pigments were dispersed in the binders by ball milling, and grinding was continued till the largest particles were 10 μm in size (Hegman scale 7). Driers (0.05 per cent Co, 0.3 per cent Pb and 0.1 per cent Ca in the form of naphthenates) were added to the paint just before application, as recommended by the manufacturer of the alkyd resins. The method of preparing the free films and the procedure for measuring the ion exchange capacities have been described in a previous publication by Ulfvarson, Khullar and Wåhlin⁴.

Electrolytic resistance of paint films

The measurements of DC resistances of detached paint films were made according to the method of Cherry and Mayne³ as described by Khullar and Ulfvarson⁶. The measurements were continued until there was no noticeable change in the conductance for several successive readings.

Conductivity measurements of the water extracts of the pigments were made according to the method of Wallgren⁷, using a conductivity meter (Philoscope). A 150 mg portion of each type of pigment was placed in a 250 ml beaker and 100ml distilled water was added to each. The solutions were stirred periodically and kept at a controlled temperature of 50°C. The conductivity of the clear solutions was measured daily at room temperature. The data were recorded for the first 26 days.

Corrosion tests

Application of paints: Cold-rolled steel panels, 15 × 7cm and 1mm thick, were degreased by washing with xylene and further cleaned by soaking for about five minutes in 1:1 hydrochloric acid containing 0.1 per cent thiourea as inhibitor, and finally washing with cold running water till the wash water was neutral to litmus paper. After drying the panels, coatings were applied by the use of a mechanical applicator. Only one side of the panel was coated with the test paint, the other side being given a thick coat of an aluminium pigmented epoxy paint. Film thickness was controlled to $18 \pm 2 \mu\text{m}$, which required a wet film thickness of about 40 μm . The panels were kept in a wire net cabinet and dried at controlled conditions of 20°C/65 per cent RH for three weeks.

Salt spray tests: The test procedure according to SIS 18, 41, 90 was followed, using a 5 per cent sodium chloride solution, but with the exception that a spraying period of 3 minutes per hour was used. After 500 hours of exposure in the salt spray chamber, the panels were removed and their degree of corrosion protection efficiency according to SIS 18 51 11 was noted.

Atmospheric exposure tests: The coated panels were mounted on a test rack at 45° facing south. The rack was placed on the top of one of the buildings of Statens Provningsanstalt, Stockholm (industrial climate). The panels were inspected periodically.

Results

Ion exchange capacities of the pigmented paint films at pH 6.15—6.25, calculated as mol kg⁻¹ of the binder, are given in Table 2. It appears from this table that zinc chromate and zinc oxide pigments decrease the ion exchange capacities of pigmented films considerably, as can be seen by comparison with the ion exchange capacities of the unpigmented films of the three binders used in this study. Red lead has a moderate effect, whereas iron oxide and titanium dioxide have least effect on the ion exchange capacities. One explanation of the reduction in the ion exchange capacities is that all the pigments are water soluble to some extent or contain water soluble salts, which possibly dissolve in the water taken up in the swollen film and thus neutralise the acid groups of the alkyd concerned. Furthermore, pigment particles, being basic, can react with the acid groups of the alkyd film. The ability of the various pigments to change the conductivity of distilled water when suspended in it is shown in Table 3. By comparing the results in Table 2 with the results in Table 3, it

can be seen that the pigments that produce the highest change in conductivity when suspended in water, zinc chromate and zinc oxide, also influence the ion exchange capacities of the three alkyd binders to the highest degree, which would be expected if the basic components of the pigments neutralise the acid groups in the film.

Table 2

Ion exchange capacity of detached pigmented paint films

Conditions: 0.1 M NaCl solution, 50°C temperature, initial pH 6.15-6.25, dry film thickness 25-30 μ m

Alkyd	Pigment	Ion exchange capacity, mol kg ⁻¹ of binder, double determinations, PVC %*							
		35		18		9		0	
A	TiO ₂	0.35	0.35	0.41	0.41	—	—	—	0.88
	ZnCrO ₄	0.00	0.00	0.00	0.00	—	—	—	—
	ZnO	0.03	0.03	—	—	—	—	—	—
	Fe ₂ O ₃	1.03	1.08	0.96	0.99	—	—	—	—
	Red lead	0.09	0.18	0.23	0.23	—	—	—	—
	Fe ₂ O ₃ + ZnCrO ₄ †	0.01	0.05	—	—	—	—	—	—
B	TiO ₂	0.26	0.26	0.27	0.32	0.43	0.46	—	0.62
	ZnCrO ₄	0.00	0.00	0.02	0.00	0.13	0.20	—	—
	ZnO	0.00	0.00	0.00	—	0.02	0.02	—	—
	Fe ₂ O ₃	0.53	0.58	0.61	0.62	0.72	0.74	—	—
	Red lead	0.10	0.10	0.25	0.25	0.26	0.26	—	—
	Oncor M 50	0.08	0.10	0.26	0.28	0.28	0.32	—	—
	Fe ₂ O ₃ + ZnCrO ₄ †	0.04	0.04	—	—	—	—	—	—
C	TiO ₂	0.15	0.20	0.18	0.20	0.21	0.21	—	0.31
	ZnCrO ₄	0.00	0.00	0.00	0.00	—	—	—	—
	ZnO	0.02	0.02	—	—	—	—	—	—
	Fe ₂ O ₃	0.25	0.25	—	—	—	—	—	—
	Red lead	0.00	0.00	0.23	0.27	—	—	—	—
	Oncor M 50	0.26	0.26	—	—	—	—	—	—

*Pigment concentration per cent by volume. †60% Fe₂O₃ + 40% ZnCrO₄.

Table 3

Conductance measurements of water extracts of different pigments

Conditions: 150mg of pigment added to 100ml of distilled water, stirred and the solution kept at 50°C temperature. All readings were taken at room temperature

Pigment	Conductance readings in μ S cm ⁻¹ (days)						
	Initial	1	3	7	14	26	
Distilled H ₂ O	3.2	3.6	4.8	5.6	6.7	6.7	
Red lead	7.1	7.1	9.1	10	10	13	
TiO ₂	4.4	9.1	14	16	25	27	
Fe ₂ O ₃	3.0	4.6	6.7	10	10	10	
ZnO	13	17	26	42	42	42	
ZnCrO ₄	500	1,000	1,000	1,000	1,000	1,700	

It is worth mentioning here that ion exchange capacities change proportionately more at the lower than at the higher PVC values, for instance in the case of titanium dioxide pigments in the different binders. In alkyd A, the ion exchange capacity per kg of binder in the film containing TiO_2 decreases compared with the ion exchange of unpigmented film, to 47 per cent at 18 per cent PVC and to 40 per cent at 35 per cent PVC. Thus, it is seen that by doubling the PVC only a small change in the ion exchange capacity took place. In the case of alkyd B at PVC values of 9, 18 and 35 per cent, the ion exchange capacity decreased to 72, 47.6 and 42 per cent respectively, and in the case of alkyd C at the same PVC values, the ion exchange capacities decreased to 68, 61 and 57 per cent respectively, which may indicate that there are different types of acid groups in the binder which possess different dissociation constants.

In a few cases, ion exchange capacities increased with the increase of the PVC, for example in the case of films pigmented with iron oxide pigments. In the case of alkyd A, the ion exchange capacity increased to 111 and 120 per cent of the ion exchange capacity of unpigmented film at PVC values of 18 and 35 per cent respectively. Similarly, with alkyd B these figures are 118, 100 and 90 per cent at PVC values of 9, 18 and 35 per cent respectively and for alkyd C at 35 per cent PVC the ion exchange capacity is 81 per cent of the value for unpigmented film. Obviously, different binders react differently with the same pigment. This situation is also well illustrated by the different PVC values of red lead. For alkyd A, the ion exchange capacity decreased to 26 and 15 per cent of the value for unpigmented film at 18 and 35 per cent PVC of red lead. For alkyd B these figures are 42, 40 and 16 per cent at 9, 18 and 35 per cent PVC values and for alkyd C the figures are 81 and 100 per cent for 18 and 35 per cent PVC. Factors which increase or decrease the ion exchange capacity of the film are the concentration and type of water soluble components of the pigments. The pigments no doubt also influence the drying process of the film and, as pointed out earlier, most of the acid groups that take part in the ion exchange are formed during the drying process of the paint film. Thus it appears that the pigments and the binder react together in a complicated manner.

Results of the resistance measurements of the detached films are given in Table 4. It appears from this table that the initial resistance values of different films vary from Mohms cm^2 to hundreds of Mohms cm^2 . These values decreased to tenths of Mohms cm^2 during the first week. Films containing red lead pigments are the only ones with high initial resistance value that remained unchanged during the first week. These films changed only slightly during a sixty day period. Films of alkyd C, which gave small ion exchange capacities, as seen in Table 4, have a resistance value that remained unchanged during the first week and required a long time before a noticeable change occurred in the resistance. Films of alkyd A, which possess the highest ion exchange capacities, correspondingly gave a lower initial resistance, a lower resistance after a week and a shorter time until further changes in resistance ceased. There are, however, exceptions to this behaviour.

Titanium dioxide with alkyd A gives relatively high initial resistance and with alkyd C low initial resistance, but after one week the relations mentioned are again found here. The film with titanium dioxide in alkyd A was unusually

Table 4

DC resistance measurements of pigmented paint films

Conditions: 0.1 M NaCl solution as electrolyte, room temperature, Ag/AgCl electrodes.

Alkyd	Pigment	PVC %	Film thickness, μm	DC resistance, Mohms cm^{-2}			
				Initial	One week	Final	Days till failure*
A	Oncor M 50	35	28	1.80	0.90	0.50	10
	TiO ₂	35	40	27.0	0.32	0.20	14
	Fe ₂ O ₃	35	28	28.0	0.36	0.36	1
	Clear	0	50	3.00	0.10	0.10	3
B	TiO ₂	35	28	180	2.50	0.53	25
	Fe ₂ O ₃	35	22	2.50	0.90	0.50	20
	ZnCrO ₄	35	22	2.70	0.001	0.001	1
	ZnCrO ₄	18	28	12.0	0.70	0.30	15
	ZnCrO ₄	9	28	42.0	0.75	0.50	20
	TiO ₂	18	18	11.0	0.24	0.12	7
	Fe ₂ O ₃	18	22	5.20	0.25	0.25	6
	Red lead	18	20	3.5	0.21	0.21	5
C	Red lead	35	28	140	140	2.00	60
	Fe ₂ O ₃	35	28	40.0	1.80	0.50	22
	TiO ₂	35	28	23.0	8.50	2.40	40
	Clear	0	50	27.0	27.0	1.30	30

* The resistance does not change further.

thick, which may explain the initial discrepancy. It is worth mentioning that the film containing zinc chromate pigments at 35 per cent PVC gives lower resistance values than those observed for any other film. The only binder tested in this case was alkyd B, and the initial resistance values and the resistance value after one week increased with the decrease of PVC.

The results of salt spray tests and outdoor exposure tests are given in Table 5. The results reported here (according to SIS 18 51 11) are in terms of degrees of paint protection efficiency, where a value of 10 means no damage to the film and a value of 1 corresponds to a surface completely covered with rust. Ion exchange capacities as mol kg^{-1} of the binder and as mol kg^{-1} of the total weight of the dried film are also shown in this table.

It is observed that of all the pigments used, zinc chromate at 35 per cent PVC gives the best corrosion protection in salt spray test. At 9 per cent PVC value the corrosion protection efficiency approaches close to that of inactive pigments. Paints with red lead are generally ranked second in order of efficiency in the salt spray test. Oncor M 50 with alkyd B gives good corrosion protection, but in combination with alkyd C the results are worse than the results with the panels coated with binder C without any pigment. Contradictions are noticed in the results of outdoor exposure tests. The binder appears to play an important role in these tests. For alkyd A, the best results are obtained with red lead and iron oxide pigments, which seems rather surprising in the case of the latter pigment. The same binder gives poor results with Oncor M 50. Zinc chromate

Table 5
Results of corrosion tests

Conditions: Salt spray test. 50°C temperature, NaCl concentration 5%, pH 6.8-7.0, spray cycle 3 minutes/hour, duration of test 500 hours. Outdoor exposure test (Stockholm). Test duration 1 year.

Binder	Pigment	PVC %	Degree of paint protection efficiency		Ion exchange capacity	
			Salt spray	Outdoor exposure	mol kg ⁻¹ dry binder (Table 2)	mol kg ⁻¹ dry paint
A	ZnCrO ₄	35	10	7	0	—
	TiO ₂	35	2	5	0.35	0.12
	ZnO	35	1	2	0.03	0.01
	Oncor M 50	35	4	5	0.33	0.11
	Fe ₂ O ₃	35	4	8	1.03	0.33
	Red lead	35	7	8	0.10	0.03
	Clear	0	2	1	0.88	0.03
B	ZnCrO ₄	35	10	9	0.0	0
	TiO ₂	35	3	4	0.26	0.1
	ZnO	35	6	5	0	0
	Oncor M 50	35	8	9	0.09	0.035
	Fe ₂ O ₃	35	1	5	0.55	0.19
	Red lead	35	7	6	0.10	0.02
	Fe ₂ O ₃ + ZnCrO ₄	35	9	9	0.04	0.02
	ZnCrO ₄	18	9	7	0.02	0.01
	ZnCrO ₄	9	5	6	0.16	0.1
	Fe ₂ O ₃	18	3	7	0.62	0.37
Fe ₂ O ₃	9	4	6	0.74	0.50	
C	TiO ₂	35	4	7	0.15	0.08
	ZnO	35	4	—	0.02	0.01
	Oncor M 50	35	5	5	0.26	0.13
	Fe ₂ O ₃	35	4	6	0.25	0.13
	Red lead	35	8	7	0	0
	Clear	0	7	8	0.30	—

and Oncor M 50 give good results in combination with alkyd B, but in this case red lead performed surprisingly poorly, whilst the results of iron oxide are as good as the results of zinc chromate at 18 per cent PVC. Oncor M 50 performed poorly again with alkyd C, which was in accordance with the results of the salt spray tests. It appears that the atmospheric corrosion test results with alkyd C are best without any pigment, the next best being red lead and titanium dioxide. Zinc chromate was not tested with this binder.

These results are to some extent unexpected and may need further confirmation, which has not yet been possible. In practice, better results should be obtained than shown by these tests because the film thickness was only about 18 μm, and no top coat was used. Generally, it can be said that the interaction between the binder and the pigment has been found to be of great importance for the final corrosion protection.

Discussion

The only reliable method of testing an anti-corrosive paint is to perform an outdoor exposure test of the complete paint system at realistic film thicknesses on a realistic substrate. Such tests can be carried out by following the procedure in Bulletin No. 26 from the Swedish Corrosion Institute. Paints which are worth consideration take several years to test. Many attempts have been made to find methods of reducing the test duration by using accelerated test methods or by means of electro-chemical tests, e.g. potentiostatic or galvanostatic investigations of painted steel panels as carried out by Clay⁸ and of water extracts of inhibitive pigments as performed by Ruf⁹. These methods do not take into consideration, however, all factors that influence the rust proofing efficiency of anti-corrosive paints. One important contribution towards this end is the measurement of the change in conductance of the paint film soaked in solutions of electrolyte with time. One indirect indication of this is the ion exchange capacity of the paint film. As has been already shown, there exists a clear relationship between the ion exchange capacity of the film and the corrosion protection efficiency of the clear varnish film. The investigations described in this paper were aimed at determining whether such a relationship existed in the case of pigmented alkyd paint films. In order to obtain a rough picture of the relationship described above, a rank correlation analysis has been made as suggested by Kendal¹⁰, and the results are shown in Table 6. From the results in this table, it appears that there is a certain correlation between the results of the salt spray tests and the ion exchange capacities, as can also be seen from Fig. 2, but there is an uncertainty about a correlation with the results of the outdoor exposure tests. It is likely that by performing a larger experiment, such a correlation would also exist for an outdoor test.

Table 6

Rank correlation coefficients (ρ_a and ρ_b) showing the relationship between the ion exchange capacity and corrosion protection efficiency of pigmented paint films

Test	Salt spray	Outdoor exposure	Ion exchange capacity		Final resistance	Days to failure by resistance measurements
			Based on binder	Based on total film weight		
Salt spray	1	0.706*	-0.482†	-0.617†	0.200	0.143
Outdoor exposure ..	—	1	-0.488	-0.628	0.207	0.147
Ion exchange capacity (based on binder)	—	—	1	0.966*	-0.405	-0.516
Ion exchange capacity (based on total weight of film)	—	—	—	1	-0.409	-0.518
Final resistance	—	—	—	—	1	0.905*
Days to failure by resistance measurements	—	—	—	—	—	1

*99.9% level of significance. †98.0% level of significance.

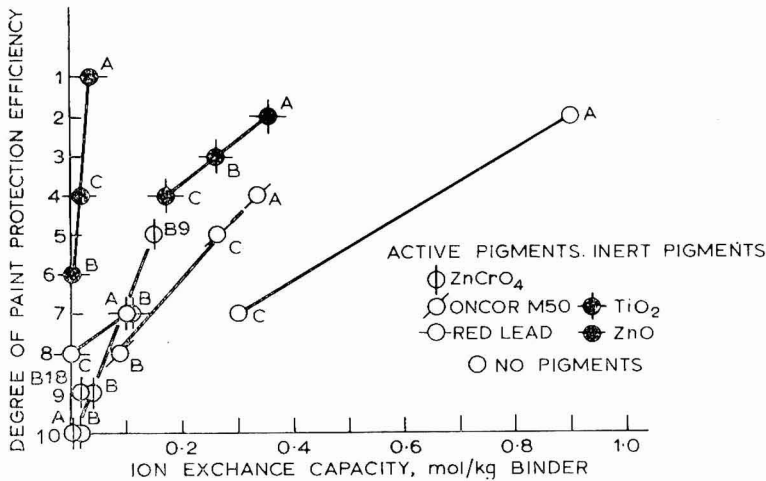


Fig. 2. Relationship between the ion exchange capacity of the binders in various paint formulations and the degree of paint protection efficiency (according to SIS 18 51 11) of paint films after exposure of panels for 500 hours in salt spray chamber according to SIS 18 41 90, but with intermittent spray 3 minutes every hour. The letters refer to the types of alkyd shown in the text

This view is supported by the fact that there already exists a significant correlation between the results of the salt spray tests and the outdoor exposure tests. It may be mentioned, however, that the corrosion protection efficiency in the case of a pigmented paint is affected by several other factors. For example, a paint containing a zinc chromate pigment is a good anti-corrosive paint not because the ion exchange capacity in this case is neutralised by the basic pigment, but because of a mechanism involving anodic protection. If this were not so, zinc oxide would give good protection, because it reduces the ion exchange capacity of the binder, but the results are poor in this case, both in the salt spray and outdoor exposure tests. The ion exchange capacity is not the dominating factor, but a secondary one. It can be said, however, that, for paints containing the same types of pigments at the same PVC values, the ion exchange capacity is the determining factor for the rank order of the corrosion protection efficiency. If the results shown in Table 5 are studied for each individual pigment, it is observed that, with the exception of iron oxide (which sometimes increased the ion exchange capacities) there exists a clear relationship between the ion exchange capacities and their corrosion protection efficiencies in both corrosion tests. In Fig. 2, the experiments with iron oxide pigments have been omitted, but in the other cases the relationship is good and, as described earlier, the lines of regression differ in their slopes. It can be concluded that ion exchange capacity may be used as a supplementary test for determining the anti-corrosive qualities of the paint system. High residual ion exchange capacity after the pigment has been added to the binder is to be considered bad. A comparison between the original and the residual ion exchange capacities after the pigment and the binder have been combined shows that a film which has a high original ion exchange capacity also has a high residual ion exchange capacity. This gives a clue to product development. Alkyds which produce a large number of acid groups or a large concentration of acid groups during the drying process

should be avoided. The ion exchange capacity cannot be used alone as an indication of the anti-corrosive value of a paint, but together with other measurements and tests this property is relevant. In a series of tests to determine the anti-corrosive efficiency of paint systems, it is worth taking into consideration how the pigment and the binder function together to produce an anti-corrosive effect. Such measurements can be made by means of potentiostatic techniques, and investigations using these techniques in the case of pigmented paint systems are in progress in the Statens Provningsanstalt.

A different way of using measurement of the ion exchange capacity is to expose panels painted with the anti-corrosive paints under test in the environment for which they are intended, and then to follow their progressive deterioration by sampling pieces of detached films and measuring the residual ion exchange capacity. This possibility has not yet been investigated.

A successive testing and recording of the conductivity through the film to its substrate could possibly replace this somewhat laborious measurement, but on the other hand purely local defects in the film would be a disturbing influence in this method.

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The characterisation of carbon black surfaces*

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Summary

To understand the relevance of the surface properties of carbon black, it is necessary to appreciate the various uses for which it is intended and the manner in which it differs from other carbons manufactured commercially, e.g. graphite, charcoal, active carbons, etc. It is also profitable to match the surface characteristics of the carbon black against the surface properties of other materials.

In this review the particle size, surface area and associated properties of carbon black, as derived from such techniques as electron microscopy and nitrogen adsorption, are outlined and details of its structure are obtained as the result of X-ray diffraction techniques.

The effect of heat treatment on the carbon blacks and the properties of oxidised carbon blacks are discussed. The adsorption upon these various carbon blacks of other gases and vapours and the manner in which such results are interpreted are discussed. Correlation of the data obtained by various techniques is an important aspect which is considered in some detail.

Keywords

Prime pigments and dyes
carbon black

Process and methods primarily associated with analysis, measurement and testing
nitrogen adsorption

Properties, characteristics and conditions primarily associated with materics in general
particle size
surface area

Miscellaneous terms
BET equation

La caractérisation des surface du noir de carbone

Résumé

Afin de comprendre l'importance des caractéristiques superficielles du noir de carbone, il est nécessaire de tenir compte des applications prévues, et de la manière en laquelle il est différent d'autres formes de carbone qui existent en commerce, e.g. graphite, charbon de bois, et des carbones activés. Il est d'ailleurs avantageux de comparer les caractéristiques des surfaces du noir de carbone avec celles d'autres matériaux.

Dans cet exposé on mentionne la grandeur particulaire, l'aire superficielle, et des caractéristiques alliées, du noir de carbone que l'on peut doser par des techniques telles que microscopie électronique et adsorption d'azote, et également la structure dont les détails sont obtenus par la technique de diffraction des rayons X.

On discute l'effet du traitement à chaud des noirs de carbone, ainsi que les caractéristiques des noirs de carbone oxydés. On discute l'adsorption des gaz et des vapeurs par ces divers types du noir de carbone et d'ailleurs la façon d'interpréter ces résultats. La corrélation des données obtenues par de diverses techniques est un aspect important que l'on considère en quelque détail.

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Die Charakterisierung von Carbon Black Oberflächen

Zusammenfassung

Um die Bedeutung der Oberflächeneigenschaften von Carbon Black verstehen zu können, muss man die verschiedenen Anwendungsgebiete, für welche es bestimmt ist, und die Art und Weise, in welcher es sich von anderen, für den Handel hergestellten Kohlenstoffen, z.B. Graphit, Holzkohle, Aktivkohle usw. unterscheidet, in Betracht ziehen. Es lohnt sich ausserdem, die Oberflächencharakteristika von Carbon Black mit denen anderer Stoffe zu vergleichen.

In dieser Betrachtung werden die Grösse der Oberfläche von Carbon Black und damit verbundene, mit Hilfe von Techniken wie der Elektronenmikroskopie und Stickstoffadsorption, feststellbare Eigenschaften sowie Einzelheiten ihrer Struktur, die man mit Hilfe von Röntgenstrahlen-Diffraktionstechniken ausfindig macht, skizziert.

Die Auswirkung von Wärmebehandlung auf Carbon Blacks, und die Eigenschaften oxidiertes Carbon Blacks werden besprochen. Erörtert wird auch die Adsorption anderer Gase und Dämpfe durch diese verschiedenen Carbon Blacks und die Art und Weise, mit welcher solche Resultate interpretiert werden.

Ein wichtiger Gesichtspunkt ist die Korrelation der bei Anwendung verschiedener Techniken erhaltenen Daten, Dies wird ziemlich eingehend in Betracht gezogen.

Характеристика сажевых поверхностей

Резюме

Для оценки применимости поверхностных свойств сажи, необходимо учесть различные употребления для которых она предназначается и в чем она отличается от других промышленно изготовляемых саж, как например графит, древесный уголь, активные углероды и. т. д. Целесообразно также сопоставить поверхностные характеристики сажи с поверхностными свойствами других материалов.

В настоящем обзоре рассматриваются величина частиц, поверхностная площадь и смежные свойства сажи, полученные путем электронной микроскопии и адсорбции азота и получены подробности ее структуры, в результате дифракции рентгеновских лучей.

Обсуждается эффект термообработки на сажи и на свойства окисленных саж. Обсуждаются также адсорбция других газов и паров на различных сажах и метод по которому интерпретируются эти результаты. Соотношения между данными полученными различными техническими методами являются важным фактором, который рассматривается несколько подробно.

Introduction

To appreciate the surface properties of carbon blacks that are of relevance, it is necessary to indicate the various uses for which it is intended and to briefly indicate its form and structure. The amorphous carbons occur in the various forms listed in Fig. 1, as well as in crystalline forms. The only crystalline form which has any bearing on the topic of carbon blacks is graphite. The carbon blacks differ from the bulk amorphous carbons such as cokes and charcoals by their particulate nature, being composed of spherical particles of colloidal dimensions. The arrangement of carbon atoms in graphite layer planes is masked by the colloidal dimensions of the carbon black particles. The structure of the carbon black particles is largely determined by X-ray diffraction studies supplemented by electron microscopy, and the subject has been reviewed in detail by Heckman¹. The carbon atoms are chemically bonded together to form plane hexagonal networks called layer planes, which are identical to the layer planes in graphite. In normal carbon blacks, the dimensions of the layer planes are much smaller than those in graphite, and it is therefore more likely

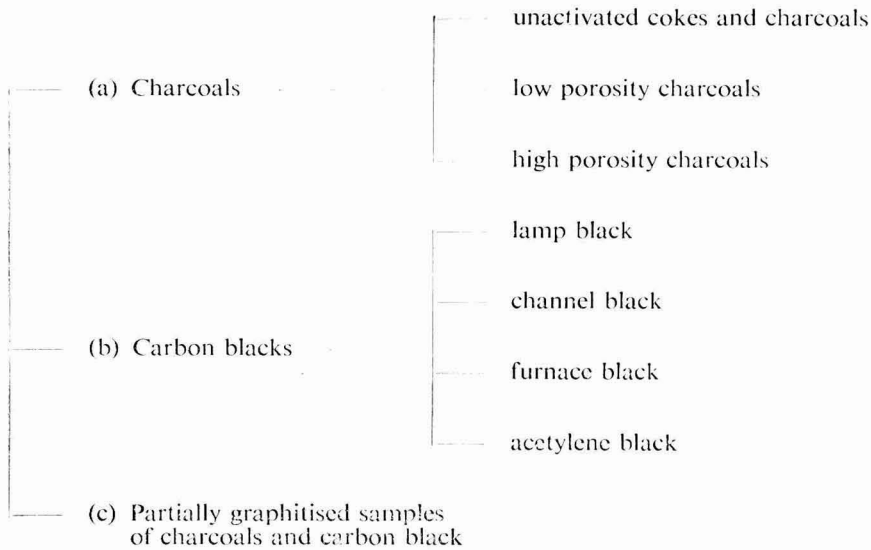


Fig. 1. Classification of amorphous carbons

that there will be a higher proportion of hydrogen attached to the "edge" of these planes. The surface of the carbon black may be covered with oxygen complexes which can be removed by heat treatment in an inert atmosphere. Heat treatment in the region 2,700-3,000°C causes graphitisation to take place, but this may be only partial.

Whereas the charcoals and derived products are prepared from solid raw materials, the carbon blacks are obtained from the partial combustion or thermal decomposition of liquid or gaseous hydrocarbons (see Fig. 2). The most recent figures show that the majority of the carbon blacks are produced by the furnace process.²

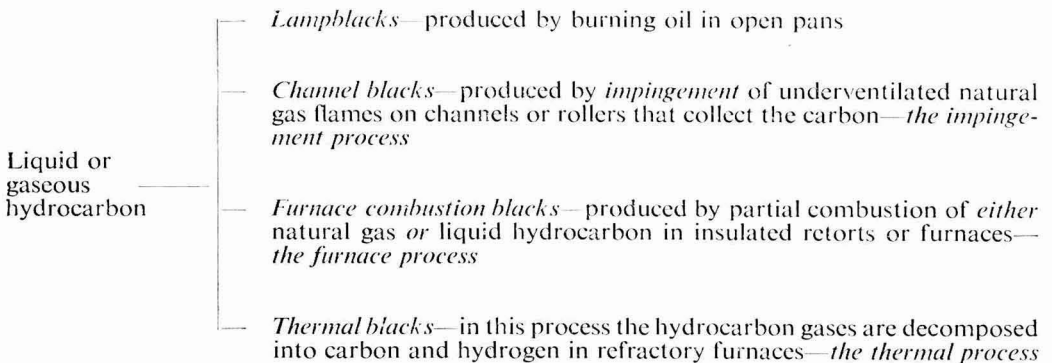


Fig. 2. The preparation of carbon blacks

The uses of the colloidal carbon black depend upon its small particle size, on its adsorption and absorption properties, on its colour, on its capacity to

absorb radiation, on its electrical conductivity, and on its chemical reactivity. Thus, its use in the grinding of Portland cement is due primarily to its small particle size, its property of decolourising is due to its adsorption capacity, its use in dry cell batteries is due to its ability to absorb the electrolyte solution, and its use as a printing ink is due to its colour. Uses based on its radiation absorption capacity include its use in soil treatment to speed germination of seeds by increasing the temperature of the soil, and its use in polyethylene and polystyrene wire and cable jackets is due to its ability to prevent the breakdown of the resin by exposure to sunlight.

Typical properties of the various classes of carbon black are listed in Table 1 and include many that are surface dependent. It can be seen that these properties taken together are often sufficient to characterise a particular type of carbon black. To appreciate the true significance of the average particle diameter, it is, of course, necessary to know the technique used for its measurement. The calculation of a surface area from nitrogen adsorption data is obviously a property dependent upon a single technique with a definite method of calculation. The electron microscope examination of carbon blacks reveals the existence of chain-like networks formed by the carbon black particles. In the soft-ball oil absorption test, the minimum amount of oil required to make 1g of carbon black cohere into a soft ball is observed, and is quoted in Table 1 as $\text{cm}^3 \text{g}^{-1}$. This quantity is related to the chain-like structure which enables the carbon mass to hold these large quantities of oil. The pH of a carbon black water slurry is a direct result of oxygen complexes at the carbon surface, and is thus related to the percent volatile content. It is now necessary to examine these properties in more detail and to study the relationships between them.

Nitrogen adsorption data

The adsorption of nitrogen at liquid nitrogen temperature and the calculation of the surface area from the data so obtained by the application of the BET theory is a widely practised technique³. In this method, the theory results in the following relationships between the amount adsorbed and the equilibrium pressure above the solid,

$$\frac{p}{x(p_0 - p)} = \frac{1}{x_m C} + \frac{C - 1}{x_m C} \times \frac{p}{p_0} \dots \dots \dots (1)$$

where x is the amount of gas adsorbed at pressure p

x_m is the monolayer coverage, and

p_0 is the saturated vapour pressure.

It can be seen that the equation contains two values to be determined, namely x_m and the constant C . A plot of $p/x(p_0 - p)$ against p/p_0 should, in the region of $p/p_0 = 0.05 \sim 0.35$, be a linear plot of slope $C - 1/x_m C$ and with an intercept of $1/x_m C$.

This allows the calculation of x_m and hence the surface area, and also of the constant C , which is a function of the heat of adsorption. However, the main use of the equation is in the calculation of the surface area.

Table 1
Typical properties needed to designate a carbon black

Type	Code	Raw material	Average particle diameter Å	Nitrogen adsorption, m ² g ⁻¹	Oil adsorption, cm ³ g ⁻¹	% Volatile content	% Benzene extract	pH
<i>Furnace Blacks</i>								
Super abrasion furnace	Oil	180-220	90-135	1.5	1.0	0.05	8-9
Intermediate super abrasion furnace	ISAF	Oil	230-250	115-130	1.3	1.0	0.05	8-9
High abrasion furnace	Oil	260-280	75-80	1.2	1.5	0.05	8-9
Fast extrusion furnace	Oil	400-450	40-45	1.3-1.4	1.0	0.05	9
General purpose furnace	Oil	500-550	25-30	0.9	1.0	0.05	9
<i>Thermal Blacks</i>								
Fine thermal	Natural gas	1,800	15	0.3-0.5	0.5	1.75	9
Medium thermal	Natural gas	4,700	5	0.3-0.5	0.5	0.3	8
<i>Channel Blacks</i>								
Easy processing channel	Natural gas	290-300	100	1.0	1	Nil	5
Medium processing channel	Natural gas	250-280	110-120	1.0	5	Nil	5
<i>Lampblack</i>	Coal tars, anthracene oils	650-1,000	20-40	1.3-2.0	0.4-10.0	0.01-0.5	3-7
<i>Acetylene</i>	Acetylene	420	65	3.4	0.3	0.1	5-7

NB—The properties are meant to be typical rather than those of a specific product, and there are other grades of carbon blacks.

Typical adsorption isotherms for nitrogen on four carbon blacks are shown in Fig. 3.⁴ Hysteresis loops were not observed, but the loss of adsorption capacity on degassing is apparent for two of the carbons. The data on the Mogul carbon black indicates porosity, and Anderson and Emmett⁴ found evidence for porosity in other carbon blacks. They point out that, in each case, the porous carbon blacks had been given an air or steam treatment that would lead to the development of pores.

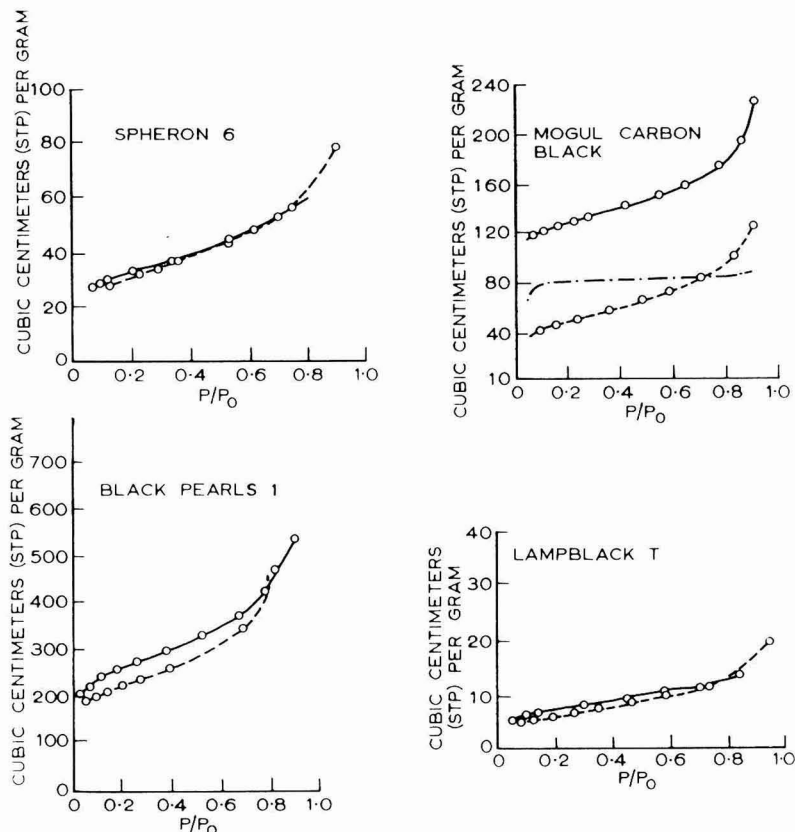


Fig. 3. Typical nitrogen adsorption isotherms on various carbon blacks (from data of Anderson and Emmett⁴)

Full lines indicate adsorption before and dotted lines after degassing at 950°-1,000°C. The line - · - · - · for Mogul carbon black represents the decrease in volume resulting from high temperature evacuation.

The surface areas of some of these carbon blacks, and the values of C , are given in Table 2. The value of $(p/p_0)_m$, i.e. the relative pressure at the monolayer, can be calculated, since substitution of this value into the BET equation gives:

$$\left(\frac{p}{p_0}\right)_m = \frac{-1 + \sqrt{C}}{C - 1} \dots\dots\dots (2)$$

Table 2

Surface areas and values of C for various carbon blacks from nitrogen adsorption at -195°C

Carbon Black	BET Surface area $\text{m}^2 \text{g}^{-1}$	Value of C	$(p/p_0)_m$
Spheron 6 original	116.4	161	0.07
Spheron 6 degassed at 950-1000 $^\circ\text{C}$	106.6	83	0.10
Black Pearls I original	942.0	246	0.06
Black Pearls I degassed at 950-1000 $^\circ\text{C}$	767.0	176	0.07
Mogul degassed at 950-1000 $^\circ\text{C}$	166.5	361	0.05
Lampblack T original	25.5	113	0.09
Lampblack T degassed at 950-1000 $^\circ\text{C}$	20.6	369	0.05
Spheron 4 original	128.5	258	0.06

Data taken from Anderson and Emmett¹

and so the value of C determines the point on the isotherm where the statistical monolayer is to be found. In the region considered here, the value of C is changing rapidly with $(p/p_0)_m$, and Table 3 lists a computer print-out of the various values of C for different values of $(p/p_0)_m$. Thus, although in Table 2 the values of C cover the range 80-370, the value of (p/p_0) varies only between 0.05 and 0.10. Lippens *et al.*⁵ calculate the function $3.54 (V/V_m) - 1$.

Table 3

C values for range of p/p_0 from 0-0.5 at $V/V_m = 1$

C	p/p_0	C	p/p_0	C	p/p_0
361.00	0.050	23.84	0.170	5.99	0.290
295.71	0.055	22.22	0.175	5.71	0.295
245.44	0.060	20.75	0.180	5.44	0.300
206.92	0.065	19.41	0.185	4.95	0.310
176.51	0.070	18.17	0.190	4.52	0.320
152.11	0.075	17.04	0.195	4.12	0.330
132.25	0.080	16.00	0.200	3.77	0.340
115.88	0.085	15.04	0.205	3.45	0.350
102.23	0.090	14.15	0.210	3.16	0.360
90.75	0.095	13.33	0.215	2.90	0.370
81.00	0.100	12.57	0.220	2.66	0.380
72.66	0.105	11.86	0.225	2.45	0.390
65.46	0.110	11.21	0.230	2.25	0.400
59.22	0.115	10.60	0.235	2.07	0.410
53.78	0.120	10.03	0.240	1.91	0.420
49.00	0.125	9.50	0.245	1.76	0.430
44.79	0.130	9.00	0.250	1.62	0.440
41.05	0.135	8.54	0.255	1.49	0.450
37.73	0.140	8.10	0.260	1.38	0.460
34.77	0.145	7.69	0.265	1.27	0.470
32.11	0.150	7.31	0.270	1.17	0.480
29.72	0.155	6.95	0.275	1.06	0.490
27.56	0.160	6.61	0.280	1.00	0.500
25.61	0.165	6.29	0.285	—	—

the statistical thickness (\AA), against pressure for a series of supposedly non-porous materials. On the master plot drawn on these plots of t (\AA) against p/p_0 the monolayer lies on a p/p_0 value of 0.085, with a scatter of points at this thickness from 0.04 \sim 0.1. This corresponds to C values of 80 to about 1,000, with average values around 120. The plot of t \AA against p/p_0 for the alumina selected in the studies of Lippens *et al* agreed with similar data for many other materials up to a relative pressure of 0.75, but deviations could be seen for graphitised carbon blacks and a fine particulate silica (Aerosil)⁶. In the carbon blacks and many oxides the values of C are relatively high and so:

$$\frac{C - 1}{C} \simeq 1$$

then,

$$\frac{p}{p_0 - p} = \frac{x}{x_m} \left(\frac{1}{C} + \frac{p}{p_0} \right) \dots \dots \dots (3)$$

To make a further approximation and ignore $1/C$ renders the relationship independent of C , but it only operates beyond the monolayer, viz.,

$$\frac{x}{x_m} = \frac{1}{1 - p/p_0} \dots \dots \dots (4)$$

Nevertheless, it has been shown that with this restriction in mind, this equation can describe many related systems⁷. The plot of this equation as x/x_m against p/p_0 , often incorrectly called a plot of the BET isotherm, gives results which lie above the master t plot of de Boer⁸ (Fig. 4). However, the insertion of a value of C (say 100—350) in equations (1) or (3) still produces a curve lying above the master t plot. In the range of relative pressure up to about $p/p_0 = 0.4$, the curves are practically identical. This helps to explain why the t plots are so successful in their application. There are carbon blacks which, in fact, give V_a-t plots which pass through the origin (Fig. 5). Others where sub-microporosity is suspected do not, and again where the carbon black is partially graphitised there are deviations from expected behaviour^{9, 10}. The explanation for the t plots not passing through the origin is that pores are present with dimensions so small that the t curve is not applicable. The best description of pores in these systems is that they are slit-shaped⁸ when the monolayer cannot be achieved in the region below $d = 2t_m$, where d is the thickness of the slit and t_m the thickness of one layer of adsorbed nitrogen (3.5 \AA). The fact that this sub-microporosity often disappears on heat-treatment is indicative of the small changes in dimensions necessary to make these pores completely inaccessible to nitrogen.

The partial graphitisation of carbon blacks

The application of heat treatment in absence of air in the range 1000° to 3100° causes varying degrees of graphitisation. This is indicated by X-ray diffraction studies¹. The electron micrographs indicate a transition from approximately spherical particles to irregular polyhedra for the graphitised samples¹¹. Adsorption studies on many carbon black surfaces demonstrated that there was a considerable degree of heterogeneity at the surface¹². On such surfaces nitrogen

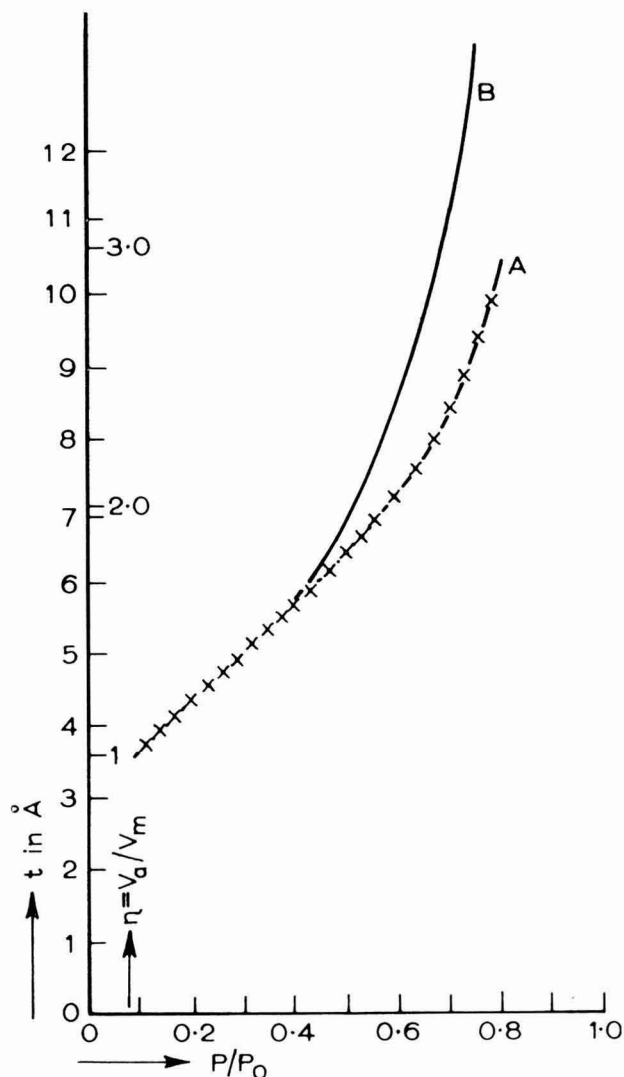


Fig. 4. The master curve for nitrogen at 78 K (curve A) compared with the simplified BET equation made independent of the value of C

adsorption isotherms were the sigmoid types discussed in the previous sections. In 1948, Halsey¹³ suggested that the sigmoid adsorption isotherm is really the superimposition of a number of stepwise adsorptions on a heterogeneous surface. It is considered that the process of graphitisation of carbon blacks is a process whereby the surface is made homogeneous. Carbon blacks heated to 3,000°C actually possess extremely uniform surfaces consisting chiefly of basal graphite planes. It should also be pointed out that the presence of oxygen complexes at the surface must be eliminated in this treatment. Theories relating to multilayer adsorption proposed by Fowler and Guggenheim¹⁴ and later by Halsey^{13, 15}, and Hill¹⁶ for adsorption on a homogeneous surface, predict that these conditions should give rise to an isotherm composed of a single series of steps.

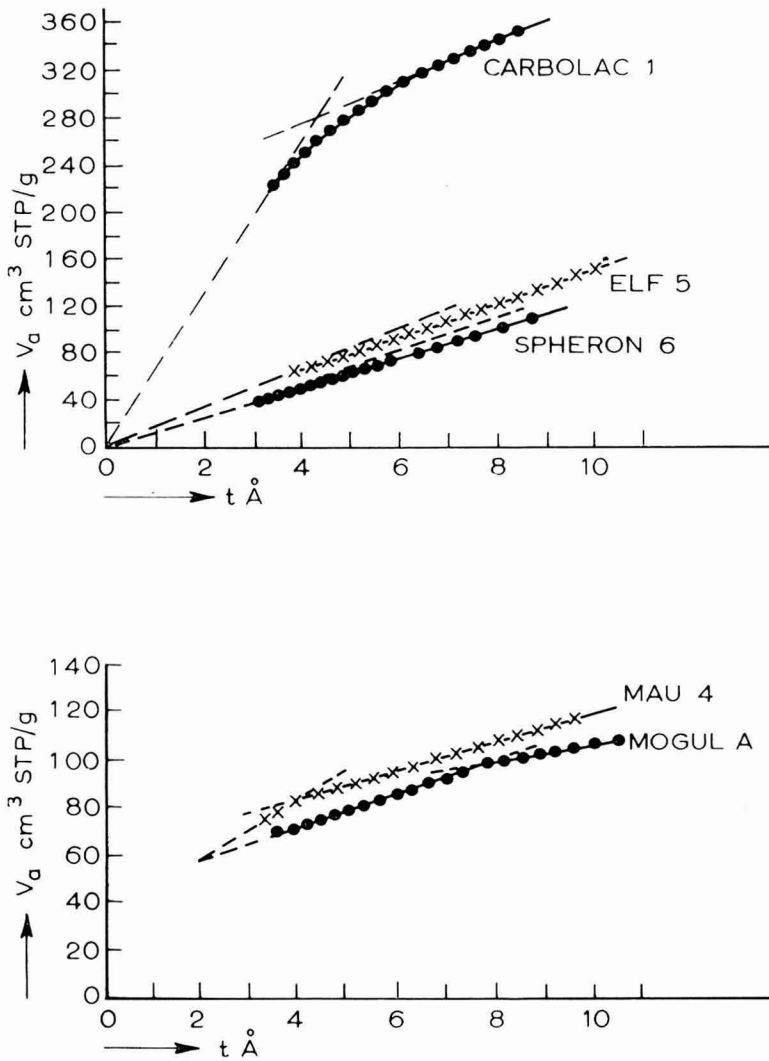


Fig. 5. $V_a - t$ plots on carbon blacks from data by de Boer et al⁹

- (a) Example of $V_a - t$ plot which passes through the origin.
 (b) Example of $V_a - t$ plot which does not pass through the origin.

These stepwise adsorption isotherms have been observed on homogeneous surfaces of carbons (i.e. partially graphitised) using argon, oxygen, nitrogen and krypton at -195°C . (Fig. 6). It has also been shown that the steps in the adsorption become more pronounced as the heat treatment is increased and graphitisation increased. The existence of stepped adsorption isotherms for methane on natural graphite has also been reported¹⁷. Stepped adsorption isotherms also occur for krypton on polyvinylidene chloride carbon, heat treated at $2,500^\circ$ and on polyvinyl chloride carbon also prepared at $2,500^\circ$ ¹⁸. These carbons, although graphitic, were not sufficiently so to show the presence at the surface of extensive graphitic basal planes.

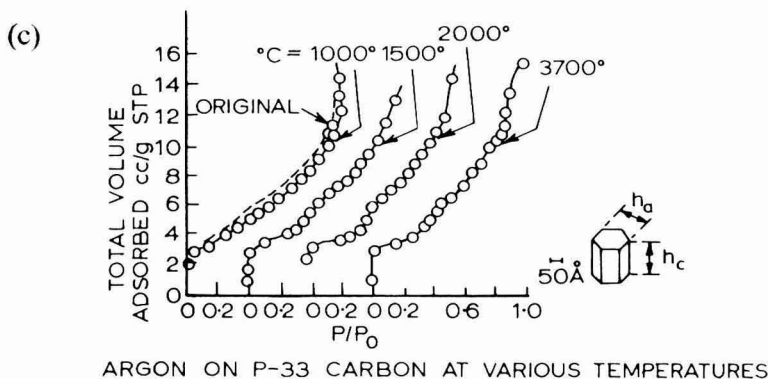
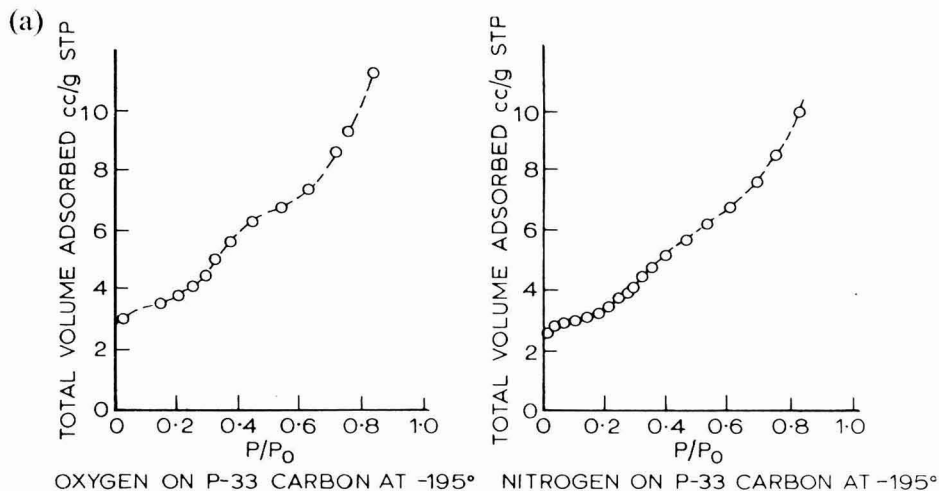


Fig. 6. Examples of stepwise adsorption isotherms on graphitised carbon blacks, from data by Polley et al.¹¹

(a) Argon on P-33 carbon at -195°C

(b) Oxygen on P-33 carbon at -195°C

(c) Nitrogen on P-33 carbon at -195°C

NB—P-33 carbon had been partially graphitised at $2,700^{\circ}\text{C}$

A further effect of a homogeneous surface on adsorption is reported by Pierce and Ewing¹⁹. In the stepped isotherms, the monolayer V_m is computed by the V/n ratio in the multilayer region, where V is the amount adsorbed at a given relative pressure by the number of statistical layers n . For nitrogen isotherms, this may conveniently be calculated by dividing V at $0.5 P_0$ by 1.70, a procedure established from many observations²⁰. The monolayer capacity so determined for nitrogen adsorption isotherms is 1.2—1.25 times larger than the BET or point B value for V_m . Pierce and Ewing have therefore suggested that the conventional nitrogen areas of uniform surface graphites are too low. Area measurements by benzene, *n*-hexane and ethyl chloride agree with nitrogen areas if the cross-section is taken as 20\AA^2 instead of 16.2\AA^2 . A proposed explanation is that nitrogen molecules are localised at graphite lattice sites so that each one fills four of the unit hexagons, an area of 21\AA^2 .

Isotherms of similar size molecules, oxygen and carbon monoxide, are in agreement with this model.

This picture of localised adsorption for nitrogen with an increased area is quite different from the situation with heterogeneous carbon black surfaces to be discussed later.

This point is also demonstrated if the data is given in the form of the t plot of de Boer. In Fig. 7, Pierce and Ewing's data is treated in this way against a standard isotherm determined on a heterogeneous non-porous graphite surface^{21,22}. This shows the effect of homogeneity on the t plots. It should be observed that the data deviates from the master plot and then returns to it at higher pressures.²³

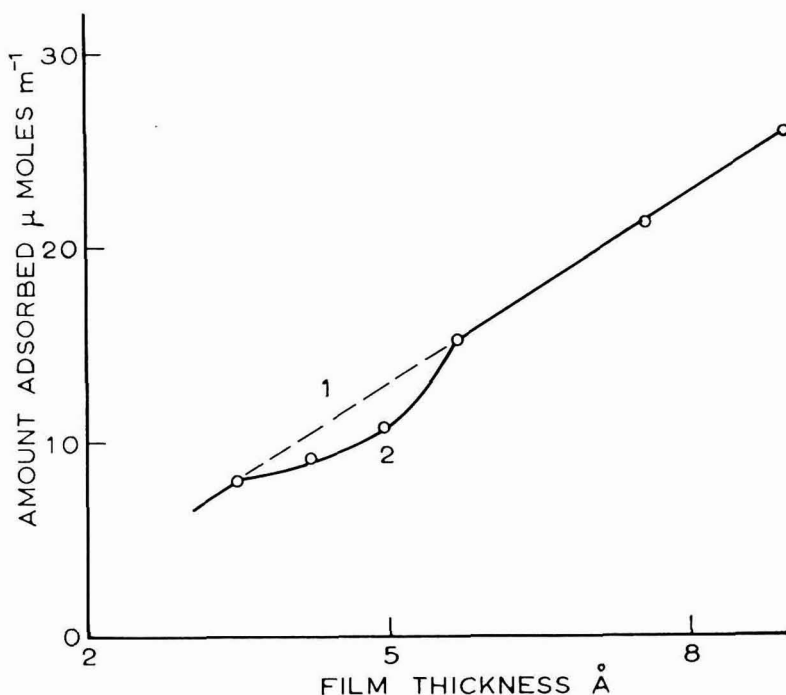


Fig. 7. Plot of amount of nitrogen adsorbed against the film thickness for a homogeneous graphitised carbon black

(1) t plot obtained from a non-porous heterogeneous graphite.²²

(2) Homogeneous graphitised carbon black nitrogen adsorption data reported by Pierce and Ewing.¹⁹

The oxidation of carbon blacks

The oxidation of carbon blacks can be considered by thinking in terms of three groups of carbon blacks, namely:

1. the oxidation of carbon blacks containing oxygen complexes at the surface,
2. the oxidation of carbon blacks that have been treated at around 1,000° and so have had the complexes removed,
3. the oxidation of graphitised carbon blacks.

Although divergence of behaviour may initially be present in the first two cases it is unlikely to persist, as oxidation is a gasification process and after the initial few per cent gasification, cases 1 and 2 become identical. Donnet and Bouland²⁴ summarise the results of gas-phase oxidation of thermal blacks. It appears that many thermal blacks display two reaction rates during oxidation. It is also possible to distinguish different degrees of texture or surface porosity among the various oxidised carbon blacks. Many display a surface of disorganised carbon 100Å thick. Electron micrographs indicate that many of the particles show two or more growth centres. Typical surface area data for a carbon black are given in Table 4. Similar results obtained in the author's

Table 4
The oxidation of Sterling FT carbon black
taken from data by Donnet and Bouland²⁴

Loss in Wt %	Surface area from electron microscopy m ² g ⁻¹	N ₂ BET Surface Area
0	16.0	18.3
4.7	19.0	29.4
10.7	19.5	48.0
14.0	19.5	80.6
24.0	19.5	137.6
33.0	19.5	199.5
60.0	19.5	283.8
78.0	19.5	388.0

laboratories on Spheron 9 show an increase in surface area upon oxidation (Table 5). In another set of experiments, Dollimore and Martin²⁵ have demonstrated that the t plot for the nitrogen adsorption isotherm on Spheron 9 passed through the origin. (Fig. 8). At 6 per cent burn off, the t plot did not pass through the origin, indicating sub-microporosity, whilst at 30 per cent burn off and beyond, the t plot consisted of two straight lines, one passing through the origin, indicating the existence of pores in the micropore region. The data on the rate of oxidation in Table 5 suggests the development during oxidation of an accessible area that is not identical with the nitrogen surface area. The development of a sub-micropore structure as a prelude to the microporous structure during oxidation suggests also that these areas may not coincide. It is, of course, possible that closed pores are opened up during the oxidation process and that this is the reason why the areas are different.

It is, in fact, possible for oxidation in air or oxygen in the temperature region 300–650°C to cause a sixfold increase in surface area of a carbon black as measured by nitrogen adsorption, whilst the electron microscope particle size does not alter appreciably,^{26, 27} as indicated in Table 4. This porosity is interpreted as arising from preferential attack of the oxygen at high energy sites on the carbon surface. These sites may be associated with the edge atoms of the graphitic parallel layer groups composing the particle. These edge atoms are more susceptible to chemical attack than are the atoms in the centre of the basal plane.

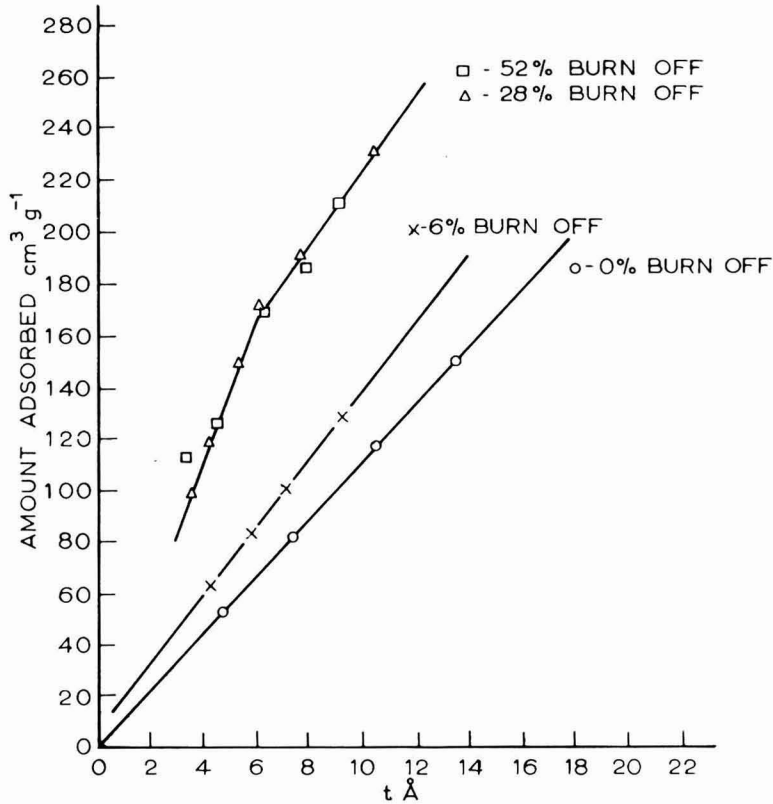


Fig. 8. Nitrogen t plots for oxidised Spheron 9
 From data in Ph.D. thesis, D. Martin, Salford, 1971.

Table 5
Oxidation of Spheron 9 at 486°C in air
 Data from Ph.D. Thesis, D. Martin, Salford, 1971.

Loss in weight. %	N ₂ BET surface area, m ² g ⁻¹	Rate of oxidation $\frac{d\alpha}{dt}$ arbitrary units (α -fraction) decomposed
0	123	0
5	255	0.9
15	270	1.0
30	308	0.8
52	225	0.5

Graphitisation in the region 2,700—3,000°C destroys these high energy sites, and thus the preferred sites for oxygen attack are either removed or greatly diminished in number²⁹. The oxygen attack should therefore occur uniformly over the surface of a graphitised carbon black, the area increase on oxidation should be proportional to the decrease in particle diameter, and there should be no development of porosity. The data demonstrating this are given in Table 6³⁰.

Table 6
The oxidation of graphitised carbon black
From data by Smith and Polley³⁰

Material	Electron microscope surface area m ² g ⁻¹	Nitrogen adsorption BET surface area, m ² g ⁻¹
Stirling FT carbon black ..	15.4	14.5
Stirling FT graphitised at 2,700°C	16.4	12.5
Graphitised Stirling FT 72% oxidised	27.9	20.2

The adsorption of other gases and vapours on carbon blacks

It is fairly obvious that, in a porous carbon, the surface area available to one adsorbate might not be available to another. It appears, however, that on the non-porous carbons there is a tendency for the surface area calculated from some vapour adsorption data on the basis of a cross-sectional area (A_m) obtained from liquid-density measurements to be smaller than the specific area derived from nitrogen adsorption^{21, 31}. It seems that, on heterogeneous carbon black surfaces, the molecules are not close-packed or that A_m values calculated from liquid density measurements are too small (Table 7). This table also indicates that reverse effects are to be found for krypton, and this should be remembered when converting adsorption data into accessible or apparent surface areas. There is also evidence to suggest that the same thing happens with the adsorption of acetylene (at -78°C), ammonia (at -46°C), water (at 25°C) *n*-butane, *n*-C₄H₁₀, (at 0°C) and methylamine, CH₃NH₂, (at 0°C)⁴. The possibility exists that these gases will adsorb on oxygen or other surface complexes so the removal of these complexes by the degassing procedure should alter the adsorption characteristics. In most cases, the surface area calculated on the basis of liquid densities (e.g. cross-sectional area, N₂, 16.2Å²; H₂O, 10.5Å²; C₄H₁₀, 32.1Å²; CH₃NH₂, 19.1Å², and C₂H₂, 18.2Å²) was smaller than that calculated from the nitrogen adsorption data, (e.g. Spheron 6 degassed, 106.6 m² g⁻¹ based on N₂ adsorption; 60.0 m² g⁻¹ based on NH₃ adsorption). The chemical nature of this series of adsorbates makes it easier to appreciate why in this case the adsorbate molecules are apparently occupying a larger area than that required by the concept of close packing. The removal of the surface complex lowers the adsorption of ammonia (e.g. Black Pearls carbon black, before degassing 858.0 m² g⁻¹ from NH₃ adsorption at -46°; after

Table 7

Cross-sectional area A_m for various vapours and gases on non-porous carbons

Adsorbate	Carbon	A_m (\AA^2)		Ref.
		From liquid density	Calculated from nitrogen adsorption	
Carbon dioxide at -78°C ..	Various carbon blacks	16.3	21.8	A
Krypton at -78°C	Various carbon blacks	21.0	18.4	A
Xenon at -78°C	Various carbon blacks	19.5	30.0	A
Methyl alcohol at 25°C ..	Graphite	17.7	24.25	B
Isopropyl alcohol at 25°C ..	Graphite	27.6	33.66	B
n-Propyl alcohol at 25°C ..	Graphite	27.3	37.0	C, D
Benzene at 25°C	Graphite	30.5	43.57	B
	Various carbon blacks	—	39-43	A
Toluene at 25°C	Graphite	31.3	53.04	B
			47.0	C, D
Carbon Tetrachloride at 25°C	Graphite	32.3	47.0	C, D
			Various carbon blacks	—
n-Heptane	Graphite	42.7	61	C, D
			42.7	61
Cyclohexane	Graphite	34.6	52	C, D
n-Butane	Spheron at 0°C	32.1	45.1	E

A. Van der Plas, T. H., "Physical and chemical aspects of adsorbents and catalysts", Ed. B. G. Linsen, 1970, New York: Academic Press, p. 425-469.

B. Broadbent, K. A., Dollimore, D., and Dollimore, J., *Carbon*, 1966, 4, 281.

C. Chessick, J. J., Zettlemyer, A. C., and Yung-Fang Yu, *J. Phys. Chem.*, 1960, 64, 530.

D. Craig, R. G., Van Voorhis, J. J., and Bartell, F. E., *J. Phys. Chem.*, 1956, 60, 1225.

E. Beebe, R. A., Polley, M. H., Smith, W. R., and Wendell, C. B., *J. Amer. Chem. Soc.*, 1947, 69, 2294.

degassing at $1,000^\circ\text{C}$; $617.0\text{ m}^2\text{ g}^{-1}$ from NH_3 adsorption at -46°). It is possible to show that the surface coverage for water increases with surface complexes present⁴ (Table 8). The water adsorption isotherms were type III or IV and were shifted in the direction of higher relative pressure for given water adsorption as the complex was removed from the surface. The ammonia or amine adsorption data may not be immediately indicative of oxygen complexes, as it is probable that the measured isotherm is a combination of adsorption at fixed

sites involving oxygen complexes and that physical adsorption also takes place elsewhere. The amine adsorbed by interaction at oxygen surface complexes is probably irreversibly adsorbed and so lost only under more severe conditions than that physically adsorbed. This is certainly the case with acid sites on aluminas, silicas and minerals investigated in the author's laboratories.

Table 8
Adsorption of water vapour as a function of surface covered by oxygen complex
From data by Anderson and Emmett⁴

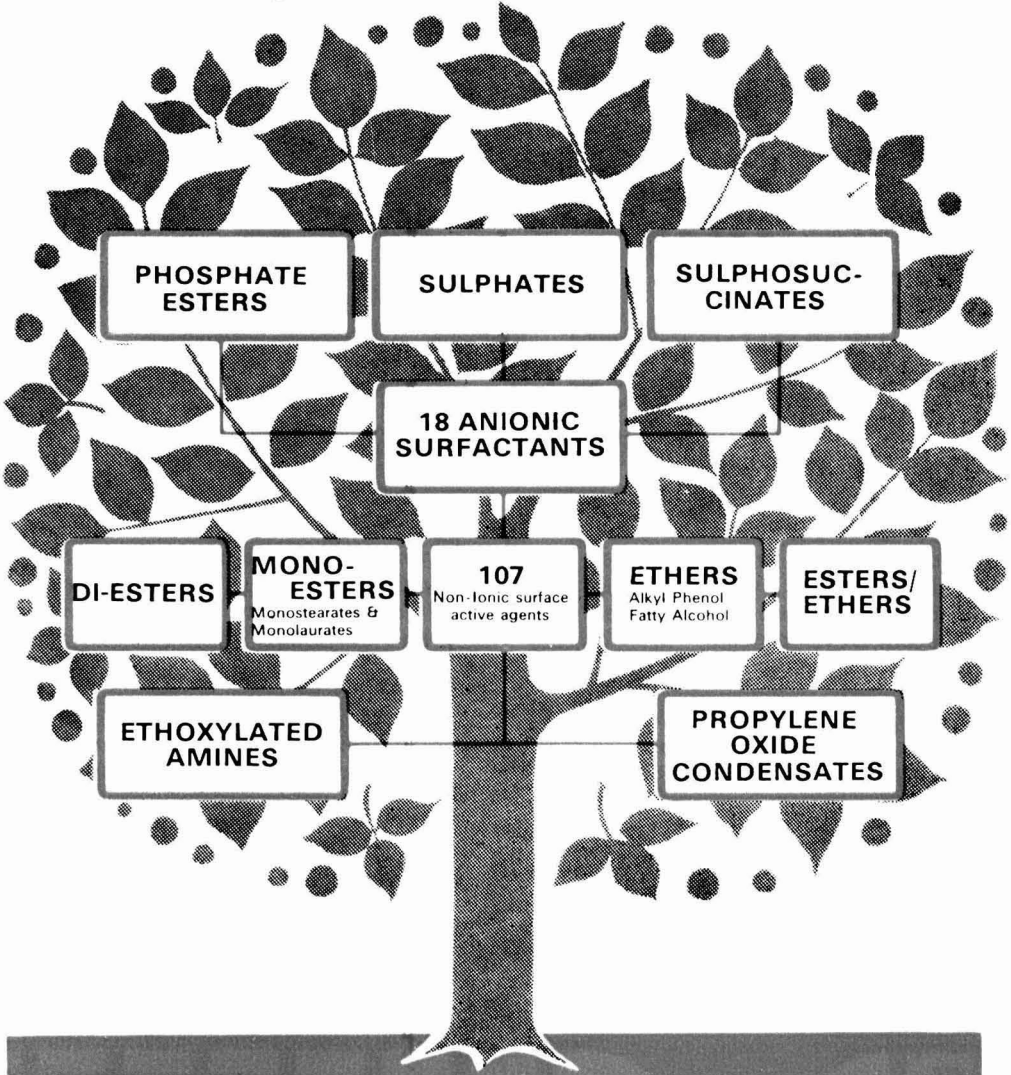
Adsorbent	% Volatile content per unit area	% Surface covered for H ₂ O adsorption at a relative pressure of 0.4
Spheron 6	4.2	67
Spheron 4	2.7	62
Mogul	2.2	49
Black Pearls 1	1.7	36
Spheron 6 degassed	0.9	4.8
Mogul degassed	0	0.7
Black Pearls 1 degassed	0	2.8

If adsorption isotherms are available at a series of temperatures for any vapour, then the use of the Clausius-Clapeyron equation enables the isosteric heat of adsorption (q_{st}) to be calculated. The equation is used in the form:

$$\frac{d \ln p}{d (1/T)} = - \frac{q_{st}}{R}$$

where p is the pressure, and q_{st} refers to the isosteric heat of adsorption at a fixed amount adsorbed (T the temperature °K, and R the gas constant). This is a differential quantity and is plotted against the degree of surface covered or the amount adsorbed. In many cases, the region of special interest is the low pressure region of the adsorption isotherm. To get information in this region, a chromatographic method of measuring the adsorption is advantageous. The measurement of adsorption isotherms of various vapours on Spheron by the elution chromatographic technique is found to be very convenient³². Typical results for a series of vapours on Spheron are given in Fig. 9. Previous results using this technique of elution chromatography have given anomalously low values of the isosteric heat of adsorption at low coverage. The method used to calculate the data in Fig. 9 involved a calculation of the adsorption isotherm starting from the top of the chromatographic peak and this overcame the difficulties previously encountered. The adsorption isotherms for these vapours were collected in the temperature region 345—480°K. In all the examples cited in Fig. 9, except for cyclohexane and hexane, there is an initial fall in the isosteric heat of adsorption followed by a horizontal or slightly decreasing value towards

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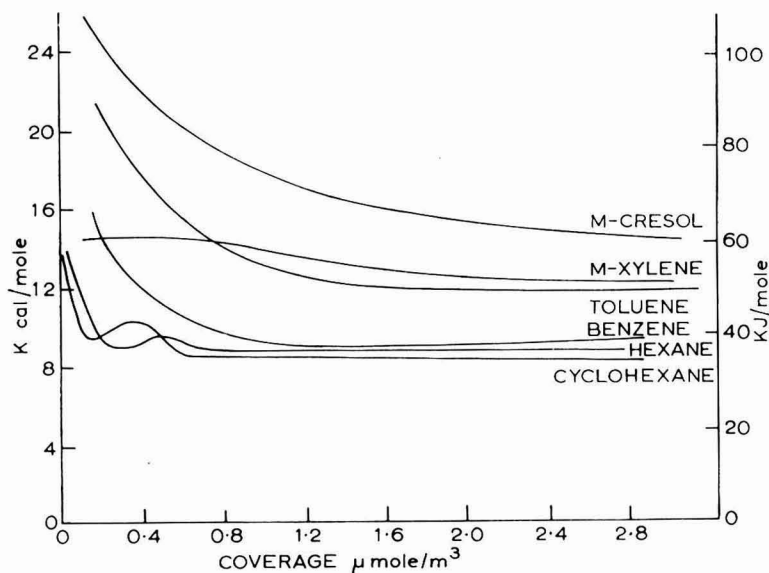


Fig. 9. The isosteric heat of adsorption of various vapours on Spheron 9
From data by Dollimore, Heal and Martin³²

the monolayer region. This is also found for the variation of q_{st} for nitrogen on a relatively heterogeneous surface of a carbon black³⁴.

The high values of q_{st} at very low coverages are probably associated with oxygen complexes at the surface. In the cases of hexane and cyclohexane, there is a small peak in the plot of the isosteric heat of adsorption against coverage at low values of coverage. Hockey and Pethica³⁵ also found a small peak in q_{st} at a coverage much less than that of a monolayer in certain silicas for benzene adsorption. They ascribe this effect to micropores in the silica and to co-operative adsorption taking place in the pores. In the results on Spheron, apart from cyclohexane and hexane, the absence of peaks indicates the absence of micropores large enough for co-operative adsorption in these samples. The peaks for cyclohexane and hexane occur at even lower coverages than in the case quoted by Hockey and Pethica. It is possible that the spherical nature of cyclohexane makes it more amenable to co-operative adsorption which might occur here at the points of contact of the small Spheron particles. It is then difficult to show why hexane also behaves in this manner. It is more useful to point out that cyclohexane and hexane are both saturated hydrocarbons and non-polar, whilst the rest are aromatic and polar, and this could be the basis for the occurrence of co-operative adsorption in the one group but not in the other.

Heats of wetting on carbon blacks

There are several reasonably obvious methods of studying the adsorption on to carbon blacks from a solution. In this case there are two components that can be adsorbed on the surface and although the resultant adsorption isotherm may only be an apparent adsorption isotherm, there is enough evidence to suggest

certain materials may be preferentially adsorbed, so that the resultant isotherm can be regarded as sufficiently correct³⁶. If, however, the carbon is immersed in a single liquid component, e.g. water, then the water will be adsorbed at the surface, but the methods employed for the determination of adsorption from solution do not apply. However, adsorption is an exothermic process and so, when an outgassed solid is immersed in a liquid, heat is evolved, and this can form the basis for surface area determinations.

The free energy of immersion of a finely divided solid material by a liquid is given by³⁷;

$$\begin{aligned} \varphi_{so/sl} &= \gamma_{so} - \gamma_{sl} \\ &= \frac{RT}{MS} \int_{p/p_0 = 0}^{p/p_0 = 1} x \, d \ln p/p_0 + \gamma_{LV}^0 \cos \theta \dots \dots \dots 6 \end{aligned}$$

term A term B

where

$\varphi_{so/sl}$ = free surface energy lowering when unit area of solid/vacuum interface is replaced by solid-liquid interface.

γ = free surface energy, the subscripts referring to the phases on either side of the surface considered so that

γ_{LV}^0 = free surface energy of a liquid in equilibrium with its saturated vapour (usually taken as the surface tension of the liquid)

θ = contact angle

p/p_0 = terms refer to the relative pressures of the adsorbate vapour above the solid at the temperature $T^\circ\text{K}$

x = weight adsorbed per g of adsorbent

R = gas constant

M = molecular weight of the adsorbate

S = surface area per g of the adsorbent.

On the basis of experimental data, the heat of wetting of comparable liquids on carbons is often held to be of the same order as the free energy of immersion ($\varphi_{so/sl}$)^{21, 38, 39, 40, 41}. The term A represents the Gibbs adsorption equation for the diminution of surface energy ($\varphi_{so/sl}$) produced by exposure to saturated vapour. The term B is often used with $\cos \theta = 1$ by making the assumption that complete wetting takes place. In this context the integrated expression may be used only over the complete range from $p/p_0 = 0$ to $p/p_0 = 1$. In this form equation (6) can be applied only to non-porous carbons, because in porous materials the effective area upon which further adsorption takes place is also altering with increasing pressure. With the presence of wider pores than are considered here, the onset of capillary condensation therefore limits the use of this equation. The microporosity that occurs in carbon blacks must also affect the application of the equation.

The term A may be evaluated by fitting a Freundlich type equation to fit the isotherm as nearby as possible²¹. Alternatively, a graphical method may be employed, from the first recorded experimental observation of adsorption to the value at saturated vapour pressure, the initial amount being calculated

analytically on the assumption that the adsorption varies linearly with pressure. This technique is superior to the use of the Freundlich isotherm, which was difficult to fit to experimental data at relative pressures beyond 0.75. The values of term A for a non-porous carbon black have not been calculated by the author directly, but the reduced isotherm for the adsorption of nitrogen on an Acheson colloid graphite has been shown to be identical with a non-porous carbon black²². Accordingly, in Table 9, the values of term A (the lowering of free surface energy in adsorption) and the terms γ_{LV}^0 and $\varphi_{so/LV}$ are set out from the results of Broadbent et al²¹ for various vapours on the graphite and also from other sources, and compared with the heat of immersion ($h_{1(SL)}$).

Table 9

Heat of wetting, net heat of adsorption, surface free energies and associated data for various organic liquids on graphite at 25°C (values in erg cm⁻²)

Liquid	Ref.	Heat of immersion $h_{1(SL)}$	h_{LV}	Net heat of adsorption $Q_{A(SV)} - Q_L$	$\phi_{SO/SL}$	$\phi_{SO/SV}$ Term A	$\frac{Td\phi_{SO/SV}}{dt}$	$\frac{d\phi_{SO/SV}}{dt}$
Methyl alcohol	A	143	45	98	90.1	67.9	30.12	0.101
	B	119	—	74	—	—	—	—
	C	102	—	57	—	—	—	—
Isopropyl alcohol	A	133	45.1	87.9	70.1	48.8	39.1	0.131
Benzene	A	161	67.6	93.4	78.5	50.1	43.28	0.145
	B	114	—	46	—	—	—	—
Toluene	A	171	60.73	110.3	74.2	46.25	64.02	0.215
Carbon tetrachloride	B	115	—	50	—	—	—	—
n-Heptane	C	112	—	—	—	—	—	—
Cyclohexane	B	101	—	44	—	—	—	—
Hexane	B	118	48	70	—	—	—	—
	C	103	—	55	—	—	—	—

- References—A. Broadbent, K. A., Dollimore, D., and Dollimore, J. *Carbon*, 1966, 4, 281.
 B. Bartell, F. E., and Suggitt, R. M., *J. Phys. Chem.*, 1954, 58, 36.
 C. Healey, F. H., Chenick, J. J., Zettlemyer, A. C., and Young, G. J., *J. Phys. Chem.*, 1954, 58, 887.

Materials— A and B. Acheson colloid graphite, but different surface areas to N₂ adsorption.
 C. Graphon.

It is an approximation to write an equality between $h_{1(SL)}$ and $\varphi_{so/LV}$, but for the purposes of comparison, it might be permissible.

If $\cos \theta$ has a value of unity, then equation (6) becomes

$$\varphi_{so/SL} = \varphi_{so/sv} + \gamma_{LV} \dots\dots\dots(7)$$

The true relationship between $\varphi_{so/SL}$ and $h_{1(SL)}$ is given by the Gibbs-Helmholtz equation:

$$h_{1(SL)} = \varphi_{so/SL} - \frac{Td\varphi_{so/SL}}{dT} \dots\dots\dots (8)$$

Combination of these equations produces;

$$h_{1(SL)} = \left(\varphi_{so/sv} - \frac{Td\varphi_{so/sv}}{dT} \right) + \left(\gamma_{LV} - \frac{Td\gamma_{LV}}{dT} \right) \dots\dots\dots (9)$$

The terms in $\varphi_{so/sv}$ represent the net heat of adsorption which is the total heat evolved ($q_{A(sv)}$) when the bare surface comes into equilibrium with the saturated vapour, less the heat required for the vaporisation of this saturating vapour (q_L). The terms in γ_{LV} represent the heat generated when a saturated surface, assumed to be liquid like, is immersed in the liquid (h_{LV}). It is therefore possible to write:

$$h_{1(SL)} = q_{A(sv)} - q_L + h_{LV} \dots\dots\dots (10)$$

Rearrangement gives

$$q_{A(sv)} - q_L = h_{1(SL)} - h_{LV} \dots\dots\dots (11)$$

Net heats of adsorption for various vapours on non-porous carbons calculated using this equation are given in Table 9. It is also possible to calculate the terms $\varphi_{so/sv}$ and h_{LV} (equal to $\gamma_{LV} - \frac{Td\gamma_{LV}}{dT}$) in equation 9. The difference $h_{1(SL)} - \varphi_{so/sv} - h_{LV}$ represents the $\frac{Td\varphi_{so/sv}}{dT}$ term from which the magnitude of $\frac{d\varphi_{so/sv}}{dT}$ in this temperature region may be evaluated. This has been done for the various vapours in Table 9.

These relationships demonstrate the connection between the heat of immersion per unit area and the net heat of adsorption ($q_{A(sv)}$) involved in adsorption from the vapour phase. From the practical point of view, when working with a non-porous carbon it is tempting to use a value of $h_{1(SL)}$ determined on a standard carbon for a particular vapour as a means of establishing the surface area on an unknown carbon. However, it must be pointed out that the non-porous nature of the carbon must be established and also the influence of various factors which can alter the established conversion factor. These factors include the degree of homogeneity of the carbon surface, the extent of graphitisation and the presence of surface oxygen complexes.

Correlation between various surface dependent properties

The data discussed so far indicates a variety of techniques used to characterise the surfaces of carbon blacks, which are either porous or non-porous as a result of their method of preparation, which may or may not possess surface complexes, which may be heterogeneous in character, or which may have this heterogeneity removed by graphitisation at a very high temperature. This all tends to make correlations between the various techniques difficult.

Taking electron micrographs as an example, and comparing data from this technique with the nitrogen adsorption BET surface areas, there should

obviously be a relationship between particle size calculated from the nitrogen adsorption surface areas and the electron micrographs if the sample is considered to be non-porous.

Now, in normal electron micrographs the estimate of area is based on a two dimensional photograph from which an estimate of particle diameter may be reasonably made on the assumption that the particles are spherical. The same procedure can be applied to the polyhedral particles of graphitised carbon blacks, noting that the departure from spherical form does not materially affect the calculation. However, in the calculation of particle size from the nitrogen adsorption data, an average diameter is calculated so that in the electron micrograph data the same calculation must be made. The distribution of particle size varies from sample to sample, and a typical example is given in Fig. 10, from work by Anderson and Emmett.⁴² If the calculation of surface area is based on an average particle size, then a figure of 25.9m g^{-1} is computed, but if the distribution is taken into account then the area can be shown to be 21.8m g^{-1} . In this case, the nitrogen BET surface area is nearly the same value. The ratio of the nitrogen BET area to the electron micrograph area serves as an indication of the surface texture. This is termed the "roughness factor." By constructing simple models without introducing any real porosity, a roughness factor of 2.5 or higher is possible. Thus, a two- or three-fold difference in surface

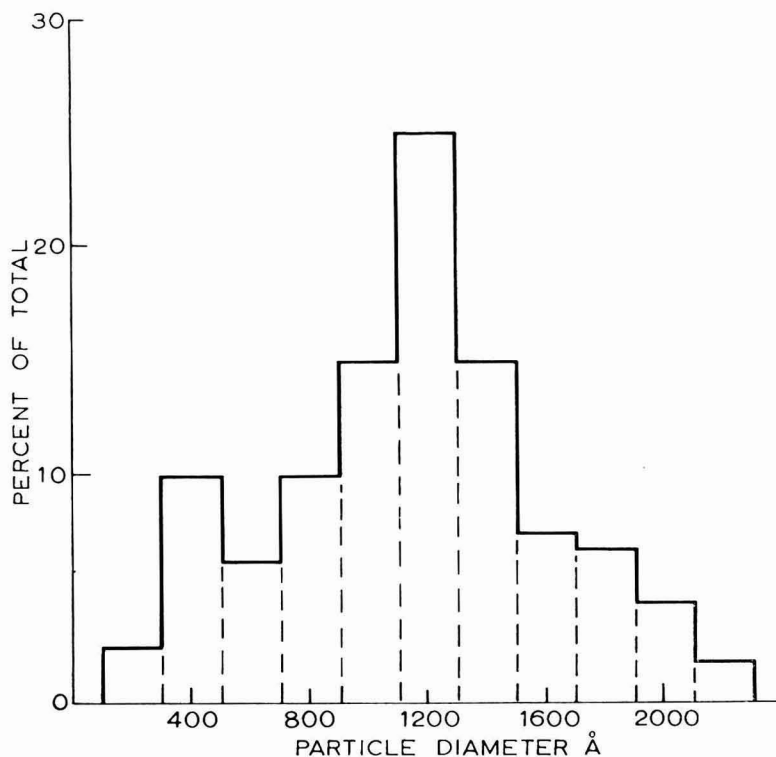


Fig. 10. Particle size distribution of a carbon black from electron micrographs
From data on carbon black P-33 reported by Anderson and Emmett⁴².

area between the two methods does not necessarily indicate the development of porosity, and it is necessary to investigate the adsorption isotherm in more detail to establish this fact.

The adsorption of materials from solution can lead to values different from those determined by nitrogen adsorption and also produce data which vary with different forms of carbon. Kipling and Wilson⁴³ quote a value for the area covered by one methylene blue molecule on Spheron 6 surface at 20°C as $102 \text{ \AA}^2 \text{ mol}^{-1}$, which is at variance with the values they calculate from a model orientated in probable directions and with various published data.

The adsorption of iodine from an aqueous iodine/potassium iodide solution is a widely used method used to determine the surface area of carbon blacks.^{44, 45}

Fig. 11 shows two relationships with the nitrogen adsorption BET area, depending on the acidic or basic nature of the surface complexes. Various methods of iodine adsorption have been examined by Puri and Bansal⁴⁶, who give details of a variation in the method which produces agreement with the nitrogen adsorption BET surface area whether the carbon is acidic or basic.

There are other tests used industrially for the specification of carbon blacks. They also are often found to be correlated in a similar fashion. The fact, however,

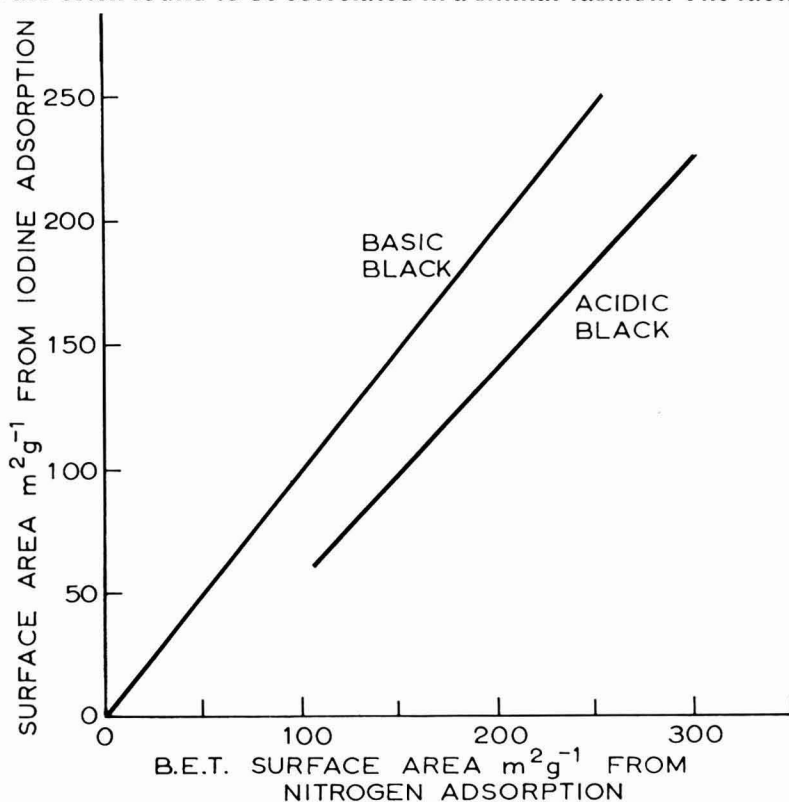


Fig. 11. Plot of iodine adsorption surface area against nitrogen adsorption area for carbon blacks

Data recorded by Studebaker⁴⁴.

that the correlation most often expressed is the data from the test under consideration against either the electron micrograph data or the nitrogen adsorption BET surface area indicates the importance felt by many investigators of these two techniques applied to carbon blacks.

Another frequently used test has a direct relationship to an important property of carbon blacks. This is the measure of oil absorption quoted in Table 1 and mentioned earlier. The variant of this test most commonly used is the "soft ball oil absorption test." This is the determination of the minimum amount of oil required to make 1g of carbon black cohere into a soft ball when carefully worked with a spatula. Linseed oil and mineral oils give similar values⁴⁴. The result of this oil, or more generally liquid, absorption is that the quantity absorbed would require a larger surface than that predicted by other methods. This is due to the carbon particles forming the chain structure which has been observed on electron micrographs.^{47, 48} This has the effect of reducing the total exposed surface by a small amount. In the absorption of liquids, these chain structures can hold large volumes of liquid. Similar chain structures are seen in some forms of non-porous silicas. This oil absorption is only reversible with difficulty, a fact which can be demonstrated using the Microscal flow microcalorimeter. Fig 12 shows a trace for linseed oil adsorption on to a carbon

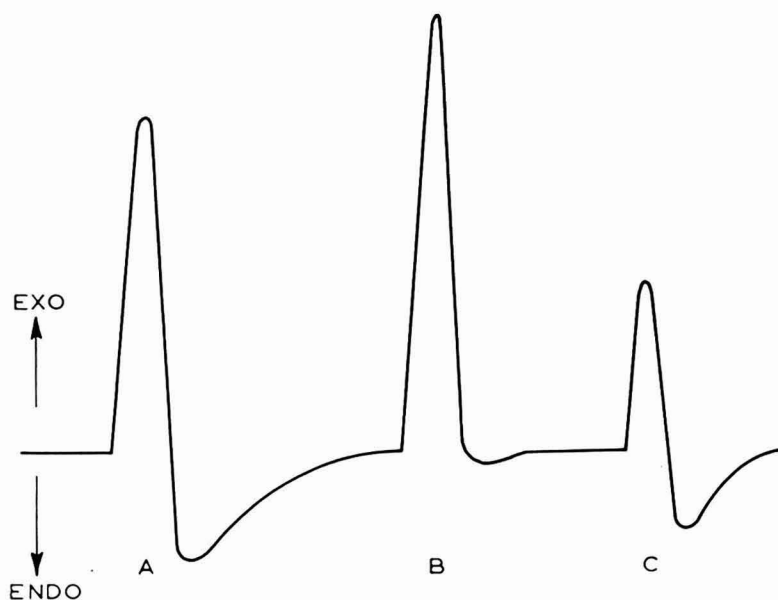


Fig. 12. Microscal flow microcalorimeter trace for linseed oil on carbon black

Carrier fluid n-Heptane

A. 40 μ l 10% cetyl alcohol solution

B. 40 μ l 10% linseed oil

C. 40 μ l 1% cetyl alcohol solution

Data supplied by C. E. Templer, Microscal Ltd.

black. It can be seen that the desorption of the linseed oil is only partial and this results in a diminished capacity for adsorption of cetyl alcohol, which is used in this test as an indicator of adsorption capacity.

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Discussion at the Joint Symposium

PROFESSOR G. D. PARFITT said that Dr Dollimore had spoken briefly about "acidity" of carbon blacks. Could he define this term in relation to the nature and number of surface groups? How were these surface groups characterised?

DR D. DOLLIMORE replied that various titration methods were used; a more accurate method was to study the adsorption of particular species in detail, including the desorption isotherms. The description of the surface sites was a matter for conjecture; they were presumably different types of oxygen/carbon complexes.

MR F. S. BAKER asked whether Dr Dollimore would elaborate on the uncertainties in the measurement of hysteresis with the conventional design of BET apparatus, compared with the Lippens and de Boer design?

DR DOLLIMORE said that with the modified design it was easier to avoid overshooting the desired pressure settings, which lead to "scanning" the isotherm.

MR M. J. KENNEDY asked what mathematical techniques were used to obtain values of the rate constants, and hence activation energies, from the plots of percentage reaction against time for the oxidation of carbon black. What theoretical expression was chosen to fit the experimental result?

DR DOLLIMORE said that the time for the half-way stage of the reaction to be reached, $t_{0.5}$, was inserted in the equations relating α to t , so removing the rate constant, K , from them; this allowed the determination of whether the runs were isokinetic. As the resulting expressions did not contain K , all the theoretical expressions could be superimposed on the experimental data, and the best fit chosen.

PROFESSOR K. S. W. SING commented that the Lippens and de Boer apparatus was satisfactory if one was not interested in low specific surface areas; it had a large dead space and so it was difficult to calibrate exactly. He considered that the q_{st} versus p curve could not be interpreted by Dr Dollimore's hypothesis. There was evidence in the literature that any highly energetic micropore would be filled first, as adsorption began. An increase in the value of ΔH was usually interpreted as an interaction between adsorbed molecules.

Professor Sing also pointed out that α versus t plots were not an alternative to $\log(V_0/V_n)$ versus t plots, but they were useful with type II or type III isotherms.

DR DOLLIMORE said that he had been very careful to select the best master plot; he would not compare a graphitised with an ungraphitised carbon black, or blacks with and without oxygen removed from them, but would use a separate standard for each series.

PROFESSOR SING said that it was better to use argon, so as to separate specific from non-specific factors.

DR F. A. P. MAGGS said that the rate of oxidation data which had been presented exhibited a maximum with respect to the amount of burn-off. He had found that the increased surface area available for reaction was roughly compensated for by the loss in weight of the solid. Did the rates quoted refer to the original weight of carbon? If so, this would explain the occurrence of the maximum.

DR DOLLIMORE replied that this was often rather obscure in the literature; if the original weight was used as the basis for weight loss, he would expect to see a maximum.

The preservation of wood with reactive fungicides

By P. M. Heertjes and J. de Jong

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Summary

The use of pentachlorophenol and other fungicides for the preservation of wood shows many disadvantages. It was felt that many of these difficulties could be overcome if the fungicides were bound chemically to the wood. Therefore the use of so-called reactive fungicides has been investigated.

Bifunctional or trifunctional agents such as trichloro-s-triazine, a diepoxide and hexamethylene-diisocyanate have been used as coupling agents for organotin fungicides. In all cases satisfactory coupling of the fungicide to the wood could be achieved, resulting in a protection comparable with, and sometimes even better than, the protection offered by pentachlorophenol. The stability of the systems against leaching out was good, and no evaporation occurred.

Keywords

Types and classes of surface

beech
wood

Miscellaneous paint additives

coupling agent
hexamethylene diisocyanate
trichloro-s-triazine

Biologically active agents

fungicide
organotin
pentachlorophenol

La préservation du bois par des fongicides réactifs

Résumé

L'utilisation du pentachlorophénol et d'autres fongicides pour la préservation du bois démontre plusieurs inconvénients. On estimait que beaucoup de ces difficultés pourraient être surmontées dans le cas où les fongicides étaient liés chimiquement au bois. Ainsi on a examiné l'emploi des fongicides soi-disant réactifs. Les composés bi ou tri-fonctionnels tels que trichloro-s-triazine, hexaméthylène diisocyanate et diépoxyde ont été utilisés en tant qu'agents de pontage pour des fongicides organo-stanniques. Dans tous les cas on peut achever une liaison acceptable entre le fongicide et le bois, qui assurait un niveau de protection comparable à celui offert par pentachlorophénol et même quelquefois supérieur. La résistance au lessivage des systèmes était bonne, et aucune séparation n'était produite.

Die Erhaltung von Holz mit Hilfe von reaktiven Fungiziden

Zusammenfassung

Der Einsatz von Pentachlorphenol und anderer Fungizide zum Holzschutz weist viele Nachteile auf. Man überlegte, ob diese nicht besser nicht da durch überwunden werden könnten, dass die Fungizide chemisch mit dem Holz verbunden würden. Daher wurde Prüfung sogenannter reaktiver Fungizide unternommen.

Zweifunktionelle oder dreifunktionelle Agenzien z.B. Trichlor-s-Triazin, ein Diepoxyd und ein Hexamethylen-Diisocyanat wurden als Kupplungsvermittler für aus organischen Zinnverbindungen bestehende Fungizide verwandt.

In allen Fällen konnte Kupplung des Fungizids erfolgreich durchgeführt werden, und die erzielte Schutzwirkung war die gleiche, wenn nicht mitunter sogar eine bessere, als die mit Pentachlorphenol erzielte. Die Beständigkeit des Systems gegen Auslaugen war gut, und es fand kein Verdampfen statt.

Предохранение дерева при помощи реактивных фунгисидов

Резюме

Применение пентахлорофенола и других фунгисидов для предохранения дерева, обнаруживает ряд недостатков. Считается что многие из этих трудностей могут быть преодолены если фунгисиды химически связаны с деревом. Поэтому исследовалось применение так называемых реактивных фунгисидов.

Двухфункциональные и трехфункциональные агенты, как например трихлор-S-триазин, диэпоксид и гексаметилен-диизоцианат, применялись в качестве сцепляющих веществ для олово-органических фунгисидов. Во всех случаях удовлетворительная связь фунгисидов с деревом может в результате дать защиту сравнимую с, а иногда даже и лучшую, чем предохранение представляемое пентахлорофенолом. Устойчивость систем против выщелачивания оказалась удовлетворительной и не наблюдалось испарения.

Introduction

Wood that is to be used as a construction material has to be protected against attack by fungi. When the wood has to be painted after such a treatment, techniques such as creosoting and treatment with carbolineum cannot be used. In such cases fungicides such as pentachlorophenol, tributyltin oxide or triphenyltin oxide, are often used. In applying formulations containing these fungicides, the fungicide may be leached out with water or evaporate during the application process, causing loss in protection. Other difficulties also exist. These are due to the fact that the fungicide is at best only adsorbed on to the wood.

For pentachlorophenol the most serious difficulties are as follows¹.

Pentachlorophenol shows a tendency to crystallise either during storage of the impregnation solution, or on the surface of the wood. Because of the rather high toxicity of this compound for animals and human beings, this last phenomenon is a serious drawback.

Because both the solubility in water (0.5 mg/100 g at 0°C²) and the vapour pressure (17×10^{-6} tor at 0°C)² of pentachlorophenol are rather high, it will tend to be leached out or to evaporate.

When wood treated with pentachlorophenol is painted, reaction of the fungicide with the paint system may occur, resulting in discoloration.

The corrosion of metals is accelerated by pentachlorophenol.

To minimise these drawbacks as far as possible, in practice resinous or oily products are added to pentachlorophenol solutions to be used for the conservation of wood. However, this then results in difficulties with overpainting. There is still the possibility of chemical reaction with the paint system. A loss of adhesion occurs due to the presence of the oily or resinous products on the wood surface. The wood surface changes its character from hydrophylic to hydrophobic with reduced adhesion to a hydrophylic paint resin.

The addition of resinous or oily products is not necessary with organotin fungicides because the solubility in water and the vapour pressure of these

products are much lower than those of pentachlorophenol. The use of organotin based wood preservatives causes less trouble in this respect. Further, the organotin fungicides are more specific as compared with pentachlorophenol; their toxicity towards the fungi is higher, whilst their toxicity towards mammals, is lower^{1,3}.

However, the depth to which the organotin compounds can penetrate into wood is not very large, and therefore the protection is not very good, despite their low solubility.

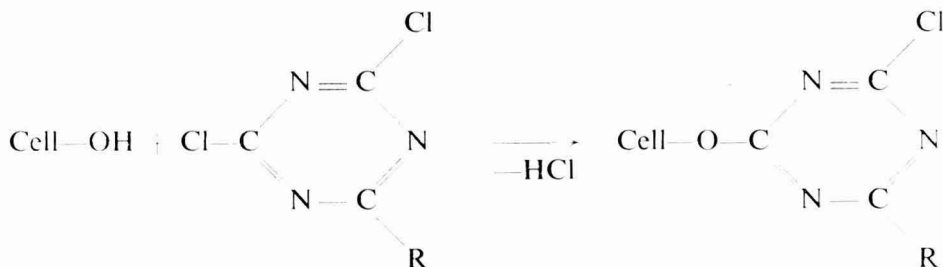
The difficulties mentioned above stem from the fact that the fungicides are only adsorbed on to the substrate, that is, bound by relatively weak forces. Many of these difficulties would be solved if the fungicides could be attached by a chemical bond to wood. A possible way of achieving this could be the use of reactive compounds, such as used in the textile industry, where the formation of a chemical bond between the material to be dyed and the dyestuff results in an extremely good fastness to washing. Recently, a paper has been published by Paulus and Pauli⁴, who have developed reactive fungicides for cotton, based on this principle.

The work to be published in this paper describes the use of reactive fungicides for the preservation of wood.

Experiments with reactive fungicides

The synthesis of the compounds studied will be discussed later on in this paper.

A first series of experiments was carried out with monosubstituted 4, 6 dichloro-s-triazine derivatives. Compounds of this type are able to form a chemical bond with a hydroxyl or amino group at room temperature in a weak alkaline solution. With cellulose this reaction results in the formation of an ether bridge between the polymer and the reactive fungicide.



The yield of this reaction can be determined by analysing the amount of nitrogen in the carefully washed off reaction product. The cellulose used was pure and nitrogen free. Some of the yields of the reaction are given in Table 1.

It can be concluded that the possibility of coupling reactive fungicides to cellulose with a good yield does exist. It is of essential importance to know if a fungicide coupled in this way will retain its toxic properties towards fungi. Therefore, pieces of beechwood were impregnated with the fungicides and, after reaction with the wood had taken place, exposed to attack by fungi that

Table 1

The yield of reaction products of some 4.6 dichloro-s-triazine derivatives with cellulose

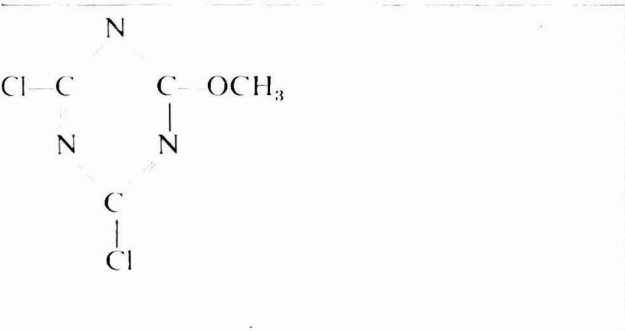
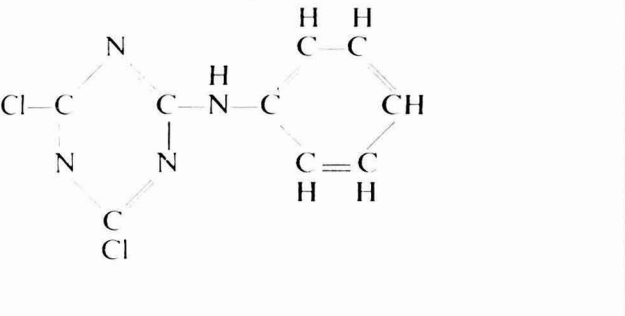
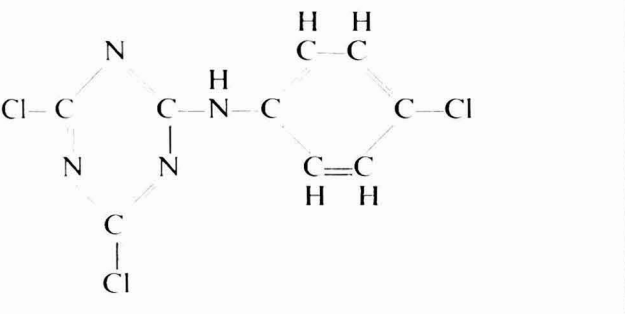
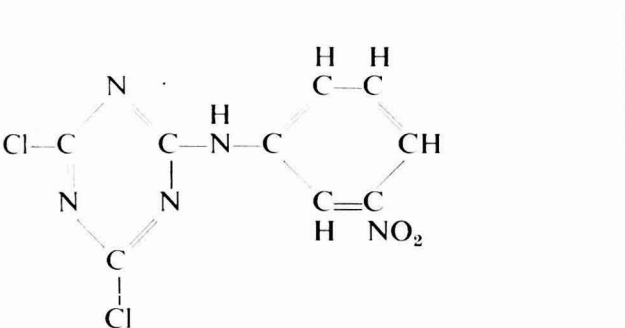
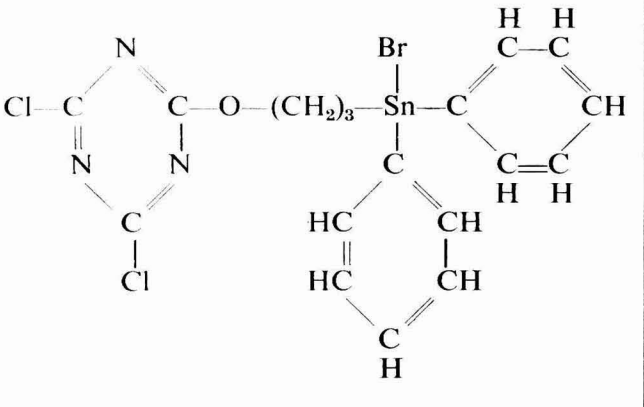
Structure	Name	Yield
	2 methoxy 4.6 dichloro-s-triazine	91%
	2 phenylamino 4.6 dichloro-s-triazine	23%
	2-(<i>p</i> -chloro) phenylamino 4.6 dichloro-s-triazine	97%
	2-(<i>m</i> -nitro) phenylamino 4.6 dichloro-s-triazine	86%

Table 1—continued

Structure	Name	Yield
	3 (0, 4,6 dichloro-s-triazyl) propoxydiphenyltinbromide	78%

cause wood decay. The technique of impregnating the wood is described in DIN 52176⁵. After impregnating the wood with a reactive fungicide in acetone and evaporation of the acetone, the pieces are then impregnated with ammonia of pH = 10 for three hours at room temperature to complete the reaction of the fungicide with the cellulose.

After removal of the unreacted fungicide by washing, and after drying, the pieces of beechwood were exposed to *Coniophora Puteana* (for 6 weeks) and *Polystictus Versicolor* (for 12 weeks) at 24°C and 70 per cent relative humidity. Pentachlorophenol was used as a reference fungicide. The results of the experiments, given as the weight loss of the pieces of wood after the experiments, are listed in Table 2, together with the concentration of the fungicide in the impregnation solution.

Before starting the experiments, the pieces of wood were dried and their weight was determined after storage at 21°C and ~ 30 per cent relative humidity. After the experiments, the pieces of wood were dried at 105°C and stored in a desiccator over CaCl₂. The weight loss of an untreated piece of wood stored at 21°C and 30 per cent RH after heating at 105°C for two hours and reconditioning over CaCl₂ is about 4 per cent. From the results given in Table 2, it follows that only the reactive organotin fungicide offers a protection which is comparable to that offered by pentachlorophenol. A disadvantage of the use of the reactive dichloro-s-triazine fungicides is that these compounds are often easily hydrolysed by water or water vapour. The ability to react with wood at room temperature is then destroyed, because monochloro-s-triazine derivatives react with hydroxyl or amino groups only at temperatures of 60-90°C. Hence, the compounds have to be stored very carefully and their application is limited. To overcome this difficulty, other bifunctional reagents were tried.

The bifunctional reagents investigated are listed below.

A diepoxide. This was a diglycidyl ether with a molecular weight of about 310. The compound is able to react with hydroxyl groups in a solution of sodium

Table 2
 Weight loss of pieces of beechwood treated with reactive fungicides after attack by fungi

Fungicide	Weight % fungicide in the impregnation solution	% weight loss after attack by:	
		<i>Coniophora P.</i>	<i>Polystictus V.</i>
2 methoxy 4,6 dichloro-s-triazine	8	16	14
	4	17	14
	2	17	18
	1	33	—
	0.5	36	—
2 phenylamino 4,6 dichloro-s-triazine	8	14	13
	4	12	17
	2	18	19
	1	36	—
	0.5	33	—
2-(<i>p</i> -chloro) phenylamino 4,6 dichloro-s-triazine	8	12	12
	4	21	11
	2	25	18
	1	34	—
	0.5	33	—
2-(<i>m</i> -nitro) phenylamino 4,6 dichloro-s-triazine	8	20	9
	4	22	9
	2	25	11
	1	35	—
	0.5	35	—
3 (0,4,6 dichloro-s-triazyl) propoxydiphenyltin-bromide	4	4	5
	2	4	9
	1	5	20
	0.5	5	25
	0.25	20	—
	0.12	33	—
Pentachlorophenol	8	5	5
	4	7	7
	2	8	17
	1	6	31
	0.5	6	—
	0.25	20	—
	0.12	35	—
Blank	0	39	40

carbonate in water. In an organic solvent, tertiary amines can be used as a catalyst for the reaction with hydroxyl groups.

Formaldehyde. In the presence of boric acid as a catalyst, formaldehyde can act in the vapour phase as a cross-linking agent for cellulose⁶. The question of whether or not a coupling between the fungicide, the cellulose and the formaldehyde in aqueous solution could take place has been investigated.

Hexamethylenediisocyanate (HMDI). This compound reacts with hydroxyl groups with cobalt naphthenate as a catalyst. Other good catalysts are organotin compounds such as tributyltin acetate and dibutyltin diacetate.

However, the yield of the reaction of diphenylhydroxypropyltin bromide with cellulose without cobalt naphthenate as a catalyst is very low.

1,5 difluor 2,4 dinitrobenzene (DFDNB). In a weakly alkaline solution, reaction with hydroxyl and amino groups is possible, as has been shown by Zahn^{7, 8}. A suitable solvent is dimethylformamide.

p, p' dinitrodiphenylcarbonate (DNDPC). This double ester of carbonic acid can react by inter-esterifying with the hydroxyl groups of cellulose and diphenylhydroxypropyltinbromide.

Adipyl chloride. Ester bonds can be formed with hydroxyl groups with the liberation of hydrochloric acid. 2, 4, 6 trimethylpyridine is used as an acceptor of the hydrochloric acid.

These bifunctional reagents were used under various conditions to couple diphenylhydroxypropyltin bromide to cellulose. The yield of the coupling reaction and the preservation of the wood after the treatment were studied. The yield of the coupling is calculated from the quantity of tin found in the cellulose. The first method used in an attempt to couple the fungicide to the cellulose was as follows. Diphenylhydroxypropyltin bromide and an equivalent amount of the diepoxide were precipitated on cellulose powder by evaporation of the solvent, acetone in this case. Then a solution of sodium carbonate in water was added and the suspension shaken. The reaction was allowed to proceed for 48 hours at room temperature. In those cases where the reaction occurs in an organic solvent the cellulose, fungicide, coupling agent and catalyst were added in that order and allowed to react for 48 hours at room temperature, the suspension being shaken occasionally (method 1). After isolation of the reaction product, all the unreacted fungicides were washed out with benzene and acetone. The amount of tin in the reaction product was determined by chemical analysis. Table 3 gives the yields of the coupling of diphenylhydroxypropyltin bromide to cellulose obtained by method 1 for each different coupling agent.

Table 3
The coupling of diphenylhydroxypropyltin bromide to cellulose (Method 1)

Coupling agent	Catalyst	Solvent	Yield (%)
Diepoxide	sodium carbonate (1 equivalent)	H ₂ O	70
DFDNB	Sodium carbonate (1 equivalent)	dimethylformamide	12
DNDPC	—	dimethylformamide	12
Formaldehyde	boric acid 0.05 equivalent	H ₂ O	—
Adipyl chloride ..	—	benzene	14
HMDI	cobalt naphthenate (2 % by weight)	benzene	11

The conclusion is that only the diepoxide gives a satisfactory coupling of the fungicide to the cellulose. In an attempt to obtain better results, the following method was applied. The diphenylhydroxypropyltin bromide was dissolved in an organic solvent together with a catalyst where required, and the equivalent amount of coupling agent was added slowly to the boiling mixture, stirring constantly. After all the coupling agent had been added, the mixture was boiled for another 1½ hours. When hydrolytic reactions were possible, the reaction was carried out in a dry organic solvent and in a nitrogen atmosphere. After cooling to room temperature, the cellulose powder was added and the suspension was allowed to react for 48 hours. During this period, the suspension was occasionally shaken. After the isolation of the reaction product, which was carefully washed to remove unreacted organotin compounds, the amount of tin in the reaction product was determined by chemical analysis, so that the yield could be calculated. The results are given in Table 4.

Table 4

The coupling of diphenylhydroxypropyltin bromide to cellulose (Method 2)

Coupling agent	Catalyst	Solvent	Yield (%)
Diepoxide	piperidine (0.1 equivalent)	benzene	85
DFDNB	2,4, 6 trimethylpyridine (1 equivalent)	benzene	52
DNDPC	—	benzene	36
Adipyl chloride ..	—	benzene	68
HMDI	cobalt naphthenate (2 % by weight)	benzene	81

Method 2 apparently gives much better yields than method 1. The best results are obtained with the diepoxide and the hexamethylenediisocyanate. Even better results can be obtained if not only the reaction of diphenylhydroxypropyltin bromide with the coupling agent to give a reaction product, but also the reaction of this product with cellulose, is carried out at a temperature of about 80°C (refluxing benzene) for six hours (method 3). The yields of the couplings obtained by this method are given in Table 5.

Both method 2 and method 3 are satisfactory. The results obtained by the last method are even better than those of the second method; however, in practice, the second method is easier in use.

To determine the fungicidal activity of the coupling products, pieces of beech wood were impregnated according to method 2 and exposed to attack by the fungi *Coniophora Puteana* and *Polystictus Versicolor*. To remove unreacted diphenylhydroxypropyltin bromide and coupling agent, the pieces of wood were extracted with benzene over two days. Pieces of wood impregnated with pentachlorophenol were used as a reference. The experiments were

carried out according to DIN 52176⁵ with some difference in the conditions in the climate room during the fungal attack (24°C, 70 per cent RH). The results are given in Table 6.

These results show that diphenylhydroxypropyltin bromide coupled to wood offers a protection as good as, and sometimes even better than, pentachloro-

Table 5
The coupling of diphenylhydroxypropyltin bromide to cellulose (Method 3)

Coupling agent	Catalyst	Solvent	Yield (%)
Diepoxide	piperidine (0.1 equivalent)	benzene	97
DFDNB	2,4, 6 trimethylpyridine (1 equivalent)	benzene	75
DNDPC	—	benzene	58
Adipylchloride	—	benzene	84
HMDI	cobalt naphthenate (0.2 % by weight)	benzene	95

Table 6

Fungicidal activity of the reaction product of diphenylhydroxypropyltin bromide, a coupling agent and cellulose

Coupling agent	Concentration of fungicide in the impregnating solution (% by weight)	% of weight loss after attack by:	
		Coniophora P (after 6 weeks)	Polystictus V (after 12 weeks)
Diepoxide	2	5	8
	1	4	15
	0.5	5	28
DFDNB	2	6	8
	1	6	14
	0.5	15	33
DNDPC	2	6	12
	1	15	21
	0.5	34	33
Adipyl chloride ..	2	7	9
	1	5	15
	0.5	8	31
HMDI	2	5	8
	1	5	15
	0.5	7	28
Pentachlorophenol ..	2	6	16
	1	6	30
	0.5	8	33
Blank	0	39	40

phenol. The possibility of leaching out the fungicides is very small when the reactive fungicides are used; when the reaction product of diphenylhydroxypropyltin bromide with hexamethylene diisocyanate and cellulose powder is extracted with streaming fresh water for two weeks, no change in the tin content of the cellulose can be detected by chemical analysis.

In view of the type of reactive compounds studied, it is to be expected that overpainting will cause no appreciable difficulties. This, however, has still to be proved on relatively large surfaces and during long periods of time.

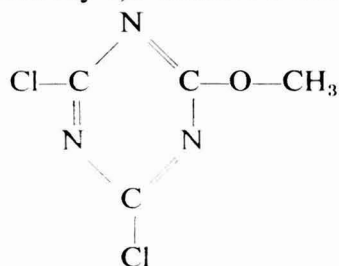
Preparation

The 4, 6 dichloro-s-triazine derivatives

Koopmans⁹ studied the synthesis of these compounds, starting from cyanuric chloride and alcohols or amines. The mechanism of these substitution reactions and the mechanism of the reaction with cellulose has been investigated by Zollinger^{10, 11, 12}.

The s-triazine derivatives used have been synthesised by the methods of Koopmans.

2 methoxy 4,6 dichloro-s-triazine



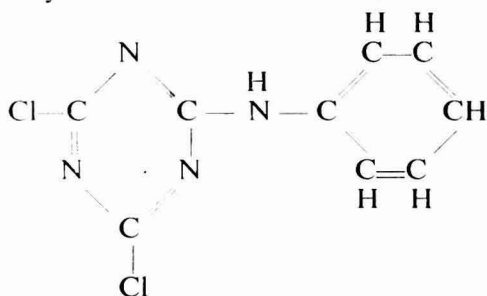
Melting point: 87-88°C. Lit. 88-89°C.
Yield: 74%

Analysis

Found—C = 26.3%
N = 23.4%
Cl = 38.6%

Calculated—C = 26.7%
N = 23.3%
Cl = 39.4%

2 phenylamino 4,6 dichloro-s-triazine

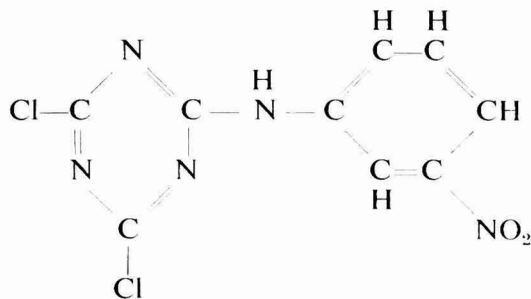


Melting point: 124.6-125.7°C
Yield: 86%

Analysis

Found—C = 45.2%
N = 22.2%
H = 29.9%

Calculated—C = 44.8%
N = 23.2%
H = 29.5%

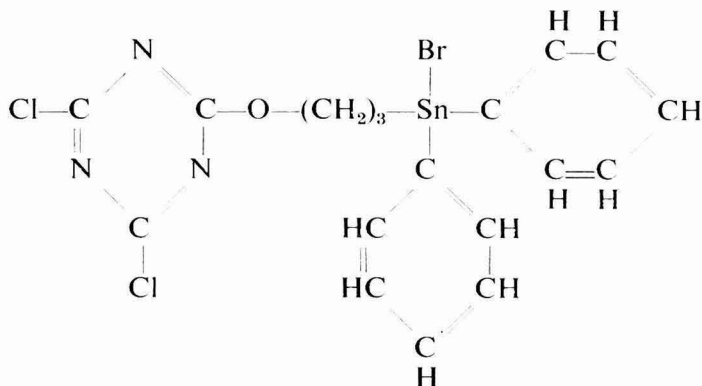
2-(*m*-nitro) phenylamino 4,6 dichloro-*s*-triazine

Melting point: 192-194°C
Yield: 69%

Analysis

Found—C = 38.4%
N = 23.7%
H = 25.9%

Calculated—C = 38.3%
N = 24.8%
H = 25.2%

3-(*o*-4,6 dichloro-*s*-triazyl) propoxydiphenyltin bromide

Oily product
Yield after
extraction with
CCl₄: 66%

Analysis

Found—Sn = 20.6%
C = 39.8%

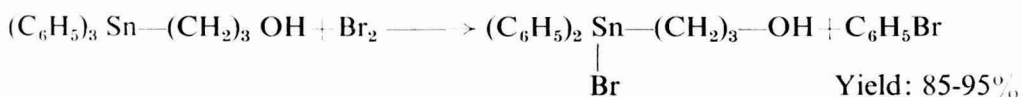
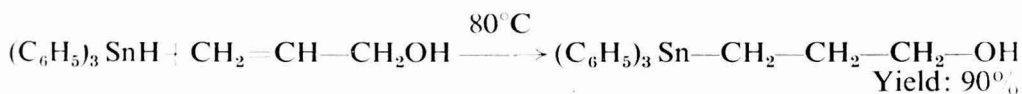
Calculated—Sn = 21.6%
C = 38.6%

The compound was dissolved in dry acetone, cellulose powder added, and finally an equivalent of 2,4,6 trimethylpyridine as a catalyst and a hydrochloric acid acceptor added. The mixture was well stirred and left to react for 24 hours at room temperature. The solid was then filtered off, washed thoroughly with acetone and water to dissolve the salt of 2,4,6 trimethylpyridine and hydrochloric acid, and dried.

Usually 2.5 grams cellulose and 0.5 gram of fungicide were used in the experiments.

Organotin compounds

The synthesis of diphenylhydroxypropyltin bromide and of its dibutyl analogue have been described by Noltes, Luyten and Van der Kerk^{13, 14}. Starting from triphenyltin chloride, the reaction scheme is as follows:



This method of preparation has also been used with a slightly different first step, as shown below.

Triphenyltin hydride

A 0.1 mole (38.6g) portion of triphenyltin chloride was dissolved in a mixture of 25ml of dry ether and 25ml of dry tetrahydrofuran. This solution was added slowly to a suspension of 2g LiAlH_4 in 80ml of dry ether placed in a four-neck 1l round bottomed flask equipped with a reflux condenser, a mechanical stirrer, a dropping funnel and a gas introduction tube. The reaction was carried out in a nitrogen atmosphere.

When the addition of the triphenyltin chloride solution was complete, the mixture was refluxed for 2.5 hours. After cooling to room temperature, 150ml water was carefully added to destroy the LiAlH_4 and separate the mixture into ether and water phases. After separation of the layers, the water phase was extracted with three 50ml portions of ether. The combined ether extracts were dried over Na_2SO_4 , filtered and the solvent of the filtrate was evaporated with the aid of a film evaporator.

A pale yellow oil remained, sometimes containing small amounts of white crystalline product, which was separated by filtration. The oily product (yield 90-95%) was sufficiently pure for the second step of the synthesis. A considerable decomposition occurred on distillation, and the yield decreased from 45% to 35%.

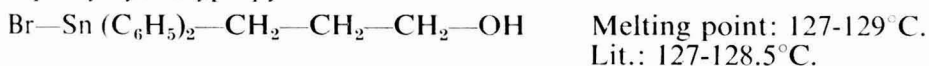
*Triphenylhydroxypropyltin*¹⁴



Analysis

Found—Sn = 28.7%	Calculated—Sn = 29.0%
C = 62.0%	C = 61.7%
H = 5.4%	H = 5.4%

*Diphenylhydroxypropyltin bromide*¹⁴



Analysis

Found—Sn = 28.7%	Calculated—Sn = 28.8%
Br = 19.5%	Br = 19.4%

Conclusions

It has been shown that wood can be protected against the attack of fungi by reactive fungicides based on s-triazyl organotin compounds.

Because of the instability of these s-triazyl compounds towards water, other possibilities of attaching an organotin compound to wood or cellulose, such as a diepoxide and a diisocyanate, have been investigated. Depending on the reaction conditions, the results of these experiments vary, but under proper conditions satisfactory coupling of the organotin compound to the wood can be obtained. Pieces of beechwood treated in this way and exposed to attack by fungi that cause wood decay are protected as well as, and sometimes even better than, when protected by pentachlorophenol.

[Received 16 November 1970]

Acknowledgment

The experiments on the preservation of wood have been carried out in co-operation with Miss T. Hof of the Wood Research Institute TNO, Delft, Holland. The authors are most grateful for her help.

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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 August issue:

"Polymeric binders containing vinyl esters of branched carboxylic acids for use in electrodeposition finishes," by W. J. van Westrenen and W. H. M. Nieuwenhuis

"The adsorption of gases and the characterisation of the surface properties of pigments," by K. S. W. Sing

"Water transport through paint films. Part V: Pigmented films," by D. Y. Perera and P. M. Heertjes

"Chemical characterisation of pigment surfaces," by G. D. Parfitt

"The characterisation of glycol ethers by gas chromatography," by J. K. Haken and V. Khenanghorn

Review

MARKOV CHAINS AND MONTE CARLO CALCULATIONS IN POLYMER SCIENCE
BY GEORGE E. LOWRY (Editor). New York: Marcel Dekker Inc. 1970 pp.
xi + 329. Price: £9.40

A Markov chain is a series of events or states of a system in which the probability of a particular step in the sequence occurring in a particular way depends upon the outcome of the n preceding steps. If $n = 0$ the process is independent of the preceding steps and we have the Bernoulli trial or Markov chain of zeroth order. The conformation of a polymer chain generated by a more or less constrained random walk process can be treated as a Markov chain of 1st, 2nd or higher order according to the degree of sophistication one wishes to achieve and the mathematical complexity which can be handled. The formation of a polymer system from a given number of monomers is another problem to which Markov chain theory can be applied, here to yield information about the distribution of molecular species and size. Both are typical applications of probabilistic models to polymer science in which Markov chain theory can provide elegant solutions.

Sometimes, however, the maths gets out of hand; the equations are found to be insoluble without unacceptable approximations, and an alternative approach may be more successful. Mathematical analysis may be replaced by simulation of the random process, with appropriate constraints, using a computer or, more simply, a roulette wheel. This is the Monte Carlo method. One observes random numbers generated in such a way as to simulate the physical random process of the original problem. It may even be possible to attack a deterministic problem in this way if a concomitant probabilistic problem can be formulated.

These brief words of introduction are intended for those readers encountering for the first time the topics with which this book is primarily concerned. Those who are not rather mathematically minded need read no further, for the liberal use of mathematical notation which riddles every chapter after the first will strike terror into their hearts. Others may take courage, for it is the profusion of mathematical symbols rather than the maths itself which appears disconcerting. The authors never use words where symbols will do, but the mathematical tools needed comprise little more than calculus, straightforward matrix algebra, rudimentary set notation and probability theory.

The first three chapters provide background theory. Their mastery is essential for an understanding of the rest of the work, but those without some familiarity with Markov chains and Monte Carlo methods will find them so concise as to be hard going. Several references, are, however, provided to more extended writings on these subjects.

The remaining two thirds of the book deals with applications; successively, polymer conformation as a Markov chain problem, polymer conformation and the excluded volume problem, higher order Markov chains and the statistical thermodynamics of linear polymers, copolymer composition and tacticity and,

finally, molecular weight distributions. The treatment is generally to take Markov chain theory as far as it will go in the present state of the art, and then to approach the problem "from the other end" by examining the application of Monte Carlo methods.

This is an important and rapidly advancing area of polymer theory, the full ramifications of which are yet to be seen. To this reviewer, however, the extraordinary non-feature of the book is the absence of any reference to the important contributions to the theory of branching processes by T. E. Harris and I. J. Good, and their strikingly successful exploitation in the polymer field by Manfred Gordon. Whatever hairs may have to be split to distinguish Gordon's approach from those here treated, this is an absurd and unforgivable omission.

A. R. H. TAWN

London Section

Southern Branch

Student Symposium

Following the successful symposium on "Surface coatings for marine use" in February 1970, the Southern Branch held another symposium on 9 February 1971 at Portsmouth, on "Biological problems associated with surface coatings." In the morning session two lectures were given, the first by Dr E. S. Pankhurst of the Gas Council, London Research Station on "Corrosion caused by micro-organisms," the second entitled "Biocidal additives for paints—are they necessary?" by Mr P. M. Proudley of Durham Raw Materials Ltd. In the afternoon two group visits were arranged: to the Dockyard Exposure Trials Station at Eastney; and to the Biological Sciences Department of the Portsmouth Polytechnic, where Dr Pankhurst and Mr Proudley had displays relevant to their lectures in the morning and Dr G. Jones of Portsmouth Polytechnic also displayed examples of polyurethane coatings which had been attacked by marine micro-organisms. At the same time, in the Chemistry Department lecture theatre, Mr B. A. Richardson gave a short lecture on "Wood preservation and painting."

Corrosion caused by micro-organisms

Dr Pankhurst introduced her lecture by outlining the three requirements for corrosion by micro-organisms to occur: a susceptible substrate, suitable flora, and an aqueous environment. Under these conditions micro-organisms could flourish and encourage chemical and electrolytic processes to occur. The various types of corrosion that occurred could be divided into five distinct categories as listed below.

The by-products of growth, for example sulphuric acid, various organic acids and hydrogen sulphide. Sulphate ions in the soil were reduced to sulphide, which could be oxidised to sulphuric acid, so that under aerobic conditions sulphuric acid would be produced, in anaerobic conditions hydrogen sulphide would be produced.

Differential aeration and oxygen cells. Colonies of organisms adhered to the surface so that there were areas of surface where anaerobic conditions prevailed, hence the corrosion products would be entirely different from those on exposed surfaces, and potential differences were set up which caused further corrosion.

Depolarisation of the cathode. At a cathodic area on the surface of a metal, hydrogen was produced, which resulted in a relatively low rate of corrosion. If, however, sulphate reducing bacteria were present, the hydrogen was utilised for the formation of hydrogen sulphide, which accelerated the corrosion.

Breakdown of protective films applied to the metal. Coal tar products had been used quite successfully as a coating for buried metal; bitumen, however, did not contain complex aromatic compounds, and was thus more biodegradable.

Breakdown of corrosion inhibitors. In hot water central heating systems, corrosion inhibitors based on sodium benzoate and sodium nitrite were used. These were very good for supporting the growth of microorganisms and hence a biocide must be added.

Unfortunately, due to a late start, there was insufficient time for questions to be put to the speaker. Questioning had to be postponed to the afternoon.

Additives for paints—are they necessary?

In introducing his lecture, Mr Proudley stressed that the views he was going to express were not necessarily those held by the company by which he was employed. The main biological problems encountered in paints could be divided into two categories, growth in the can and growth on, or under, the applied film. Growth in the can only occurred with water-based paints. Bacteria or yeasts attacked the colloid or plasticiser, thus bringing about a reduction in the viscosity of the paint. Only in very rare cases was the polymer attacked. This problem had to be solved by the use of biocidal additives.

Biological attack of the surface occurred with emulsion and decorative paints. Both fungi and bacteria grew on the surface, but since fungi preferred acid conditions, say pH 4.5–6.5, they were more or less confined to decorative paints, since emulsion paint surfaces were usually alkaline. A soft linseed oil paint was much more easily attacked than the harder alkyds and urethanes.

The speaker pointed out that there was a tendency nowadays to put an additive into a formulation to control one factor, resulting in the need to introduce more additives to control the side effects of the first one. Thus it would be much more sensible to go back and re-examine the basic formulation. As mentioned earlier, if the film hardness was increased then the possibility of attack would be reduced. Choice of pigmentation also affected the performance of paint. Titanium dioxide was now virtually the only white pigment used; as far as pigmentation was concerned it was very satisfactory, but it possessed virtually no fungistatic properties, whereas zinc oxide, particularly micronised zinc oxide, possessed considerable fungistatic activity. Unfortunately zinc oxide was not compatible with alkyds because of the high acid values of these resins. There was a possibility that extending the pigmentation with, say, calcium carbonate might increase the alkalinity of the film and thus reduce growth of fungi.

Mr Proudley concluded his lecture by giving a list of requirements for the ideal biocidal additive: it must be of low toxicity to mammals, readily incorporated into the formulation, unaffected by light, it must not adversely affect the performance of the coating, and it must be cheap. It can safely be said that no one additive fulfils these requirements at the present time.

T.R.G.C.

Manchester Section

The problems of painting timber

On Wednesday 7 April a Student Meeting of the Manchester Section was held at the Manchester Literary and Philosophical Society under the Chairmanship of Mr F. Redman to hear a paper "The problems of painting timber" presented

by Mr G. W. Rothwell of the Building Research Station. There were 46 student members and guests present.

Mr Rothwell commenced by outlining the effect of type and source of timber on the effectiveness of paint protection, particularly under exterior conditions. With the increased demand for timber, softer and faster growing timbers were now being used. These were less durable, and unless adequately protected could have lives of as little as five years, compared with earlier traditional timbers with a life of 20-30 years. The method of drying timber, direction of grain, proportions of oil and resin in the timber (particularly in hard woods) were all important in determining the degree of penetration and paint adhesion.

It was estimated that maintenance costs for timber in the UK were of the order of £100m per year. Water was the main cause of failure and this was accelerated by the inadequate use of rebates, and "overhangs," and the use of undersized timber, resulting in warping and distortion.

Extreme conditions of temperature and humidity should be avoided during painting, and water trapped between joints should be removed to prevent premature failure of the paint film. Contact of unprotected wood with water or damp masonry and excessive condensation on internal surfaces led to early failure.

Premature failure could be minimised by attention to the following points: design detail of fittings with respect to rebates/overhangs and construction of joints,

use of recommended type of wood preservative,

ensuring that timber was thoroughly dry after treatment with preservative, compatibility of the paint system with the type of preservative used.

Four main types of paint primers were available. Lead based primers were toxic and slow drying, but generally gave the best protection. Non-lead based primers dried quickly when formulated on oxidising resin media, but were less satisfactory due to low flexibility and high permeability. Primers based on aluminium flake gave very good water resistance, sealed in resins and stains but sometimes became brittle, and if water penetration occurred there was loss of adhesion. Emulsion primers gave low toxicity and low flammability, were flexible and dried quickly under normal conditions, but dried slowly at low temperatures and at high humidities. Emulsion primers were generally considered to be slightly inferior in durability to lead primers but better than non-lead and aluminium-based primers. However, emulsion primers could cause difficulties. There was a tendency to raise the grain by dipping, casement putties dried slowly when applied over primed surfaces, and the long-term adhesion of putties applied over emulsion primers was suspect. Combined preservative/primers were available, but it was difficult to combine good penetration with an adequate paint primer film.

Treatment with preservative and primer was followed by an undercoat and one coat of finish. Traditional alkyd resin paint systems were being challenged by polyurethanes but there was no significant advantage in durability and the harder film formed could cause cracking. Emulsion systems were generally less durable at the present time than alkyd and urethane systems, but should improve in the developing field of gloss emulsion paints.

Recommendations were given for test procedures designed to cater for a range of different types of woods with various grain orientations. It was emphasised that the exposure of paint panels at 45° was not always a realistic test and it was necessary to carry out exposures as closely as possible to conditions of actual usage. Artificial weathering was found to be a useful accelerated test for film hardness and graphs of film hardness as measured by a micro indentation tester were shown for different paint systems.

Finally Mr Rothwell concluded by comparing the durability of clear coatings with pigmented paint systems, and said that experience had shown that four coats of the most durable types of varnishes only gave a life of three years and were much more expensive than traditional paint systems. Phenolic varnishes, one-pack urethanes and the best traditional alkyds gave comparable durability and were easier to use on-site than two-pack polyurethanes. In practice preservative stainer types, although not as durable as the other systems, had been found to be cheaper both in initial cost and cost of application/maintenance.

The presentation of this paper was followed by a lively question and discussion period and the number of questions amply demonstrated the interest in the subject of painting timber.

G.R.R.

Thames Valley Section

Modern solvents

The inaugural meeting of the Thames Valley Section Student Group was held at Slough College on Tuesday 2 March 1971, when Mr L. A. Tysall of Shell Research Limited gave a talk entitled "Modern solvents."

Mr Tysall opened by classifying solvents into two basic groups, hydrocarbons and chemical solvents, the latter group including esters, ketones, alcohols and glycol ethers. The manufacture of both types was discussed. A graph illustrated boiling range of hydrocarbons relative to the different constituents. Chemical solvents were derived from crude oil cuts, which were then cracked giving olefines, from which were further derived the alcohols, esters, ketones and glycol ethers by the well known chemical routes.

He then went on to discuss important criteria for the assessment of the utility of solvents. Firstly there was solvency, which involved the correct choice of solvent for a particular resin with respect to the viscosity desired; here the primary emphasis rested with the chemical nature of the resin or resins involved. He contrasted the behaviour of resin/solvent systems, which quite often showed minimum solubility, with crystalline solute/solvent systems (e.g. salt in water), which showed maximum solubility. A further important criterion was the volatility. There was no direct correlation between boiling point, evaporation rate and drying time. Many paint chemists confused evaporation rate and drying time. He spoke of the non-ideal behaviour of mixed solvent systems which evaporated at rates not directly related to the individual rates of their components.

Lastly Mr Tysall touched on solubility parameters, and by means of examples showed their value as a formulating tool, using three dimensional plots of the

solubility parameters of some common solvents. Mr J. Wilton, one of the student members, proposed the vote of thanks, which was warmly acclaimed by the eight Student members and 37 visitors present.

A full programme has been arranged for the 1971-72 winter session.

P.MCM.

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.)

A new type of silicone antifoaming agent designed specifically for high-temperature, high-pressure jet dyeing systems, has been introduced by **ICI Limited, Nobel Division**. The new product, *Silcolapse 5005*, is water soluble, and is based on a siloxane copolymer. Since it is soluble, *Silcolapse 5005* does not give rise to plating out or spotting of the silicone, a phenomenon encountered when using silicone emulsions. It has inverse solubility characteristics, being completely soluble at temperatures below 30°C, and progressively less soluble as the temperature rises, giving rise to its antifoaming effect.

It has recently been announced that **M & B Plastics Limited**, a subsidiary of **May & Baker Limited**, is to act as UK and Eire agent for products from the **Redis** division of **Pechiney-Saint-Gobain**, a member of the **Rhone-Poulenc** group. A selection of products from the *Stratyl* range of unsaturated polyester resins, for use in speciality surface coatings, varnishes and glass fibre, will be marketed.

Orel polyester filament for use in high quality paint brushes is now available in Europe, the **Du Pont Company** has recently announced. The result of 15 years' research, *Orel* is claimed to be impervious to all common paint solvents, to have an abrasion resistance three times that of natural bristle, and to have excellent stiffness properties under both low and high temperature conditions. The polyester used is not believed to be available outside the Du Pont group.

Three silicone treatments for modifying the handling properties of powder have been developed by **Dow Corning International Limited**. *Dow Corning 1107 fluid*, when used with a room temperature active catalyst, imparts a high degree of water repellency in powders, leading to good flow and freedom from lumps.

Dow Corning 470A fluid, mixed with the powder in concentrations of 0.01 to 0.5 per cent, gives improved wettability.

Dow Corning 200 fluid, in concentrations of 0.1 to 0.5 per cent, promotes faster grinding and uniform particle size by forming a semi-organic coating on the particles. When used in pigment grinding, easier mixing and more uniform colour strength are claimed.

Dow Corning has also introduced three new silicone additives for latex and solvent based paints.

Dow Corning 12 and *13* paint additives are especially designed to increase the mar resistance of solvent based paints, and are particularly recommended for urethane coatings.

Dow Corning 17 paint additive is a water based silicone for latex paints, claimed to reduce foaming and improve levelling, flow-out and mar resistance.

A new 12-page brochure on methods of bulk storage and handling of latices has been issued by **Dow Chemical Company Limited**. Entitled "Bulk storage and handling of Dow latexes," copies of the brochure are available from Dow on request.

A new departure in the field of instruments has been announced by **Pye Unicam Limited**. This company is to become the first in its field to supply its instruments on a leasing basis. Any Pye Unicam instrument of more than £400 in value can be leased

in this scheme, the financial arrangements being carried out by the "in house" company **Communication Services Limited**, a company jointly owned by Pye and Philips. The advantages of leasing are said to be that equipment can be obtained well in advance of proposed budgets for capital expenditure, and that, as the rental is fixed by contract at the time of the arrangement, the cost of the equipment will not be affected by inflation.

In view of doubts in the industry on the future of high grade channel blacks caused by stricter air pollution control regulations in the USA and Europe, **Degussa** has announced that it will still be in a position to supply high colour channel blacks to the market. The gas black process used by Degussa meets the stringent air pollution control requirements of the Federal Republic of Germany, and the high quality channel blacks produced by the process will continue to be available.

The latest in the range of weight operated filling machines produced by **Albro Fillers & Engineering Company Limited** is designed for 5 gallon polythene containers with off-centre vents. Liquids with a range of viscosities from solvents to finished paints can be handled, and accuracies of $\frac{1}{2}$ per cent on the gross weight are claimed. The machines, which require no power of any kind, can also be adjusted to fill conventional free-standing containers.

Badische Anilin- & Soda-Fabrik AG has made additions to three of its product ranges.

Two new colours have been added to the *Luconyl* range. *Luconyl Yellow 107* is a high fastness product for outdoor paints, and *Luconyl White X22*, also having good fastness properties, is recommended for speciality paints.

Fanal Green PM9370 is added to the *Fanal* range. Recommended for use in printing inks, the new pigment is claimed to be 20 per cent stronger, slightly yellower and cleaner in shade than *Fanal Green PTM9340*.

The *Paliogen* range has been supplemented with *Paliogen Violet 5890*, a dioxazine derivative. Intended to replace *Paliogen Violet 5990*, the new pigment is claimed to be markedly stronger, rather redder and cleaner, and more easily dispersible than the old grade. Excellent light fastness and weather resistance, and good fastness to over-spraying, heat and solvent-resistance are also claimed.

It has recently been announced that the range of temperature recording and measuring instruments manufactured in Germany by **Braun Electronic GmbH** is to be marketed in the UK by **Colstar Limited**. The products handled will include the *Tastotherm* range, covering a spread of temperature from -60° to $+600^{\circ}\text{C}$, the *Tastomed* range for medical applications, and the *Infratherm*, which, since it measures the infra-red rays emitted by the object, does not have to be in direct contact.

The Penetone Company Limited has introduced a newly formulated version of *Solvo-Strypp* paint and plastics stripping agent. Stripping times with the new formulation of this solvent stripper, which contains new activating additives, have been reduced by 5-40 per cent, it is claimed.

A new service for firms wishing to give advanced and specific technological training to more senior staff is now available from **H. Warson (Chemical Consultant) Limited**. Aware of the difficulties involved in this aspect of staff training, the company has brought together a team of lecturers covering a range of topics including resins,

paints, rubbers, adhesives, industrial organic chemicals, food chemistry, chemical plant problems, industrial research and development in relation to marketing, management and some legal aspects. Each lecturer is an acknowledged expert in his subjects, with over 25 years' practical experience. The lecturer will travel to the company concerned, and will be prepared to speak on a number of his own specialist subjects.

Rates for the service will depend on location and preparation involved; favourable rates will be quoted for a series of seminars for the same organisation. Full details are available from H. Warson (Chemical Consultant) Limited.

Heyden & Son Limited has recently issued a catalogue of publications of the American Society for Testing and Materials (ASTM) that are now available from Heyden, the ASTM's European agent. A catalogue of Heyden's own publications on analytical chemistry is also available.

Agreement has been reached between **Anchor Chemical Company Limited** and **Paragon Rubber Company (Pty) Limited**, of South Africa, for Paragon to manufacture, under licence, the Anchor range of factices. The factices will be sold by Anchor's wholly owned subsidiary **Anchor Chemical Company (South Africa) (Pty) Limited**, in Johannesburg.

The Paint Research Association has launched a titles-only current awareness bulletin, "Paint Titles" (PT). Issued weekly, PT complements the other PRA publication, "World Surface Coatings Abstracts," bringing to the reader's attention articles virtually before they could be read in the original. Initially circulated to PRA staff, PT was evaluated by RA members, the response being encouraging enough for the PRA to offer the publication at a subscription rate of £20 per annum to members, and £50 per annum to non-members.

Annual Report of the Council for 1970

Adopted at the Ninth Annual General Meeting, held at the Palace Hotel, Torquay, Devon on 7 May 1971.

General

Perhaps the most important single development in a year in which progress was made in many projects was the holding of the Association's Annual Technical Exhibition for the first time at the Empire Hall, Olympia, London, W14. This took place from 27 to 30 April and a report appears later under the Exhibition Committee's Report. A review of the Exhibition appeared in the June issue of the *Journal*.

The Eighth Annual General Meeting of the Incorporated Association took place on Thursday 21 May at the Ballerup Hall, East Kilbride, Lanarkshire when Mr A. W. Blenkinsop was appointed President-Designate and the following Vice-Presidents were elected:

Dr. S. H. Bell
Mr A. H. McEwan
Mr W. J. McWaters
Mr I. S. Moll
Mr C. H. Morris
Mr F. Schollick
Mr L. H. Silver

The Honorary Officers were elected as follows:

Honorary Secretary	Mr D. S. Newton
Honorary Treasurer	Mr F. Cooper
Honorary Editor	Mr S. R. Finn
Honorary Research and Development Officer	Mr A. R. H. Tawn

The report of the Auditors on the scrutiny of the postal votes was received and it was announced that the following members had been elected to the Council for the years 1970-72:

Mr J. E. Mitchell
Mr A. G. Holt
Mr D. M. James

Honorary Membership of the Association was conferred upon Dr H. A. Hampton (President 1961-63) and Mr F. Sowerbutts (President 1967-69) but unfortunately neither member was able to be present (Dr Hampton on medical advice and Mr Sowerbutts because Mrs Sowerbutts had just undergone an operation) at the Annual General Meeting to receive the Scrolls from the President, but these were presented at the Foundation Lecture on 8 October in London.

Votes of thanks to Retiring Council Members, the Honorary Officers of the Association, and to the Chairman of the meeting were carried with acclamation.

The Annual General Meeting was held in conjunction with a Symposium organised by the Scottish Section entitled "Dispersion in theory and practice." The technical sessions were held in the Ballerup Hall and nearly 300 delegates and ladies attended. A small exhibition of some ten companies displaying dispersing machinery was also held in the Civic Centre for the period of the Symposium.

The Symposium commenced with a civic reception on Wednesday 20 May by the Burgh of East Kilbride for the lecturers, overseas visitors and Association officers and following the Annual General Meeting on the evening of 21 May an informal dinner was held in the Carrick Suite at the Bruce Hotel when a true Scottish atmosphere was given to the evening.

The proceedings of the Annual General Meeting and a report of the Symposium, with photographs, appeared in the August issue of the *Journal*.

Other symposia organised by Sections included two for Students. The first, held in February by the Southern Branch of the London Section, was attended by 135 delegates, and had the title "Ships' paints and compositions;" it took place in the Portsmouth Polytechnic and included technical visits to HM Dockyard and the Eastney Testing Station.

In April the Bristol Section held a Symposium for Students at the University of Bristol which was attended by approximately 100 people. In addition to the lectures three technical films on paint and titanium pigments and emulsions were shown.

The 1970-71 session opened in the West Riding Section with a two-day Seminar at the University of Leeds on "Future trends in surface coatings" and incorporated the use of films made by speakers to illustrate various or particular aspects of their research work. This was attended by 115 people.

In March the London Section held a half-day *Conversazione* on "Paint user test methods" at the Borough Polytechnic attended by nearly 70 members and guests and in November the Section joined with the Colloid & Surface Chemistry Group of the Society of Chemical Industry in organising a one-day Symposium, having the theme "The characterisation of pigment surfaces" at the Brunel University, attended by 165 people.

In addition to these special meetings, all Sections have held their usual programmes of technical meetings and social activities.

In June, the Auckland and Wellington Sections held another successful Convention at Wairakei. In the September issue of the New Zealand quarterly *Chemistry and Industry*, 20 pages were devoted to the background of the Association and the activities of the two New Zealand Sections. The necessary material was supplied by members in New Zealand and the congratulations of the Council were extended to the New Zealand Sections on achieving this splendid publicity for the Association's aims and activities.

The Third National Convention of the South African Section was held in September at the Cathedral Peak Hotel in the Drakensberg area, the theme on this occasion being "The principles of electrophoretic deposition of coatings."

At the end of May, the Biennial Dinner and Dance took place at the Savoy Hotel, London, WC2 when over 300 members and guests were present. The guests and their ladies were received by the President and Mrs Fraser, and on this occasion five other societies were represented.

After the Dinner the toast to the Association was proposed by Dr E. S. Paice, President of the Research Association of Paint, Colour & Varnish Manufacturers. The President replied and then welcomed the guests and ladies. Mr G. Isserlis, President of the Institute of Metal Finishing, responded on behalf of the guests. After the speeches, dancing continued until 1 a.m. with a break at 11.30 p.m. for refreshments and a cabaret.

As indicated earlier, the fifth Foundation Lecture took place on 8 October at the Painter Stainers Hall, Little Trinity Lane, London, EC4 when nearly 100 members gathered to hear Sir Paul Chambers, KBE, CB, CIE, formerly Chairman of ICI Ltd. and currently Chairman of the Royal Insurance Co., speak on "Human relationships and communications in industry."

The Lecture was followed by an informal reception before dinner. During his address of welcome after the dinner, the President explained that this function incorporated the annual reunion dinner for Founder Members, Past Presidents, Past Honorary Officers and Members of Council and he was glad, on this occasion to be able to present Dr H. A. Hampton and Mr F. Sowerbutts with their Scrolls of Honorary Membership—an honour conferred upon them at the Annual General Meeting but which both of them had been prevented from attending.

An account of the Foundation Lecture, with photographs, appeared in the December issue of the *Journal* and the lecture by Sir Paul Chambers will be reproduced in full in the January 1971 issue.

The President represented the Association at the Sixth Congress of the Federation of Scandinavian Paint and Varnish Technologists held in Copenhagen in September and conveyed greetings from the Association to the Congress. The official Association paper was presented by Mr L. A. Tysall. The Presidents of the Association's three sister societies were also present and an account, together with a photograph, appeared in the December issue of the *Journal*.

Mr A. R. H. Tawn (Honorary Research and Development Officer) represented the President at the Tenth FATIPEC Congress in Montreux in June, when the official Association paper

at a plenary session was presented by Dr W. Hughes. Mr Tawn also visited the United States during the year, when he lectured to various societies of the Federation of Societies for Paint Technology and at the Paint Research Institute's Annual Meeting. On all these occasions Mr Tawn conveyed to the respective organisations the greetings of the Association.

At the Annual Meeting of the Federation of Societies for Paint Technology held in Boston in October, Mr A. G. North presented a paper on behalf of the Association. Dr W. Carr, a member of the Association, also presented a paper at the meeting for which he received a Roon Award.

Council was saddened to learn of the death during the year of two members who had rendered considerable service during the early years of the Association. In November Mr R. P. L. Britton, a Founder Member, died. An obituary notice will appear in the *January* 1971 issue of the *Journal*. In December Mr T. Hedley Barry, Honorary Editor 1921-24, died. An appreciation will appear in the March 1971 issue of the *Journal*.

During the year the Director & Secretary has been pleased to help members when they visited the Association's office and from overseas was particularly pleased to meet the following:

In June, Mr. R. W. Matlack, (Executive Secretary of the Federation of Societies for Paint Technology).

In July, Mr L. A. Hill (Honorary Editor of OCCAA "Proceedings and News") when Mr D. S. Newton and Mr A. R. H. Tawn joined in the discussions, and

In September, Mr K. M. Engelbert (Honorary Treasurer of the South African Section and former Vice-President):

Mr P. B. Hunt (first recipient overseas of the Commendation Award, Past Chairman of the Auckland Section and former Vice-President), when Mr F. Sowerbutts joined in the discussions:

Mr W. W. Vasterling (President of the Federation of Societies for Paint Technology).

The Council records its thanks to the Director and Secretary and his staff for their efforts in furthering the development of the Association.

Membership of the Association

There were 242 elections during the year compared with 273 in 1969. The table shows the total strength of the Association as at 31 December 1970.

<i>Section</i>	<i>Ordinary</i>	<i>Associate</i>	<i>Honorary</i>	<i>Student</i>	<i>Total</i>
Bristol	79	16	—	4	99
Hull	77	6	—	3	86
Irish	45	22	—	6	73
London (including Southern Branch)	627	93	5	15	740
Manchester	361	65	2	20	448
Midlands (including Trent Valley Branch)	186	31	1	3	221
Newcastle	140	8	—	12	160
Scottish (including Eastern Branch)	108	31	—	24	163
Thames Valley	112	17	—	9	138
West Riding	65	18	—	16	99
Auckland	56	41	—	2	99
Wellington	54	26	—	—	80
South African	204	50	—	4	258
General Overseas	350	22	2	—	374
Total 1970	2,464	446	10	118	3,038
Total 1969	2,477	448	9	147	3,081
Net increase/decrease during 1970	-13	-2	+1	-29	-43

It is pointed out that there has been a decrease in the number of Students and it is felt that the recommendations of the Working Party on Education, Training and Qualifications may

well, if implemented in 1971, prove a source of encouragement to younger personnel in the industries to associate themselves with the Association. Mergers and amalgamations of companies during 1970 contributed to the slight decrease in the overall membership.

The Council

During the calendar year the Council has met four times, the average attendance being 23. All meetings were held in London.

Committees of the Council

The Committees of Council met as set forth below:

Exhibition Committee	2
Finance Committee	2
President's Advisory Committee	4
Working Party on Education, Training and Qualifications	2
Sub-Committee of the Working Party on Forward Thinking	1

Exhibition Committee

Chairman—The Honorary Treasurer, Mr F. Cooper

The Twenty-Second Annual Technical Exhibition, the first at the Empire Hall, Olympia, London was held from 27 to 30 April and proved to be the most successful exhibition held by the Association. Plans to move to Olympia were made at short notice and thus it was possible for the Exhibition to be open on four days only, but despite this the total number of visitors who passed through the turnstiles amounted to 14,500, including representatives from 38 overseas countries.

The Exhibition Luncheon was held at the Savoy Hotel, London, WC2 on 27 April and was attended by 250 members, exhibitors and other guests. The Principal Guest on this occasion was Lord Sherfield, GCB, GCMG, President of the Parliamentary and Scientific Committee.

The President of the Association in his address of welcome referred to the encouraging support for the Exhibition Committee's decision to change the venue of the Exhibition and after outlining the various moves associated with the progress of the Exhibition since its modest beginnings in the early years, expressed the hope that Olympia might become a permanent centre for the Exhibition. Lord Sherfield, in his reply, congratulated the Committee on achieving the present scale and scope of the Exhibition, which had already acquired an international reputation as a centre for information. On arriving at the Empire Hall after the Luncheon Lord Sherfield performed the official opening ceremony and made a tour of the stands accompanied by the President, the then Chairman of the Exhibition Committee (Mr A. W. Blenkinsop) and the Director & Secretary.

The theme of the Technical Education Stand on this occasion was "Newer methods of paint application" and it was again staffed by representatives from technical colleges and the paint and printing ink industries. Parties of sixth form science students visited the Exhibition and before touring the stands were given an introductory talk by Mr G. H. Hutchinson on the variety of scientific interests involved in the industry and the opportunity for careers.

A review of the Exhibition appeared in the June issue of the *Journal* and the Exhibition Committee is particularly grateful to Mr J. A. L. Hawkey (past Chairman of the London Section) who organised the reporting and collated the reports and comments received from a team of some 37 reporters.

Finance Committee

Chairman—The Honorary Treasurer, Mr F. Cooper

This was the first full year in which the Association received the benefit of registration as a charity.

During the year the Committee continued its policy of building up the Association's reserves, so that the investments at the end of the year stood at £50,705 compared with £40,428 at the end of 1969. Some adjustments have been made as a result of certain Government Stock reaching maturity, the resulting funds having been re-invested in equities. The market value

of the Association's investments at the end of the year showed that the Government securities stood at £1,346 below their purchase price and the other quoted investments stood at £513 above their purchase price, i.e. the total market value of all investments was £833 below their purchase price.

President's Advisory Committee

Chairman—The President

It will be recalled that, in the Report for 1968, reference was made to the setting up of the President's Advisory Committee, comprising the Honorary Officers of the Association together with three Section Chairmen, normally in their second year of office. For the 1970-71 session Mr A. S. Fraser invited the Chairmen of the London Section (Mr J. E. Pooley), the Newcastle Section (Mr D. H. Tate) and the West Riding Section (Dr L. J. Watkinson) to serve on this Committee.

Publications Committee

Chairman—The Honorary Editor, Mr S. R. Finn

During 1970, fifty-three papers were published, compared with forty-five in 1969 and forty-three in 1968. The overall size of the *Journal* was 1,132 pages, compared with 1,212 and 1,062 pages in 1969 and 1968 respectively. The number of pages covered by "Transactions" and "Communications" was 740 (65.4 per cent) against 750 pages (61.9 per cent) in 1969 and 638 pages (60.1 per cent) in 1968.

The papers from the Symposia organised by the Manchester and Midlands Sections during 1969 appeared in full in the *Journal* during 1970 and during this latter year further symposia were arranged by the Scottish and West Riding Sections. The papers from the former event will commence to appear in the *Journal* in January 1971. One of the main purposes of the West Riding meeting was to demonstrate the use of visual aids at such an event; this resulted in papers which would have lost much of their value in the purely printed form and it was, therefore, agreed with the Section concerned not to reproduce them in the *Journal*.

A Convention on Electrodeposition was held by the South African Section, the papers from which have been submitted for publication. It is anticipated that these will be published in the *Journal* in due course.

During the year less correspondence with the Honorary Editor was published in the *Journal* (7 letters), compared with 16 in 1969.

A total of eighteen book reviews appeared during the year; the standard of reviewing has been well maintained and the Committee wishes to thank all those members who have undertaken this work. The Honorary Editor also wishes to express his thanks to the Hon. Publications Officers for the large number of "Section Reports" produced during the year.

The "Student Review" section introduced in 1968 contained only three papers in 1970. None are on hand at present and the Committee would very much appreciate suitable contributions to this worthwhile section.

The Resins, Drying Oils, Varnishes and Paints Report for 1969, reprinted from the Annual Reports of the Society of Chemical Industry, was published in November and authors have been invited to prepare the Report for 1970.

Volume VII of the Paint Technology Manuals was completed during the year and was submitted to the publishers. Sales of the first six volumes of the Manuals continue satisfactorily and it will shortly be necessary to re-print more volumes.

Unfortunately it was not possible to hold a meeting of the Committee during the year owing to the difficulty of finding a date upon which a sufficient number of members could attend.

The most gratifying aspect of the year has been the large number of papers submitted for publication, particularly from direct sources. Many of these are of very high quality and it is considered that the interest and standard of the *Journal* should be well maintained during 1971. Some authors have expressed their gratification at the number of requests they have received for reprints.

Survey of published papers:

<i>Section</i>	1968	1969	1970
Bristol	2	1	—
Hull	6	1	1
Irish	—	—	—
London	4	6	2
Manchester	1	2	13
Midlands	—	—	5
Newcastle	1	—	1
New Zealand	—	—	—
Scottish	1	—	—
South African	—	3	—
Thames Valley	—	—	1
West Riding	2	—	—
<i>Direct</i>			
United Kingdom	11	9	15
Overseas	13	14	15
<i>Conference</i>	—	9	—
<i>Foundation Lecture</i>	1	—	—*
	43	45	53

*The 1970 Foundation Lecture will appear in the January 1971 issue.

Jordan Award Committee

Chairman—The Honorary Research and Development Officer, Mr A. R. H. Tawn

It is hoped to present the second Jordan Award at the time of the Association's next Conference in May 1971 and applications have been invited, through the pages of the *Journal*, at regular intervals during the course of the period under review. The closing date is 1 January 1971 and soon after that date the Committee will be meeting to consider the applications received.

Liaison Committee

Chairman—The President

An exchange of information, as discussed at the meeting of the Liaison Committee held during the course of the Association's Conference in 1969 (referred to in the last Report), has taken place and, as indicated in the general part of this Report, the Presidents of the four societies (Fédération d'Associations de Techniciens des Industries des Peintures, Vernis, Emaux et Encres d'Imprimerie de l'Europe Continentale, Federation of Societies for Paint Technology, Federation of Scandinavian Paint and Varnish Technologists and Oil and Colour Chemists' Association) met at the Sixth Congress of the Federation of Scandinavian Paint and Varnish Technologists in Copenhagen in September and discussed matters of common interest.

Technical Education Committee

Chairman—Dr H. W. Keenan

It will be recalled that in 1968 it was reported that the Technical Education Committee was being retained with a membership comprising only the President, Honorary Secretary, Honorary Editor and Dr H. W. Keenan until such time as the deliberations of the Working Party on Education, Training and Qualifications (of which Dr Keenan is also Chairman) were complete. Mr C. J. A. Taylor, as Editor-in-Chief of the Paint Technology Manuals, who was formerly a member of the Technical Education Committee, is now serving as a member of the Publications Committee and details of the current position of the Manuals is given in the report of that Committee.

Light Fastness Committee

Chairman—Dr S. H. Bell

Although no meetings of this Committee have been held during the period under review co-operation has been maintained with other committees in this field.

Working Party on Education, Training and Qualifications

Chairman—Dr H. W. Keenan

Considerable progress has been made this year on the proposal to introduce an optional professional grade for Ordinary Members and, at the end of the year the Council had been presented for consideration by the Working Party with a comprehensive document setting out the steps and procedure necessary for implementing this proposal.

Working Party on Forward Thinking

Chairman—The President

During the year a sub-committee of this Working Party was formed to consider whether an overall summary of all the Section questionnaires on Forward Thinking could be published in the *Journal*. The sub-committee consisted of:

Mr M. P. Ford (Bristol Section)
 Mr F. D. Robinson (Hull Section)
 Mr D. A. Bayliss (London Section)
 Mr D. Morris (West Riding Section)

A considerable amount of work was undertaken by these members individually and their report was first accepted by the Working Party, which then passed it to Council for its January 1971 Meeting.

Representation on other organisations

The Association was represented on other organisations, as follows:

Technical Training Board for the Printing Ink and Roller Making Industry: Mr H. C. Worsdall and Mr R. M. W. W. Wilson.

Paint Apprenticeship Council: Dr H. W. Keenan and Mr G. Copping.

Paint Trade Benevolent Fund: Mr G. Copping and Mr D. E. Roe.

The Parliamentary and Scientific Committee: The President and the Director & Secretary.

The British National Committee for Chemistry: Mr A. R. H. Tawn.

City and Guilds Advisory Committee No. 9—Technology of Pigments, Paints, Varnishes and Lacquers: Dr J. G. Gillan.

East Ham Technical College Advisory Committee: Mr R. M. W. W. Wilson.

Association of Exhibition Organisers: The Director & Secretary.

Programme Liaison Committee: The Honorary Programmes Officer of the London Section and the Director & Secretary.

The Paintmakers Association Training and Technical Education Committee: Dr H. W. Keenan and the Director & Secretary or the Honorary Secretary.

The Society of Dyers and Colourists Terms and Definitions Committee: Dr F. M. Smith and Dr J. Toole.

The Society of Dyers and Colourists Review of Coloration Progress Committee: Dr F. M. Smith.

The Colour Group (Great Britain): Mr R. Smith.

The British Colour Council Colour Institute Committee: The Director & Secretary.

Joint Society of Chemical Industry/Plastics Institute/Institution of the Rubber Industry/Society of Dyers and Colourists and Oil and Colour Chemists' Association Conference Committee: The Honorary Research and Development Officer and the Director & Secretary.

Institution of Corrosion Technology Education Committee: Dr J. B. Harrison and the Honorary Secretary.

British Standards Institution:

PVC	Pigments, Paints and Varnishes Industry Committee	Dr J. B. Harrison
PVC/1	Pigments	Mr A. S. Lewis
PVC/1/9	Black Pigments	Mr J. S. Marsh
PVC/1/11	Extenders	Mr S. A. Ray
PVC/1/18	Zinc Dust Pigments	Mr D. S. Newton
PVC/3	Oils, Varnishes, Putty etc.	Mr G. H. Hutchinson
PVC/3/5	Test Methods for Paint Media	Mr S. R. Finn
PVC/4 and PVC/4/1	Lac	Dr B. S. Gidvani
PVC/6	Cement Paints	Mr W. O. Nutt
PVC/8	Plastic Wood	Mr V. P. Gellay
PVC/10	Test Methods for Paints	Mr A. N. McKelvie
PVC/15	Water Paints and Distempers	Mr T. W. Wilkinson
PVC/16	Ready Mixed Paints	Mr G. A. Newell
PVC/19	Bituminous Paint	Dr H. B. Footner
PVC/20	Calcium Plumbate Priming Paints	Mr A. G. Walker
PVC/23	Zinc Rich Paints	Dr D. Atherton
PVC/24	Water Thinned Priming Paints	Mr J. E. Pooley
PVC/25	Organic Finishes for Aluminium Windows	Dr J. B. Ley
LGE/9	Artificial Daylight for Colour Matching	Miss O. Rawland
C/17	Viscosity	Mr A. N. McKelvie
C/17/2	Revision of BS.188 (Drafting)	Mr A. N. McKelvie
CHE/43	Test Sieves	Mr M. J. F. Meason
CHE/50	Test Methods for Powder Properties	Mr D. S. Newton
CIC/4	Solvents and Allied Products	Dr L. A. O'Neill
OFFA/6	Glycerine	Mr S. R. Finn
OFFA/7	Sampling Oilseeds, Oils and Fats	Mr N. F. Lythgoe
OFFA/12	Vegetable Oils	Mr N. F. Lythgoe
OFFA/24	Analysis of Oilseeds, Oils and Fats	Mr N. F. Lythgoe
ELE/16/53/6	Varnishes	Mr J. McGowan
ACE/44	Aircraft Finishes	Mr J. B. G. Lewin
BLCP/18	Code of Practice: Painting	Mr P. J. Gay
M/36	Artists' Materials	Mr J. A. L. Hawkey
RDE/25	Road Marking Compounds	Mr T. R. Bullett
OC/20/4/12	Chemistry and Chemical Technology	Mr J. Orpwood

Reports from the above representatives may be seen by members at the Association's offices.

The Association was also represented on overseas organisations as follows:

New Zealand Corrosion Association: Mr P. B. Hunt.

New Zealand Standards Association: Mr T. Whitfield.

Standards Association of New Zealand—Paints and Coatings Sectional Committee: Mr T. W. Slinn.

Appendix

Report of the Council in accordance with the Companies Act 1967.

1. The Council presents herewith the audited accounts of the Association for the year ended 31 December 1970.

2. Results

The results for the year and the appropriation thereof are set out in the Income and Expenditure Accounts on pages 14-16.

3. Principal Activities of the Association

The Association has continued in its work of furthering the development of the science and technology of the oil and colour industries.



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range of dispersible
pigments comprises

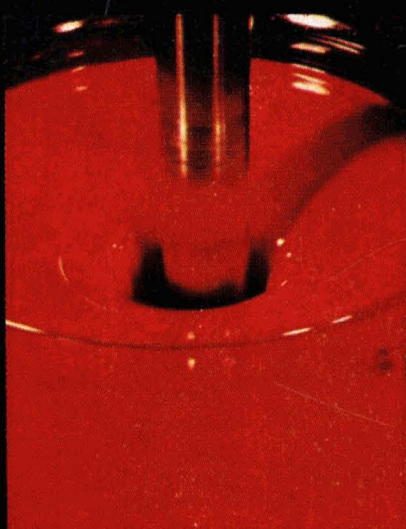
Irgalite Yellow PDS1
arylamide yellow G

Irgalite Yellow PDS2
arylamide yellow 10G

Irgalite Red PDS3
yellow shade toluidine red

Irgalite Red PDS4
blue shade toluidine red

Irgalite Blue PDS5
phthalocyanine blue



CIBA—GEIGY

Pigments Division
CIBA-GEIGY (UK) Limited
Wythenshawe Manchester
M23 9ND

4. *Changes in fixed assets*

The movement in fixed assets during the year is set out in the table on page 15. There were no significant changes during the year.

5. *The Council*

The following were members of Council at 31 December 1970.

A. S. Fraser	
A. W. Blenkinsop	
D. S. Newton, AMCT, CGIA, FInstCorrT	
F. Cooper, BSc	elected 21 May 1970
S. R. Finn, BSc, FRIC	
A. R. H. Tawn, FRIC, FInstPet, FIMF	
F. Sowerbutts, BScTech	
A. H. McEwan	
W. J. McWaters	
S. H. Bell, PhD, DIC, ARCS, FRIC	elected 21 May 1970
I. S. Moll	
C. H. Morris	elected 21 May 1970
L. H. Silver	elected 21 May 1970
I. C. R. Bews, BSc, ARIC	
R. N. Wheeler, BA, ARIC	
H. C. Worsdall	
A. G. Holt, BSc, BPharm	elected 21 May 1970
D. M. James, BSc, FRIC	elected 21 May 1970
J. E. Mitchell, BSc, FRIC	elected 21 May 1970
J. R. Taylor, BSc, FRIC	
P. L. Gollop, ARIC	elected 30 April 1970
N. F. Lythgoe, FRIC	
F. D. Robinson, BSc	elected 8 April 1970
S. McWade	
F. D. H. Sharp	elected 19 March 1970
J. E. Pooley, BSc, ARIC	
D. E. Eddowes, BSc	elected 16 April 1970
F. M. Smith, BSc, PhD, ARIC	
S. Duckworth, ARIC	elected 3 July 1970
H. J. Griffiths, ACT	elected 24 April 1970
R. F. Hill, BSc, ARIC, ACT, API	
D. H. Tate	
A. A. Duell, ARIC	
R. G. Gardiner	elected 10 April 1970
E. M. Burns	elected 10 April 1970
B. Jacob	
K. R. W. Chitty	
L. J. Watkinson, MSc, PhD, ARIC	
Mrs K. Driver	
T. W. Slinn	
O. E. Rutledge	elected 19 March 1970
L. F. Saunders	elected 29 April 1970
F. Schollick, BSc, FRIC	elected 21 May 1970
A. Lowe, MSc, PhD	
G. Willison, FRIC	
D. M. D. Stewart, BSc, ARACI,	
(co-opted as President of the Oil and Colour Chemists' Association Australia)	

In addition the following were members of Council at 1 January 1970 and served during the year; the date shown after each names denotes when service on Council terminated:

D. Atherton, BSc, PhD	(21 May 1970)
L. J. Brooke	(21 May 1970)
K. M. Engelbert	(21 May 1970)
H. Meyer, MSc	(21 May 1970)
H. A. Hampton, BSc, PhD	(21 May 1970)
T. A. Banfield, BSc, PhD, DIC, ARCS, FRIC	(21 May 1970)
A. E. Claxton, BSc, ARCS	(21 May 1970)
E. A. Brown	(8 April 1970)
W. F. McDonnell, FRIC, AMBIM	(17 April 1970)
D. J. Morris	(24 April 1970)
J. Miller	(10 April 1970)
W. A. Grainger	(19 March 1970)
J. Tooke-Kirby	(16 April 1970)
D. Rowley	(10 April 1970)
P. A. Draper	(29 April 1970)
G. J. Juster	(19 March 1970)

6. *Auditors*

The auditors, Cooper Brothers & Co., will continue in office in accordance with Section 159(2) of the Companies Act, 1948.

By Order of the Council

ROBERT HAMBLIN
Director and Secretary.

1 January 1971

INCOME & EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31 DECEMBER 1970

1969			1970	
£	£		£	£
		Membership and general income		
	14,698	Subscriptions	14,236	
	142	Entrance fees	118	
	1,046	Sundry publications	570	
	2,701	Investment income (gross) ..	3,314	
	229	Surplus on sale of investments	281	
	1,194	Refund of SET for prior years	—	
	—	Profit on sale of furniture ..	259	
	<u>20,010</u>		<u>18,778</u>	
		Journal receipts		
	13,026	Advertising	13,235	
	10,295	Sales	10,298	
	1,961	Capitation fees OCCA Australia	2,298	
	1,253	Reprints	1,413	
	<u>26,535</u>		<u>27,244</u>	
	40,506	Exhibition receipts	54,854	
87,051				100,876
EXPENDITURE				
		Membership and general expenses		
	7,844	Administration expenses		
		(Note 4)	8,470	
	8,855	Journal	9,398	
	4,052	Postage, printing and stationery	3,453	
	1,028	Publications	961	
	1,447	Section expenditure (Note 5) ..	1,256	
	239	Past Presidents' Dinner	—	
	686	United Kingdom taxation	—	
	100	Provision for Paint Technology		
		Manuals	100	
	247	Eastbourne Conference	—	
	179	Recruitment Circular	—	
	—	Dinner Dance and Foundation		
	—	Lecture	394	
	—	Section and Past Chairmen's		
		Badges	207	
	1,894	General expenses (including		
		Accountancy Charge)	2,108	
	<u>26,571</u>		<u>26,347</u>	
		Journal expenses		
	7,844	Administration expenses		
		(Note 4)	8,470	
	10,821	Printing and publication	11,485	
	928	Reprints	983	
	1,755	Postage and stationery	1,510	
	180	Provision for bad debts	—	
	473	General expenses	490	
	<u>22,001</u>		<u>22,938</u>	
		Exhibition expenses		
	23,190	Direct expenses	32,495	
	7,844	Administration expenses		
		(Note 4)	8,469	
	473	General expenses	490	
	<u>31,507</u>		<u>41,454</u>	
80,079				90,739
<u>£6,972</u>		Surplus for the year		<u>£10,137</u>

NOTES ON THE ACCOUNTS

1. *Fixed Assets*

Cost	£	£
At 31 December 1969	7,303	
Additions	2,236	
	<u>9,539</u>	
Less Disposals	1,066	
		8,473
<i>Depreciation</i>		
At 31 December 1969	4,962	
Charged to Income and Expenditure Account	913	
	<u>5,875</u>	
Less Disposals	754	
		5,121
Net book value at 31 December 1970		<u>£3,352</u>

2. *Foreign Currencies*

Owing to the postal dispute, it has not been possible to obtain final figures from the Sections overseas, but the half year returns have been used as a basis for estimated figures. (See Report of Auditor at the foot of the Balance Sheet.)

(a) Foreign currencies and liabilities have been converted at the following rates:

New Zealand \$2.1425

South Africa Rands 1.714

(b) Overseas section expenditure has been converted to sterling at the above rates.

(c) The basis of conversion of New Zealand and South African membership subscriptions is the sterling rate of £5 5s 0d per full member and £1 1s 0d per student member. Entrance fees have been converted at 10s per member.

3. The Ethel Behrens Fund and the Jordan Award Fund have not been incorporated in the Association's Income and Expenditure Account and Balance Sheet but have been shown as separate accounts.

4. *Administration Expenses*

Administration expenses have been equally apportioned between the three main headings of expenditure in the Income and Expenditure Account on the basis of staff time involved. These expenses are:

1969		1970
£		£
17,347	Salaries	19,019
692	Temporary staff	577
657	Welfare	732
3,918	Rent, rates, lighting, telephone	3,805
263	Audit fee	263
100	Provision for dilapidations	100
555	Provision for depreciation	913
<u>£23,532</u>		<u>£25,409</u>

The charge to each heading is therefore } (1969 £7,844)
 £8,470 Membership
 £8,470 Journal
 £8,469 Exhibition

5. *Section Expenditure*

The section expenditure is as follows:

1969		1970
£		£
92	Bristol	15
47	Hull	46
214	Irish	2
515	London	401
	(Southern Branch £59)	
(459)	Manchester	347
220	Midlands	178
	(Trent Valley Branch £79)	
117	Newcastle	124
247	Scottish	(332)
	(Eastern Branch £55)	
97	Thames Valley	132
66	West Riding	33
82	Auckland	90
114	Wellington	78
95	South Africa	142
<u>£1,447</u>		<u>£1,256</u>

Ethel Behrens Fund**INCOME & EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31 DECEMBER 1970**

1969		1969	
£	Expenditure	£	Income
28	Tax on Investment Interest	56	Interest on Investments (gross)
—	FATIPEC Congress—Travelling expenses	103	Deficit for year
107	Surplus for year	—	
<u>135</u>		<u>159</u>	<u>159</u>

BALANCE SHEET as at 31 December 1970

1969		1969	
£	Liabilities	£	Assets
2,549	Accumulated Fund	2,525	British Government Securities at cost ..
		107	Balance at Bankers
<u>2,549</u>		<u>2,525</u>	<u>2,525</u>

Jordan Award Fund**INCOME & EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31 DECEMBER 1970**

1969		1969	
£	Expenditure	£	Income
100	Awards	—	Interest on Investments (gross)
5	Printing	10	Deficit
—	Surplus for year	56	
<u>105</u>		<u>66</u>	<u>66</u>

BALANCE SHEET as at 31 December 1970

1969		1969	
£	Liabilities	£	Assets
1,089	Accumulated Fund	1,145	British Government Securities at cost ..
		89	Balance at Bankers
<u>1,089</u>		<u>1,145</u>	<u>1,145</u>

Proceedings of the Annual General Meeting

The Ninth Annual General Meeting of the Incorporated Association was held on 7 May 1971 at 2.15 p.m., at the Palace Hotel, Torquay, Devon, with the President (Mr A. S. Fraser) in the Chair.

The notice convening the meeting was read.

Apologies

Apologies for absence were received from Mr I. S. Moll, Mr S. A. Ray, and Mr L. H. Silver.

Minutes

The President asked the meeting to take as read the Minutes of the Eighth Annual General Meeting held on 21 May 1970, as printed and circulated in *JOCCA*, pp. 730-734 inclusive, August 1970. There being no comments the adoption of the Minutes was put to the Meeting and carried unanimously. The President then signed the Minutes.

Report of the Auditors to the Members

The Report of the Auditors to the Members was read.

Annual Report of the Council for 1970

Mr D. S. Newton (Honorary Secretary) moved the adoption of the Annual Report of the Council and the Statement of Accounts for 1970.

In seconding the adoption of the Annual Report of the Council and Statement of Accounts for 1970, Mr F. Cooper (Honorary Treasurer) drew attention to the surplus of over £10,000, which had been achieved during a year that was not generally considered favourable from a financial point of view and which he felt was most satisfactory.

There being no comments or questions on the Annual Report of the Council and Statement of Accounts, these were formally adopted by the meeting.

Presentation of Jordan Award

The President indicated that he now had the pleasant duty of presenting a certificate, and a cheque to the value of £100, to the winner of the 1970 Jordan Award, referred to in the Annual Report of the Council for 1970.

For the benefit of those present he explained that the Jordan Award had been instituted in 1967 by Mrs Marjorie Jordan, in memory of her late husband, Dr L. A. Jordan, who was President of the Association 1947-49 and became an Honorary Member in 1955. Mrs Jordan, who had since died, wished the Award of £100 to be made for the best contribution to the science or technology of surface coating by a member, under the age of 35, of any nationality working in either the academic or industrial field.

On this occasion the Jordan Award Committee had decided to make the Award to Mr J. R. Groom for his paper entitled "Milling—a printing ink variable" which



Mr J. Groom (left) receiving the Jordan Award from the President,
Mr A. S. Fraser

appeared in the March 1971 issue of the *Journal*. Mr Groom was a member attached to the West Riding Section and presented the paper to that Section in December 1970.

The President then presented the certificate and cheque to Mr Groom with acclamation.

Election of President

Mr Fraser stated that, as indicated on the Agenda, Mr A. W. Blenkinsop had been nominated by Council as President of the Association and he now asked the Annual General Meeting to accept the nomination.

This was carried unanimously with acclamation.

Mr Blenkinsop thanked the meeting for the honour bestowed upon him and stated that he would do his best to uphold the dignity and good work carried out by former Presidents of the Association. He then asked Mr Fraser to take the Chair for the remainder of the meeting and to preside at the Dinner later in the day.

Election of Vice-Presidents of the Association

The President read the nominations of the Council, as printed on the Agenda and the addendum thereto, and asked the meeting to accept them *en bloc*. This was agreed. The following were then elected as Vice-Presidents:

(a) Vice-Presidents who have not been President

- (i) Mr I. S. Moll
- (ii) Mr C. H. Morris
- (iii) Mr F. Schollick
- (iv) Mr N. H. Seymour
- (v) Mr L. H. Silver
- (vi) Mr T. Whitfield

(b) Vice-President who has been President

Dr S. H. Bell

Election of Honorary Officers of the Association

It was unanimously agreed to elect the Honorary Officers as follows:

Honorary Secretary	Mr D. S. Newton
Honorary Treasurer	Mr F. Cooper
Honorary Editor	Mr S. R. Finn
Honorary Research and Development Officer	Mr A. R. H. Tawn

Announcement of election of three Elective Members to Council 1971-73

The President read the following report which had been received from the Auditors:

We have scrutinised the voting papers for the three elected members of the Council received from the members in the United Kingdom and General Overseas Sections, and certify that the votes cast, including those notified by letter from the South African Section, show that the following obtained the largest number of votes:

A. T. S. Rudram V. T. Crowl D. J. Morris

Five voting papers were rejected as not being in order.

London, 28 April 1971

COOPER BROTHERS & Co.,

Chartered Accountants

The President then declared the three members listed elected to Council.

Chairmen of Sections for the coming session

The names of the Section Chairmen for the coming year were given as follows:

Auckland	Mr O. E. Rutledge
Bristol	Mr P. L. Gollop
Hull	Mr N. F. Lythgoe
Irish	Mr F. D. H. Sharp
London	Mr D. E. Eddowes
Manchester	Dr F. M. Smith
Midlands	Mr H. J. Griffiths
Newcastle	Mr A. A. Duell
Scottish	Mr R. G. Gardiner
South African	Mr L. F. Saunders
Thames Valley	Mr B. Jacob
Wellington	Mr T. W. Slinn
West Riding	Mrs K. Driver

The President drew attention to the fact that Mrs Driver was the first lady to be elected as Chairman of a Section and he took the opportunity of wishing her a successful term of office.

Reappointment of Auditors and fixing the remuneration thereof

It was proposed by Mr H. J. Griffiths that Cooper Brothers & Company (Chartered Accountants) be reappointed Auditors of the Association and that their fee be £350'00. This was seconded by Dr H. R. Hamburg and carried unanimously.

Vote of thanks to retiring President

In proposing the vote of thanks to the retiring President, Mr F. Sowerbutts stated that the duties of Presidents of the Association became more and more onerous and time-consuming with each successive year, and the fact that it had become almost

traditional to ask the Immediate Past President to propose the vote of thanks to his successor would seem to imply that the last incumbent was the most likely to know just how much work was involved. The day to day affairs of the Association were very capably handled by the Association's Director & Secretary who, in addition to his normal duties, acted as guide, philosopher and friend to one President following another, but it still fell on the President to preside at an increasing number of meetings, including those of the Council and his Advisory Committee and so on. Equally, or perhaps more important, were the public and social occasions such as this Conference, the Annual Luncheon prior to the Technical Exhibition, the Past Presidents' Dinner, Section Dinner Dances and, in addition, the functions of kindred societies both at home and abroad where the President was expected to uphold the traditions and prestige of the Association. Speaking from experience, Mr Sowerbutts pointed out that these responsibilities fell heavily even on a man retired from business, but in the case of one still in harness it required a tremendous amount of enthusiasm and grit coupled with the support and co-operation of his company, to which the Association owed a debt of gratitude.

Mr Fraser had carried out these traditions with dignity and good humour and in this he had been ably assisted by Mrs Fraser to whom a vote of thanks would be moved by Mr Blenkinsop at the Dinner that evening.

Mr Sowerbutts then asked the members to show in the usual way their appreciation and thanks to Mr Fraser for the services he had rendered during the last two years.

The vote of thanks was carried unanimously with acclamation.

Mr Fraser thanked Mr Sowerbutts for his kind remarks.

Vote of thanks to retiring Council Members

The President called upon Mr J. Smethurst to propose a vote of thanks to the members retiring from Council.

Mr Smethurst expressed the view that in this age of highly organised industrial activity with its demands on the time of all concerned, all too frequently the dedicated actions of those prepared to sacrifice their personal time to ensure the success of the Oil and Colour Chemists' Association could go unrewarded. He was, therefore, delighted to have been asked to propose a vote of thanks to the retiring Council members.

The retiring members, whether elected as Vice-Presidents, Section Chairmen or Elective Members, had had to make considerable personal adjustment to ensure their attendance at meetings in London, and for these efforts the meeting was deeply grateful. The successful endeavours of all past members of the Council since the Association was founded was reflected in the strength and size of the Association, and its recognition on an international basis had only been achieved by a lot of effort by members spending time to foster the Association over the years. The members now retiring from the Council had played their part in continuing this successful story. Mr Smethurst was aware from his own experience that members felt honoured to be elected to Council, but this was no reason why their endeavours should not be appreciated and he asked the meeting to express their gratitude in the usual manner to all the retiring Council members.

This was carried with acclamation.

Vote of thanks to Honorary Officers of the Association

Mr A. T. S. Rudram pointed out that much of what Mr Smethurst had said in respect of Council members applied equally to the Honorary Officers, but their terms of office were longer. The Association was fortunate to have Honorary Officers who managed

to find the time to carry out their duties and it was with great pleasure, having been an Honorary Officer for a time, that he had accepted the invitation to propose this vote of thanks.

This Conference was one example of what the Honorary Research and Development Officer and the Honorary Editor were doing, as was the *Journal* but, of course, the duties undertaken by the Honorary Secretary and the Honorary Treasurer were important to the President and the Director and Secretary in organising the activities of the Association. Mr Rudram then asked the meeting to show its gratitude to the Honorary Officers.

This was carried with acclamation.

Other competent business

The President asked the meeting if there was any competent business which any member wished to raise.

Dr Bell reported that just before he left Teddington he had received a letter from Dr H. W. Talen (Vice-President of the Association 1965-67) expressing his regret at not being able to attend the Torquay Conference, but conveying his greetings to the Association and requesting that his apologies for absence be recorded.

Mr Fraser concluded the meeting by expressing his thanks for the help and support he had received during his term of office as President from all the Honorary Officers, members of Council, the President's Advisory Committee and all Section Chairmen. When he and Mrs Fraser had visited the various Sections throughout the country they had been greatly impressed by the courtesy and friendliness shown to them by Section Chairmen and their ladies.

Mr Fraser also thanked the Director & Secretary (Mr R. H. Hamblin) and members of the staff at Wax Chandlers' Hall, in particular those present at the Conference—Miss J. M. Varney (Senior Secretary), Mr R. Wood (Assistant Editor) and Mr P. L. Smith (Administrative Assistant)—for all they had done to assist him during the last two years.

There being no other competent business, the President declared the meeting closed at 2.40 p.m.

Section Proceedings

Bristol

Aerosols

The March meeting of the Bristol Section was held at the Royal Hotel, Bristol, on Friday 26 March under the chairmanship of Mr J. R. Taylor, when Mr T. Jones of Swallowfield-Serta Ltd. presented a paper entitled "Aerosols."

Mr Jones outlined the historical development of aerosols from the crude bug-bombs developed for the US Forces during the second world war to the sophisticated products available today. The tremendous growth of this market was demonstrated, with figures for the UK market which increased from between 2 and 5,000 units in 1950, the second year of UK manufacture, to 264 millions in 1969. The largest single outlet of approximately one-third was for hair lacquers, with paint applications accounting for less than 5 per cent of the total.

Aerosol containers were usually prepared from coated tinfoil, and consequently possessed a soldered seam which could creep under stress and result in leakage. Seamless containers could be produced, and glass containers were also available, usually coated with a plastic, e.g. pvc, for improved safety during handling. Various types of valves were available and the choice usually depended on the characteristics of the material to be sprayed. The range and choice of propellants were discussed in some detail. These were usually hydrocarbons e.g. propane, butane, and were often used in conjunction with halogenated hydrocarbons, which functioned as diluents to reduce the pressure within the container. Propellants and diluents had to be inert and non-toxic to be acceptable. Mr Jones concluded his talk by describing the problems involved in formulating aerosols for satisfactory storage and application properties and how these problems could be overcome in practice.

The discussion was opened by Mr. L. J. Brooke and several questions were dealt with by the speaker reflecting the considerable interest in this topic. Finally, a vote of thanks was moved by Mr T. I. Price and warmly supported by all members and visitors present.

T.I.P.

London

Southern Branch

The function of phosphoric acid in wash primers

The date of the student symposium, reported elsewhere in this issue, had been arranged to coincide with the Southern Branch third technical meeting of the session, which was held in the Chemistry Department lecture theatre, Portsmouth Polytechnic, where a lecture entitled "The function of phosphoric acid in wash primers" by Herr Lampe of Farbwerke Hoechst AG was presented by Dr Lehmann of the same company.

The introduction to the lecture was a brief survey of the formulations used as primers on steel surfaces. These were based on polyvinylbutyral with, more recently, acid hardening phenolic resins. Chromates were used as corrosion inhibiting pigments, and orthophosphoric acid was also included.

A two-pack primer with phosphoric acid in propan-2-ol as one part and polyvinylbutyral and pigments in propan-2-ol with toluene as diluent as the other was the best of the two-pack type. When the two parts were mixed various changes occurred; there was an initial rapid decrease in the amount of free phosphoric acid and there was a slow colour change from yellow to brown or green indicating reduction of chromate.

Protection of the steel by this primer system was due to the formation of $Zn_3(PO_4)_2 \cdot 4H_2O$, γFe_2O_3 and amorphous $CrPO_4$ on the surface.

The pot life of a two-pack primer was only about eight hours, and it would thus be an advantage to have a one-pack primer with a reasonable shelf-life. The use of an acid-hardening phenolic resin with polyvinylbutyral gave a much better film. The amount of phosphoric acid to be added was very critical since there must be sufficient to react with iron, but as the concentration of phosphoric acid increased, the shelf-life decreased. Also, any unreacted acid in the film would leach out and make the film permeable. The problem of finding the correct quantity of acid was solved by arranging a column of water on the film and measuring the change in conductivity as free phosphoric acid was leached out; measurement of the change in pH was found to be insufficiently reproducible. The conclusions from this test agreed with the results obtained from salt spray tests, the optimum amount of phosphoric acid being about 5-10 per cent of the polyvinylbutyral content.

During the lecture, references were made to the thickness of a two-pack primer coating, not greater than $10\mu m$, and to the fact that a one-pack primer dried in about five minutes and therefore coated the peaks in the metal surface, so that it did not have to fill the troughs in the surface. These comments brought forth many questions, but difficulties were encountered with Continental versus British practice in grit, sand, shot or other blasting of the surface and, of course, the problem of a different native tongue.

T.R.G.C.

Thames Valley

Where paint and ink meet

It is customary for Thames Valley to have one lecture dealing with the printing ink industry. This session there have now been two, including Mr Sutherland's earlier paper on the wallpaper industry. Mr R. G. Kinsman of Winstones Limited gave the second lecture under the above title on Thursday 15 February at the Beech Tree, Beaconsfield, before an audience of 35 Members and visitors.

Mr Kinsman's talk was a carefully considered contribution to the paint technologist's understanding of the ink industry's problems. He managed to bridge the gap between the two technologies most effectively. First, he described the basic printing processes; this was followed with an excellent rundown on the technical similarities and differences between the two industries.

Letterpress or relief printing required very thin films of ink which were at the most 8μ wet. A multi-roll technique enabled this to be achieved, the film weight being reduced by half at each roll. It was a high speed process in which ink drying relied on binder absorption into the substrate and on speedy solvent evaporation. Rates of shear at the moment of "squash" were far greater than in paint application. A common problem was ink spread or halation.

In the lithographic process halation was not a problem, as the water on the plate surface arrested ink flow. Offset printing inks were used, which could only rely on rapid oxidation and polymerisation for drying, there being no possibility of adsorption on to the base. In this process film thicknesses were often of the order of 1 to 3μ and thus the opacity of coloured materials became critical. In contrast to the paint industry, it was quite common to use two coats of a white ink with a titanium dioxide content of 60 per cent.

In gravure printing, the coating principle was entirely different in that the ink was held below the level of the cylinder surface. The process gave very fine detail by direct transfer (for paper and board). On rougher surfaces offset gravure was the more

usual. This was a high speed process (800ft/min) and inks dried by evaporation in a maximum time of four seconds.

The silk screen or stencil process was the only one in which the inks bore a close similarity to the classical paint compositions, the ink being held within an absorbent mesh. The process was much used on plastics, road signs and tinplate and was relatively slow.

Mr Kinsman then moved to an explanation of the similarities and differences between the two industries. First of all the differences of scale were most striking. In printing, multi-colour effects were achieved with very few basic colour materials, using a dot process and additive and subtractive effects, whereas paint colour was just the opposite, requiring a separate mixing for each shade. He tabled many properties in which overlapping occurred in both industries by his reference to the pigments, solvents, film formers, additives, manufacturing methods, film formation and properties. He dealt with each of these in turn and very clearly pointed to the common ground. For example, ink manufacturers used similar equipment, but their aim was to obtain much smaller particles, to overcome excessive abrasion during the printing process. In film formation, very marked differences occurred in evaporation rate, substrate penetration, rate of hardening and polymerisation.

Mr Kinsman concluded by expressing the hope that it might be possible to bring the two industries closer together by arranging joint educational programmes. Much of his lecture showed the good sense in this proposal.

He illustrated his talk throughout with many practical examples of the graphic art which were very interesting in their own right.

The meeting concluded with Mr B. Jacob's vote of thanks which was warmly supported by all present.

R.E.G.

Additives for paint

Mr W. K. H. Lakin, of Hardman & Holden Ltd., gave a talk entitled "Additives for paint" to 32 Members of the Thames Valley Section and 10 visitors, at the Beech Tree, Beaconsfield, on Thursday 18 March.

He began by discussing drier additives in long oil alkyd brushing paints, laying particular stress on the advantages to be gained by synthetic acids over naphthenates and octoates. He presented tabular data to support this, and stressed the need for a minimum acid/metal ratio. Notable among its benefits were improved drying rate, resistance to yellowing in the dark and reduced odour. Furthermore, cost comparisons were favourable.

He then turned to some interesting effects in the use of thickeners in a typical white acrylic latex paint, in this case a cellulose ether solution. Besides its effect on consistency, the thickening agent was chosen for its other significant effects on flow, levelling, colour uniformity, water resistance, and ease of brushing. The rheological effect was dependent on the molecular weight chosen, the concentration, and pH of the paint system. Through a range of pH values, there was usually peak viscosity value.

Mr Lakin described how he approached the rheological influence of thickeners by considering the difference in viscosities at a set rate of shear. If it was desired to increase the thixotropic nature of the paint, then bonds must be introduced which were stable under no-shear conditions and yet which had bond energy levels low enough to be broken by shear force. These were the energy levels which were involved in co-ordination bonding when a stable compound was formed by the complexing of molecules which in themselves were stable. Among the metals which were capable of forming such systems in emulsion paints, zirconium and titanium were outstanding.

Mr Lakin illustrated the effect of zirconium complexing with hydroxyl groups of cellulose ethers by means of a small practical demonstration in a white emulsion paint.

After some useful questions, Mr K. Chitty, a past Chairman of Thames Valley, offered a warm vote of thanks to the speaker.

R.E.G.

Torquay Diary



The lecture room at the Palace Hotel. A high level of attendance was maintained at all sessions

Surface properties and appearance

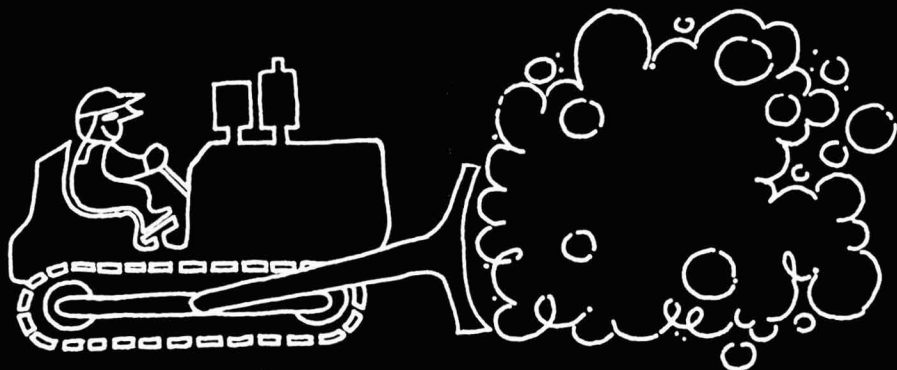
The venue for the Association's 1971 Conference, "Surface properties and appearance", was Torquay, and the earlier-than-usual date of 4-8 May meant that Devonshire was in full blossom to welcome nearly 280 delegates and ladies. The headquarters of the Conference was the Palace Hotel, where most delegates were accommodated, but four other hotels, the Babbacombe Cliff, the Osborne, the Queens and the Victoria were also used, special coach services being arranged between the outlying hotels and the Palace.

There was a slight decrease in numbers compared with attendances at previous conferences, but in view of the postal strike earlier in the year, which severely reduced the amount of publicity that could be distributed, particularly to non-members, the difference was hardly significant. Certainly the slight fall in numbers was not reflected in any reduction in the participation in the discussions at the Technical and Workshop Sessions.

Thursday 4 May

The first function of the Conference was the reception held by the President, together with the Honorary Officers and the Director & Secretary, for overseas Members and visitors, held before dinner. Delegates from 14 overseas countries—Belgium, Canada, Denmark, Finland, France, Germany, Holland, India, Italy, Japan, Norway, Sweden, Switzerland and the USA—registered for the Conference, and the Association was pleased to have present at the Overseas Reception the Presidents of the other three societies of the international liaison, Dr M. Bono (FATIPEC)—who made a special visit to the Conference to be present at this reception—Mr S. L. Davidson (Federation of Societies for Paint Technology), and Mr A. O. Brantsaeter (Federation of Scandinavian Paint and Varnish Technologists).

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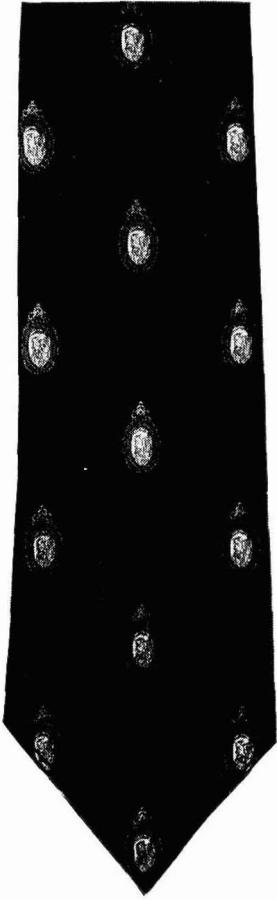
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The tie is blue terylene, with the Association's insignia woven in red and gold silk.

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.



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(state bar or grille)

(All prices include postage and packing)

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Total Remitted

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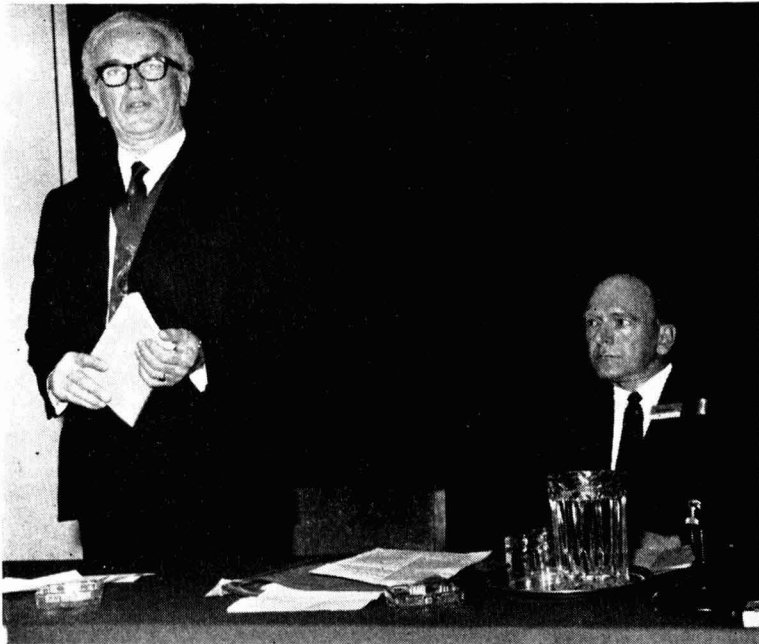
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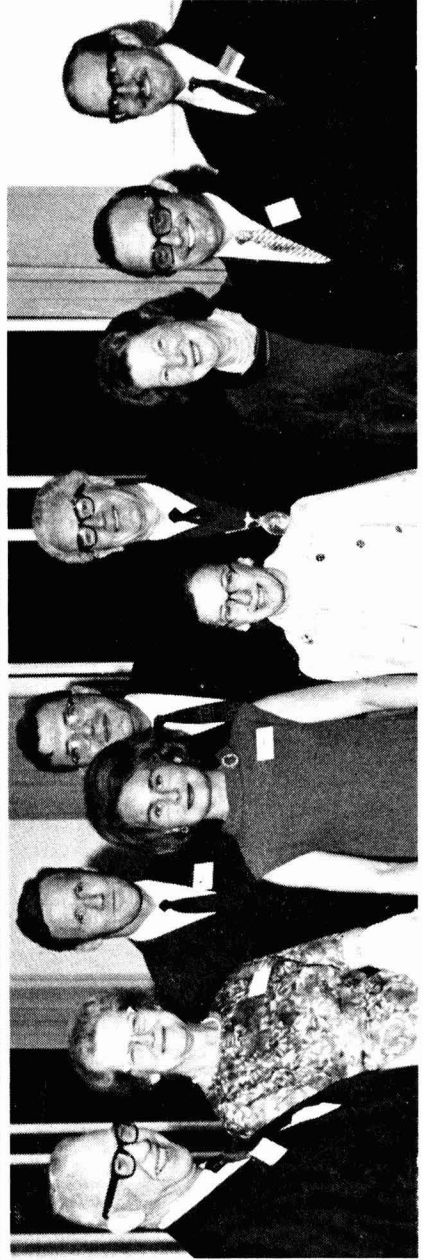
The ties will be supplied from stock; all other items are made to order. Only the tie can be supplied by airmail at an extra cost of 35p.



The Civic Reception. The Mayor of Torbay, Alderman K. G. M. Walke (right) greets the President, Mr A. S. Fraser, with Mrs Walke (left) and Mrs Fraser



The President, Mr A. S. Fraser, opening the Technical Sessions, watched by Mr A. R. H. Tawn, the Honorary Research and Development Officer



Top. The lecturers meeting. Below. The Overseas reception. See facing page for key



Key to facing page

Upper picture, see key above. 1. Dr D. A. Plant (Convenor) 2. Mr A. G. Holt (Convenor) 3. Mr P. Bennet 4. Mr H. Meyer (Chairman) 5. Mr T. R. Bullett 6. Mr G. W. Rothwell 7. Mr P. Whiteley 8. Dr W. Funke (Chairman) 9. Mr K. A. Safe (Convenor) 10. Dr J. Dunderdale 11. Mr D. F. Tunstall 12. Dr W. Carr 13. Mr D. G. Dowling 14. Dr G. de W. Anderson (Chairman) 15. Dr W. E. Craker 16. Mr J. H. Colling 17. Mr H. Foster 18. Mr K. McLaren 19. Mr A. R. H. Tawn (Hon. Research and Development Officer) 20. The President (Mr A. S. Fraser) 21. Mr S. R. Finn (Hon. Editor) 22. Dr K. H. Riechert 23. Dr R. Bult (Chairman)

Lower picture (left to right) Mr R. W. Matlack (Executive Secretary, FSPT), Mrs Matlack, Mr A. O. Brantsaeter (President, SLF) Mrs Brantsaeter, Mr S. I. Davidson (President, FSPT), Mrs Davidson, The President (Mr A. S. Fraser), Mrs Fraser, Dr M. Bono (President, FATIPEC) Mr R. H. Hamblin (Director & Secretary)

After dinner, the Honorary Research and Development Officer, Mr A. R. H. Tawn, gathered together the lecturers and chairmen, and the convenors of the Workshop Sessions, to discuss the way in which the technical part of the Conference would be conducted.

Meetings were also held to organise the golf, tennis and table tennis tournaments, and thanks are due to Mr K. Chitty (golf), Mr C. Williams (tennis) and Mr R. M. W. W. Wilson (table tennis), whose hard work and unsinkable optimism made the events successful and enjoyable.

Wednesday 5 May

At 9.30 a.m., the President, Mr A. S. Fraser, set in motion the Conference proper by opening the first Technical Session. After a brief introduction and welcome to delegates, Mr Fraser handed over to the Honorary Research and Development Officer, who was to chair the first session, commencing with the Keynote Address by Mr T. R. Bullett.

All papers from the Conference, together with the ensuing discussions, will be published in full in the *Journal* later in the year, and no attempt at reportage will be made here. However, it must be noted that the discussions following the papers were both lively and long, reflecting the interest aroused by the speakers. Compliments are due both to the contributors to the discussions, and to the chairmen, who encouraged, controlled, and, in many cases, closed the discussions in a prudent and tactful manner.

After the first Technical Session, Mr and Mrs Fraser welcomed all delegates at an informal reception before lunch.

In the afternoon, while the ladies were visiting Widdecombe—made famous in the song *Tom Cobbley*—and Buckland Moor on the first coach tour of the Conference,



The Presidents of the four societies of the international liaison left to right: Mr A. O. Brantsaeter (SLF), Mr S. L. Davidson (FSPT), Mr A. S. Fraser (OCCA), Dr M. Bono (FATIPEC)

the members were occupied with the Workshop Sessions and the Management Session.

This was the first time that a Management Session had been held at an OCCA Conference, and a measure of the interest in this new "science" can be gained from the fact that the Chairman, Dr G. de W. Anderson, was forced to call back all three speakers at the close of the time allotted for the discussion to the last paper, so that questions for which there had been no time earlier could be asked. The session thus ran over its schedule by some 30 minutes.

The three Workshop Sessions—"Powder coatings—a threat to stoving enamels" (convenor: Dr D. A. Plant), "Is the gloss emulsion paint a myth?" (convenor: Mr K. A. Safe), and "How will pollution control affect the paint industry?" (convenor: Mr A. G. Holt)—also produced vigorous discussions. The Association's policy of not recording the proceedings, in order to foster a freer interchange of ideas, was proved successful once again, and Council thanks each of the convenors for his help.

After dinner, the Mayor of Torbay, Alderman K. G. M. Walke, and the Mayoress, together with the President and Mrs Fraser, received delegates at a Civic Reception, which was followed by dancing until midnight.

Thursday 6 May

The Technical Session on Thursday morning was chaired by Dr W. Funke, of the Forschungsinstitut für Pigmente und Lacke, in Stuttgart, a Member attached to the General Overseas Section.

The ladies, meanwhile, were being entertained by a coach trip to Torre Abbey and to Oldway House, the home of the Singer family, the sewing machine pioneers. The famous dancer Isadora Duncan was married to one of the Singers, and the film of her life, *Isadora*, starring Vanessa Redgrave, was filmed at Oldway House.

In the afternoon a further Technical Session was held, chaired by Dr R. Bult, the Director of the Verfinstitut TNO in Holland, and a Member attached to the General Overseas Section.

A coach tour was also organised to Steps Bridge, by way of the Lustleigh and Teign Valleys.



At the Dinner Dance, (left to right): Sir Frederick Bennett (MP for Torquay), Lady Bennett, the President, (Mr A. S. Fraser), Mrs Fraser, Alderman K. G. M. Walke (Mayor of Torbay) and Mrs Walke, Mr A. W. Blenkinsop (President-Designate) and Mrs Blenkinsop



Seen at the Dinner and Dance, Mr F. Cooper (Hon. Treasurer) and Mrs Cooper (left) and Mr D. S. Newton (Hon. Secretary) and Mrs Newton

An early dinner was arranged in most hotels, so that delegates could join the party visiting the Princess Theatre, where the D'Oyly Carte Opera Company was performing *Iolanthe*.

Friday 7 May

The final Technical Session of the Conference was chaired by Mr H. Meyer, the Honorary Editor of *Farg och Lack*, the Scandinavian equivalent of this *Journal*, and a former Vice-President of the Association. At the close of the session, the President, Mr A. S. Fraser, made a short speech bringing to a close the technical part of the Conference, and thanking all those who had helped to make it successful, in particular the lecturers, the chairmen, and those Members who had helped in the distribution of the microphones for the discussions (Mr D. S. Newton and Mr D. J. Silsby).



At the Dinner and Dance (left to right) Dr S. H. Bell (President 1965-67) Mrs Blenkinsop, Mr A. W. Blenkinsop (the President), Mrs Sowerbutts, Mr F. Sowerbutts (President 1967-69)



Relaxing after a successful conference, Mr A. R. H. Tawn (Hon. Research and Development Officer) and Mrs Tawn

The Annual General Meeting of the Association was held at 2.15 p.m., and a full report appears elsewhere in this issue.

Following the AGM, delegates had the opportunity of a coach tour to Haldon, Dawlish and Teignmouth.

The evening saw the final event of the Conference, the Association's Dinner and Dance, held in the Palace Hotel. Delegates and their ladies were received by the President and Mrs Fraser, and the Mayor and Mayoress of Torbay, together with Sir Frederic Bennett, MP for Torbay, and Lady Bennett, joined the top table party, who were clapped to their places in what has now become a Conference tradition.

Mr Fraser opened the after-dinner proceedings by proposing the Loyal Toast. He was followed by Mr A. O. Brantsaeter, the President of the Federation of Scandinavian Paint and Varnish Technologists, who proposed the toast to the Association. Mr Brantsaeter stressed the pleasure which both the SLF and OCCA had in maintaining their close liaison. Not only was there an interchange of lecturers for conferences and other meetings, but also many SLF members subscribed to the Association's *Journal*. Whilst on the subject of liaison, it was particularly pleasing to see the Presidents of the four participating societies—FATIPEC, the American FSPT, OCCA and the SLF—together at an OCCA Conference.

Mr Brantsaeter went on to refer to the Association's Technical Exhibitions; these were enjoyed by many members of the Scandinavian Federation, and he knew that many were looking forward to OCCA 23, to be held at Olympia in June.

Finally, on behalf of the SLF, he issued an invitation to all Members of the Association to attend the next SLF Congress, to be held in the autumn of 1973, at the time of the 20th anniversary of the formation of the SLF.

The President replied on behalf of the Association, thanking Mr Brantsaeter for his good wishes. It was with great pleasure that he had learned that Mr and Mrs Brantsaeter would be able to attend the Conference. Although Mr Brantsaeter had attended previous Association functions, he believed that this was the first time that Mrs Brantsaeter had visited Britain, and hoped that they would both take away as many happy memories of Torquay as he had from the SLF Congress in Copenhagen in 1970.

Mr Fraser also gained great satisfaction from the close ties between OCCA and the SLF, and with FATIPEC and the American Federation, and looked forward to seeing members of all three societies at the Exhibition in June.



Mr A. S. Fraser (left) invests Mr A. W. Blenkinsop with the Presidential insignia



Following his investiture as President, Mr A. W. Blenkinsop presents Mrs Fraser with a stereo-record player in recognition of her work as President's Lady

It was his pleasure to welcome also the Association's other guests on this occasion. In welcoming the Mayor and Mayoress of Torbay, Alderman and Mrs K. G. M. Walke, he wished to thank the Borough for the Civic Reception it had provided on the Wednesday of the Conference. Alderman Walke had rendered considerable service to the locality, in several local government positions as well as being the third Mayor of the newly formed County Borough of Torbay, which he represented in the "Come to South Devon" movement. Since the Association had held four conferences in Torquay since 1957, he could assure the Mayor that these words would be borne in mind when planning future conferences.

The Association was very pleased to welcome the President of the Federation of Societies for Paint Technology, Mr S. L. Davidson and Mrs Davidson, who were also making their first trip to the UK. He hoped that this would be the first of many visits to Association functions, and that they would have pleasant memories of the country and the Association. The Association was again happy to see the Executive Secretary of the FSPT, Mr R. W. Matlack, and Mrs Matlack, and Mr Fraser recalled with pleasure the toast to the Association that Mr Matlack had proposed on the occasion of its 50th Anniversary celebrations. The Association was delighted at the number of Members of the FSPT who took the Association's *Journal*; in return many OCCA Members subscribed to the *Journal of Paint Technology*, the FSPT publication.

The President welcomed also the lecturers and chairmen of sessions, and thanked them for their work in the running of the Conference.

Finally, Mr Fraser extended a special welcome to the ladies; this Conference had contained more Technical Sessions than on any previous occasion, and he hoped that they did not feel that they had been neglected. He thanked them for their patience and forbearance, not only for this week, but also for the remainder of the year. He called on all Members of the Association to rise and drink a toast to the ladies and

guests, coupled with the name of the Mayor of the County Borough of Torbay, Alderman K. G. M. Walke.

In his reply, Alderman Walke thanked Mr Fraser for his welcome; his tenure of office as Mayor was nearly at a close, and he was pleased that it had included such a pleasant and friendly Conference.

Following Alderman Walke's speech, the ceremony of the presentation of the Presidential Insignia to Mr A. W. Blenkinsop, who had been elected President at the Association's AGM that afternoon, took place. Mr Fraser, in investing Mr Blenkinsop, used the traditional form of words:

Arthur Willis Blenkinsop, in accordance with the resolution passed at the Annual General Meeting this afternoon, it is now my duty to invest you with the insignia as President of this Association, and I charge you to guard well the interests of our Association and at all times to uphold the dignity of our high office.

Mr Blenkinsop then presented Mr Fraser with his Past President's Medallion, engraved with his years of office, and paid tribute to the fine way in which he had carried out his duties during his term as President. In this he had, of course, been ably supported by Mrs Fraser. Mr Blenkinsop thanked Mrs Fraser for her work as President's Lady, particularly in her visits to the various functions of the Sections of the Association, where she had charmed everyone.

In recognition of the considerable part she had played in helping the President during his term of office, Mr Blenkinsop presented her, on behalf of the Association, with a stereo record-player.

Mrs Fraser thanked Mr Blenkinsop and the Members of the Association for their kindness in making this presentation for what had been a very pleasant and interesting, as well as happy, two years. She had much enjoyed visiting the Sections of the Association and meeting so many Members and their ladies, and would treasure the gift in the years to come as a happy memento of this time.

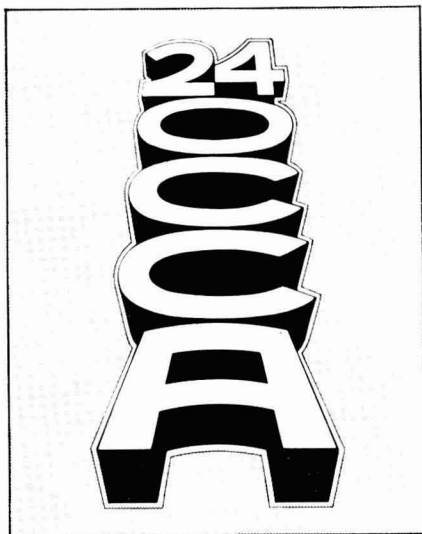
Following the speeches, the top table party left the dining room, and the assembled company made its way to the ballroom for the dance.

During the dance, the new President's Lady, Mrs A. W. Blenkinsop, presented the prizes for the various tournaments. The winners were: *Golf*—The Sam Sharp Conference Trophy and sweep, Dr J. Dunaerdale. *Men's Tennis and Table Tennis*, Mr H. Foster. *Ladies' Tennis and Table Tennis*, Mrs H. Foster. Dancing continued until 1.00 a.m.

Saturday 8 May

Saturday saw the dispersal of delegates. Once again the verdict was that an enjoyable and successful Conference had been held.

R.W.



Technical Exhibition

17-21 April 1972

The Association's next Technical Exhibition of raw materials, machinery and equipment will be held at the Empire Hall, Olympia, London W14, from 17 to 21 April 1972.

The special motif for 24 OCCA (which, as for many years past, has been designed by the Director & Secretary) is reproduced above in black and white, but the colour scheme will be mandarin red and cascade blue, these colours being used for the fascia felts.

The Exhibition will be open on the following dates and times:

Monday 17 April	..	15.00-18.30
Tuesday 18 April	..	09.30-18.30
Wednesday 19 April	..	09.30-18.30
Thursday 20 April	..	09.30-18.30
Friday 21 April	..	09.30-16.00

The last Exhibition, in which over 200 companies, research organisations, etc. participated on more than 120 stands, was held 21-25 June 1971.

The Invitation to Exhibit is now being despatched to companies both in the United Kingdom and overseas, and any company intending to exhibit must

return a completed application form not later than **1 October 1971**.

The Exhibition is believed to be unique in that it is entirely technical, and is aimed at ensuring that technical advances are passed on as quickly as possible to the technical personnel in the paint, printing ink and allied industries. The technical advances may relate to new products, new knowledge of existing products and their uses, or, in suitable cases, existing knowledge which has not been available to the consuming industries.

Copies of the *Official Guide* to the Exhibition will be sent individually to chemists and technologists in the paint and allied industries in Western Europe, to consuming firms in this country and to all members of the Association wherever resident. Copies can also be obtained free of charge from the Association's offices: admission to the Exhibition is free.

Each copy of the *Official Guide* will contain a form of application for tickets for the Exhibition Luncheon, which will be held at the Savoy Hotel, London WC2, on Monday 17 April 1972.

Also being prepared for distribution on the Continent is a leaflet in English, French, German, Italian, Russian and Spanish, containing information on the

Exhibition, and copies can be obtained without charge from the Association's office.

Any companies wishing to apply for

stand space at 24 OCCA who have not previously exhibited should write immediately to the Director & Secretary at the Association's offices.

London Section

33rd Annual General Meeting

The 33rd Annual General Meeting was held on 23 April 1971 at the Polytechnic of the South Bank, London SE1, with Mr D. E. Eddowes in the chair.

Members stood in silence for a few moments in memory of the Section Chairman, Mr Jack Pooley.

The minutes of the 32nd AGM were taken as read and adopted unanimously. In proposing the adoption of the Annual Report, Mr R. H. E. Munn referred to the inclusion of fringe subjects in the lecture programme, which had proved to be popular, and would continue next session. The half-day symposium was also very well attended, and a further one would be held next session, continuing on the theme of "Coatings—their use and abuse." The joint symposium with the Colloid and Surface Chemistry Group of the SCI, held at Brunel University, had also been extremely well supported. The proposal was seconded by Dr A. Hudson, and adopted unanimously.

In proposing the adoption of the Financial Report, Dr H. R. Hamburg spoke of the lower attendance at the Ladies Night, which had resulted in a slight loss; however, it had still been possible to reduce the grant from Council by £50 for the year. The report was

seconded by Mr J. J. Pemberton, and adopted unanimously.

The Officers and Committee Members for the coming year were elected as follows:

Chairman: Mr D. E. Eddowes. *Honorary Secretary:* Mr R. H. E. Munn. *Honorary Treasurer:* Dr H. R. Hamburg. *Honorary Publications Officer:* Dr V. T. Crowl. *Honorary Programmes Officer:* Mr D. A. Bayliss. *Honorary Auditor:* Mr A. H. Soane. *Committee Members:* Mr J. K. B. Burke, Mr K. A. Chippington, Mr K. J. Hedgecock, Mr H. A. Hipwood; (newly elected) Mr A. K. Unsworth, Mr R. M. W. Wilson, and Mr H. C. Worsdall.

Mr J. T. Tooke-Kirby referred to Southern Branch's activities during the session; four successful meetings had been held, together with a very well attended student meeting, and their Annual General Meeting had been held at Winchester followed by a reception by the Mayor of Winchester and a dinner.

The meeting was followed by a buffet meal, at which members were joined by the ladies, after which Dr S. H. Bell, a past-President of the Association, gave a fascinating talk, illustrated by numerous slides, on "Art, colour and heraldry."

V.T.C.

New Zealand Sections

A regular quarterly feature on the activities of the New Zealand Sections of the Association is now published in the monthly publication *Chemistry and Industry in New Zealand*, and it was interesting to see, in the latest OCCA feature, that Miss P. J. McQuarrie has recently achieved the distinction of becoming the first lady Member of the New Zealand Sections.

It seems particularly appropriate that this event occurred in a year in which the first lady chairman of a Section, Mrs K. Driver of West Riding, was elected, and in which there are two ladies on Council, Mrs Driver, and Miss P. Magee, of the Irish Section. Obviously the ladies of New Zealand are not far behind those of Great Britain in seeking equality.

Thames Valley Section

Works visits

The lecture by Mr R. G. Kinsman, reported elsewhere in this *Journal*, was backed up by works visits on two occasions to Sun Printers at Watford. These visits were arranged through the courtesy of Mr Kinsman and Dr Fuchs of Sun Printers.

The tour began in the ink manufacturing department, where points of interest were the high speed Kady mills used for dispersing colours, and the large

varnish tanks, where up to 22 different types of medium were stored. The cleanliness and efficiency of the plant impressed all the visitors.

On moving to the main printing works, a rapid and yet concise explanation followed of the steps in processing the cylinder. They were plated, photographed and, after additional corrective work, were ready for the presses. Finally the group saw the impressive photogravure presses in action.

R.E.G.

Obituaries

Mr F. A. Walker

It is with regret that we announce that Mr F. A. Walker, an Ordinary Member attached to the Manchester Section, died on 16 May following a long illness. Mr Walker had a long and distinguished career in the pigment industry, and was active in the Manchester Section, being a committee member 1940-43, 1947-50, and 1954-56, Hon. Publications Officer 1950-54, and Hon. Auditor 1962-71. The

condolences of the Association are passed to his widow and family.

Mr D. T. Young

Members will be saddened to learn of the death of Mr D. T. Young, an Ordinary Member attached to the West Riding Section, and that Section's Social Secretary, in a motor accident on the morning of 1 May. Mr Young leaves a wife and two children, to whom our sincere sympathy is offered.

FSPT Annual Meeting and Paint Show

Further details of the programme for the Annual Meeting of the Federation of Societies for Paint Technology, to be held at Cobo Hall, Detroit, 27-30 October 1971, have been released.

Three seminars are to be held, on waste disposal, dispersion and communications. The seminars will be open to all registrants, and there will be no report or publication based on their proceedings.

As well as the annual Paint Research Institute Symposium, there will be three symposia on colour: "New optical effects", "Design" and "New techniques".

A photographic salon and competition is to be sponsored by the FSPT during the Annual Meeting, open to all members

of the paint industry and their families.

PA to offer associate membership to overseas firms

The Paintmakers Association has decided to offer associate membership to paint manufacturers located outside the UK, but with a UK trading entity. If an associate member in this category subsequently establishes UK production facilities, it will cease to be eligible, but may apply for full membership.

Interfinish 1972

The 8th Interfinish congress is to be held 5-9 September 1972 in Basle, in the lecture halls of the Swiss Industries Fair. The congress will be concurrent with the

international surface treatment exhibition, Surface.

The technical programme will be centred on progress in surface treatment with special regard to the corrosion resistance and other properties of protective and functional coatings, and authors are invited to submit papers in this field to the Organising Committee, Interfinish, Postfach CH-400 Basle 21, Switzerland.

IAEA set up analytical quality control service

The International Atomic Energy Agency has set up a new service, analytical quality central services (AQCS). To overcome difficulties in determinations of trace amounts of elements in materials, AQCS will distribute reference materials, standards and samples for intercomparison, thus supplying a means of checking the precision of trace analyses in individual laboratories.

Register of Members

The following elections to membership have been approved by Council. The Section to which new members are attached are given in *Italics*.

Ordinary Members

WILDASH, PETER JOHN, BSc, British Titan Products Co. Ltd., Billingham. (*London*)

DEE, GERALD PHILIP, 17 Osney Walk, Carshalton, Surrey. (*London*)

BULBECK, ROBIN ANDREW, Flat 5, 67 Upton Park, Slough, Buckinghamshire. (*Thames Valley*)

BONO, MARCO, D.CHEM., Strada, S. Brigida 44, Moncalieri, Italy. (*Overseas*)

McKITTRICK, JOHN NEVILLE, c/o Bermuda Paint Co. Brighton Hill, Devonshire, Bermuda. (*Overseas*)

Associate Members

STEAR, JOHN MICHAEL, 2 High Park Cres., Heaton, Bradford BD9 6HT. (*West Riding*)

POUGNET, M. O. E. PHILIPPE, 21 Club Road, Vacoas, Mauritius. (*Overseas*)

Student Members

WATERER, ANDREW JOHN, 72 Holland Pines, Bracknell, Berks RG12 40Z. (*Thames Valley*)

SEARLE, MARION, 333a High Street, Slough, Bucks. (*Thames Valley*)

WILTON, JOHN HOWARD, Flat 2, Rear of 25 Alma Road, Windsor, Berks. (*Thames Valley*)

PING, JOHN DAVID, 24 King Edward Street, Slough, Bucks. (*Thames Valley*)

Oil and Colour Chemists' Association

President: A. W. BLENKINSOP

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 Encre 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.

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.

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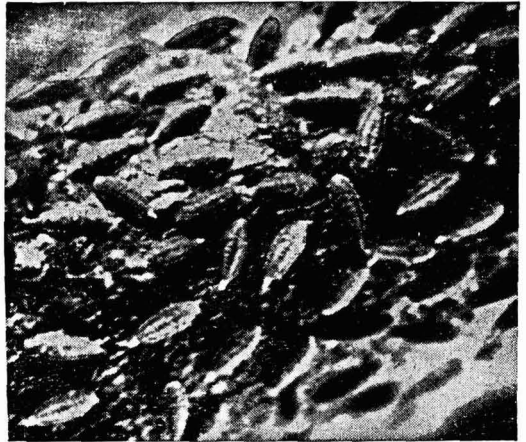
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