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OCCA 23 Technical Review

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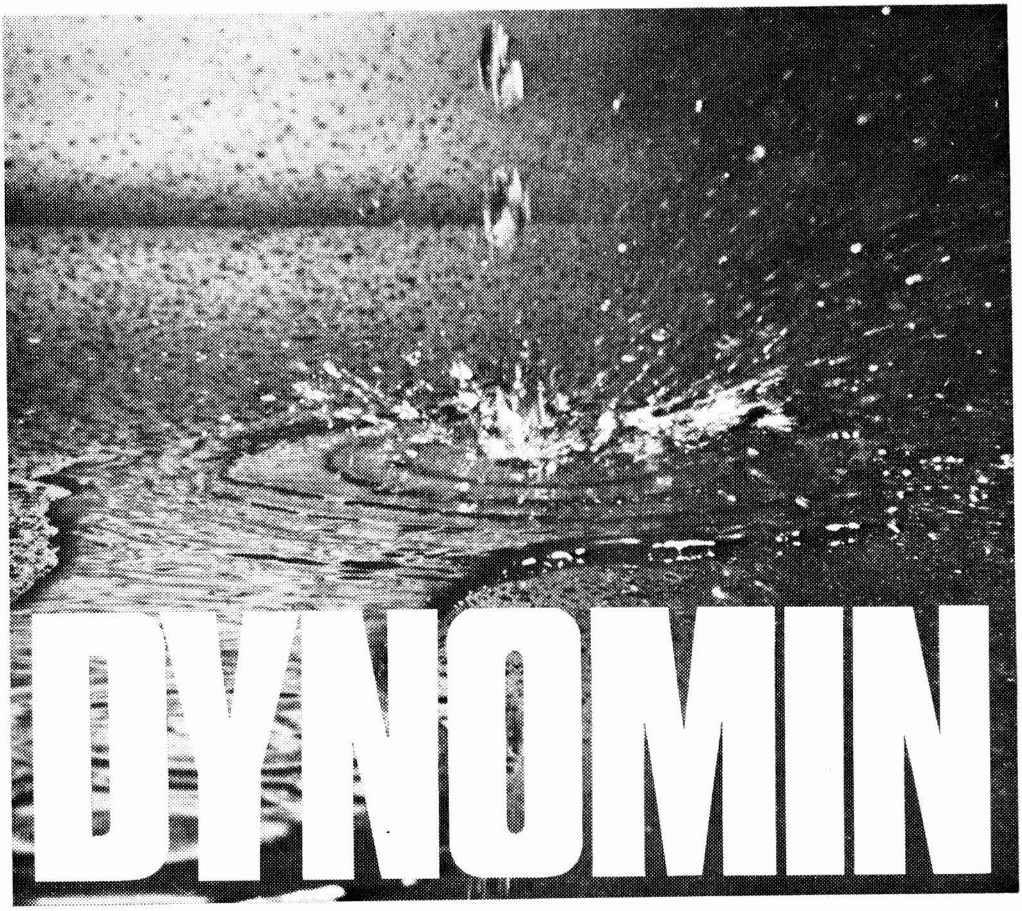

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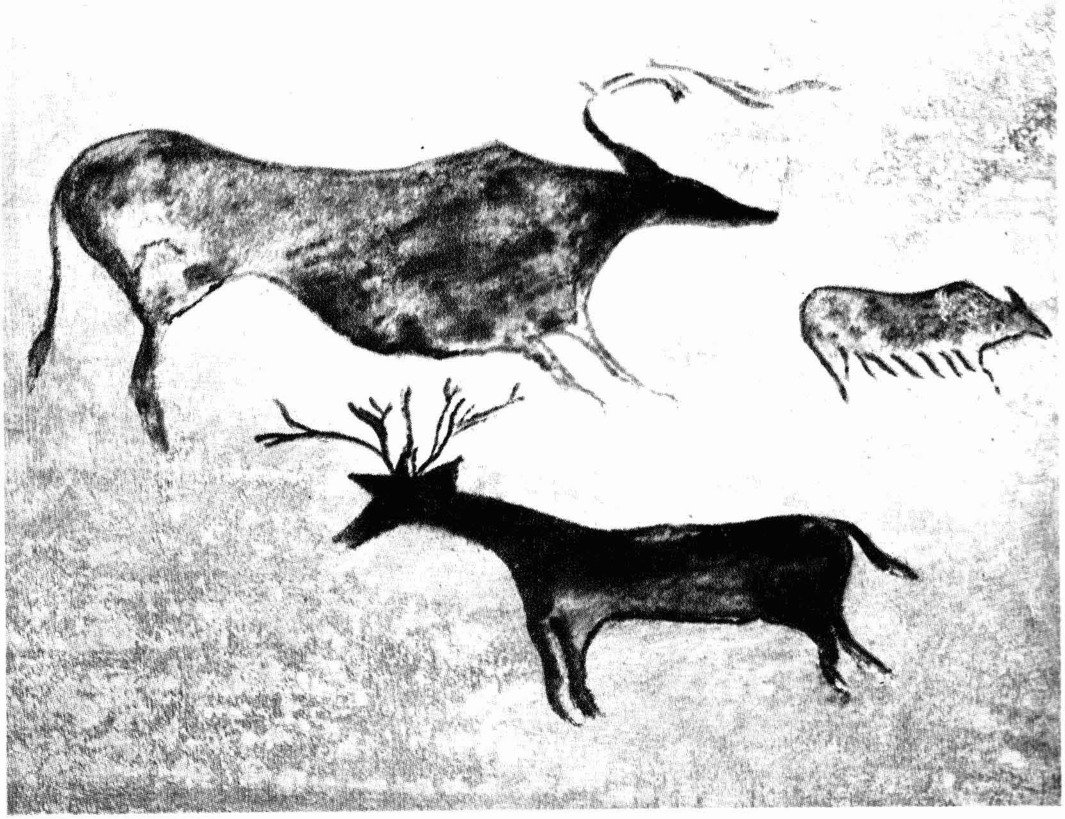

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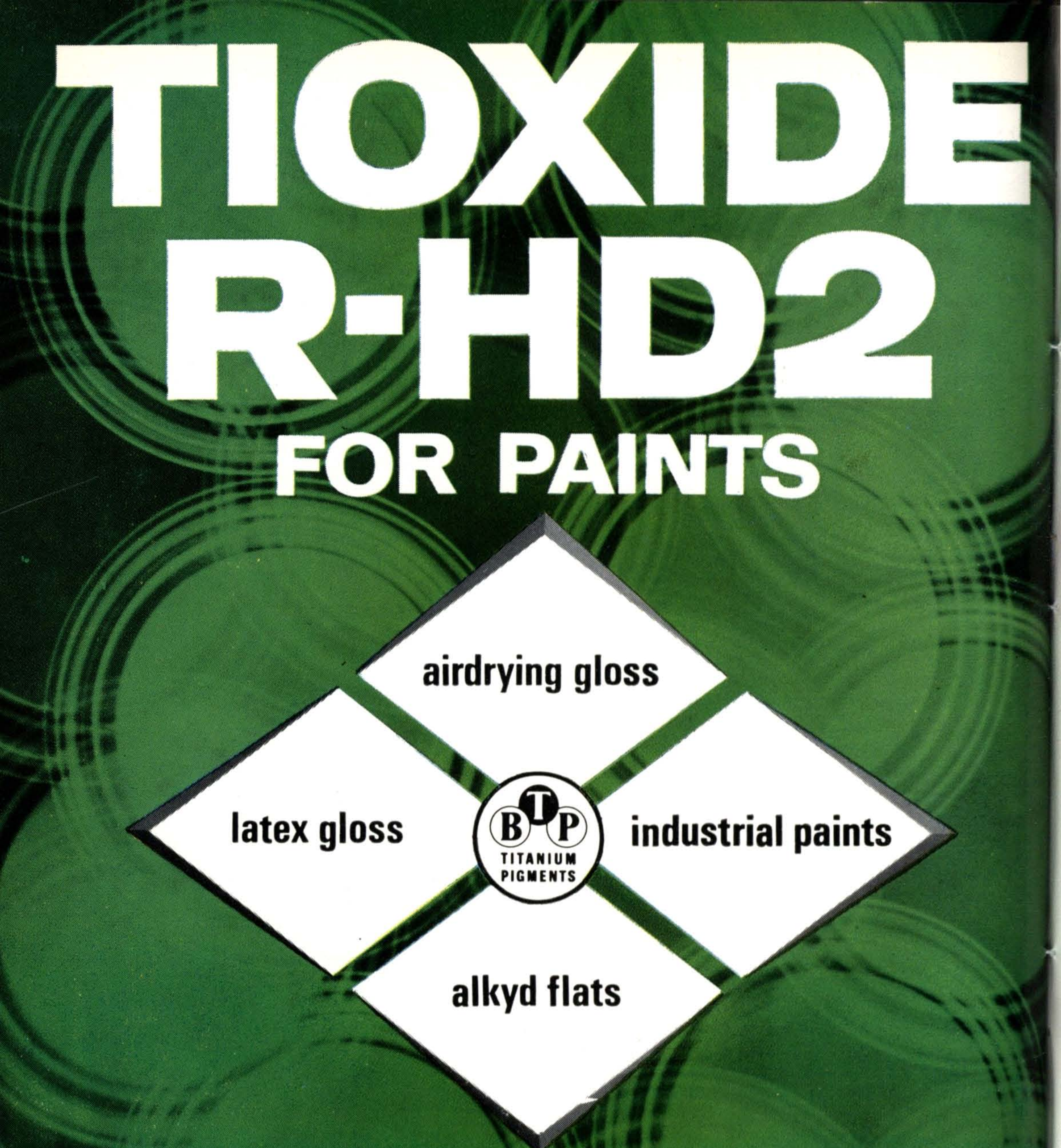
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Transactions and Communications

Chemical characterisation of pigment surfaces*

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Summary

The knowledge of the nature of the surface of titanium dioxide surfaces gained by means of infra-red and electrophoretic methods is discussed.

The effect of coating the surfaces with silica and/or alumina on the number and form of the surface hydroxyl groups is considered.

Dehydration experiments give information on the nature and stability of the hydroxyl group. The adsorption of ammonia and pyridine on the surface gives further information on the nature of these groups.

Keywords

Prime pigments and dyes
titanium dioxide

Process and methods primarily associated with analysis, measurement, and testing
electrophoresis
infra-red spectroscopy

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

La nature des caractéristiques chimiques des surfaces pigmentaires

Résumé

On discute la connaissance de la nature de la surface du dioxyde de titane, au moyens des méthodes infra-rouge ou d'électrophorèse.

On considère l'effet qu'exerce un enrobement de la surface par la silice, l'alumine ou tous les deux composés, sur le nombre et la forme des groupements hydroxyles superficiels.

Des expériences de déshydration donnent de l'information sur la nature et la stabilité du groupement hydroxle. L'adsorption de pyridine par les surfaces rend d'autre information sur la nature de ces groupements.

Chemische Charakterisierung von Pigmentoberflächen

Zusammenfassung

Die im Wege der Infrarot-und Elektrophoresemethoden über die Natur der Titandioxideberflächen gewonnenen Kenntnisse werden besprochen.

Die Auswirkung der Beschichtung der Oberflächen mit Kieselerde und/oder Tonerde auf die Anzahl und Form der an der Oberfläche befindlichen Hydroxylgruppen wird in Betracht gezogen.

Dehydrierungsexperimente verschaffen Auskunft über die Natur und Stabilität der Hydroxylgruppen. Die Adsorption von Pyridin an der Oberfläche gibt weitere Auskunft über die Natur dieser Gruppen.

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*Presented to a joint meeting of the London Section and the Colloid and Surface Chemistry Group of the Society of Chemical Industry, 25 November 1970.

Химическая характеризация пигментных поверхностей

Резюме

Обсуждается оценка природы поверхностей двуокиси титана, формулированная при помощи инфракрасных и электрофорезных методов.

Рассматривается эффект покрытия поверхностей двуокисью кремния и/или окисью алюминия, на число и форму поверхностных гидроксильных групп.

Опыты по дегидратации дают информацию о природе и устойчивости гидроксильных групп. Адсорбция пиридина на поверхности дает добавочные сведения о природе этих групп.

Introduction

It is well known that titanium dioxide pigments are coated with both inorganic and organic compounds for the purpose of optimising their efficiency in dispersion and durability. The coatings play a large part in the present day success of titania pigments. To obtain a complete understanding of the surface of the coated material and of the interactions that take place during the coating process, it is necessary to characterise the surface, both of the underlying base material and of the final product. This characterisation must be in terms both of its physical form (porosity, density of coating etc.) and its chemical nature (type and number of surface sites, impurity effects, etc.). For the former, it is common to use such techniques as gas adsorption and electron microscopy, and for the latter, infra-red spectroscopy, adsorption from gas and solution phases, and electrophoresis are proving increasingly useful.

To define explicitly the chemical character of the surface of a pure oxide is in itself a complex task and much progress has been made during the past decade, but for mixed oxides the understanding of the surface is less developed. It is the latter, of course, which is of great relevance to the pigment industry.

This paper briefly summarises current thinking in the application of infra-red spectroscopy and electrophoresis to the study of the chemical character of oxide surfaces. Such surfaces, under normal conditions, contain hydroxyl groups and adsorbed species such as water and carbon dioxide, as well as anions which arise from the preparation, e.g. chloride and sulphate. Infra-red spectroscopy may be used to study the behaviour of these various surface species, their relation to the surface chemistry of the oxide, and how this is affected by external conditions such as heat treatment, humidity, etc. This technique also permits a study of the interaction between the oxide and the adsorbates, such as those of relevance to the treatment of pigments with organic compounds and to the interaction of pigments with paint media, etc. Certain adsorbates may also be used to give information on the surface as, for example, in the use of amines to study the acidity of surface groups.

The literature contains a large amount of infra-red data on silica, alumina and silica/alumina catalysts, the interest in these materials being obviously related to their catalytic potential[1, 2]. The amount of fundamental work on titanium dioxide surfaces is increasing, and during the next decade it is anticipated that our knowledge of these surfaces will have reached the state current for silica. Future development along the lines of coated oxides is a vital part of pigment technology.

The technique of electrophoresis has, for many years, been used successfully in the characterisation of colloidal dispersions, and more recently for defining the acid/base character of powder surfaces. Oxides have received considerable attention, because the nature of the surface hydroxyl groups determines how the electrophoretic mobility varies with pH. Each oxide has its own zero point of mobility, i.e. the pH at which there is no overall charge on the particle and hence no movement in an electric field[3]. For pH values higher than the zero point, the particles are negatively charged, and are positively charged for values below it. This reflects the dissociation of the hydroxyl groups by the mechanism

$$M - OH_2^+ \rightleftharpoons M - OH \rightleftharpoons MO^- + H^+$$

$$\xleftarrow[\text{decreasing pH}]{\qquad\qquad} \qquad\qquad \xrightarrow[\text{increasing pH}]{\qquad\qquad}$$

The zero point of mobility (or point of zero zeta potential, pzz) should not be confused with the zero point of charge obtained from titration experiments, although in certain cases the difference between them is trivial[4]. We would expect the pzz for pure silica to be pH 1-2, for pure titania pH 4.5—5.5, and for pure alumina pH 8-9 [3]. Hence, the establishment of a pzz for a pure or coated oxide gives information on the character of the surface hydroxyl groups and could therefore be used to define the nature of the external surface of coated pigments.

Infra-red studies of oxide surfaces

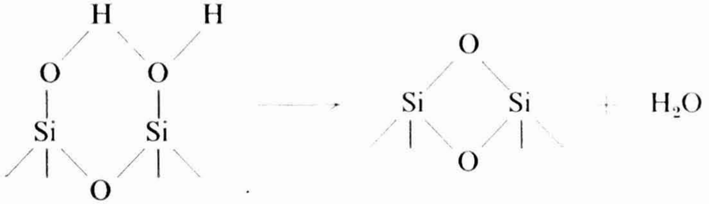
Particle size is an important factor in determining the resolution of absorption bands in the infra-red. The technique commonly used is to compress the powder into a disc (either self-supporting or with KBr) and to support this disc in the infra-red beam using an appropriate glass cell, of which several useful designs have been published[1]. Whether or not bands are observed, and the resolution of fine structure in the bands, depend on the precision of the instrument in use, as well as the degree of scattering of the radiation by the small particles. This scattering is approximately proportional to the third power of the particle size and inversely to the fourth power of the wavelength. Hence, small particles and long wavelengths tend to reduce the scattering effect; thus, care must be taken not to relate the lack of absorption bands to the absence of surface species without first ensuring that the particles are sufficiently small. The assignment of structures to the absorption bands is normally based on a comparison with those published for molecules in the bulk liquid or solid phases, which assumes that the physical state of the species at the solid surface is of a similar kind and that similar restriction occurs in molecular vibration and rotation as exists in these phases. For example, the position of the absorption band due to the vibration of a hydroxyl group on an oxide surface is close to that found for the same group in alcohols and, from a comparison with the spectra of dilute and concentrated alcohol solutions in hydrocarbon media, it is possible to derive significant information on the hydrogen bonding interaction of adjacent hydroxyl groups. Several examples of such assignments are published in Little's book[2] and there are numerous cases of good correlation between observed spectra and anticipated surface structures.

The contributions made by infra-red spectroscopy to the understanding of the chemistry of oxide surfaces will now be considered, first on the individual oxides silica, alumina, and titania, and then on the mixed silica/alumina type oxides, which are more closely related to the surface of pigmentary titanium dioxide.

Silica

This oxide has been the subject of a great deal of research, and coupled with those from thermogravimetric methods the data from infra-red analysis have led to a satisfactory description of the concentration, coordination and stereochemistry of the surface hydroxyl groups.

A review of the infra-red literature on silica gels and powders shows that the hydroxyl stretching region (3000-3800 cm^{-1}) of the spectrum has two distinct features, the relative magnitude of each depending on the pretreatment of the silica. The sharp absorption band at 3740 ± 10 cm^{-1} is assigned to isolated hydroxyl groups on the surface and these predominate when the oxide is heated in vacuo at high temperatures (> 500°C). A broad band centred at about 3500 cm^{-1} is due to hydrogen bonded hydroxyl groups which are progressively removed on heating silicas above ambient temperature in vacuo, and are virtually all gone at about 500°C according to the reaction



The effect is clearly shown in the infra-red spectra and illustrated in Fig. 1. Hydroxyl groups in the bulk of the oxide, i.e. not accessible to adsorbates and therefore taking no direct part in the oxide's surface chemistry, also give absorption bands in this region, but by simple interaction with deuterium or deuterium oxide vapour their location is readily established, since the exchange converts OH to OD and the bands appear at higher wavelengths (lower wavenumber) in the region 2700-2750 cm^{-1}.

Various studies of the concentration of surface hydroxyls on silica (using thermogravimetric, spectroscopic and chemical techniques) suggest that, after evacuation at 150-200°C to remove physically adsorbed molecular water, there are 4.5—5 hydroxyl groups per 100 Å^2 of surface, corresponding to one hydroxyl per silicon atom in the surface[2]. There has been speculation as to whether this number represents the concentration on a "fully" hydroxylated surface, since the definition of the latter requires an assumption of what crystal planes predominate in the surface, e.g. the rhombohedral face of β-tridymite has 4.6 silicon atoms per 100 Å^2 whereas the 100 face of β-cristobalite would be fully hydroxylated, with each silicon atom carrying two hydroxyl groups, giving a theoretical maximum of 7.9 hydroxyls per 100 Å^2. Recent studies[5] of the stoichiometry of the reactions of $SiMe_2Cl_2$, $TiCl_4$ and BCl_3 with silica hydroxyl groups demonstrate that the fully hydroxylated surface contains two

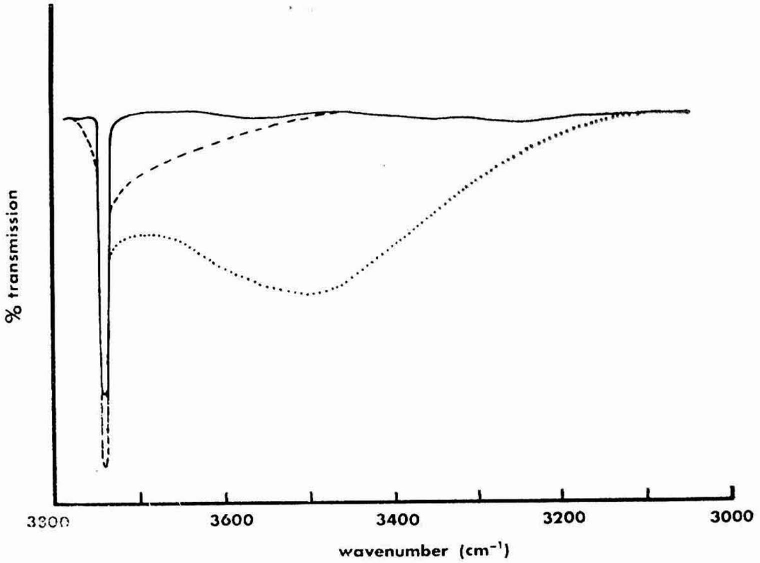


Fig. 1. Infra-red spectra of silica after evacuating at room temperature (dotted line), 500°C (broken line), and 940°C (continuous line)

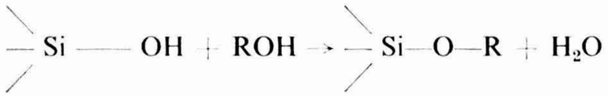
distinct types of hydroxyl sites. These are single surface hydroxyls at 1.4 ± 0.1 per 100 Å^2, and interacting (hydrogen bonded) hydroxyls in pairs at 1.6 ± 0.1 per 100 Å^2, giving a total hydroxyl population of 4.6 per 100 Å^2. The interacting groups are lost by evacuation at ∼ 500°C, while the concentration of single hydroxyls remains approximately constant up to 600 ± 50°C. At higher temperatures, further loss of hydroxyls occurs but the details are not well defined. There is no definitive evidence on the extent of dehydroxylation of silica evacuated at room temperature, but it seems likely that some occurs. To explain the numbers quoted above, it is necessary to consider that the surface corresponds to an array of different crystal planes, some with hydroxyl groups far enough apart to preclude hydrogen bonding and others with hydroxyls sufficiently close to interact.

Infra-red spectroscopy also gives information on rehydration and rehydroxylation processes, although analysis of the spectra is not without problems. Again, coupled with thermogravimetric data, a picture emerges suggesting that, for a surface evacuated at high ($>$800°C) temperatures, interaction with saturated water vapour at room temperature does not lead to significant rehydroxylation of the surface, although at lower activation temperatures the hydroxylation process is to some extent reversible[6]. However, the exact behaviour depends on the nature and previous treatment of the particular silica under consideration.

The existence of acidic sites on oxide surfaces is well known in catalysis. Two types are considered; Lewis acid sites, capable of accepting electrons from adsorbate molecules, and Brönsted acid sites, which donate protons to the adsorbate molecule. Characterisation of these sites on oxides is possible by studying the infra-red spectra of adsorbed amines and, by varying the strength of the amine, the relative acidity of the sites may be defined, e.g. pyridine

(pK_B ~9) only reacts with the stronger acid sites since it is a weak Lewis base and therefore should be more selective in its reaction with surface sites than ammonia ($pK_B = 5$). Infra-red spectroscopy readily distinguishes between pyridine coordinated with surface Lewis acid sites and the pyridinium ion formed on interaction with a Brönsted acid site. Experiments with silicas indicate that pyridine hydrogen bonds only with the surface, since the spectra are similar to that for pyridine in chloroform solution, no interaction with Lewis or Brönsted acid sites being observed[7]. Similar results are obtained with ammonia, suggesting the absence of Lewis and Brönsted acid sites on pure silica[8].

Physical adsorption of molecules on silica surfaces is frequently observed, and the displacement of the hydroxyl bands to lower frequencies as a result of this interaction gives useful information on the nature and energy of short range molecular interactions as well as on the character of the surface. Kiselev[9] has shown that the shift of the absorption band of silica surface single (isolated) hydroxyl groups is closely related to the extent and heat of adsorption for a variety of adsorbate molecules, and by judicious choice of adsorbate the adsorption process may be defined in terms of the nature of the substrate surface. Infra-red spectroscopy is also an important tool in the investigation of chemical reactions between surface groups and adsorbate molecules, e.g. the silica hydroxyl reacts in the same manner as an alcoholic hydroxyl group as, for example, in the formation of surface alkoxides with alcohols:



$$\equiv Si—OH + ROH \rightarrow \equiv Si—O—R + H_2O$$

A study of the surface reactions is important in the production of surfaces with specific properties as, for example, in the treatment of pigment surfaces with organic molecules, and infra-red spectroscopy is particularly valuable since it is the only technique yet developed that provides a ready means of identifying surface species. Such information on reactions of silica surfaces with hydrocarbons, Grignard reagents, silicones, alcohols etc. is reviewed in the books by Little[2] and Hair[1].

Alumina

The hydroxyl stretching region of the infra-red spectrum is more complex in the case of alumina. Peri[10] reports five distinct bands between 3810 and 3680 cm^{-1} after outgassing at high temperature, and using "Monte Carlo" statistical methods[11] has predicted the existence of five different isolated hydroxyl positions in which the group is adjacent to differing numbers of surface oxide ions from 0 to 4. These isolated hydroxyls and their respective absorption bands arise after all hydrogen-bonded hydroxyls have been removed by heat treatment. The Monte Carlo technique has also been used for silica[12], but its value depends, of course, on how close to reality is the model used for the surface.

The spectra obtained for pyridine adsorbed on alumina[7] show bands similar to those observed for the pyridine/boron trihydride complex in solution, and therefore the adsorbed pyridine is assumed to be coordinated to Lewis acid sites (surface cations). No evidence for the pyridinium ion has been reported, suggesting absence of Brönsted activity on pure alumina surfaces.

The value of infra-red spectroscopy in the study of surface reactions is well illustrated by the interaction of alumina with ethanol. Greenler's experiments[13] show that ethanol reacts with hydroxyls to form surface ethoxide species, some of which, when heated at 170°C in the presence of ethanol, are converted to acetate ions; the appropriate spectra were compared with those of aluminium ethoxide and acetate.

Titanium dioxide

To date, less infra-red work has been reported on titania than on silica and alumina, although quite a number of papers are currently in the press. From available information, it would appear that there are two distinct types of isolated hydroxyl group on the rutile (and probably anatase) surface. Spectra showing the hydroxyl stretching bands and the changes brought about by evacuating pure rutile at elevated temperatures[14], are shown in Fig. 2. The sharp bands at 3700 and 3670 cm^{-1} are assigned to two isolated hydroxyl groups in different stereochemical environments, and the broad band centred at about 3400 cm^{-1} results from absorption by hydrogen-bonded surface species (hydroxyls and water). The spectra clearly show the disappearance of the hydroxyls as the temperature is raised, until at 400°C the surface appears to contain very few of these groups. After such treatment, the hydroxyls are readily replaced by exposing the surface to saturated water vapour, as shown by the reversible character of the spectra. It should be noted that impurities of the type remaining after rutile preparations (chloride and sulphate) have a profound effect on the spectra[14], suggesting exchange of these species with the hydroxyls, and as such they play a significant role in the dehydroxylation process. The extent to which such effects take part in similar treatment of the other oxides has not yet been established.

The interaction of ammonia and pyridine with pure rutile is of particular interest. Ammonia, the stronger of the two bases, gives spectra[15] which indicate coordination to two different cation sites, i.e. four bands are observed in the 3100-3500 cm^{-1} region (Fig. 3) rather than the two expected for adsorbed ammonia[2]. These two different cation (Lewis acid) sites might be those associated with the two different hydroxyls discussed above. Also, neither suggests the presence of ammonium ion, as would be expected if Brönsted acidity was involved. Adsorption of pyridine[16] gives only one set of four bands in the 1400-1650 cm^{-1} region (Fig. 4) showing that only one of the sites is sufficiently strong to coordinate with this weaker base, and demonstrating the selectivity of pyridine as an adsorbate.

Silica/alumina

Some of the studies on silica/alumina catalysts provide a useful guide in the characterisation of coated pigment surfaces. A variety of methods may be used to prepare the mixed oxide, and therefore the constituents of the silica/alumina system are likely to be present in various states of intermixing, ranging

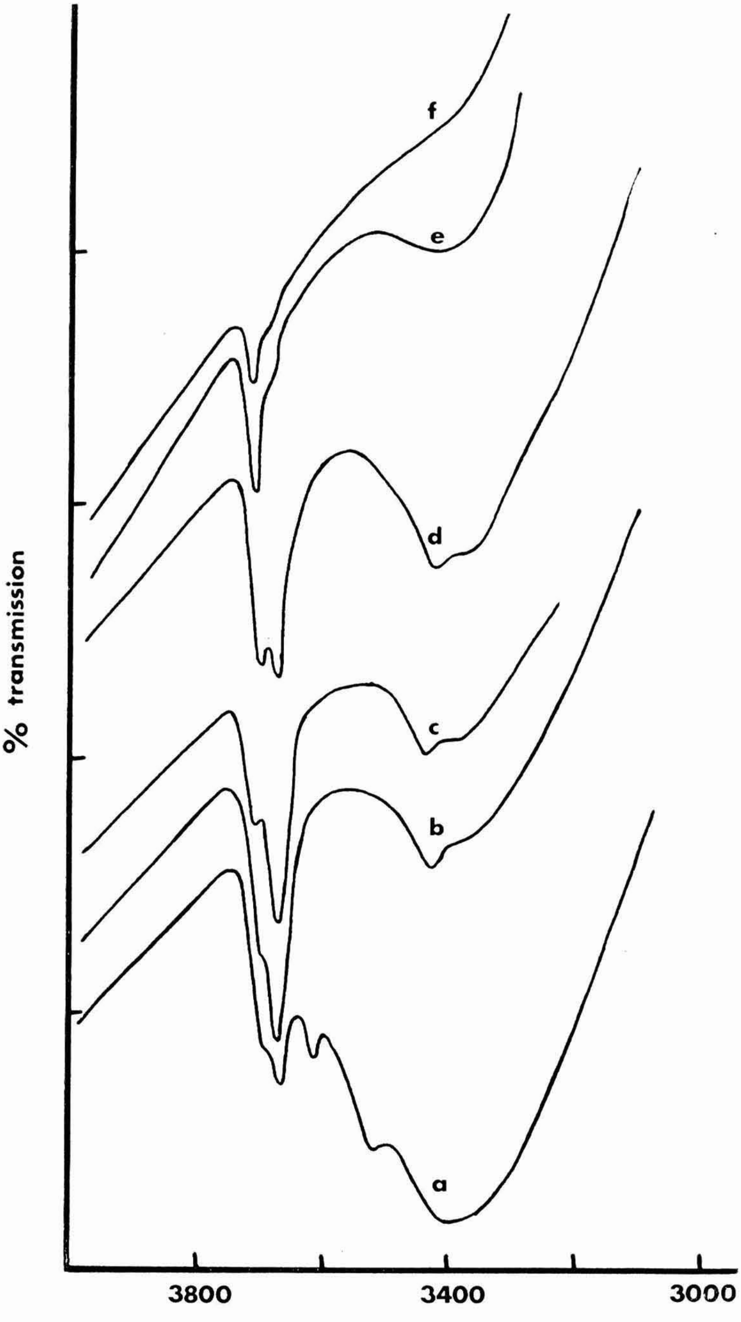


Fig. 2. Infra-red spectra of rutile after evacuating at room temperature (a), at 100°C (b), at 150°C (c), at 200°C (d), at 300°C (e), and at 400°C (f)

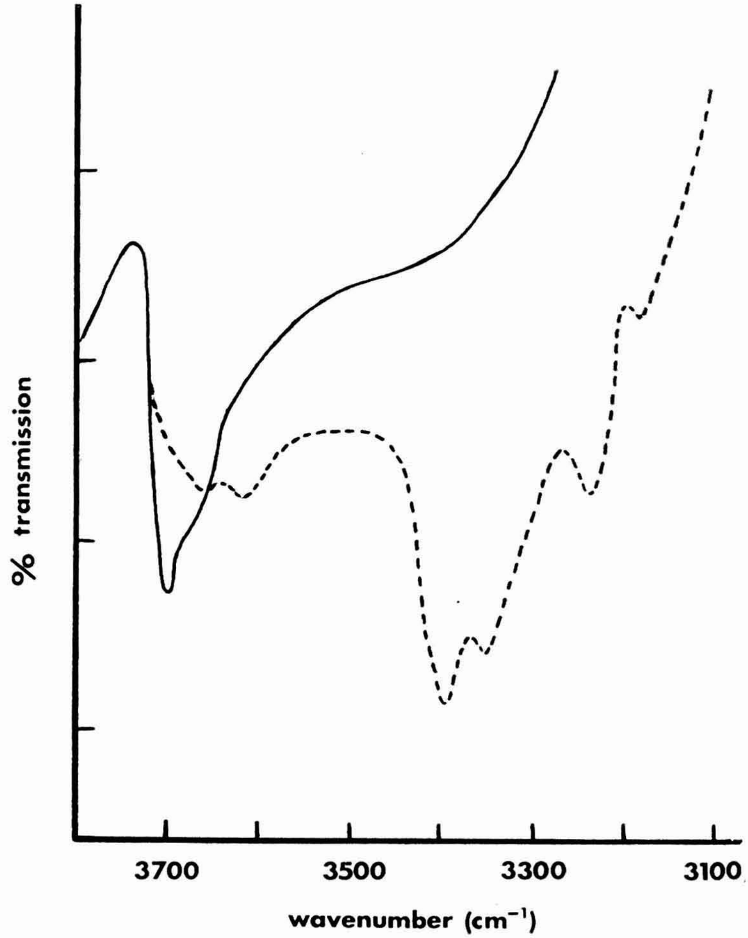


Fig. 3. Infra-red spectra of ammonia adsorbed on rutile. Continuous line, starting surface; broken line, after adsorption

from perfect alternation of silica and alumina to regions containing bulk silica or bulk alumina. Both Lewis and Brönsted acidity have been detected by pyridine adsorption on silica/alumina catalysts[2], and the conversion of Lewis sites on a dehydrated surface to Brönsted sites by adding water vapour is well known. A recent paper by Bourne, Cannings and Pitkethly[17] describes the preparation of two silica/alumina systems, one in which the aluminium atoms are incorporated (by ion-exchange) on to a silica surface, and one in which the aluminium is co-precipitated with the silica so that it is incorporated into the lattice. In both cases the aluminium atoms have only oxygen and silicon atoms as near neighbours and are therefore potential catalytic sites. Using pyridine, it was demonstrated that, for the aluminium sites in the first system, there is both Lewis and Brönsted acidity, the amount of each depending on the pre-treatment and surface water content; the conversion of Lewis acid sites to Brönsted sites is reversible. However, when the aluminium is buried within the silica, only Brönsted sites were detected after dehydration, suggesting that,

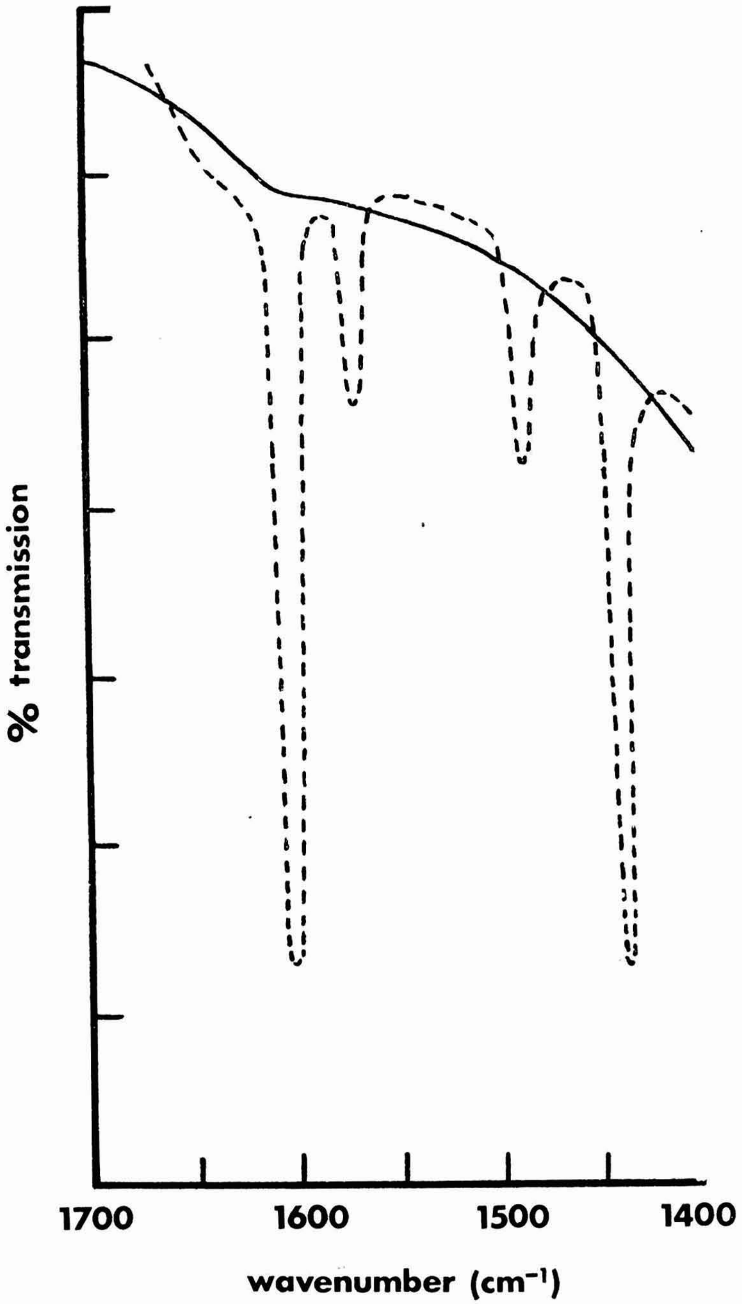


Fig. 4. Infra-red spectra of pyridine adsorbed on rutile. Continuous line, starting surface; broken line, after adsorption

after heat treatment, protons are retained within the lattice in the vicinity of the aluminium. These slowly migrate to the surface when water is present, forming pyridinium ions with adsorbed pyridine. Thus infra-red studies using pyridine provide an effective method for locating the position of aluminium in the silica/alumina lattice, and also for defining potential catalytic activity, both being of relevance to pigment surfaces.

Electrophoresis

Although the charge characteristics of pure oxide surfaces in aqueous media have been quite well defined by electrochemical experiments, the same cannot be said for mixed oxides, and in particular the literature contains very little definitive information on the behaviour of titanium dioxide pigment surfaces involving coatings of mixed oxides laid down on a "pure" oxide. From what has been said above, it is clear that infra-red spectroscopy would be useful, especially if coupled with electrophoretic experiments, in defining the location and behaviour of the coating components. No such infra-red studies have yet been reported, but recent electrophoretic data on titanium dioxide pigments containing varying proportions of silica and alumina in the coatings/demonstrate the potential of such an approach[18].

The details of the pigments are given in Table 1, and the variation in pH at the pzz with proportion of alumina in the coating is illustrated in Fig. 5.

Table 1

Details of surface treatments of TiO_2 pigments

Pigment No.	Al_2O_3 (%)	SiO_2 (%)	Proportion of Al_2O_3 in surface treatment
1	0.55	1.88	0.23
2	0.97	1.86	0.34
3	1.75	1.84	0.49
4	2.16	1.84	0.54
5	2.18	0.98	0.69
6	2.14	0.56	0.80
7	2.20	0.15	0.94

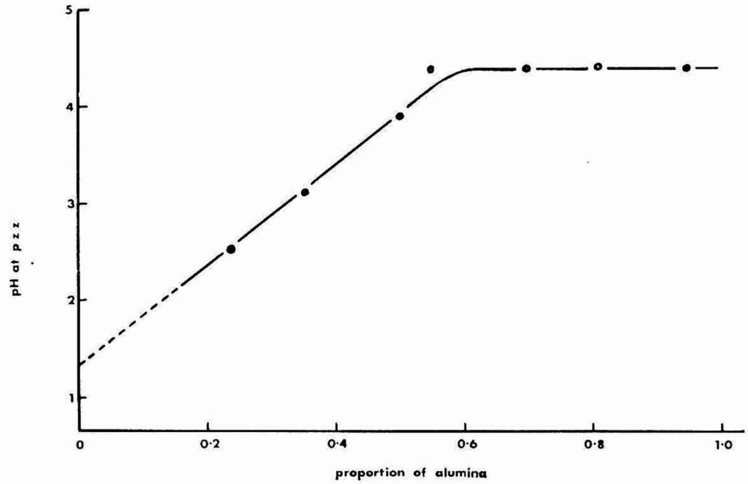


Fig. 5. Variation of pH at the pzz with proportion of alumina in the coating

Clearly the pzz is related directly to the amount of aluminium species in the coating, since the pzz remains constant at pH 4.4 ± 0.1 for pigments 4-7 having approximately identical alumina content, and decreases with the alumina content for pigments 1-3 until it reaches the extrapolated value of about pH 1.5 for zero alumina, corresponding to what might be expected for a pure silica surface. The constancy in pzz with alumina content, and the fact that this pzz is not approaching pH 9 (expected for pure alumina) suggests that the surfaces of pigments 4-7 are similar and contain predominantly aluminium associated with silicon and oxygen as near neighbours; infra-red studies with pyridine should confirm this hypothesis.

Conclusions

Infra-red spectroscopy is now sufficiently well developed to be used for the definitive characterisation of titanium dioxide pigments. Dehydration experiments lead to information on the nature and thermal stability of surface hydroxyl groups, and from analysis of surface species formed by adsorbed pyridine the acid sites (Brönsted and Lewis) present are defined. The location and reactivity of the various components of surface coatings may also be established. Coupled with electrophoretic data, the infra-red technique provides a valuable tool for obtaining useful information on the chemical character of the pigment surface in relation to its dispersion and durability behaviour.

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Discussion at the London Section

DR TH. F. TADROS commented that Professor Parfitt had said that silica surfaces were fully hydroxylated with about 4.5 OH groups per 100 Å^2. It had been mentioned in Iler's book that, based on model calculations, a silica surface should contain 8 OH groups for 100 Å^2. Was there any explanation of why a figure of between 4 and 5 hydroxyl groups was obtained experimentally?

Professor G. D. Parfitt said that this depended upon the assumptions made in the theoretical model, i.e. which planes were available for adsorption. A fully hydroxylated surface meant that every available site was hydroxylated.

Dr Tadros, referring to the point of zero zeta potential in alumina/silica mixtures, said that he had carried out micro-electrophoresis measurements on glass that contained silica and alumina. He had found that the point of zero zeta potential was about pH 2 in KCl solutions, whereas the titration curves in a number of monovalent chlorides would suggest a point of zero charge around pH 6. The difference between the pzz and the pzc was large for glass, whereas this was not so for silica. Could it be expected that the same would occur for pigment surfaces? What electrolyte was used for the electrophoretic measurements?

Professor Parfitt said that the ions adsorbed on the surface were determined directly in titration experiments. On measuring the pH of a pigment suspension a different result would be obtained from electrophoresis because here a point of zero charge was found, not zero zeta potential. Potassium nitrate was used in the electrophoretic experiments.

Mr T. D. Blake made the point that it was very difficult to decide from the structure of the bulk oxide what the structure of the surface might be. For example, one estimate of the maximum hydroxyl concentration on the γ-alumina surface (based on the oxygen concentration of the 111 plane) gave about 20 OH's per 100 Å^2, whereas the experimental value was closer to 10 per 100 Å^2.

Professor Parfitt agreed that the choice of crystal plane would greatly affect the value obtained.

Mr A. J. Groszek wondered whether any work had been done on the adsorption of fatty acids on to alumina and titanium dioxide. Did the fatty acids chemisorb exclusively on to the Lewis sites or perhaps Si OH groups, and had this been demonstrated by IR spectroscopy?

Professor Parfitt said that adsorption of a fatty acid on an OH site would yield an ester. Interactions with particular sites were difficult to detect, and he knew of no IR work that had given definite information on this topic.

Dr R. R. Ford referred to recent IR studies of carbon monoxide adsorbed on metals, where it had been observed that only a small percentage of the adsorbed phase was IR active in the carboxyl region. Was it possible to be sure that all the OH groups on the metal oxide surface interacted with the IR beam?

Professor Parfitt said that the interaction of OH groups with D_2O and various other adsorbates could be followed and thus the number of OH groups available could be measured quantitatively, and related to the infra-red data. Published comparisons did not suggest that some surface OH groups were not infra-red active.

Dr D. Dollimore remarked that the structure of a surface would be different from the structure in the bulk mass of material. Therefore, although a particular layer plane exposed at the surface might be considered, this would have different spacings from the spacings of the same layer plane in the interior. This point was largely ignored in calculating the theoretical number of hydroxyl sites at a surface.

One further point was the danger of merely equating weight loss to loss of water. In many cases he had found other species to be present, and a series of experiments came to mind in which hydrogen was detected from the thermal treatment of kaolin.

Professor Parfitt expressed his agreement with these comments.

Professor K. S. W. Sing referred to differences between silica and alumina, in dehydration and re-hydration. On dehydration, silica was rendered hydrophobic, and it took some time to recover the surface. On the other hand, high temperature

γ-alumina re-hydrated quite rapidly. Concerning alcohol adsorption, chemisorption at room temperatures had been mentioned. With silica, higher temperatures were necessary to obtain ethylation of the surface.

Professor Parfitt agreed. It was clear that titanium dioxide behaved more like alumina than silica.

Dr Dollimore said that he had found that a small amount of polymer (e.g. polyacrylamide) which was quite insufficient to cover a significant proportion of the surface was, however, sufficient to alter the rate and nature of the loss of water from oxides and clays. Could Professor Parfitt suggest how this process could operate, as many industrial oxides were coated with organic materials?

Professor Parfitt suggested that one polymer molecule could cover a very large area of surface, and hence restrict a large number of OH groups, to which it might be attached. The relative effect of a small overall coverage of polymer would obviously depend on the degree of hydroxylation of the oxide.

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The adsorption of gases and the characterisation of the surface properties of pigments*

By K. S. W. Sing

Department of Chemistry, Brunel University, Uxbridge, Middx.

Summary

Gas adsorption techniques are now widely used for the determination of the surface area and pore size distribution of pigments and similar materials. In the analysis of physical adsorption data obtained on different gas-solid systems it is useful to distinguish between specific and non-specific adsorbent/adsorbate interactions. The specific interactions are encountered when polar molecules are adsorbed on ionic or heteropolar solids, whereas non-specific interactions are the result of the universal dispersion forces.

The BET monolayer capacity is of doubtful validity unless the isotherm exhibits a sharp knee (well-defined point B); this condition generally demands an appreciable interaction energy, which may arise through either high dispersion potentials or specific adsorbent/adsorbate interactions. An empirical method of isotherm analysis may be employed to check the BET areas and to assist in the interpretation of the mechanism of adsorption.

Two different mechanisms of pore filling may influence the course of an adsorption isotherm: micropore filling, associated with the overlap of adsorption potentials and occurring at low relative pressure; and capillary condensation in mesopores, taking place over the multilayer range of relative pressure and involving meniscus formation. The application of the Kelvin equation for pore size distribution calculations should be restricted to mesoporous solids. The empirical method can be employed to assess the micropore volume, provided that standard adsorption data are available on an appropriate non-porous solid.

Keywords

Miscellaneous terms
Brunauer Emmett Teller equation

Prime pigments and dyes
carbon black

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

Properties, characteristics and conditions primarily associated with materials in general
surface area

L'adsorption des gaz et la caractérisation des propriétés superficielles de pigments

Résumé

Les techniques de l'adsorption des gaz sont largement utilisées actuellement pour déterminer l'aire superficielle et la répartition de la grandeur des pores de pigments et de matières semblables. Au cours de l'analyse des cotes de l'adsorption physique, dérivées des systèmes gaz/solide, il est convenable de faire une distinction entre les interactions spécifiques de l'adsorbant et de l'adsorbat et celles qui ne sont pas spécifiques. Les interactions spécifiques sont abordées dans le cas où des molécules polaires sont adsorbées sur les solides ioniques ou hétéropolaires, tandis que les interactions non-spécifiques résultent des forces universelles de dispersion.

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*Presented to a joint meeting of the London Section and the Colloid and Surface Chemistry Group of the Society of Chemical Industry on 25 November 1970.

La capacité monocouche BET est d'une validité douteuse sinon l'isotherme démontre "un genou aigu," (un point B bien défini); en général cette condition exige une énergie d'interaction appréciable qui peut arriver soit par des potentiels dispersion élevés, soit par des interactions adsorbant/adsorbat spécifiques. On peut s'en servir d'une méthode empirique pour analyser les isothermes afin de vérifier les aires BET et de faciliter l'interprétation des mécanismes d'adsorption.

Deux différents mécanismes du remplissage de pores peuvent exercer une influence sur le tracé d'une isotherme d'adsorption: remplissage des micropores qui se produit aux pressions relativement basses, et qui est lié au chevauchement des potentiels d'adsorption; condensation capillaire dans les micropores ayant lieu à travers la gamme multicouche de pression relative et accompagné de la formation de ménisque. L'application de l'équation de Kelvin pour calculer la répartition de la grandeur des pores devrait être limitée aux solides mésoporeux. On peut employer la méthode empirique pour apprécier le volume des micropores, pourvu que les données normales d'adsorption d'un solide non-poreux et approprié soient disponibles.

Die Adsorption von Gasen und die Charakterisierung der Oberflächeneigenschaften von Pigmenten

Zusammenfassung

Gasadsorptionstechniken werden heutzutage häufig zur Bestimmung der Oberflächengrösse und Verteilung von Poren verschiedener Grösse bei Pigmenten und ähnlichen Stoffen benutzt. Bei verschiedenen Gas- Festkörper Systemen der Analyse physikalischer Adsorptionsdaten ist es zweckmässig zwischen spezifischen und nicht-spezifischen Reaktionen von Adsorbans mit Adsorbat zu unterscheiden. Die spezifischen Reaktionen trifft man dann an, wenn polare Moleküle auf ionischen oder heteropolaren Festsubstanzen adsorbiert werden; die nicht-spezifischen Reaktionen sind dagegen das Ergebnis der universellen Dispersionskräfte.

Die Aufnahmefähigkeit der BET Monomolekularschicht ist zweifelhaft, es sei denn, dass die Isotherme ein scharfes Knie zeigt (klar definierter Punkt B); dieser Zustand erfordert für die Reaktion im allgemeinen erheblichen Energieaufwand, welcher entweder durch hohe Dispersionspotentiale oder spezifische Adsorbans/Adsorbat Reaktionen entstehen kann.

Eine empirische Methode der Isothermen-Analyse kann angewandt werden, um die BET Oberflächen nachzuprüfen und bei der Interpretierung des Adsorptionsmechanismus zu helfen.

Zwei verschiedene Mechanismen für das Füllen von Poren können den Ablauf einer Adsorptionsisotherme beeinflussen: Mikroporenbildung in Verbindung mit dem Überschneiden von Adsorptionspotentialen und bei niedrigem relativen Druck vorkommend; sowie kapillare Kondensation in Mesoporen im mehrlagigen Bereiche relativen Druckes und Meniskusbildung mit sich bringend. Die Anwendung der Kelvin Gleichung für die Berechnung der Verteilung von Porengrössen sollte auf Festkörper mit Mesoporen beschränkt werden. Die empirische Methode kann benutzt werden, um das Mikroporenvolumen zu schätzen vorausgesetzt, dass Standard-Adsorptionsdaten für eine entsprechende nichtporöse Festsubstanz vorliegen.

Адсорбция газов и характеризация поверхностных свойств пигментов

Резюме

Технология газовой адсорбции в настоящее время широко применяется для определения распределения поверхностной площади и величины пор пигментов и аналогичных материалов. При анализе физических данных адсорбции полученных в различных системах «газ-твердое тело», целесообразно различать между специфическими и не специфическими адсорбент/адсорбатными взаимодействиями. Специфические взаимодействия имеют место когда полярные молекулы адсорбируются на ионных или гетерополярных твердых телах, тогда как не специфические взаимодействия являются результатом универсальных дисперсионных сил.

Однослойная емкость BET обладает сомнительной ценностью, если изотерма не проявляет острого изгиба (хорошо выраженной точки B); это условие обычно требует значительной энергии взаимодействия, которая может возникнуть либо за счет высоких дисперсионных потенциалов или специфических адсорбент/адсорбатных взаимодействий. Эмпирический метод изотермического анализа может быть применен для проверки поверхностей ВЕТ и для пособия в интерпретации механизма адсорбции.

Два различных механизма наполнения пор могут повлиять на ход адсорбционной изотермы: микропористое наполнение, связанное с перекрытием потенциалов адсорбции и имеющее место при низких относительных давлениях и капиллярная конденсация в мезопорах, имеющая место в многослойном диапазоне относительных давлений и вызывающая образование мениска. Применение уравнения Келвина для вычисления распределения величины пор, должно ограничиваться мезопористыми телами. Эмпирический метод может применяться для оценки микропористого объема, если имеются на лицо стандартные адсорбционные данные для соответствующего непористого тела.

Introduction

The use of the physical adsorption of gases for the determination of surface area and pore size distribution is now well established in many different fields of scientific investigation. In view of the vast literature on the subject[1, 2] and the variety of commercial equipment available, it might be supposed that the interpretation of adsorption data no longer presents a serious problem. In principle, the amount of gas adsorbed per unit mass of adsorbent may be expressed as a function of the pressure, temperature and the surface properties of the solid, i.e. its chemistry, area and porosity. In practice, however, an unambiguous interpretation of the adsorption data is not always possible.

It is customary to record adsorption data in the form of the adsorption isotherm, i.e. the adsorption measured at various equilibrium pressures, all other variables being held constant. Many attempts have been made to analyse mathematically the adsorption isotherm in terms of surface coverage and pore filling mechanisms. Most solid surfaces of industrial importance (e.g. catalysts or pigments) are heterogeneous and they are often associated with either polydisperse systems of particles or porous structures (or both). Is is hardly surprising, therefore, that adsorption isotherms on such surfaces are not amenable to theoretical analysis by any relatively simple model.

In spite of these difficulties, the BET (Brunauer-Emmett-Teller) method[3] has provided for some systems a simple and remarkably successful means of isotherm analysis. The method is still the most widely used procedure for surface area determination, and it has been adopted recently as the basis for a BSI method for the determination of the specific surface area of powders[4]. A good deal of the experimental evidence in support of the validity of BET areas[2] has been obtained for nitrogen adsorption on oxides, hydroxides and carbon blacks. Much less information is available on the adsorptive properties of organic solids. However, recent studies[5, 6] have revealed significant differences in specificity between various physical adsorption systems, and it is now possible to make useful comparisons of different types of solid surfaces by studying their interactions with selected adsorbate molecules. It is the aim of this short review to discuss the various aspects of physical adsorption that must be taken into account if the method is to be exploited successfully for the characterisation of the texture and surface chemistry of pigments and similar materials.

Thermodynamics of adsorption and physical interaction energies

From the thermodynamic standpoint, the affinity between the adsorbate and adsorbent at the relative pressure, p/p_0 may be expressed as the difference in chemical potential of the vapour in equilibrium with the adsorbed phase and that of the vapour at the standard saturation pressure, p_0. Thus:

$$\Delta\mu = RT \ln(p/p_0)$$

and also

$$\Delta\mu = \Delta\overline{H} - T\Delta\overline{S}$$

where $-\Delta\overline{H}$ is the isosteric heat of adsorption, q_{st}, and $\Delta\overline{S}$ is the differential entropy of adsorption.

It can be seen from the second equation that the change in chemical potential can be separated in the usual way into the heat and entropy terms: thus, the affinity of adsorption at a particular value of p/p_0 is governed not only by the exothermic release of heat energy, but also by a difference in entropy between the vapour and the adsorbed state. The entropy term itself has thermal and configurational components, the latter varying with surface coverage according to the arrangement of adsorbate molecules on the surface.

Model adsorption systems may be postulated (e.g. localised or mobile monolayers) and the variation of differential heat and entropy with coverage calculated[7]. In practice, however, it is difficult to distinguish clearly between such models because of overlap in the effects of energetic heterogeneity with respect to the adsorbent/adsorbate interactions and the effects of the lateral interactions between adsorbate molecules.

In spite of the uncertainties in the quantitative analysis of adsorption heat data, it is nevertheless useful to separate the various interaction energy contributions. This approach provides a basis for the comparison of different physical adsorption systems and the study of the physical and chemical nature of a solid surface.

Because of their universality, the dispersion energy, φ_D, and short-range repulsion, φ_R, contributions are regarded as non-specific interactions. On the other hand, the polarisation, φ_P, field-dipole, $\varphi_{F\mu}$ and field gradient-quadrupole, φ_{FQ}, terms are examples of specific interaction energies, which are significant only in the case of particular adsorbent-adsorbate systems[5].

The dispersion energy is calculated by the summation of the pairwise interactions between the fluctuating dipoles (and where appropriate quadrupoles) in the adsorbate molecule and those in the assembly of atoms or ions in the solid adsorbent. The value of φ_D depends, therefore, not only on the polarisabilities of the interacting atomic and molecular species, but also on the structure of the solid (bulk and surface) and the orientation of the adsorbate molecule. The value of φ_D will be enhanced if the adsorbate molecule can fit into surface indentations or penetrate into very narrow pores.

Specific interactions are encountered with ionic, or heteropolar, solids; the contribution of φ_P is usually small, but $\varphi_{F\mu}$ or φ_{FQ} may be very important in the case of adsorbate molecules having permanent electric moments. In general, the specific interactions are the result of the concentration of negative or positive charges on the peripheries of adsorbate molecules[5]. They are not confined to molecules with permanent dipole moments, but are also important


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in the case of molecules with permanent quadrupole moments (e.g. N_2, CO_2) interacting with the field gradient over an ionic or heteropolar surface.

Progress has been made in recent years by the study (both theoretical and experimental) of graphitised carbon blacks as adsorbents[5]. High temperature graphitisation of carbon black produces a regular and energetically uniform surface, which is essentially that of the basal face of graphite. After graphitisation of carbon black, the variation in the differential heat of adsorption with surface coverage is greatly reduced. Moreover, the characteristic feature of graphitised carbon as an adsorbent is the high potential of dispersion forces above the close-packed basal plane. The interactions between adsorbate molecules and graphite are therefore essentially non-specific, even with polar molecules, since the impurity centres, which would otherwise give specific interactions, have been removed. Kiselev and his co-workers[5] have investigated the adsorption of a number of vapours on graphitised carbons in detail. By studying various homologous series of hydrocarbons (*n*-alkanes, alkylbenzenes etc.), they have confirmed the principle of additivity of the pairwise dispersion interactions by showing that, for each series, the differential heat at low coverage varies linearly with the number of carbon atoms.

In the estimation of the relative importance of specific and non-specific interactions, it is useful to compare the heats of adsorption on various adsorbents of two selected adsorbate molecules, one polar and the other non-polar, of similar size and polarisability. Such comparisons are made in Tables 1 and 2. Taking the case first of argon and nitrogen (Table 1), it will be noted that the isosteric heat values (recorded at half-coverage) are higher for nitrogen than for argon in every case in which the specific interactions are significant. On carbon black, polypropylene, polytetrafluoroethylene and dehydroxylated silica, the two corresponding values of the heat are not very different, but there is an appreciable difference in the individual values, the extremes being on the graphitised carbon and polytetrafluoroethylene. Clearly, in the latter case (and also with polypropylene) the less dense solid structure

Table 1

Isotherm character and isosteric heats of adsorption of argon and nitrogen on non-porous solids

Adsorbent	Isosteric heat at $V/V_m = 0.5$		Point B well-defined	
	Argon (kcal mole^{-1})	Nitrogen (kcal mole^{-1}	Argon	Nitrogen
Carbon black[8, 9]	2.7	2.7, 2.8	Yes	Yes
Graph. carbon black[8, 9, 10]	2.7, 2.8	2.9	Yes	Yes
Hydroxylated silica[5, 11]	2.1	2.8	No	Yes
Dehydroxylated silica[5, 11]	2.1	2.2	No	No
γ-alumina[12]	2.0	2.7	No	Yes
α-alumina[12]	2.5	3.2	Yes	Yes
Rutile[13, 14]	2.5, 2.3	3.3, 2.7	Yes	Yes
Anatase[14, 15]	—	3.4, 3.1	—	Yes
Polypropylene[16]	1.6	1.7	No	No
Polytetrafluoroethylene[17]	1.7	1.4	No	No

has greatly reduced the overall dispersion interactions. The comparison between *n*-hexane and benzene (Table 2) is also of interest. The high value of the heat for *n*-hexane on graphitised carbon is partly the result of lateral interactions between adsorbed molecules, since the value at low surface coverage is 11.4 kcal mole^{-1} (i.e. closer to the benzene heat). It will be noted that dehydration of the silica and magnesium hydroxide has resulted in an appreciable decrease in the benzene heat, without altering very much the hexane value. This is undoubtedly due to the much lower specific interaction contribution in the case of the dehydrated surface. The modification of the silanol surface by reacting it with $(CH_3)_3$ Si Cl has led to a reduction in the specific interaction for benzene, but has also resulted in a marked decrease in the dispersion field.

Table 2

Differential heats of adsorption of n-hexane and benzene

Adsorbent	Differential heat of adsorption (kcal mole^{-1}) at $V/V_m = 0.5$	
	n-Hexane	Benzene
Graphitised carbon black[18]	12.5	10.3
Magnesium hydroxide[19]	9.0	9.6
Magnesium oxide[19, 20]	9.4	9.1, 9.2
Hydroxylated silica[5]	8.8	10.2
Dehydroxylated silica[5]	8.8	8.6
Chemically modified silica [$(CH)_5Si$—][5, 19]	7.5	7.7

The adsorption isotherm

In view of the differences in interaction energies and hence differential heats of adsorption, it is not surprising to find that the adsorption isotherm for a particular vapour varies considerably in character from one solid to another. The case of adsorption on non-porous solids will be discussed first, examining in particular the monolayer region of the isotherm.

Curve (a) in Fig. 1 is a typical isotherm for a system in which the adsorbent-adsorbate interaction energy is high. Examples are argon, nitrogen, *n*-hexane, on graphitised carbon[8,9,10,18] and nitrogen on α-alumina[12] and titania[13,14,15,21]. Isotherms of nitrogen on low-temperature carbon blacks[8, 9], hydroxylated silica[5] or γ-alumina[12] are similar to curve (b). It is noteworthy that, with the change of γ-alumina to the close-packed α-alumina (corundum) structure, the dispersion potential is enhanced (Table 1) and the character of the nitrogen and argon isotherms is changed from (b) to (a). A similar change in isotherm shape has been noted with the dehydroxylation of titania, but the effect of dehydroxylation of silica is different[5]; in the latter case the oxygen structure remains practically unchanged and the dispersion potential relatively weak (see Table 1). Thus, dehydroxylation of silica has very little effect on argon adsorption, whereas the specific interactions with nitrogen are reduced.

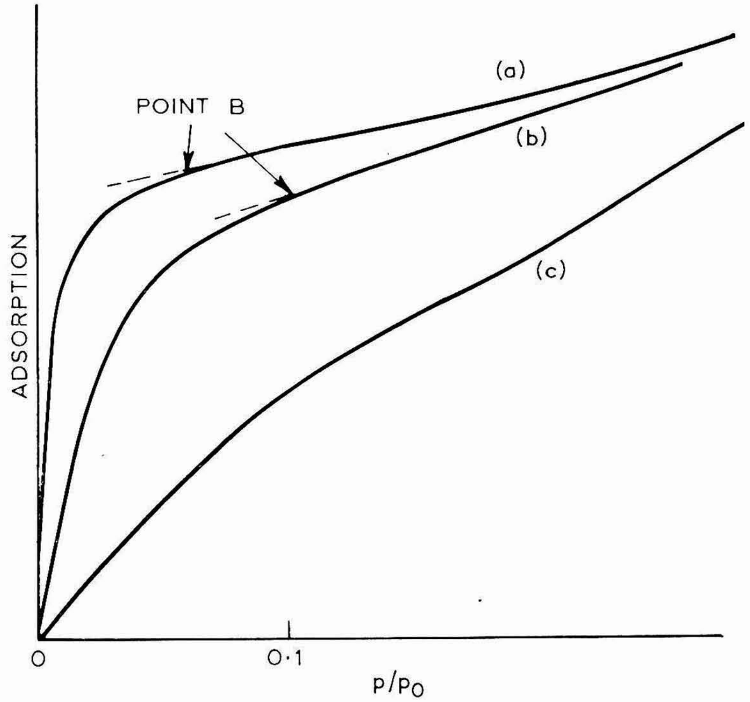

Fig. 1. Adsorption isotherms on non-porous solids

Isotherms similar to curve (c) have been obtained with argon and nitrogen on polyolefins[16] and polytetrafluoroethylene[17, 22], with benzene on chemically modified silica (—$Si(CH_3)_3$)[5] and with water on carbon[5] and dehydroxylated silica[23]. The adsorption of water vapour is a special case which depends primarily on specific interactions. This is why the uptake of water vapour by high-area graphitised carbon is very low—indeed, quite difficult to detect until $p/p_0 \rightarrow 1$.

The effect of porosity on isotherm shape may now be considered. The three most important isotherm types in the Brunauer classification[24] are shown in Fig. 2. Isotherms II and IV are drawn as a common curve up to a certain level of p/p_0, where capillary condensation has caused IV to swing upwards. Isotherms of type IV are obtained with mesoporous solids (formerly called transitional porous) with pore widths in the approximate range 20-200Å. An important aspect of capillary condensation is that it involves meniscus formation in pores which are already lined with an adsorbed layer. The process of micropore filling, which is identified by the type I (or Langmuir) isotherm, is quite different in character. In this case, pore filling occurs at low p/p_0, i.e. within the usual monolayer region of the isotherm, and is the result of the enhanced adsorption potential within very narrow pores (pore width $<$ 20Å). The experimental evidence now available with a number of adsorption systems confirms the effect of micropore filling in distorting the isotherm as indicated in Fig. 2 and in being accompanied by an enhanced heat of adsorption over that given by the surface coverage of the mesoporous, maeroporous ($d >$ 200Å) or non-porous surface[2, 23, 25].

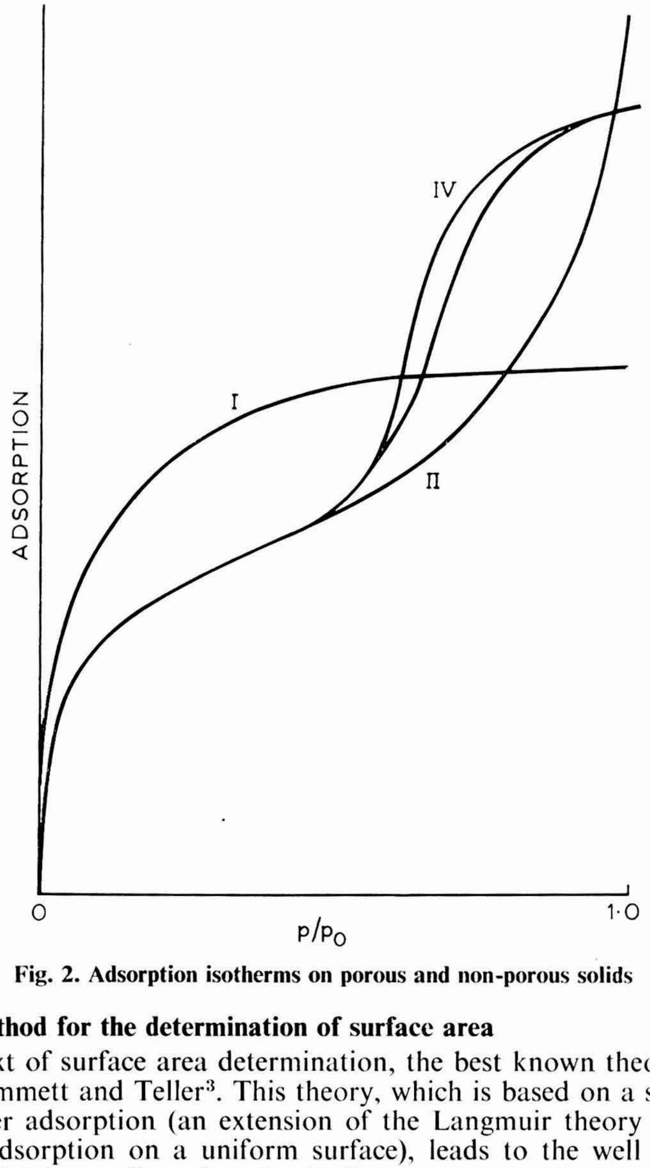

Fig. 2. Adsorption isotherms on porous and non-porous solids

The BET method for the determination of surface area

In the context of surface area determination, the best known theory is that of Brunauer, Emmett and Teller[3]. This theory, which is based on a simple model for multilayer adsorption (an extension of the Langmuir theory for localised monolayer adsorption on a uniform surface), leads to the well known BET equation, which is usually written in the form

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{p}{p_0}$$

where V is the amount adsorbed (mass, volume or mole) at the equilibrium relative pressure p/p_0, V_m is the monolayer capacity and C is a constant related exponentially to the first layer heat of adsorption. It is clear that the BET equation demands a linear relation between $p/V(p_0 - p)$ and p/p_0 (i.e. the BET plot), and that if this is the case it is a simple matter to calculate V_m and C.

In practice, the range of linearity of the BET plot is always restricted to a part of the isotherm (e.g. p/p_0 of 0.05-0.3), even with non-porous solids. Indeed, there appears to be no connection between the range of linearity of the BET plot and the validity of V_m.

In their early work, Emmett and Brunauer[26] designated point B as the point corresponding to the beginning of the middle nearly linear part of a type II isotherm (see Figs. 1 and 2); on empirical grounds they suggested that point B may be taken as an indication of the completion of the monolayer. Later Brunauer, Emmett and Teller[3] argued that the close agreement often found between the value of V_m and the uptake at point B supported their claim for the validity of V_m. In fact, it is now clear that the correspondence between point B and the BET monolayer capacity is only given if point B lies within the linear range of the BET plot[27]. Halsey[28] and others[1] have proposed that point B is more trustworthy than is the BET plot in providing a measure of the true monolayer capacity. Indeed, many workers[2] now agree that it is doubtful whether an isotherm without a clear point B should be used for the evaluation of monolayer capacity by the BET method. In fact, point B cannot be located with accuracy if C values are less than 70-80. This implies that values of the BET monolayer capacity are not reliable for a number of the adsorption systems in Tables 1 and 2.

The second stage in the application of the BET method is the calculation of the surface area from the monolayer capacity by means of an equation of the form

$$S_{BET} = \frac{V_m}{M} \cdot N_0 \cdot A_m \times 10^{-20}$$

Here, S_{BET} is the specific surface (m^2 g^{-1}), V_m is expressed in grams adsorbate per gram solid, M is the molecular weight of the adsorbate, N_0 is Avogadro's Constant (6.023×10^{23} molecules/mole) and A_m is the average area occupied by the adsorbate molecule in the completed monolayer.

Alternatively, if V_m is expressed in cm^3 (stp)g^{-1}, the equation becomes

$$S_{BET} = \frac{V_m}{22414} \cdot N_0 \cdot A_m \times 10^{-20}$$

A difficulty in the calculation of S_{BET} from V_m is the lack of independent evidence on the correct values for A_m. Emmett and Brunauer[26] assumed that the close-packing of adsorbate molecules in the monolayer is very nearly the same as in the bulk solid or liquid. For nitrogen as the adsorbate and taking the liquid density this calculation gives the value $A_m = 16.2$Å^2 at -196°C.

Little is known about the exact mode of packing of the adsorbed molecules in the monolayer, but on *a priori* grounds some degree of localisation and a variation in the value of A_m from one surface to another might be expected. It is remarkable that the value of A_m for nitrogen appears to be reasonably constant and close to 16.2Å^2 with hydrated oxides and some other solids[2]. Recent evidence, however, suggests that the nitrogen monolayer is localised on graphitised carbon[29] and α-alumina[12] surfaces, with values of A_m of about 20 and 18Å^2, respectively. It is noteworthy that in both of these cases the nitrogen isotherm is similar to curve (a) in Fig. 1, the knee being sharp ($C \sim 300$) and point B especially well defined at low p/p_0.

The position with other adsorbates is still very confused. Many attempts[30] have been made to adjust the areas assigned to the adsorbate molecules to bring the BET areas into agreement—based on the nitrogen value of $A_m = 16.2$Å^2. For example, krypton, which has been used extensively for the determination of low surface areas of pigments and other materials[2], appears to occupy about 19.5Å^2/molecule in the completed monolayer rather than 15.2Å^2/molecule, the value calculated for a close-packed "liquid" monolayer. The BET C values for krypton extend from about 10, with organic solids, to over 2000 with clean metal films[31]. Campbell and Duthrie[32] have drawn attention to the pronounced alteration in the low pressure region of the krypton isotherm produced by the chemisorption of oxygen on nickel and have suggested that this is probably linked with a variation in the effective area occupied by each adsorbed krypton atom. Although this is probably the case, it must be re-emphasised that the use of the BET plot as a means of locating the monolayer capacity is not satisfactory in the case of isotherms of type (c) in Fig. 1. Indeed, this is confirmed by the recent work of Whalen, Wade and Porter[22] on Teflon, in which it was found that the area obtained from electron microscopy was larger than the *maximum* BET area which could be calculated from the nitrogen isotherm.

Empirical methods

There are a number of ways in which isotherms may be compared with standard or "universal" isotherm data obtained on non-porous reference solids. The best known of these empirical methods is probably the *t*-method of Lippens and de Boer[33], which provides a simple and direct means of analysing nitrogen isotherms on some solids. The amount of nitrogen adsorbed by the sample under test is plotted against t, the multilayer thickness of nitrogen (at corresponding relative pressures) on the non-porous solid. Any deviation in shape from the standard *t*-curve is therefore detected on the *t*-plot as a departure from linearity. The so-called "universal *t*-curve" of de Boer and his co-workers has been criticised on the grounds that it cannot represent precisely the nitrogen isotherm on all non-porous solids. It should be clear from the above discussion of interaction energies that the structure of the adsorbed layer must depend on the nature of the particular adsorption system. In its early form, the *t*-method did not take micropore filling into account; the method was amended by Sing[34] to provide (in the absence of mesoporosity) an assessment of the micropore volume*. The most serious limitation of the *t*-method is that it is necessarily dependent on the BET evaluation of the monolayer capacity, since t is itself calculated from V/V_m. The *t*-method is therefore restricted to those systems where V_m is well defined.

Recently, the *t*-method has been modified[25] and t replaced by $(V/V_x)_s$—which will be called α_s—where V_x is the amount adsorbed by the non-porous reference solid at the selected relative pressure $(p/p_0)_x$. The master curve for the standard data is therefore plotted as α_s against p/p_0 and the α_s-plot is constructed as amount adsorbed on the test sample against α_s for the standard.

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*The influence of micropore filling on the nature of the *t*-plot was also discussed by Day and Parfitt (Day, R.E., and Parfitt, G.D., *Trans. Faraday Soc.* 1963, **63**, 708).

The values of α_s are thus obtained directly from the adsorption data without the need to calculate V_m first. It is important to stress that the α_s method is essentially a means of comparing the mathematical form of isotherms and that in principle α_s could be placed equal to unity at any convenient point on the standard isotherm. In practice it is usually convenient to place $\alpha_s = 1$ at $(p/p_0)_x = 0.4$ since monolayer coverage and micropore filling occur at $p/p_0 < 0.4$ whereas capillary condensation (along with any hysteresis) takes place at $p/p_0 > 0.4$.

Three typical α_s-plots are given in Fig. 3, corresponding to the isotherms in Fig. 2: curve (a) is the result of unrestricted monolayer-multilayer adsorption (type II isotherm) on a non-porous solid, whilst the upward departure of (b)

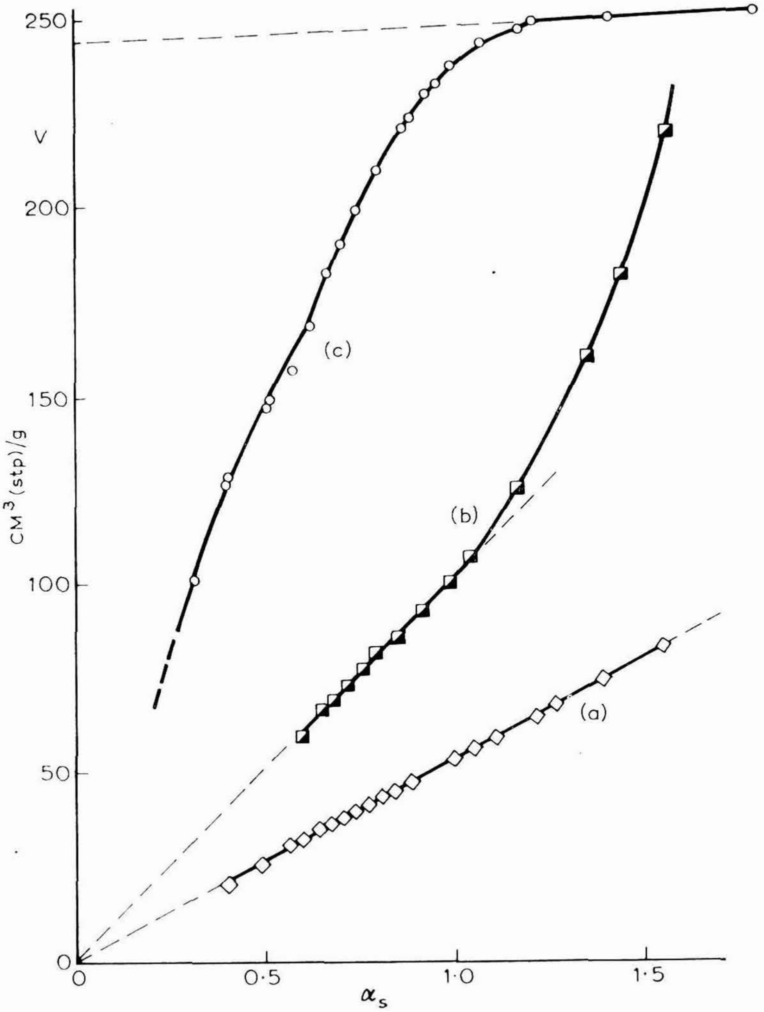

Fig. 3. α_s plots for nitrogen on silicas

◇ non-porous silica (Tμ 800)
◪ mesoporous silica
○ microporous gel

from linearity indicates capillary condensation (type IV isotherm) on a mesoporous solid, and the restricted adsorption in the case of (c) (type I isotherm) is caused by the filling of micropores.

Values of surface area, S_s, are readily calculated from the slopes of the linear regions of the α_s-plots by the use of a proportionality (or normalising) factor which is obtained from the standard isotherm on the non-porous reference material of known BET surface area. In the case of nitrogen adsorption on hydroxylated silica[25], the appropriate relationship is:

$$S_s = 2.89 \ . \ V/\alpha_s$$

which, when applied to α_s-plots similar to (a) and (b) in Fig. 3, gives values of S_s in excellent agreement with those of S_{BET} (usually to within 1 per cent). With type I isotherms, on the other hand, S_s must be calculated from the upper linear part of the α_s-plot and now the surface areas are considerably smaller than the corresponding BET areas. In the latter case, the value of S_s calculated from the multilayer region of the isotherm, provided that this is linear, gives a measure of the external surface area.

Once the standard isotherm has been obtained on the non-porous reference solid, the α_s-method provides a convenient diagnostic test for micropore filling and capillary condensation and a routine method for surface area determination. The approach may also be employed to reveal the effect of specific interactions or enhanced (or reduced) dispersion interactions on the structure of the adsorbed layer[12]. The α_s-method is more versatile than the t-method because it may be applied to type III (or near type III) isotherms. It seems likely that α_s-areas calculated from isotherms with low C values are more reliable than the corresponding BET areas. Thus, the α_s-method can be applied to adsorption systems that exhibit low interaction energies in Tables 1 and 2. Particular care is, of course, required to ensure that the α_s-plot is restricted to that part of the isotherm covered by reliable standard data.

Assessment of porosity

The Kelvin equation is generally used as the basis of pore size distribution calculations[2]. With the correction introduced for multilayer thickness, t, the pore radius, r_p, is given by the equation:

$$r_p = \frac{2 \ V_L \gamma}{RT \ \ln(p_0/p)} + t$$

where V_L is the molar volume and γ is the surface tension of the liquid. Condensation in the pore at p/p_0 is assumed to entail the formation of a hemispherical meniscus. For the case of condensation in a set of cylindrical pores, the equation becomes:

$$V_p - V_a = \int_{r_p}^{\infty} \pi \ (r_p - t)^2 L(r) \mathrm{d}r$$

where V_p is the total pore volume, and V_a is the volume adsorbed at the relative pressure at which all pores having radii less than r_p are full. Various methods have been used to obtain the pore size distribution function $L(r)$: it is now customary to use numerical integration rather than assume a mathematical form for the distribution.

It is clear that the application of the Kelvin equation is restricted to capillary condensation in mesoporous solids. However, even in the ideal case of perfect wetting of cylindrical pores, it is very doubtful whether the bulk values of V_L and γ are appropriate with pore radii < 100Å. The pore shape should also be taken into account, but with most porous adsorbents this is unknown. Hysteresis is another complication and it is still uncertain whether pore size distribution calculations should be applied to the adsorption or the desorption branch of the hysteresis loop. Indeed, it seems likely that the correct procedure will depend on the pore shape, since meniscus formation is likely to be delayed in the case of slit-shaped or open-ended pores[35]. In view of these complications, the method can only be expected to provide a semi-quantitative estimate of the pore size distribution, which is nevertheless useful in the comparison of the surface properties of closely related catalysts or pigments.

Attempts have been made by Brunauer[36] and Dubinin[37] to assess the micropore size distribution. Brunauer and his co-workers have used an extension of the *t*-method, whereas the Russian workers have adapted the potential theory of Polanyi making the assumption of a Gaussian function for the adsorption potential.

As mentioned earlier, Sing[34] has also modified the *t*-method in order to assess the micropore volume. It was suggested that, in the case of microporous solids, the backward extrapolation of the linear *t*-plot, or α_s-plot, to the V-axis (see Fig. 3) would provide a measure of the micropore volume—provided that mesoporosity is negligible. A compensating effect can occur with certain isotherms, i.e. a combination of curves (b) and (c), giving rise to an almost linear α_s-plot over a very wide range of p/p_0, and thus masking micropore filling and capillary condensation. This situation may be identified[25] by making a systematic study using adsorbate molecules of different size and polarisability in order to check the constancy of S_s and the linearity of the different α_s-plots on the same adsorbent.

General conclusions

A considerable amount of evidence is available which suggests that BET areas are not always reliable and, in practice, the validity of the area must be assessed empirically for each gas/solid system. Unfortunately, many of the experimental investigations reported in the literature were undertaken with poorly characterised solids and the numerous attempts to adjust molecular cross-sectional areas were often made on an arbitrary basis. In fact, the calculation of the area is not justifiable unless the monolayer capacity is itself valid.

There are at least two adsorbent systems for which the BET monolayer capacity is in error. In the first case, the adsorbent/adsorbate interaction is so weak that the statistical monolayer is not manifested as any well-defined feature of the isotherm, i.e. the C value is low ($C < 50$) and the location of point B is uncertain. Secondly, if micropore filling occurs along with monolayer coverage (at $p/p_0 < 0.1$), although C may be high ($C > 100$) and point B sharp, the BET monolayer capacity is false unless proper allowance is made for the micropore filling component of the isotherm.

The use of gas adsorption for the characterisation of solid surfaces can only be fully exploited if standard adsorption data are obtained on well-characterised non-porous solids. Progress in this direction has been made in recent years, but it is important that the range of adsorption systems be extended to include organic solids.

The method offers considerable promise for the study of pigments and coated materials, since physical adsorption isotherms and heats of adsorption are sensitive to changes in the chemistry and the structure of solid surfaces. Thus, the coating of a titanium dioxide surface by an organic polymer or silica would be expected to reduce the interaction energy and hence change the shape of the adsorption isotherm of, say, nitrogen or benzene vapour. On the other hand, microporosity in the coating would give rise to an enhanced differential heat over that given by coverage (under the same conditions of p/p_0) of the open surface. With a judicious selection of adsorbate molecules of different size, polarisability, and specific properties, it should be possible to improve the understanding of the chemistry and the texture of the exposed pigment surface.

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Discussion at the London Section

DR D. DOLLIMORE remarked that some of the isotherms on graphitised surfaces were stepped. What kind of treatment should be applied to such isotherms?

PROFESSOR K. S. W. SING said that this was quite an important feature; in the last 10 or 15 years a number of stepped isotherms had been found, e.g. argon or krypton on graphitised carbon, or on other uniform surfaces. The work of Prenzlow and Halsey had shown that the tread of the steps sharpened with a decrease in temperature, but the height of the steps remained the same. These results could be interpreted in terms of localised site adsorption with some lateral interaction between adsorbed molecules. Strictly speaking, one should not apply the BET equation to such systems.

DR A. J. GROSZEK said that graphitised carbon blacks were shown by electron microscopy to be strongly aggregated. For this reason one would expect that this adsorbent would have spaces between the particles which might act as micropores, and the filling of these pores might contribute to the sharp knee that was observed for graphon, in the first monolayer.

PROFESSOR SING commented that this was an ingenious idea, but the steps extended up into the multilayer region. The steps were quite well defined, and he thought that this was due to the regularity of the graphite structure, and that adsorption was taking place layer by layer. The edge effects would probably be quite small.

PROFESSOR G. D. PARFITT respectfully reminded Professor Sing that graphitised carbon black was not a pigment, although one appreciated the need for the use of well-defined surfaces in the development of fundamental knowledge. He asked which technique was likely to be of the greatest value to the industrial chemist in the characterisation of surface area and surface features. Professor Sing's α_s plot would seem to be very useful.

PROFESSOR SING referred to the recent publication of the proceedings of the Bristol SCI symposium on the determination of surface area. Essentially the α_s plot was an extension of Lippens and de Boer's t-plot, which had gained a lot of attention in the last few years. One set up a standard isotherm for nitrogen, plotting the multilayer thickness (t) against p/p_0, and used this to compare with the isotherm under test. One plotted Va against t and with a non-porous solid obtained a straight line; deviations from this were of interest. Professor Sing had developed from this a method in which one replaced t by V/V_0, where V_0 was the uptake at a particular relative pressure, e.g. $p/p_0 = 0.4$. One was no longer restricted to a type II isotherm. One could distinguish between the processes of surface coverage, micropore filling, and capillary condensation.

MR J. D. COHEN said that he spoke as an ink maker, whose task was to get the maximum value for money, notably the maximum dispersibility, from the pigments available. Some very important organic pigments, such as phthalocyanine blue and benzidine yellow, had surfaces of relatively low energy. Professor Sing had pointed out that the BET method could not be used for polyisopropylene and polytetrafluoroethylene. These materials also had low energy surfaces, and he asked Professor Sing to comment on adsorption on such surfaces, particularly concerning the forces involved.

PROFESSOR SING replied that he could not do justice to this topic, as little was known about adsorption on such low energy surfaces. One could probably obtain a rough guide to the surface area by the use of the BET method. In the simplest case the interaction was primarily due to dispersion forces. There might be other contributions from the pigments, due to the polar groups present. One could begin to see a sharpening of the isotherms, due to the effect of specific interactions. It should be possible to apply the α_s method in such cases provided that standard adsorption data could be obtained on reference materials. Analysis of the α_s plots of various vapours (e.g. nitrogen, argon, alcohols) should yield information on the chemistry and the texture of the exposed pigment surface.

DR TH. F. TADROS, referring to the t or α_s plots, said that he could understand why one could obtain an upward deviation, but it was not clear to him how a downward deviation could be interpreted. He had obtained such downward deviations on glass, using the standard curve for amorphous silica. Did this mean that one had slit-shaped micropores that were inaccessible to the adsorbate molecules?

PROFESSOR SING said that this depended upon the reference material used. The system must be chemically similar to the material under examination; he did not believe in a universal t isotherm. The downward swing under such circumstances must be due to micropore filling.

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Polymeric binders containing vinyl esters of branched carboxylic acids for use in electrodeposition finishes*

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Summary

Solution polymers designed for use in water-soluble binders for electrodeposition finishes have been prepared from vinyl esters of branched fatty acids ("VeoVa" 10), (meth) acrylic acid and hydroxyethyl methacrylate with styrene and/or methyl methacrylate.

Semi-batch polymerisation procedures have been developed for preparation in high conversion of products which proved very stable in aqueous solutions. White pigmented electrodeposition finishes from these polymers, cured with melamine/formaldehyde resin, showed the high chemical resistance characteristically imparted by the branched-chain esters to surface coatings.

Keywords

Types and classes of coating
electrocoating
water-soluble coating

Processes and methods primarily associated with manufacture or synthesis
solution polymerisation

Binders—resins etc
copolymer resin
acrylic resin
melamine/formaldehyde resin
methacrylate resin
styrene
VeoVa resin

Liants polymères contenant des esters vinyliques des acides carboxyliques, à chaîne ramifiée, destinés être utilisés en finitions pour application par électrodéposition

Résumé

Des polymères solubles destinés à être utilisés en liants, soluble dans l'eau, des finitions pour application par électrodéposition ont été preparés à partir des esters vinyliques des acides gras à chaîne ramifiée (Véova 10), de l'acide (méth) acrylique, du méthacrylate d'hydroxyéthyle, avec styrolène et/ou méthacrylate de méthyle.

On a mis au point des procédés de polymérisation à l'échelle pilote pour la préparation, à un taux de conversion élevé, des produits qui se démontrent très stables en solutions aqueuses. Des finitions blanches pour application par électrodéposition, préparées à partir de ces polymères et durcies par résine mélamine-formol ont démontré la bonne résistance aux agents chimiques qui est une caractéristique accordée aux revêtements par les esters à chaîne ramifiée.

Vinylester Verzweigter Karbonsäuren Enthaltende Polymere Bindemittel für Elektrotauchlacke

Zusammenfassung

Aus Vinylestern verzweigter Fettsäuren ("VeoVa" 10), (Meth-) Akrylsäure und Hydroxyäthylmethakrylat mit Styrol und/oder Methylmethakrylat wurden Lösungspolymere zur Verwendung in wasserlöslichen, für Elektrotauchlacke bestimmten Bindemittln hergestellt.

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Polymerisationsverfahren mit halben Ansätzen wurden zur Herstellung stark umgewandelter Produkte entwickelt, welche sich in wässrigen Lösungen sehr stabil verhielten. Weisspigmentierte mit Melaminformaldehydharz gehärtete Elektrotauchlacke aus diesen Polymeren wiesen die hohe Chemikalienbeständigkeit auf, welche charakteristischer Weise Beschichtungsmitteln von Estern mit verzweigten Ketten verliehen wird.

Полимерные крепители содержащие виниловые эфиры разветвленных карбоновых кислот, для применения в отделках электролитических осаждений

Резюме

Растворные полимеры, предназначенные для применения в водорастворимых крепителях для отделок электролитического осаждения, приготовлялись из виниловых эфиров разветвленных жирных кислот («Veo Va» 10), (мет) акриловой кислоты и гидроксиэтил метакрилата со стиролом и/или метил метакрилатом.

Разработаны полудозировочные процессы полимеризации для приготовления, в широком преобразовании, продуктов которые оказались весьма устойчивыми в водных растворах. Белые пигментированные отделки электролитических осаждений из этих полимеров, высушенные меламино/формальдегидной смолой, обнаружили высокое химическое сопротивление, характеристически придаваемое разветвленно—цепными эфирами поверхностным покрытиям.

Introduction

Vinyl esters of branched fatty acids have been widely known in the paint industry for a number of years, in particular as base materials for the preparation of paint latices[1, 2]. Improved alkali resistance and outdoor durability are among the characteristics which result from the introduction of the branched fatty acid structure in these copolymer latices. In earlier work, the beneficial effect of the same branched acid structures in alkyd type resins has been demonstrated[3]. The glycidyl ester of the acids was used to incorporate the branched acid structure into the alkyd molecules. More recently[4] attention has also been paid to a third category of binders increasingly finding use in the industrial paint field—solution polymers of a molecular weight between that of emulsion polymers and condensation resins.

The present paper describes solution polymers of this third category that are specially designed for use in electrodeposition finishes. These copolymers are prepared from four or five different monomers.

Considerations on the choice of monomers

When considering the technical requirements of polymers of the type to be used in electrodeposition finishes, one inevitably concludes that it is necessary to use systems composed of at least three monomers. Each monomer has to contribute towards achieving a given essential polymer property. The following are the requirements concerned.

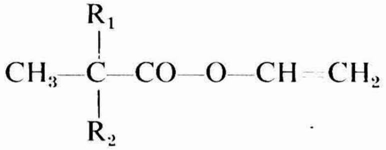
In order to obtain adequate water solubility, the polymer should have a number of carboxyl groups attached to its chains. As known from experience, their concentration should be such that the final acid value of the product is about 90meq/100g.

The polymer should have the inherent capability of being cross-linked by stoving in paints to form a system with good physical and chemical resistance properties. Either self-curing or, a better alternative, cross-linking with amino-curing resins, can be considered.

A polymer entirely consisting of a carboxylic acid monomer and a functional monomer, from the point of view of curing, could be designed theoretically but in practice, for economic reasons, cheaper monomers have to be used as well. These monomers must impart to the polymer the desired balance of hardness and flexibility. This is usually achieved by selecting a combination of a "hard" and a "soft" monomer.

In the literature[5] some mention has been made of the feasibility of curing products containing carboxyl groups with special amino resins. In early investigations polymers were made from vinyl acetate/vinyl esters of branched fatty acids and acrylic acid.

The branched chain vinyl esters will be referred to, for convenience, as VeoVa 10, and consist of esters of branched chain saturated acids of the general structure:



$$CH_3\text{—}\underset{\displaystyle R_2}{\overset{\displaystyle R_1}{C}}\text{—}CO\text{—}O\text{—}CH{=}CH_2$$

It soon became clear that, in conjunction with amino resins, no proper cure could be attained. Variations in acid value and changes in stoving temperature and amino resin concentration were made without leading to acceptable improvements; hence, it was concluded that the presence of hydroxyl groups was indispensable for an adequate cure.

Thus, the use of four types of monomer is generally involved in considering the possibility of using VeoVa 10 in a water-soluble solution polymer, a COOH-monomer, an OH-monomer, a "hard" monomer and a "soft" monomer. VeoVa 10 is classified under the last of these types. Representative and readily available monomers of each type are:

COOH-monomers—acrylic acid, methacrylic acid
OH-monomers—hydroxy ethyl methacrylate
"hard" monomers—methyl methacrylate, styrene
"soft" monomers—VeoVa 10, acrylic esters such as butyl acrylate.

Systematic exploitation of multi-component polymer systems is still in its infancy as far as the knowledge of the molecular structures obtained is concerned. Nevertheless, in practice, four-component polymers have received considerable attention in technological applications for a number of years. Examples of such polymers are acrylic systems. This paper will be restricted specifically to water-soluble acrylic systems.

Typical water-solubel acrylates are composed of monomers such as acrylic acid, hydroxyl ethyl methacrylate, butyl acrylate and styrene. Although exact data on the course of the copolymerisation of four-component systems of this type are scarce, in practice not many difficulties are encountered in obtaining polymer solutions homogeneous in appearance and of good conversion under reasonable reaction conditions.

This is because the mutual relative reactivity ratios of the monomers are not too far apart. When the "soft" flexibilising monomer is replaced by a vinyl ester, the picture changes drastically. As can be seen in Table 1, which gives rate constants for radical-initiated polymerisations from the literature[6], the homopolymerisation rate of vinyl acetate is much lower than its free radical copolymerisation rates with methylmethacrylate and styrene, whereas the homopolymerisation rates of methylmethacrylate and styrene are much higher than their free-radical copolymerisation rate with vinyl acetate. VeoVa 10 is apparently not very different from vinyl acetate in reactivity[7]. The large differences in rate constant ratios mean that the initial copolymer from the system vinyl ester/methyl methacrylate contains much less vinyl compound than is present in the monomer mixture. The same is true of vinyl ester/styrene; here, moreover, the extremely low reactivity of vinyl monomer with the styrene radical lowers the overall rate of polymerisation so drastically that a small amount of styrene acts as an inhibitor for vinyl polymerisation.

Table 1

Rate constants for radical initiated polymerisation (60°C) (Walling[6])

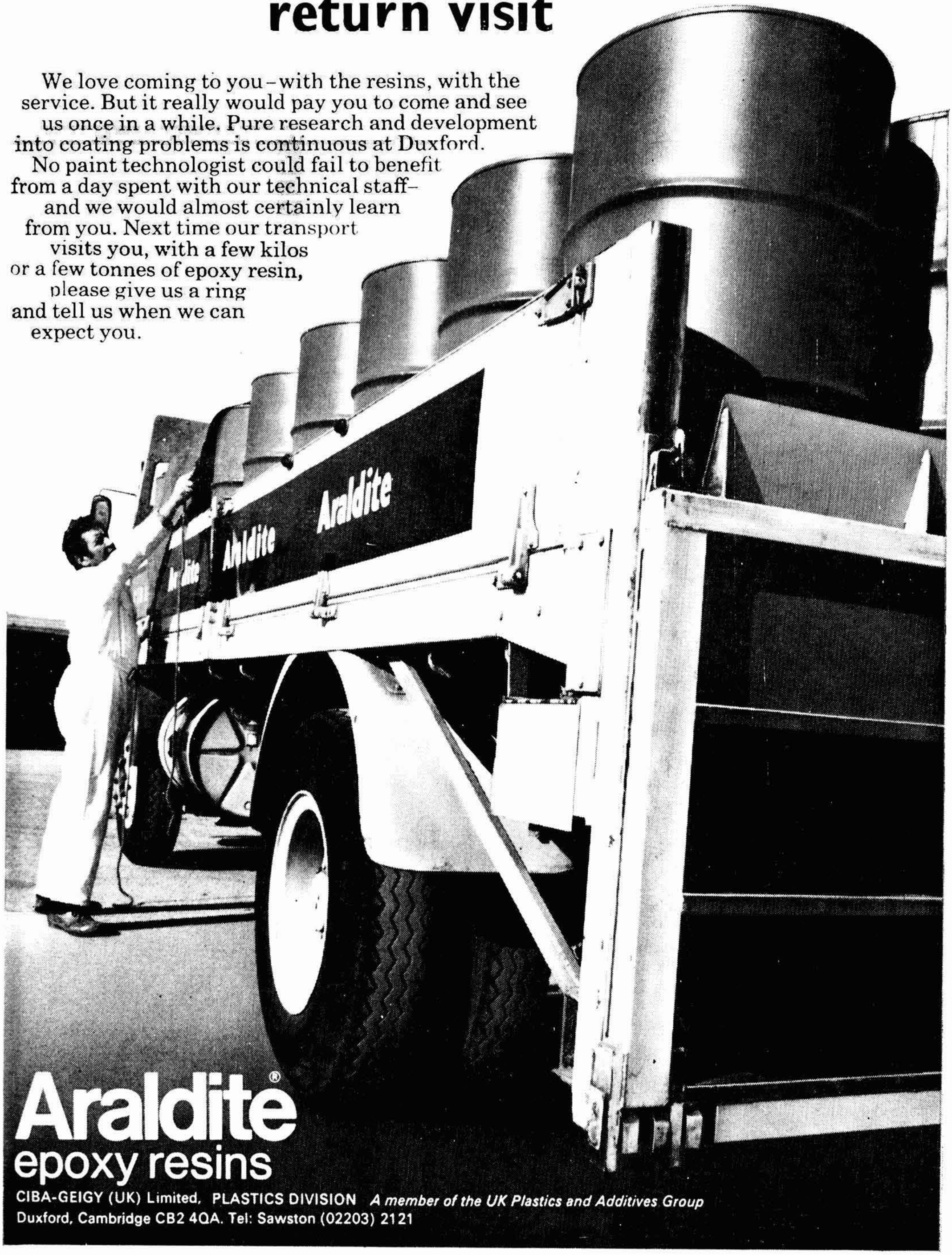
Monomer	Radical		
	Styrene	Methyl methacrylate	Vinyl acetate
Styrene	145	1,520	> 100,000
Methyl methacrylate ..	278	705	> 100,000
Vinyl acetate	3	35	2,300

The situation becomes somewhat different when ternary systems are considered. It has been stated[8] that it is possible to copolymerise styrene and vinyl acetate in the presence of an acrylate monomer. The latter can be considered to be a "coupling" monomer. No detail is, however, given in this patent reference on the preparation of such a product and, in fact, in the final patent specification no mention of styrene appears at all.

The work on VeoVa in such systems was therefore simply started with exploratory experiments in order to gain some insight into the actual phenomena that would occur in practice.

Polymerisation procedures

The laboratory apparatus that has been used for the polymerisation work is schematically illustrated in Fig. 1. Basically, it consists of a normal glass reactor fitted with an anchor stirrer, thermometer, condenser, nitrogen-inlet tube. The reactor is connected via glass tubes with a metering vessel and a micro-pump. Bearing in mind the differences in reactivity, in most of the procedures the reactor was precharged with VeoVa monomer, while the more reactive monomers were gradually added over periods varying from 12-24 hours. This addition was started after the reactor contents had been heated to 80°C. During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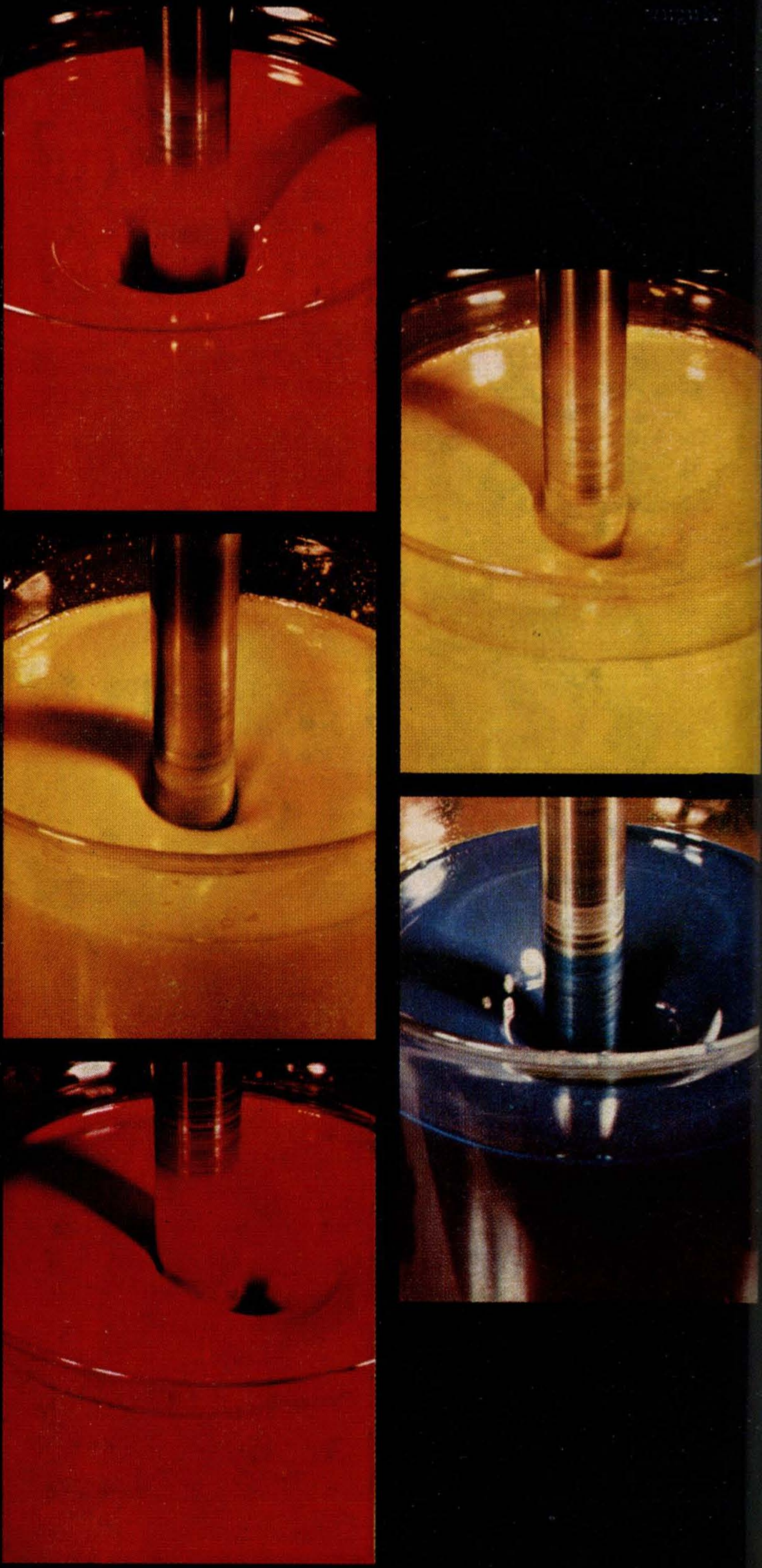

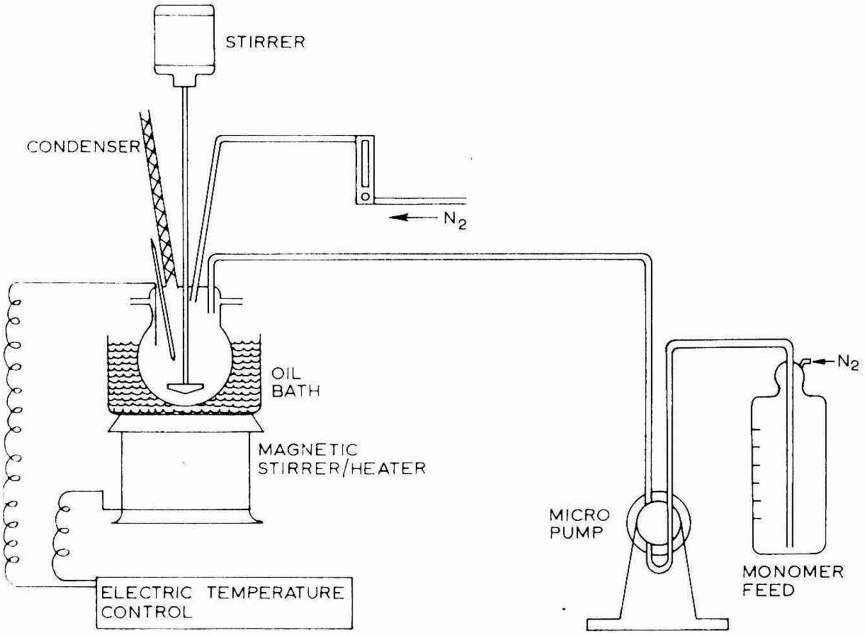

Fig. 1. Laboratory polymerisation apparatus

the addition period the temperature was allowed to increase to 115-120°C. A typical scheme of such a procedure is given in Table 2. All acrylic types of monomers have been given the common heading of "acryl", although it is realised that between certain of these monomers some variations in reactivity may exist.

Table 2

Polymerisation procedure 1

Reaction		Steps	Constituents				Initiator
Time	°C		VeoVa	"Acryl"	Styrene	Solvent	
—	—	charge	a	0.1 b	0.1 c	3	0.18*
12hr	115	addition	—	0.9 b	0.9 c	27	0.35**
5hr	110	post-reaction					0.50**

a + b + c = 70wt parts; total monomers/solvent 70/30

*DTBP (di tert. butyl peroxide)

**BPO (benzoyl peroxide)

Using this technique, a number of polymers was prepared with final acid values of 90-100meq/100g and an OH-content of 80-90meq/100g. The monomer compositions are given in Table 3.

Table 3
Composition of polymers

Ref. No.	2108 W	1009 F	0710 F	0910 P	0711 F	2711 F
VeoVa	36.4	44.9	53.6	60.0	50.0	50.0
AA	6.4	6.6	7.7	6.6	6.6	6.6
HEMA ..	10.0	10.3	12.0	10.3	10.3	10.3
MMA	17.3	17.7	26.7	23.1	17.1	17.1
ST	29.9	20.5	—	—	16.0	16.0
solvent	ethyl ether of ethylene glycol				butanol	benzyl alc/ BuOx 2/1

BuOx = butyl Oxitol (butyl ether of ethylene glycol)
AA = acrylic acid
HEMA = hydroxy ethyl methacrylate
MMA = methyl methacrylate
ST = styrene

The styrene containing polymeric solutions were all clear in appearance and stable; however, the two formulations prepared without styrene showed phase separations quite rapidly, undoubtedly caused by too great a polymer inhomogeneity. On separation of the two phases and removal of their solvents, it appeared that one phase was sticky, while the other phase was considerably "harder". The acid value of the latter phase was more than twice that of the first.

The four styrene-containing polymer solutions, after neutralisation with triethylamine, could be diluted easily with water. Solutions of 10 per cent solids, although sometimes milky in appearance, showed very good stability, as judged from storage tests at 40°C, where, even after three months, no obvious changes had shown up. White finishes were formulated from these binders in combination with a low-reactive butylated melamine resin. The base resin/curing resin ratio was 80/20, the pigment/binder ratio 0.33 and the binder solids content of the electrodeposition (E/D) paints was 10 per cent. The main features of this preliminary evaluation are summarised in Table 4.

Table 4
Evaluation data on preliminary experiments

Ref. No.	2108 W	1009 F	0711 F	2711 F
Film appearance	matt	matt	matt	smooth, glossy
Rupture voltage	450	450	160	130
Thickness, μ	12-18	15-20	30	30
Flexibility	very poor	very poor	poor	moderate
5% NaOH, 23°C	2 d soft	7 d soft	—	7 d v.sl.bl.
Mins. to be softened by				
xylene	8	8	6	25
MIBK	10	10	4	24
Buchholz hardness	—	125	105	105

Stoving: 30min 150°C; d-days; v.sl.bl.—very slight blistering

On studying these results, it becomes obvious that the first two polymers give films that are too brittle, but whose solvent resistance indicates a reasonable degree of cure. The high rupture voltages may, moreover, be typical of the presence of acidic polystyrene of a fairly high molecular weight. In the other two formulations, the reduction of the styrene content indeed resulted in an improvement in flexibility. An interesting observation was that the matt films obtained improved considerably in gloss when, after deposition and just prior to stoving, a superficial rinse with some organic solvent was carried out. This suggests that only a slight improvement in flow is actually required. The product polymerised in benzyl alcohol/ethylene glycol butyl ether gives a good gloss without any treatment. The resistance of this E/D film to alkali is considered to be very good.

In additional, more elaborate, polymerisation work a number of variations was examined, including the effect of:

type and concentration of the monomers to be used in the initial reactor charge and of the monomers to be added,

addition period or addition sequence of the various monomers,

temperature,

type of solvents and initiators, and

post-reaction conditions.

It was found that an increase in the amount of styrene in the formulations invariably reduced the final monomer conversion. This effect could be partly overcome by simultaneously increasing the hydroxy ethyl methacrylate (HEMA) concentration, but for economic reasons this is not very attractive. For an adequate cure, 10 per cent of HEMA, corresponding with 80meq OH/100g, is sufficient. Styrene monomer concentrations around 15 per cent offer no serious polymerisation problems. A final acidity of 90meq/100g is a good compromise between good colloidal solution stability and E/D characteristics, which means that the quantities of acrylic acid or methacrylic acid should be in the range of 6-7 per cent.

Precharging the reactor with all of the vinyl ester remained in every case advisable in order to obtain good conversions. Initially, it seemed better to add the more reactive styrene and the acrylic monomers gradually to the vinyl monomer, the styrene somewhat more quickly than the acrylic monomer. In the course of the experiments aimed at reducing the processing time from about twenty-four hours to about six hours, it also appeared quite possible to precharge the reactor with all of the vinyl and styrene and then gradually to add the acrylic monomer mixture. Some polymers showed an increased inhomogeneity when prepared at a higher speed. This manifested itself by slow phase separations on storage in the 70 per cent polymer solutions. The reduction in processing time can also be effected by raising the reaction temperature; in this case a gradual addition of styrene prevents any slow phase separation.

Certain solvents had a very pronounced effect on the copolymerisation. An example of such a solvent is benzyl alcohol which strongly affects polymerisation, thereby causing the vinyl conversion to be retarded quite appreciably.

Temperature and type of initiator are, of course, interrelated. For the polymerisations carried out at 115-120°C, benzoyl peroxide was used. At higher temperatures (140°C) a blend of di-*t*-butyl peroxide/*t*-butyl perbenzoate was used. Conversion improves with increasing temperature.

Finally, the various stages of development in the preparation procedure are given in Table 5. A selection of the polymers prepared will be considered further and details of their composition are given in Table 6.

Table 5

Various preparation procedures

Ref. No.	Reaction		Steps	Constituents				Initiator (BPO)
	Time	°C		VeoVa	"Acryl"	Styrene	Solvent	
II	—	115	charge	a	0.1 b	0.1 c	12	—
	18hrs		addition 1	—	0.8 b	0.9 c	15	0.8
	2		addition 2	—	0.1 b	—	3	0.2
	4		post-reaction	—	—	—	—	0.5
III	—	115	charge	a	—	c	12	0.1
	5		addition	—	b	—	18	0.9
	$1\frac{3}{4}$		post-reaction	—	—	—	—	3 × 0.167
IV	—	140	charge	a	—	0.2 c	12	0.2*
	$4\frac{1}{2}$		addition 1	—	0.9 b	0.8 c	15	0.8**
	$\frac{1}{2}$		addition 2	—	0.1 b	—	3	0.2**
	$1\frac{3}{4}$		post-reaction	—	—	—	—	3 × 0.167

all wt. parts a + b + c = 70

*di-t-butyl peroxide

**t-butyl perbenzoate

Evaluation

Solution stability

A first impression of the suitability of any polymer for electrodeposition is always obtained by assessing the water dilutability of the pre-neutralised polymer solutions. For neutralisation, amines such as triethylamine or dimethyl ethanolamine are quite common. The aqueous systems obtained should be stable at solids concentrations around 10 per cent, in the sense that on storage at temperatures up to 40°C no rapid phase separations should occur, nor a serious drift in pH, or rather in conductivity, due to hydrolysis of the binder. This breakdown by saponification is governed by the relation:

$$R = \{K_1(\mathrm{OH}^-) + K_2(\mathrm{H_2O}) + K_3(\mathrm{H}^+)\}\ x\ (\text{ester})$$

The main hydrolysis is in practice the alkaline saponification, and the others can be ignored in the present case. In order to learn something about the apparent acidity of the carboxyl groups in the VeoVa polymers, pH values were measured in relation to the degree of neutralisation (α). Results have

Table 6

Details of polymers investigated

Ref. No.	0302 F	0309	0316	0262	0279	0337	0409
VeoVa 10	50.0	57.0	—	70.3	—	73.4	50.0
Butyl acrylate	—	—	57.0	—	70.3	—	—
Acrylic acid	6.6	—	—	—	—	—	6.6
Methacrylic acid	—	6.9	6.9	6.9	6.9	6.9	—
HEMA	10.3	22.8	22.8	22.8	22.8	13.0	10.3
Methyl methacrylate ..	17.1	—	—	—	—	—	17.1
Styrene	16.0	13.3	13.3	—	—	6.7	16.0
Prep. techn.	II	II	II	II*	II*	III	IV
Conversion %	80	99	100	100	100	97	95
Solvents**	benz. alc/BuOx 20/10	MeOx/THF 25/5	BuOx/THF 25/5	MeOx/THF 25/5	MeOx/THF 25/5	BuOx	BuOx

*modified, charge 0.2 a, 1st addition 0.8 a + 0.9 b, 2nd addition 0.1 b

**BuOx = butyl Oxitol, MeOx = methyl Oxitol, THF = tetra hydrofuran been plotted in Fig. 2. For comparison, calculated titration curves of a weak base ($pK_b = 4.6$) versus acids of various pK_a's have been plotted as well. In addition, the change in pH, which results from the addition of Versatic 10 (branched C10 acid) to completely neutralised VeoVa polymer, has been plotted.

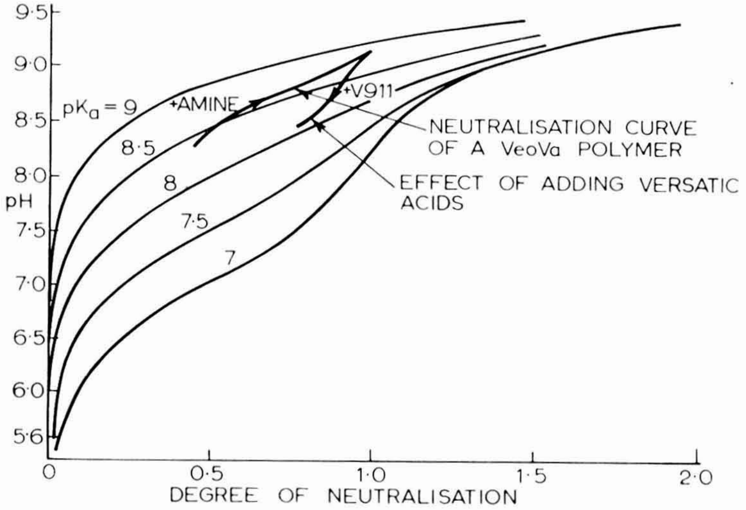

Fig. 2. Neutralisation curves of various acids with a weak base ($p^kb = 4.6$)

The polymer acids behave like a very weak acid. In Fig. 3 the two extreme pH/neutralisation relations have been replotted. Furthermore, the initial pH at equivalent neutralisation has been indicated for a representative VeoVa polymer (0309), a corresponding acrylic polymer (0316), a typical commercial acrylate polymer and a water-soluble alkyd based on the glycidyl ester* of the same branched acids as those in VeoVa.

After storage of the neutralised solutions at 40°C, for six months for the polymer systems but only 14 days for the alkyd system owing to early phase separation, the resultant increase in acid value was determined. From these values the decreased neutralisation degree was calculated; these values are also given in Fig. 3.

It can be seen that the rate of saponification of the VeoVa polymers is extremely low and slightly lower than that of acrylate polymers. The acid liberated is very weak, as is also the case with corresponding acrylate polymers. The HEMA in the VeoVa polymer probably hydrolyses faster than the Versatic esters. The binder acids of the alkyd (phthalic monoesters) are stronger than the polymer acids. The pH decreases much faster, which causes slowing down of the process, but in practice unfavourable effects such as discolorations of the deposited films have then already shown up. The very small degree of saponification observed with VeoVa polymers could possibly be reduced further by using a different hydroxy-containing monomer (hydroxypropyl methacrylate).

As regards phase separations of diluted polymer solutions upon storage, it

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*trade-name Cardura E

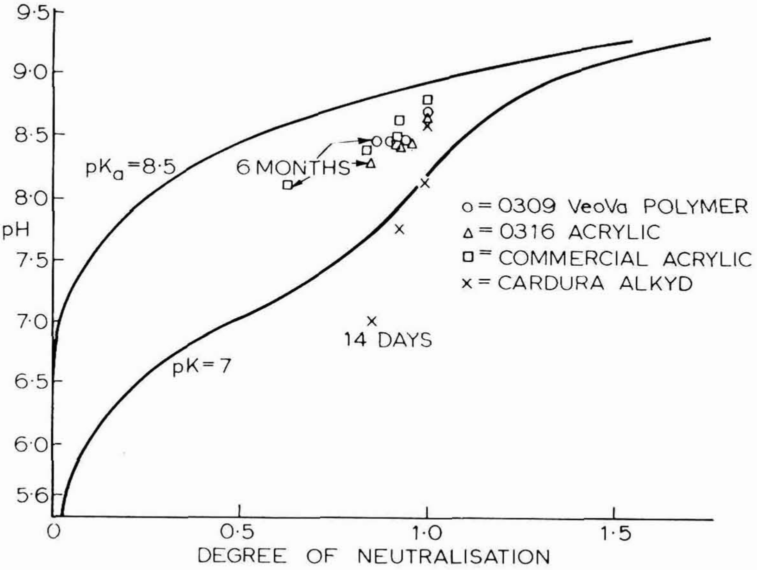

Fig. 3. Saponification of various polymeric binders

has to be remarked that these are not always due to mere saponification. Phase separations have also been observed with systems that could have hardly suffered from saponification. It is interesting to note that these observations were made only with systems without styrene. The styrene-containing polymers could also be more easily (quickly) thinned down with water than the vinyl/acrylate systems.

Electrodeposition of paints

There is no need to stress the importance of electrodeposition as a method of paint application; after all, the process has been commercially operational now for more than seven years and the number of installations commissioned has increased considerably over that period[9]. The technical problems associated with electrodeposition primers, such as bath control, have largely been solved; industry is now approaching the stage of demanding additional performance properties from these binders. Hitherto, the more successful binders have been those of the "oleo-resinous" type, including phenolic or hard resin modified styrene/allyl alcohol copolymers and epoxy ester systems. For electrophoretic application of white or slightly tinted systems, these binders fail, however, to offer good colour and colour consistency. The polymeric binders discussed here have intrinsically more attractive characteristics in this respect, and have therefore been tested in white electrodeposition paints.

The preferred method of preparing white electrodeposition paints is first to blend the polymer with the amino-curing resin, to neutralise this blend with amines and then to dilute this system with demineralised water to about 25 per cent solids. Part of this solution is used for making a "slush" type pigment dispersion in a pebble mill. The laboratory electrodeposition coating technique is sufficiently common these days and hardly needs further explanation. For testing the paint stability properties circulation tests or stirring tests were used. These have been found to be sufficiently severe to obtain a reliable impression of the actual usefulness ot the systems under practical conditions.

The melamine resins suitable for these applications can be of the low molecular weight solvent-free type,[10] but more conventional low-reactive butylated amino resins, available as solutions in butanol, can also be used.

A collection of the major electrodeposition paint test results on the selected binders is given in Table 7. In general, the degree of neutralisation was 1.0, which resulted in pH values of the final paints of approximately 9, using dimethyl ethanolamine or triethylamine. The value of the specific resistance of the paints as used varied from 900 to 1,200 Ωcm at 10 per cent total solids. For comparison, results of similar tests carried out on one of the commercial acrylic type polymers used for reference have been included.

The VeoVa containing polymers gave films of a good whiteness. In contrast to previous experience of water-soluble alkyd systems, the colour proved to be much more consistent with ageing of the paints. Another interesting feature is the good chemical resistance of these systems, which is superior to that of four commercial acrylates used as reference (the results of the best acrylate are given in Table 7). In straight comparisons between similarly prepared VeoVa/HEMA/methacrylic acid copolymers and butyl acrylate/HEMA/methacrylic acid copolymers, the former systems have a better chemical resistance. In a comparison between two such polymers where a certain amount of styrene has been used, the difference in performance is less obvious, but is still in favour of VeoVa polymers.

It can be seen that, for one of the first polymers prepared (0302 F), the conversion as given in Table 6 is fairly low. The unconverted monomer is mainly VeoVa. This means that the final paint (10 per cent binder solids) contained 1.6 per cent free VeoVa 10, but this did not affect the colour or the stability of the paint. Of course, the actual polymer in the paint films is then different in composition (VeoVa 10/AA/HEMA/MMA/ST 37.5/8.2/12.9/21.4 19.9) and this explains the better chemical resistance, in comparison with VeoVa polymers of higher conversion.

The gloss of the electrodeposited paint films on bonderised steel (Bonderite 97) is a property which is very sensitive to polymer preparation procedures. On plain degreased steel, this is far less critical, as can be seen from results obtained with 0309 polymer. Attempts to trace the course of this phenomenon by studying the molecular weight characteristics have not yet been successful. The curves obtained from the relevant gel permeation chromatograph gave an apparent uniform molecular weight distribution for the VeoVa polymers. The non-VeoVa containing acrylate polymers, admittedly prepared according to a technique which is somewhat unusual for these polymers, did show anomalous peaks in their GPC curves. So far preparation method IV for VeoVa polymers has been the most promising in this respect.

Terpolymerisation model tests

For a better understanding of the actual course of events during polymerisation when using VeoVa 10, acrylic monomers and styrene, a special test was developed which allowed regular gas chromatographic analysis of unreacted

Table 7

Collection of results of E/D paint testing

Polymer ref. No.		0302 F	0309	0316	0262	0279	0337	0409	Commercial
Gloss on Bonderite 97		84	14	—	19	—	28	55	64
Gloss on steel		75	74	34	39	68	21	77	74
Stoving °C, 30 min		150	175	175	175	175	175	175	160
Application, V		90	300	280	280	150	200	150	100
Thickness, μ		33	24	26	28	29	28	22	28
Mandrel bend		$\frac{1}{4}$in	$\frac{1}{8}$in	$\frac{1}{16}$ in	$\frac{1}{8}$in	$\frac{1}{8}$in	$\frac{1}{8}$in	$\frac{1}{8}$in	$\frac{1}{16}$ in
Buchholz hardness		100	91	100	87	77	80	100	98
Erichsen pen., mm		5.5	6.9	6.8	5.8	6.7	> 8	> 9	> 9
5% NaOH, 23°C, 2 d.		10	9	9	7	6	10	10	0
5% NaOH, 23°C, 7 d.		10	6	5	5	0	8	8	—
5% HAC, 23°C, 2 d.		10	8	4	9	3	10	10	—
5% HAC, 23°C, 7 d.		9	4	4	7	2	7	10	—
MIBK, (15 min)		B	5B	4B	6B	6B	> 6B	2B	> 6B
Xylene, (15 min)		B	2B	4B	4B	5B	5B	2B	> 6B
Salt spray, 240 hr (ASTM)		1-2mm	—	—	—	—	—	2-4mm	—
Type of MF resin		M96	XM 1116	XM 1116	XM 1116	XM 1116	XM 1116	XM 1116	Self curing
P/B	Bath	0.41	0.3	0.3	0.3	0.3	0.3	0.3	0.5
Pol/MF		74/26	70/30	70/30	70/30	70/30	70/30	70/30	Self curing
P/B	Film	0.53	0.39	0.38	0.36	—	0.35	0.40	—
Pol/MF		69/31	79/21	81/19	80/20	—	80/20	78/22	—

monomer during the process. In order to facilitate the analysis, more volatile model compounds had to be selected. The vinyl ester of pivalic acid was used to represent VeoVa as a class of monomers and methyl methacrylate was chosen in place of HEMA and methacrylic acid.

As an example, the results are given of a model experiment following polymerisation procedure III.

After the reaction temperature of 110°C was reached, samples were taken at half-hour intervals and analysed. The information obtained from this analysis was fed into a computer in order to calculate the effect of changes in concentrations of the various constituents in the reaction mixture. The initial monomer ratio was adjusted to correspond with the ratios used with the VeoVa 10 polymers evaluated for electrodeposition finishes. Fig. 4 shows the quantities of monomer plotted against the reaction time.

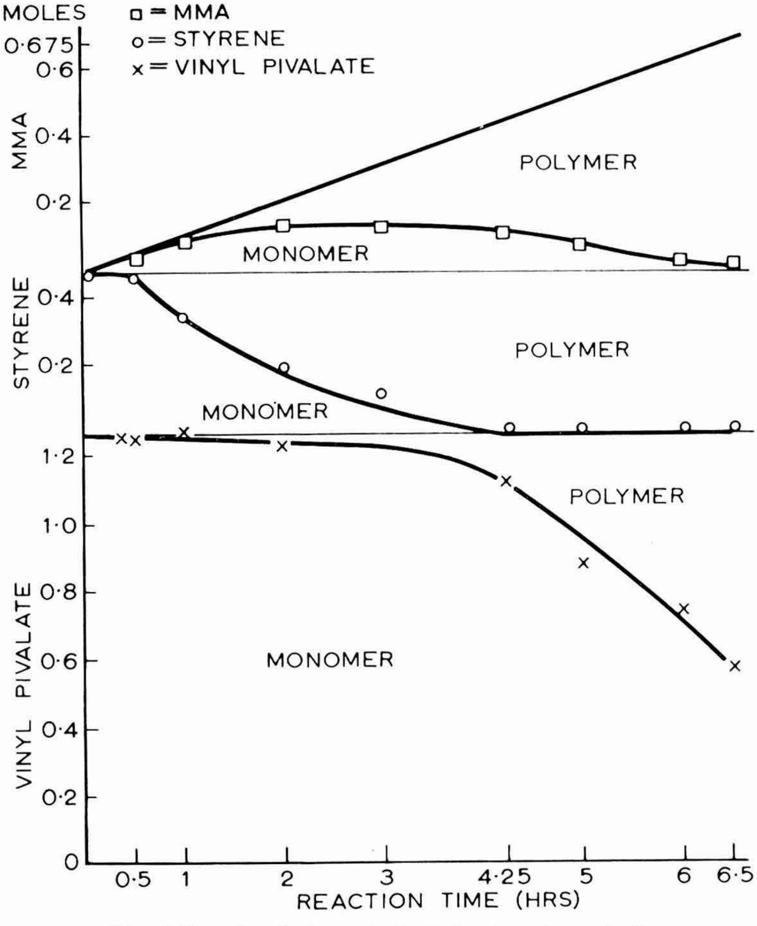

Fig. 4. Results of glc analysis during terpolymerisation

In the first hours of the reaction, after a short inhibition period, styrene and acrylate almost exclusively take part in the polymerisation. The vinyl ester only enters the copolymer when the styrene monomer concentration has been reduced appreciably. In Fig. 5 the polymer composition distribution, as computed from the difference between total and measured residual monomer quantities, has been plotted as a function of the total monomer conversion. The theoretical instantaneous polymer composition calculated from the relative reactivity ratios from literature has been plotted as well and shows very reasonable agreement with the practical results.

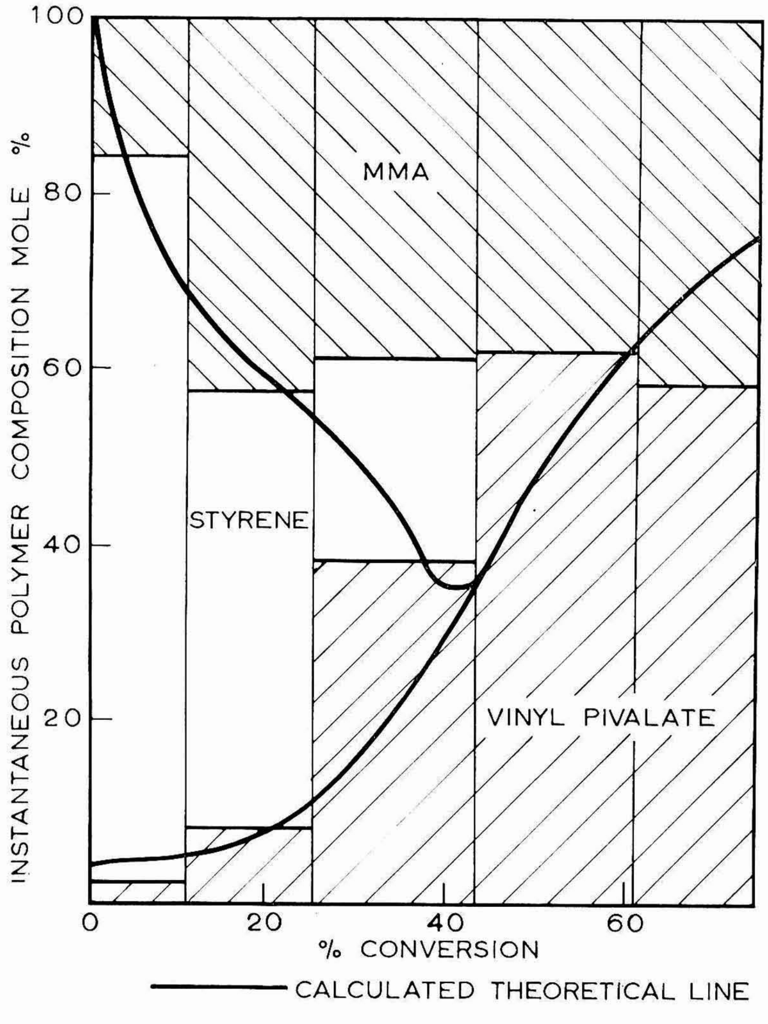

Fig. 5

It is, however, obvious that more studies of this type are required to elucidate the relationship between process conditions and polymer build-up, to enable the ultimate preparation of a copolymer of predetermined structure.

Conclusions

The work described here has shown that, under suitable process conditions, polymeric water-soluble binders can be prepared from VeoVa 10 and styrene, together with acrylic type monomers, such as hydroxyethyl methacrylate, (meth), acrylic acid and methyl methacrylate.

Tests on relevant model compounds have indicated that such polymers vary in chemical composition during polymerisation. However, in spite of this drift in composition with conversion, these polymers have attractive characteristics for the formulation of white pigmented electrodeposition finishes. After neutralisation with amines they are readily dilutable with water and hardly suffer from hydrolysis or phase separation when stored as aqueous solutions at 40°C. In conjunction with melamine/formaldehyde resins, electrodeposition finishes can be prepared which show an attractive level of film properties, of which good colour and alkali resistance are most notable.

Acknowledgment

The authors wish to thank Mr J. W. J. Koop, Miss C. H. van Lienden and Miss J. P. E. Smid, who carried out the experimental work and contributed helpful suggestions.

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Discussion at the London Section

Dr M. Ellinger asked how the colour of the films compared with that of acrylics, in the case of pure whites. Also, what stoving times and temperatures were used?

Mr van Westrenen said that the whiteness was quite as good as that with acrylics. A normal stoving schedule of 30 minutes at 150°C was used when the polymer systems in question were combined with conventional butylated melamine resins. In the case of low molecular weight solvent-free melamine resins of the hexamethoxymethyl melamine type a stoving temperature of 175°C was used, in view of the low reactivity of these melamine resins.

Mr S. Teller, referring to polymers in which butyl acrylate had been used, asked how the overall reactivity of the system would be affected if the butyl acrylate were replaced by 2-ethylhexyl acrylate.

Mr van Westrenen replied that the two monomers had roughly comparable reactivities and hence the polymerisation could be expected to proceed very similarly.

MR P. J. SCAMMELL asked whether the specially developed addition techniques for polymerising vinyl esters of branched fatty acids with acrylate monomers and styrene could be of value for applications other than electrodeposition e.g. conventional solvent borne systems.

MR VAN WESTRENEN said that this was certainly possible. In the screening of melamine resins to be used for the electrodeposition binders discussed, first draw-downs of the systems, only containing the solvents (no water, no amines) were always prepared and then stoved for an assessment of the curing characteristics. This assessment had clearly indicated that, when applied only in solvents, these systems possessed interesting properties. For such an application in practice, however, one would re-adjust the compositions of the polymer to some extent, as for example less carboxyl monomer was strictly needed or even desirable. Similarly, by re-adjusting the quantities of carboxyl and hydroxyl monomers, polymers could be prepared which were suitable for isocyanate cure.

MR D. E. EDDOWES, commenting on the range of systems examined, asked whether the transport number was the same in all cases.

MR VAN WESTRENEN said that one was dealing with a colloidal system which could not really be seen as a collection of individual ions. What was really important was that there should be an equilibrium between the feed material and the material drawn out of the bath by electrodeposition.

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The characterisation of glycol ethers by gas chromatography

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Summary

The gas chromatography of glycol ethers and their acetate esters is reported, using three polysiloxane stationary phases of varying polar character which exhibit essentially non-polar, donor and electron accepting properties. The esters find some application and may be used as derivatives formed by reaction in the column to confirm the presence of the glycol ethers.

Keywords

Solvents
glycol ethers

Processes and methods primarily associated with analysis, measurement and testing
gas chromatography

La caractérisation des éthers glycoliques par chromatographie en phase gazeuse

Résumé

On rend compte d'une investigation des éthers glycoliques et leurs esters acétiques par chromatographie en phase gazeuse, utilisant en tant que phase stationnaire trois formes de polysiloxane ayant de différentes caractéristiques polaires, à savoir non-polaire, donateur ou accepteur d'électrons. Ces esters ont des possibilités, et lors de leur formation sur la colonne ils peuvent être utilisés pour confirmer la présence des éthers glycoliques.

Die Charakterisierung von Glykoläthern mittels Gaschromatographie

Zusammenfassung

Ein Bericht über die Gaschromatographie von Glykoläthern und deren Azetatestern. Bei diesen Untersuchungen wurden drei stationäre Phasen von unterschiedlichem polaren Charakter benutzt, welche wesentliche nicht-polare Donor- und Akzeptor-Eigenschaften aufweisen. Für die Ester gibt es eine Anzahl von Anwendungsgebieten; sie können als Derivate, welche sich während der Reaktion in der Kolonne bildeten, benutzt werden, um die Anwesenheit des Glykoläthers zu bestätigen.

Характеризация гликолевых эфиров при помощи газовой хроматографии

Резюме

Описывается газовая хроматография гликолевых эфиров и их ацетатных эфиров, применяя три полисилоксановые стационарные фазы различной полярной характеристики, проявляющие преимущественно неполярные свойства доноров и электронных акцепторов. Эфиры находят некоторое применение и могут употребляться в качестве производных образующихся реакцией в колонне, для подтверждения присутствия гликолевых эфиров.

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Introduction

Whilst gas chromatography has found extensive acceptance in the surface coatings industry and is widely used for the characterisation of solvent mixtures and monomers, the emphasis has tended to be directed towards the lower boiling compounds. Detailed examinations have not yet been reported on the available glycol ethers and their homologues, which appear to be finding greater application in the apparently ever increasing number of speciality coatings and inks.

As unambiguous identification is not possible from a single gas chromatographic examination, a variety of supplementary procedures have been described. Whitham[1] examined fractions of solvent mixtures obtained by the use of the fluorescent indicator technique developed by Ellis and Le Tourneau[2]. Haslam and his co-workers[3] used two columns of different polarity and infra-red spectrophotometry to resolve complex mixtures. Gatrell[4] used a mixed stationary phase under isothermal conditions whilst Esposito and Swann[5] have used temperature programmed gas chromatography. Haken and McKay[6] have reported a method of analysis using sequential application of solubility tests supplemented, if necessary, with several effluent colour reactions.

Limited retention data on glycol ethers and their esters have been reported[6, 7, 8], the most extensive work being that of Esposito and Wagner[9], who used temperature programmed operation with two polar stationary phases. The use of gas chromatography in the examination of coating solvents has recently been reviewed[10] and retention data from a number of early reports concerning solvent analysis have been tabulated by Hundert[11].

Gas chromatographic retention data for glycol ethers, obtained by isothermal operation, are reported in this work, using three polysiloxane stationary phases of varying polar character. These are: the essentially non-polar phase OV-1, dimethyl polysiloxane; OV-25, with 50 per cent phenyl substitution and exhibiting some donor properties; and OV-210, with 50 per cent trifluoropropyl substitution and exhibiting electron accepting properties.

The acetate esters and several other high boiling solvents have also been examined, as certain of these find industrial use, whilst the esters are also of interest as derivatives which may be used to confirm the presence of the glycol ethers. The esters may be prepared as derivatives either externally or by reaction in the column, using a peak-shifting technique[12].

Experimental

Gas chromatography

The retention data were obtained on a modified F & M 810/29 Research Chromatograph with simultaneous flame ionisation and thermal conductivity detection, and fitted with an improved flow control system. Two 12ft × $\frac{1}{4}$in OD aluminium columns were packed with 10 per cent of the stationary phase on 60-80 mesh acid-washed and silanised Celite 560, and operated isothermally at 150°C.

With thermal conductivity detection, the following conditions were used: injection temperature, 190°C; detector temperature 220°C; bridge current, 150 ma; carrier gas, helium, with an inlet pressure of 40 psi.

Table 1
Retention data

Compound	Stationary phase									
	OV-1			OV-25			OV-210			
	V_g	V_R	I_R	V_g	V_R	I_R	V_g	V_R	I_R	Solubility % v/v
Methyl Cellosolve	0.189	0.27	620	0.462	0.72	837	0.482	0.91	872	c
Cellosolve	0.252	0.36	680	0.616	0.96	885	0.583	1.06	915	c
Butyl Cellosolve	0.681	0.973	889	1.611	2.511	1682	1.462	2.66	1145	c
Hexyl Cellosolve	1.82	2.60	1102	3.974	6.19	1270	3.413	6.44	1347	s (1.0)
Isopropyl Cellosolve	0.352	0.503	751	0.673	1.048	906	0.774	1.46	990	c
Isobutyl Cellosolve	0.603	0.862	866	1.088	1.695	1003	1.214	2.29	1100	c
Phenyl Cellosolve	3.486	4.95	1237	14.573	22.7	1528	8.692	16.40	1575	s
Ethyl-butyl Cellosolve	1.526	2.18	1064	2.889	4.50	1203	2.798	5.28	1152	s
Ucar LM	0.217	0.31	648	0.446	0.699	828	0.462	0.872	866	c
Ucar 2 LM	1.078	1.54	990	2.465	3.84	1172	2.210	4.17	1242	c
Propasol P	0.520	0.743	838	0.928	1.445	975	0.96	1.815	1043	c
Propasol B	0.789	1.14	928	1.445	2.25	1063	1.359	2.56	1126	s (7.0)
Methyl Carbitol	0.791	1.13	924	2.825	4.40	1198	2.13	4.02	1234	c
Carbitol	1.078	1.54	984	3.351	5.22	1235	2.412	4.55	1265	c
Butyl Carbitol	2.618	3.74	1177	7.832	12.2	1406	5.194	9.80	1447	c
Hexyl Carbitol	7.056	8.65	1354	19.838	30.9	1590	11.925	22.5	1646	s (2.0)
Diethyl Carbitol	1.442	2.06	1051	3.640	5.67	1250	2.035	3.84	1201	c
Dibutyl Carbitol	8.365	11.95	1421	19.324	30.1	1585	7.696	14.52	1563	i
Methyl Tri-Icinol	3.15	4.50	1217	12.615	19.65	1502	8.00	15.1	1552	c
Tri-Icinol	4.13	5.901	1274	15.158	23.61	1537	9.169	17.3	1585	c
Butyl Tri-Icinol	9.359	13.37	1448	35.31	55.0	1715	19.61	37.0	1768	c
Methyl Cellosolve acetate	0.434	0.62	795	1.271	1.98	1040	1.235	2.33	1101	c
Cellosolve acetate	0.588	0.84	858	1.650	2.57	1089	1.436	2.71	1139	p (23.0)
Butyl Cellosolve acetate	1.519	2.17	1063	4.032	6.28	1271	3.159	5.96	1330	s (1.6)
Hexyl Cellosolve acetate	3.92	5.60	1263	9.835	15.32	1453	6.864	12.95	1516	i
Isopropyl Cellosolve acetate	0.749	1.07	912	1.817	2.83	1110	1.945	3.67	1210	p
Isobutyl Cellosolve acetate	1.341	1.915	1031	2.767	4.31	1196	2.899	5.47	1306	i
Phenyl Cellosolve acetate	7.035	10.05	1385	30.94	48.2	1678	17.177	32.41	1736	s
Ucar LM acetate	0.511	0.73	825	1.194	1.86	1023	1.251	2.36	1106	c
Ucar 2LM acetate	2.198	3.14	1142	5.534	8.62	1335	4.653	8.78	1421	c
Propasol P acetate	1.113	1.59	995	2.208	3.44	1149	2.221	4.19	1245	s
Propasol B acetate	1.729	2.47	1090	3.422	5.33	1238	3.169	5.98	1528	i
Methyl Carbitol acetate	1.757	2.51	1094	6.42	10.0	1365	5.003	9.44	1437	c
Carbitol acetate	2.317	3.31	1152	7.897	12.30	1410	5.867	11.07	1475	[illegible]

	[illegible]	[illegible]	1090	[illegible]	[illegible]	1238	[illegible]	5.98	1528	[illegible]
Methyl Carbitol acetate	1.757	2.51	1094	6.42	10.0	1365	5.003	9.44	1437	c
Carbitol acetate	2.317	3.31	1152	7.897	12.30	1410	5.867	11.07	1475	c
Butyl Carbitol acetate	5.614	8.02	1137	18.49	28.8	1575	12.031	22.70	1650	s (6.6)
Hexyl Carbitol acetate	13.648	19.50	1526	43.977	68.5	1748	25.546	48.2	1832	i
Methyl Tri-Icinol acetate	6.72	9.6	1375	29.628	46.15	1670	18.921	35.7	1760	c
Tri-Icinol acetate	8.66	12.37	1430	35.182	54.8	1705	21.624	40.8	1794	c
Butyl Tri-Icinol acetate	19.39	27.7	1602	76.398	119.0	1865	46.11	87.0	1972	s
Ethylene glycol diacetate	0.924	1.32	953	3.030	4.72	1215	4.129	7.79	1389	c
3-Methoxy butyl acetate	0.973	1.39	966	2.253	3.51	1152	2.629	4.96	1285	c
3-Methoxy butanol	0.487	0.695	826	1.114	1.735	1009	1.364	2.46	1116	c
Pentoxol***	0.806	1.151	928	1.685	2.625	1093	1.977	3.73	1216	c
Methoxy hexanone	0.707	1.01	900	1.644	2.561	1090	2.306	4.35	1253	i
Methyl-isoamyl ketone	0.537	0.767	840	1.003	1.562	986	1.733	3.27	1184	i
Methyl-*n*-amyl ketone	0.614	0.878	869	1.297	2.02	1037	2.009	3.79	1220	i
Isophorone****	2.492	3.56	1168	6.812	10.61	1376	11.24	21.2	1631	i
Di-isobutyl ketone	0.549	1.356	962	1.451	2.26	1065	2.220	4.19	1245	i
Hexane	0.174	0.248	600	0.14	0.218	600	0.149	0.280	600	i
Heptane	0.276	0.395	700	0.232	0.361	700	0.232	0.438	700	i
Octane	0.431	0.630	800	0.400	0.622	800	0.356	0.661	800	i
Nonane	0.70	1.00	900	0.643	1.00	900	0.530	1.00	900	i
Decane	1.127	1.611	1000	1.050	1.630	1000	0.805	1.519	1000	i
Undecane	1.816	2.595	1100	1.731	2.691	1100	1.22	2.301	1100	i
Dodecane	2.927	4.180	1200	2.84	4.410	1200	1.85	3.490	1200	i
Tridecane	4.776	6.682	1300	4.632	7.195	1300	2.82	5.321	1300	i
Tetradecane			1400							
Hexadecane			1600							

***Registered trade name of Shell Chem. Ltd.

****3, 3, 5-Trimethylcyclohexene-2-one-1.

Key c completely soluble, p partially soluble, s sparingly soluble, i insoluble

The retention data of the compounds examined are shown in Table 1 as net retention (V_g), relative retention (V_R) using nonane as standard, and as retention indices (I_R).

The majority of the esters were prepared in the atlaborory using conventional esterification procedures with sulphuric acid or ion-exchange resins as catalysts, and were purified before use.

On-column reaction

The peak-shifting technique involves *in situ* chemical reaction of the hydroxyl group with the formation of the ester derivative in the column. The injection of the sample (0.1μl) was followed within 2-5 seconds by an injection (0.5μl) of the esterifying agent. Acetic anhydride containing 0.5 per cent sulphuric acid is satisfactory, whilst almost quantitative conversion is achieved using acetyl chloride[12].

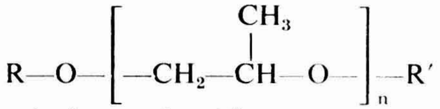
Nomenclature

While the compounds examined have many trade names[13] the Union Carbide product names are widely known and, for convenience, these are used where applicable.

The series of glycol ethers studied have the general structure

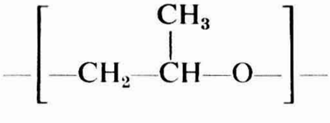
$$\mathrm{R{-}O{-}[{-}CH_2{-}CH_2{-}O{-}]_n{-}R'}$$

where R is an alkyl group, R′ is a hydrogen atom or acetate group, and n is the number of ($CH_2{-}CH_2{-}O$) groups. When n is one, two or three, a homologous series of ethylene glycol, diethylene glycol, and triethylene glycol monoalkyl ethers result, and are represented by the Cellosolve*, Carbitol* and Tri-Icinol** series, respectively.

A similar series has the basic structure 

$$\mathrm{R{-}O{-}}\left[\mathrm{{-}CH_2{-}}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}\mathrm{{-}O{-}}\right]_n\mathrm{{-}R'}$$

where R and R′ are as described above and n is the number of



$$\mathrm{{-}}\left[\mathrm{{-}CH_2{-}}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}\mathrm{{-}O{-}}\right]\mathrm{{-}}$$

groups.

The compounds Ucar LM*, Proposol P* and Proposol B*, where n has a value of one and R values of 1, 3 and 4 carbon atoms respectively, were examined, together with Ucar 2LM*, where n is 2 and R is 1. In each case the hydroxyl compound and the acetylated derivative were used.

Results

The retention data of the compounds examined are shown in Table 1. The

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*Registered trade name of Union Carbide Corporation.

**Registered trade name of ICI Ltd.

various homologous series are plotted in Fig. 1 on the three stationary phases, from which it is apparent that the retention indices of the polar compounds are increased as the general polar character of the column is increased. The

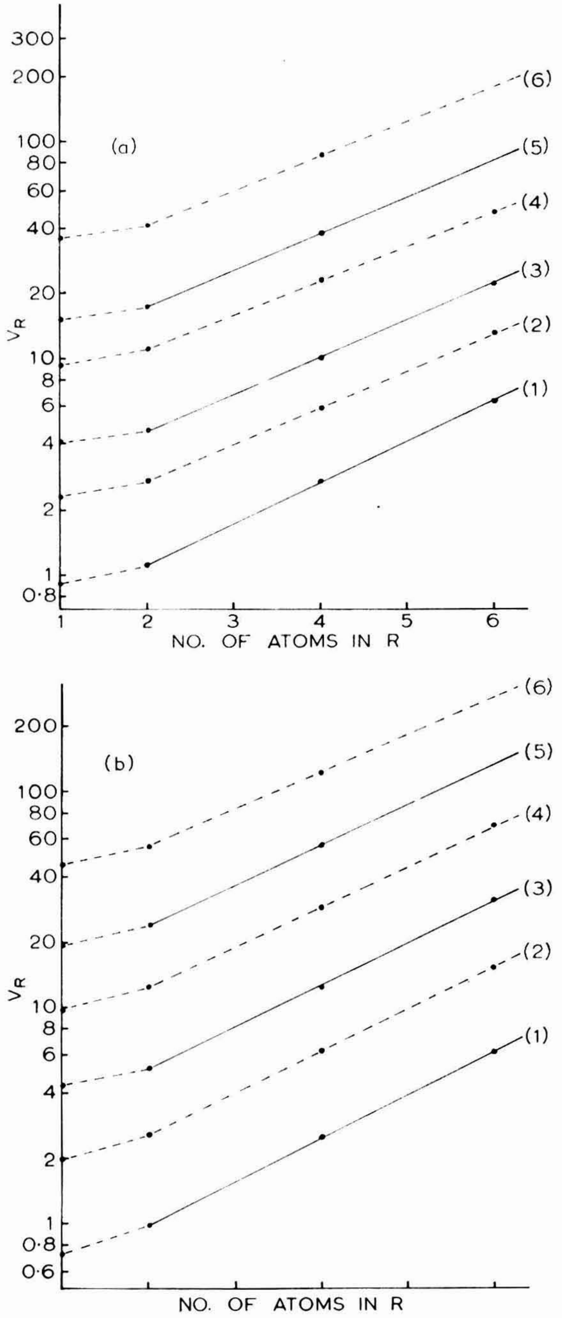

Fig. 1 (see over)

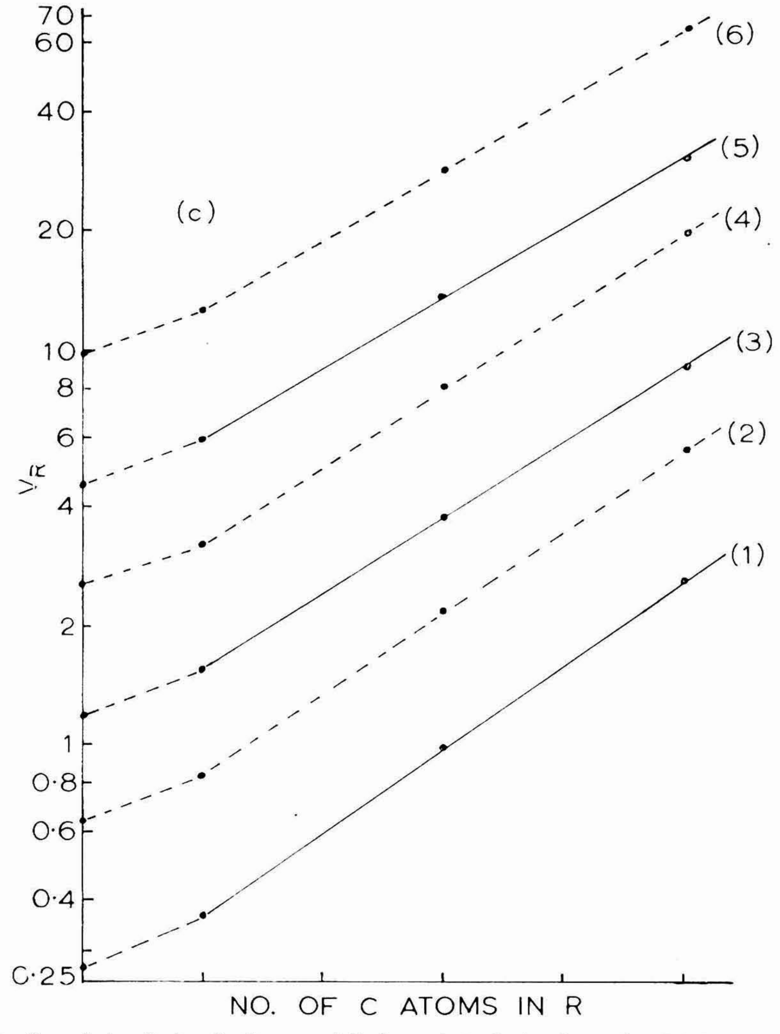

Fig. 1. Retention plots of glycol ethers and their acetate derivatives with (a) OV-210 dimethyl trifluoropropyl (50%) polysiloxane (b) OV-25 dimethyl phenyl (50%) polysiloxane and (c) OV-1 dimethyl polysiloxane as the stationary phase. Series: (1) Cellosolve, (2) Cellosolve acetate, (3) Carbitol, (4) Carbitol acetate, (5) Tri-Icinol, (6) Tri-Icinol acetate

effect of non-polar compounds is shown by the behaviour of the paraffinic hydrocarbons used as reference compounds, which are more rapidly eluted as the general polar character of the phase is increased. A nearly parallel series of plots is observed with the various series on the three phases. The slopes of the three sets of data are not equal, as the OV-1 plots have a considerably greater slope than that observed with the other two columns.

An alternative representation of the data is shown in Fig. 2, where the number of ether groups present forms the abscissa. A series of parallel linear relationships is observed for the methyl, ethyl, butyl and hexyl ethers, and such plots may be used to estimate the retention of a homologue that may not be available. This type of relationship, which considers some structural feature of a portion of the molecule rather than the total molecule, i.e. carbon number, has been used with success in the tentative identification of a variety of unsaturated esters[14, 15]. Confidence in a tentative identification is enhanced by the use of two columns of varied polarity. The particular behaviour of the compounds on the two stationary phases is apparent from Fig. 2 by the relative separation of the plots of the individual series.

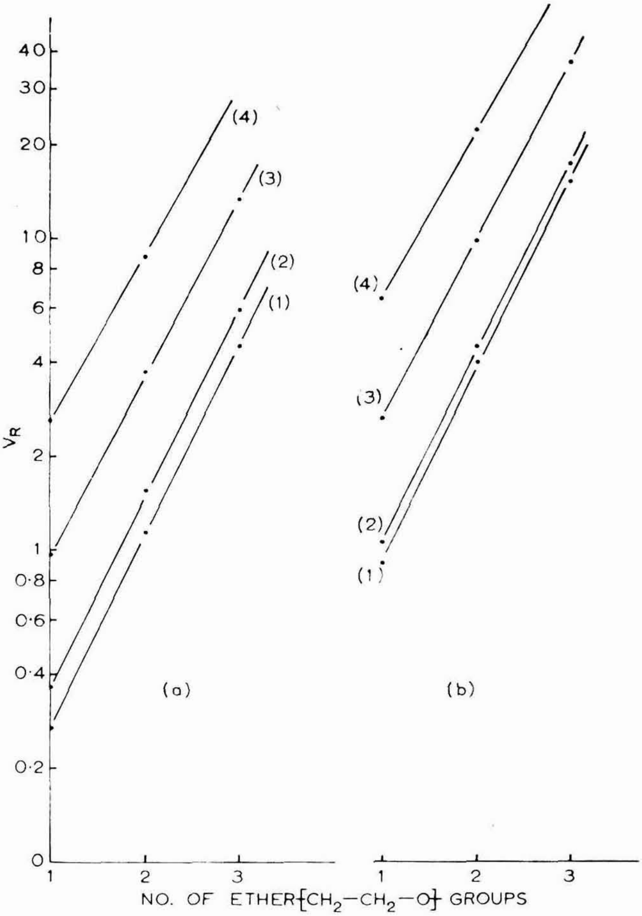

Fig. 2. Retention plots showing (1) methyl (2) ethyl (3) butyl and (4) hexyl ethers on (a) OV-1 and (b) OV-210 stationary phases

The formation of the acetate derivative by chemical reaction in the column is shown in Fig. 3. The chromatogram (a) is that of 0.1μl of a mixture of Cellosolve and methyl Carbitol. The chromatogram (b) shows the peak-shifting technique by the appearance of peaks due to the acetate esters formed by *in situ* reaction of the sample with 0.5μl of the acetylating agent. The technique is of particular value where peaks may be superimposed, as frequently occurs with, for instance, hydrocarbon fractions, where a separation of the peaks assists in the identification. With hydrocarbons and superimposition of the glycol ethers, a change in column polarity is also frequently advantageous. With an increase in the general polar character of the column material, hydrocarbons of similar retention on a non-polar phase, i.e. elution essentially following boiling point, tend to be separated owing to structure with elution order paraffins, olefins, and aromatics, whilst the elution of glycol ethers is significantly retarded with this polarity change.

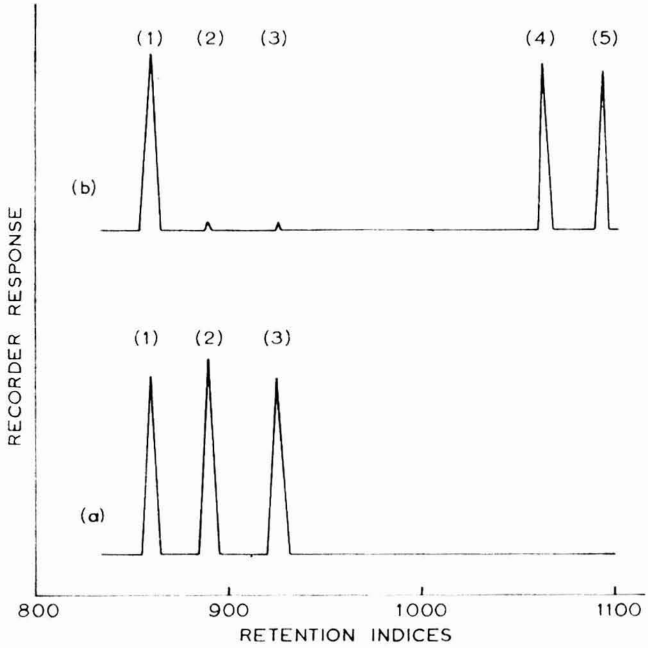

Fig. 3. On-column chemical reaction. Chromatogram (a) is that of a mixture of (1) Cellosolve acetate (2) butyl Cellosolve and (3) methyl Carbitol. Chromatogram (b) after reaction shows peaks (4) butyl Cellosolve acetate and (5) methyl Carbitol acetate

Whilst a series of chromatographic injections and the application of reaction gas chromatography require only a few microlitres of sample, a difference in the chromatogram may often be achieved by solvent extraction if larger samples are available[6, 10]. Relatively few of the higher boiling solvents are water soluble and the glycol ethers may be removed by shaking 2.5ml of sample with an equal volume of water in a 5ml graduated cylinder. The sample size may be reduced if smaller graduated vessels are available, but with small diameter vessels a metal probe is required to facilitate mixing. The solubility of the glycol ethers is shown in Table 1 and, considering the example shown in Fig. 3, it is apparent that the first peak in chromatogram (a) will remain after aqueous extraction, whilst the other two will essentially be removed. Chromatography of the resulting organic layer after extraction by vigorous shaking will show that minor residual glycol ether peaks, i.e. usually less than 0.2 per cent, remain.

Acknowledgments

One of us (V. Khemangkorn) is grateful for the award of a Colombo Plan Scholarship during the period over which this investigation was conducted.

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Water transport through paint films Part V: Pigmented films

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Summary

The water transport in paint films consisting of two binders with two different pigments has been investigated. The variation of the permeability, solubility and diffusion coefficients with the pigment volume fraction under varying conditions has been determined.

The two pigments used were an untreated titanium dioxide and a non-setting red lead, representing two quite different types of the many pigments used in paint manufacture. It was found that the two pigments caused large differences in the water transport through the paint films.

The experimental results are qualitatively in accordance with a model proposed to describe the water permeation in pigmented films. For an impermeable and inert pigment incorporated in a binder, a decrease of the permeability coefficient with increase of the pigment volume fraction is to be expected. When pigment aggregates are formed in the film, higher values were found for the permeability coefficient than would be expected.

It was shown that this was caused by the air entrapped in the film. For the system alkyd resin/red lead, lower permeability coefficients than those expected were found. This was explained on the basis that the pigment interacted with the binder.

Keywords

Prime pigments and dyes
red lead
titanium dioxide

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

Binders, resins, etc.
alkyd resin
epoxy resin

Transport de l'eau à travers des feuils de peintures. Vème. Partie: Feuils pigmentés

Résumé

On a examiné le transport de l'eau à travers les feuils de peintures composés de deux liants et de deux pigments différents. On a déterminé, sous des conditions variées, la variation des coéfficients de perméabilité, de solubilité, et de diffusion en fonction de la fraction pigmentaire par volume.

Les deux pigments, un dioxyde de titane non-traité, et un minium de plomb "non-setting," représentent deux types tout à fait différents parmi les plusieurs pigments utilisés dans la fabrication de peintures. On a trouvé que ces deux pigments provoquent des différences importantes dans le transport de l'eau à travers les feuils de peintures.

Les résultats expérimentaux sont en accord, au titre qualitatif, avec le modèle proposé pour décrire la pénétration de l'eau en feuils pigmentés. On doit s'attendre une diminution de la coéfficient de la fraction pigmentaire par volume, dans le cas où il s'agit d'un pigment, inerte et imperméable, incorporé dans un liant. Quand des agrégats pigmentaires se forment dans le feuil on trouve des coéfficients de perméabilité plus élevés que l'on devrait s'attendre. On a demontré que cela est provoqué par l'air occlus dedans le feuil. A l'égard du système résine alkyde/minium de plomb, on a trouve les coéfficients de perméabilité plus bas que l'on devrait s'attendre. C'était expliqué sur la base d'une interaction pigment/liant.

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Wassertransport durch Anstrichfilme. Teil V: Pigmentierte Filme

Zusammenfassung

Der Wassertransport in aus zwei Bindemitteln und zwei verschiedenen Pigmenten bestehenden Anstrichfilmen wurde geprüft. Die Änderung von Durchlässigkeit, Löslichkeit und Diffusionskoeffizienten mit der Pigmentvolumenfraktion unter verschiedenen Bedingungen wurde bestimmmt.

Die beiden benutzten Pigmente waren ein unbehandeltes Titandioxid und eine nichtabsetzende Bleimennige. Diese stellten zwei ganz verschiedene Typs unter den zahlreichen in der Lackfabrikation benutzten Pigmenten dar. Es wurde gefunden, dass die beiden Pigmente grosse Unterschiede im Wassertransport durch die Anstrichfilme verursachten.

Die experimentellen Resultate stehen qualitativ in Einklang mit einem Modell, das vorgeschlagen wird, um die Wasserdurchdringung pigmentierter Filme zu beschreiben. Für ein undurchlässiges und inertes Pigment in einem Bindemittel ist Verminderung des Durchlässigkeitskoeffizienten bei Vergrösserung der Pigmentvolumenfraktion zu erwarten. Wenn sich im Film Pigmentaggregate bildeten, wurden für den Durchlässigkeitskoeffizienten höhere Werte als erwartet gefunden.

Es wurde festgestellt, dass dies durch Lufteinschlüsse im Film hervorgerufen wird. Für das System Alkydharz Bleimennige wurden niedrigere Durchlässigkeitskoeffizienten als erwartet, gefunden. Die Erklärung dafür war, dass das Pigment mit dem Bindemittel reagierte.

Перенос воды в красочных пленках
Часть V. Пигментированные пленки

Резюме

Анализировался перенос воды в красочных пленках состоящих из двух крепителей с двумя различными пигментами. Определялось изменение в коэффициентах проницаемости, растворимости и диффузии с изменением пигментной объемной фракции в различных условиях.

Применялись два пигмента: необработанная двуокись титана и неоседающий свинцовый сурик, которые являются двумя совершенно разными типами среди многих пигментов применяемых в красочной промышленности. Найдено что эти два пигмента вызвали большую разницу в переносе воды в красочных пленках.

Экспериментальные результаты согласуются качественно с моделью предложенной для описания проникания воды в пигментированных пленках. Для непроницаемого и инертного пигмента включенного в крепителе, можно ожидать уменьшения в коэффициенте проницаемости с увеличением пигментной объемной фракции. Когда пигментные агрегаты образуются в пленке, обнаруживались более высокие значения коэффициента проницаемости чем можно было ожидать.

Показано что это вызывалось воздухом улавливаемым в пленке. Для системы алкидная смола/свинцовый сурик, были найдены более низкие коэффициенты проницаемости чем ожидаемые. Это объяснялось тем фактом что пигмент реагировал с крепителем.

Introduction

To investigate the process of water transport through pigmented films is obviously of practical, as well as of theoretical, interest. However, owing to the pigment incorporation, the number of factors to be considered in such investigations is greater than with non-pigmented films.

A quantitative treatment has only been given[1] for certain penetrants, such as simple gases and non-polar vapours and liquids, and for media consisting of polymers and a well dispersed filler having a well defined particle form and size (*q.v.*).

For more complicated systems, only qualitative treatments could be found in the literature[2, 3, 4]. No rigorous treatment exists for the water transport through filled media.

With respect to paints, relatively few attempts to investigate water transport through pigmented films have been made. Most of the published work[5, 6, 7] is only descriptive. The possible effects of pigmentation on water permeation were discussed by Michaels[8]. He pointed out that the incorporation of the pigment into the binder may reduce or increase the permeability of water relative to that of the binder, depending on the pigment volume fraction, the chemical constitution and geometry of the pigment, degree of dispersion, etc. Funke *et al.*[9, 10] found that the water absorbed by the pigmented films may be related to the pigment volume fraction (λ_p) in three different ways, viz: the water absorption is independent or decreases with the increase of λ_p; the water absorption increases steadily with increasing λ_p; and the water absorption has a maximum at relatively low λ_p. They related these dependencies to the strength of adhesion between the pigment and the binder.

In the previous papers[11, 12, 13, 14] on transport of water through non-pigmented films, large differences in the water permeation, sorption and diffusion were found for different materials. This was due to the specific water/polymer interaction and the formation of clusters of water in the film.

This paper deals with the influence of pigmentation on the water transport for a non-treated titanium dioxide and for a non-setting red lead in two different binders.

A permeation model for pigmented films

A model is proposed to describe water permeation through pigmented films. The arrangement of the binder (*b*) and the pigment (*p*) in the film is assumed to be as follows: a part of the binder is in series with the pigment, while the rest of the binder is in parallel with this system.

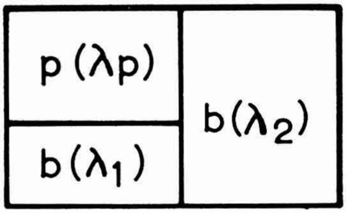

Fig. 1. Permeation model for pigmented films

The volume fraction of the binder in series with the pigment is denoted by λ_1, and the rest of the binder (in parallel) is denoted by λ_2 (see Fig. 1).

If, for the whole system:

$$\lambda_p + \lambda_1 + \lambda_2 = 1 \quad \text{.........................}(1)$$

then the permeability coefficient of the total system, P_t, is:

$$P_t\,(\lambda_p + \lambda_1 + \lambda_2) = P_t = \lambda_l P_l + \lambda_2\, P_b \quad \text{...............}(2)$$

In this equation

$$\lambda_I = \lambda_1 + \lambda_p \quad \ldots\ldots\ldots\ldots (3)$$

where in equation 2:

P_b = permeability coefficient of the binder,

P_I = permeability coefficient of that part of the model in which the pigment and the binder are in series. In this region reciprocal permeabilities are additive:

$$\frac{\lambda_I}{P_I} = \frac{\lambda_1 + \lambda_p}{P_I} = \frac{\lambda_1}{P_b} + \frac{\lambda_p}{P_p}$$

or,

$$P_I = \frac{(\lambda_1 + \lambda_p)\, P_b P_p}{\lambda_1 P_p + \lambda_p P_b} \quad \ldots\ldots\ldots\ldots (4)$$

Introduction of equations 3 and 4 into equation 2 gives:

$$P_t = \frac{(\lambda_1 + \lambda_p)^2\, P_b P_p}{\lambda_1 P_p + \lambda_p P_b} + \lambda_2 P_b \quad \ldots\ldots\ldots\ldots (5)$$

By denoting:

$$\frac{\lambda_1}{\lambda_p} = \alpha \quad \ldots\ldots\ldots\ldots (6)$$

$$\text{and } \lambda_1 + \lambda_2 = \lambda_b \quad \ldots\ldots\ldots\ldots (7)$$

where λ_b is the volume fraction of the binder in the film, equation (5) can be rewritten as:

$$P_t = \frac{P_p P_b \lambda_p (1 + \alpha)^2}{P_b + \alpha P_p} + (\lambda_b - \alpha\lambda_p)\, P_b \quad \ldots\ldots\ldots\ldots (8)$$

When the permeation of water through the pigment is zero ($P_p = 0$) (which for the pigments under consideration seems to be a reasonable approach) the repartition factor α can easily be determined. Then equation (8) transforms to:

$$P_t = (\lambda_b - \alpha\lambda_p)\, P_b \quad \ldots\ldots\ldots\ldots (9)$$

since $\lambda_b + \lambda_p = 1$, equation (9) can be rewritten as:

$$P_t = (1 - \lambda_p - \alpha\lambda_p)\, P_b \quad \ldots\ldots\ldots\ldots (10)$$

From which:

$$\alpha = \frac{P_b - P_t}{P_b\, \lambda_p} - 1 \quad \ldots\ldots\ldots\ldots (11)$$

Since P_b and P_t can be determined experimentally, the repartition factor α can be calculated.

If the pigment particles are incompletely wetted by the binder, pigment aggregates containing air can be formed in the film. For such a situation, the model must describe a three-component system. As a function of the volume fraction of air which actually takes part in the permeation process, P_t may have higher, the same, or lower values than P_b. This situation will be considered later. Other complications may arise if the pigment particles interact with the binder, and the resultant product has different properties from those of the bulk binder.

Another model which could be used takes into consideration the tortuosity, i.e. the increase in the diffusion length, caused by the presence of the pigment particles in the film[1, 2, 3]. Thus, for a pigmented film—composed of an inert pigment impermeable to the penetrant action, but perfectly dispersed into a binder—for which the fraction of area occupied by the binder in any cross-section is taken to be equal to the volume fraction of the binder, it follows that:

$$P_t = \frac{1}{k} \lambda_b P_b = \frac{1}{k} (1 - \lambda_p) P_b \quad \ldots\ldots (12)$$

The tortuosity factor k, as introduced in equation (12), depends on λ_p and on the pigment geometry.

For a perfect dispersion of particles of a well-defined form and size, such as spheres, cubes and plates, the dependence of k on λ_p can be calculated[2, 3, 15].

In the case where the pigment particle size approaches zero, k will approach 1 and α will approach zero. Thus, it follows from equations (10) and (12) that:

$$P_t = (1 - \lambda_p) P_b \quad \ldots\ldots (13)$$

The advantage of the model described by equation (8) when compared with the tortuosity model, equation (12), is that it can predict the minimum permeability through pigmented films without considering the tortuosity. In most cases, the pigment particles in the paint films are present as aggregates of different forms and sizes. Therefore, the tortuosity factor can rarely be determined accurately. The model proposed can also be used when the pigment particles (or aggregates) are permeable to the penetrant.

Experimental

The influence of pigmentation on the water transport was investigated using two pigments and two binders.

Pigments: A well water-washed, non-treated titanium dioxide (Kronos R, d = 4.2), and a reactive pigment—red lead (non-setting, PbO_2 34 per cent, d = 8.9).

Binders: An air drying medium oil length alkyd, and an epoxy resin.

The properties of the binders were described in an earlier paper[11]. Concentrated pastes were prepared in white (porcelain) ball mills, until the fineness of grind reached 7-8 Hegman units for the titanium dioxide, and 5-6 Hegman units for the red lead.

Paints having different pigment volume fractions were prepared by dilution of the paste with binder, according to:

$$\lambda_p = \frac{V_p}{V_p + V_b} \quad \ldots\ldots (14)$$

In equation (14), V_p and V_b represent the volume of pigment and binder in the dry film, respectively. For ageing, the paints were left on a roll (for 30 days) after milling. The film preparation technique was identical to that used for the non-pigmented films[11].

Method

The sorption and the permeation measurements were carried out under the same conditions of time, temperature and relative humidities, as for the non-pigmented films[11]. Each measurement was made in triplicate.

Results and discussion

Because the pigmented films investigated behave differently, the results from each will be discussed separately.

Films pigmented with TiO_2

Permeation measurements: The permeability coefficients P_t as calculated from the permeation measurements are shown in Table 1, and in Figs. 2 and 3 for the alkyd resin and the epoxy resin, respectively.

Table 1

Permeability coefficients under different experimental conditions

Film	$p_1 - p_2$ mm Hg		$Pt \times 10^9$ (g cm^{-1} h^{-1} mmHg^{-1})							
			λ_p							
			0	0.5	0.10	0.15	0.20	0.25	0.3	0.4
AT	17.53	15.78	63.5	60.5	—	56.7	51.0	—	45.7	—
	17.53	13.15	47.6	45.6	—	39.4	35.0	—	32.2	—
	17.53	0	28.0	26.0	—	22.4	21.0	—	19.0	—
	2.63	0	9.6	8.5	—	7.2	6.4	—	6.2	—
ET	17.53	15.78	21.2	—	21.1	22.4	21.2	23.0	22.6	—
	17.53	13.15	16.5	—	15.4	15.4	15.6	16.0	15.9	—
	17.53	0	12.00	—	11.9	12.8	11.5	11.5	11.5	—
	2.63	0	6.35	—	6.0	6.3	6.0	6.1	5.6	—
AR	17.53	15.78	63.5	33.5	31.1	—	29.9	—	26.5	24.2
	17.53	13.15	47.6	27.5	26.8	—	23.5	—	20.8	18.1
	17.53	0	28.0	19.5	17.4	—	15.2	—	13.9	11.0
	2.63	0	9.6	6.5	5.7	—	5.3	—	4.6	4.1
ER	17.53	15.78	21.2	—	20.5	—	18.3	—	16.3	14.3
	17.53	13.15	16.5	—	16.0	—	14.6	—	12.9	11.0
	17.53	0	12.0	—	12.0	—	11.1	—	10.0	9.1

AT = alkyd resin with TiO_2; ET = epoxy resin with TiO_2; AR = alkyd resin with red lead; ER = epoxy resin with red lead; p_1 and p_2 = water vapour pressures on both sides of the film; λ_p = pigment volume fraction.

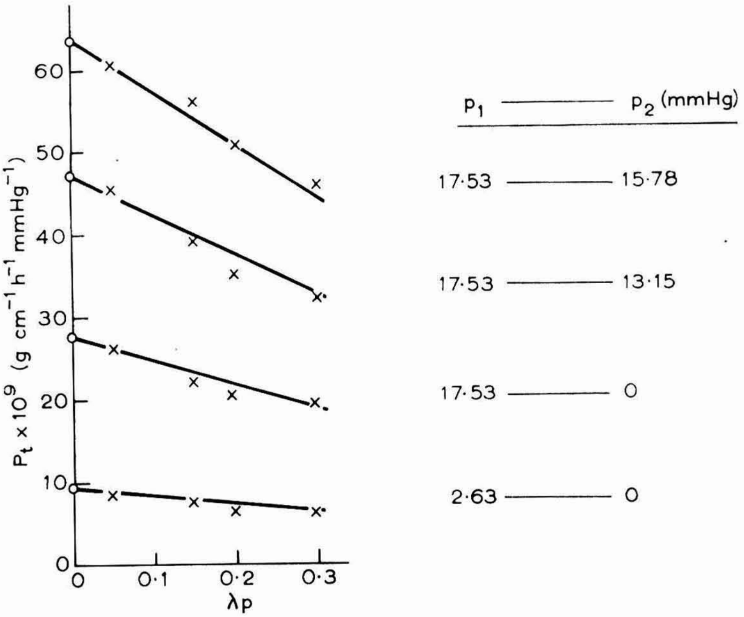

Fig. 2. **Alkyd resin/TiO$_2$. Permeability coefficient (P$_t$) versus pigment volume fraction (λ$_p$), under different experimental conditions**

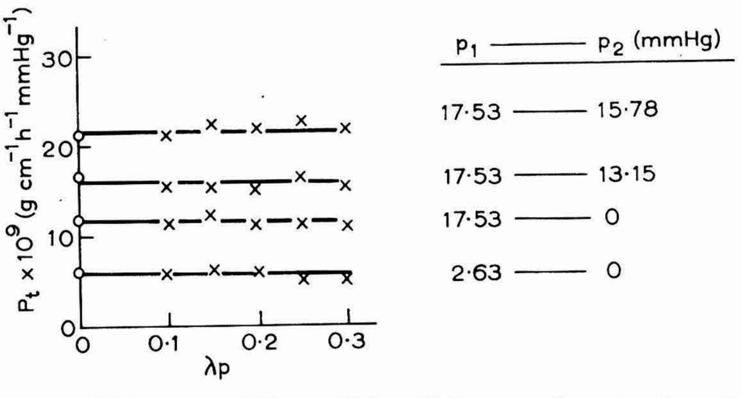

Fig. 3. **Epoxy resin/TiO$_2$. Permeability coefficient (P$_t$) versus pigment volume fraction (λ$_p$), under different experimental conditions**

For the alkyd resin (AT), it was found that the experimental results fit the curves expressed by:

$$P_t = \lambda_b P_b = (1 - \lambda_p) P_b \qquad (13)$$

As already shown, such behaviour is to be expected if the pigment particles in the film are impermeable to water ($P_p = 0$), small ($\alpha \simeq 0$, or $k \simeq 1$), and well dispersed. An examination of a cross-section, see Fig. 4, confirms that the pigment particles are small (0.2 — 0.4μm) and well dispersed in the binder.

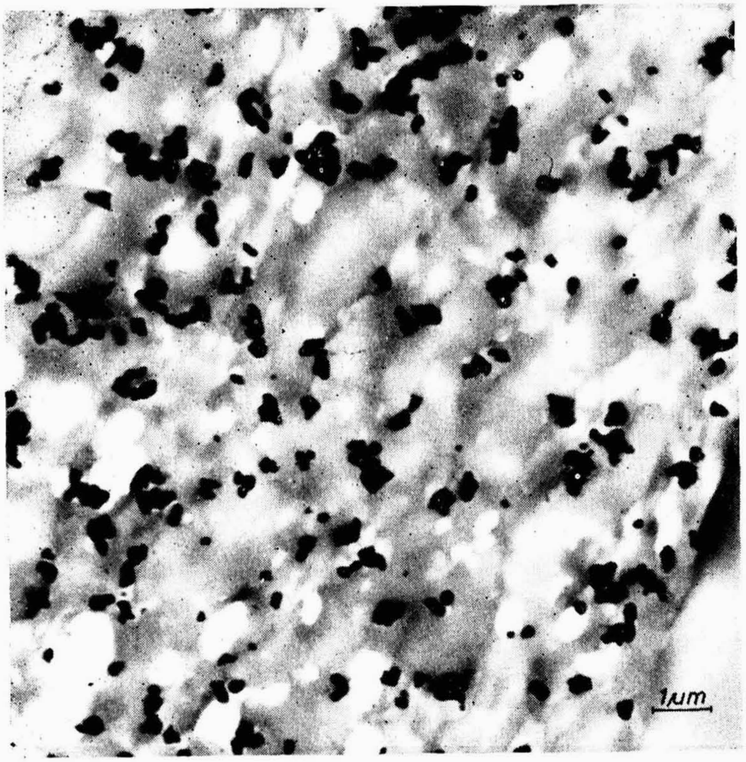

Fig. 4. Part of a cross-section (× 11,700) of an alkyd resin/TiO_2 film ($\lambda_p = 0.1$)

For the epoxy resin (ET), the results are quite different. P_t appears to be equal to the permeability coefficient of the binder, P_b, for all λ_p-values investigated, and independent of the experimental conditions. This finding can only be explained on the basis of equation (8) if the water permeability of the pigment and that of the binder are equal ($P_p = P_b$). This cannot be true, because the pigment itself is not permeable to water. However, as previously shown, the pigment particles may be incompletely wetted by binder. In this case, porous aggregates which contain air may be present in the film[1, 2]. An examination of a cross-section, as well as density measurements of the films, show this to be the case for the system epoxy resin/TiO_2. Fig. 5 shows that the pigment particles are unequally dispersed in binder. From Fig. 6 and Table 2, it can be seen that the determined densities (d_t) have lower values than those given[2] by:

$$d_c = \lambda_b d_b + \lambda_p d_p \qquad \ldots\ldots\ldots\ldots\ldots\ldots (15)$$

in which the additivity of volumes was assumed. In equation (15), d_b and d_p represent the density of binder and pigment, respectively.

Fig. 5. Part of a cross-section (× 11,700) of an epoxy resin/TiO_2 film ($\lambda_p = 0.1$)

The volume fraction of air, λ_a, present in ET-films, as estimated from the values of d_c and d_t, is about 0.06-0.07. For AT (see Table 2), the values of d_c are in agreement with those observed experimentally, d_t.

The volume fraction of air which influences the permeation process can be approximated. For this purpose, a model representing the porous aggregates will be used (see Fig. 7). This model, in which the pigment particles, λ_p, are

Table 2

d_c (density values as calculated from equation (15)); and d_t (determined density) of some pigmented films

		λ_p						
		0.5	0.1	0.15	0.2	0.25	0.3	0.4
AT—	d_c ..	1.36	—	1.66	1.81	—	2.11	—
	d_t ..	1.30	—	1.68	1.80	—	2.10	—
ET—	d_c ..	—	1.46	1.61	1.77	1.92	2.07	—
	d_t ..	—	1.36	1.51	1.62	1.80	1.90	—
ER—	d_c ..	—	1.93	—	2.70	—	3.48	4.25
	d_t ..	—	1.73	—	2.38	—	3.18	3.85

$d_{\mathrm{TiO_2}} = 4.2$; $d_{\text{alkyd resin}} = 1.22$; $d_{\text{red lead}} = 8.9$; $d_{\text{epoxy resin}} = 1.16$.

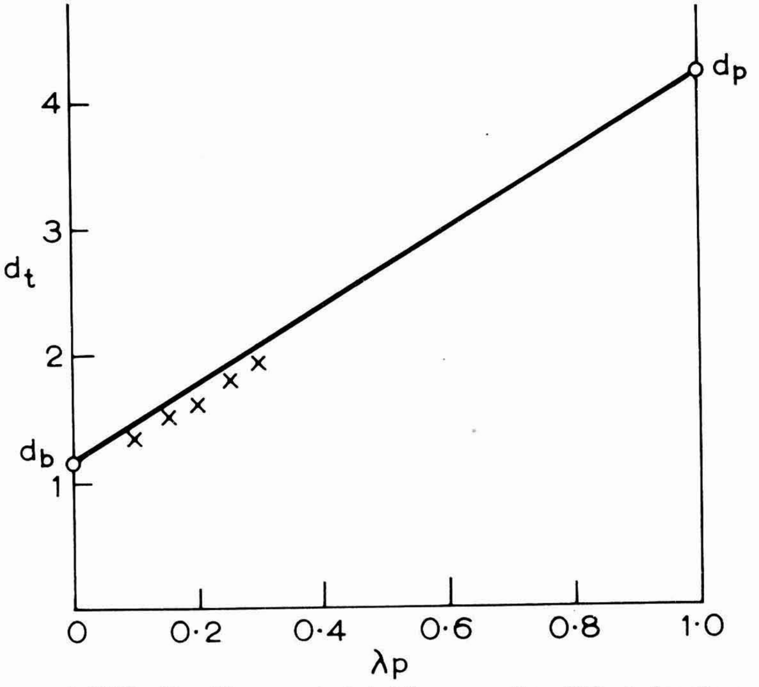

Fig. 6. Epoxy resin/TiO$_2$. Densities as calculated from equation (15), d_c (continuous line) and observed densities d_t(X) versus λ_p

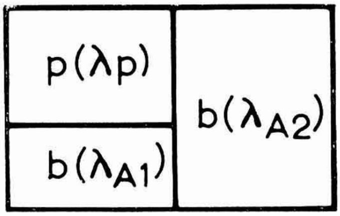

Fig. 7. Permeation model for porous aggregates

assumed to be arranged with air, in series, λ_{A_1}, and in parallel, λ_{A_2}, is similar to the one already described (see Fig. 1). Therefore:

$$P_{tp} = \frac{P_A P_p (\lambda_{A_1} + \lambda_p)^2}{\lambda_{A_1} P_p + \lambda_p P_A} + \lambda_{A_2} P_A \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

In this equation P_{tp}, P_p and P_A represent the permeability coefficients of water in the porous aggregate, of the pigment particles, and of air, respectively. Because the TiO_2 particles are impermeable to water ($P_p = 0$), it follows that equation (16) can be reduced to:

$$P_{tp} = \lambda_{A_2} P_A$$

As already shown for ET-films, P_{tp}, equal to P_b . P_A, was found in the literature[16] to be $\simeq 10^{-4}$ ($gcm^{-1}h^{-1}mm\ Hg^{-1}$). From which, $\lambda_{A_2} \simeq 0.0002$. It follows that the volume of air ($\lambda_a = \lambda_{A_1} + \lambda_{A_2}$) incorporated in the porous aggregates is more than sufficient to increase the water permeability through the porous aggregates to a value close to that of the binder.

Sorption measurements: From the sorption measurements the solubility coefficients, S_t, were calculated. Some of the results obtained are represented in Figs. 8 and 9 for AT and ET, respectively (see also Table 3).

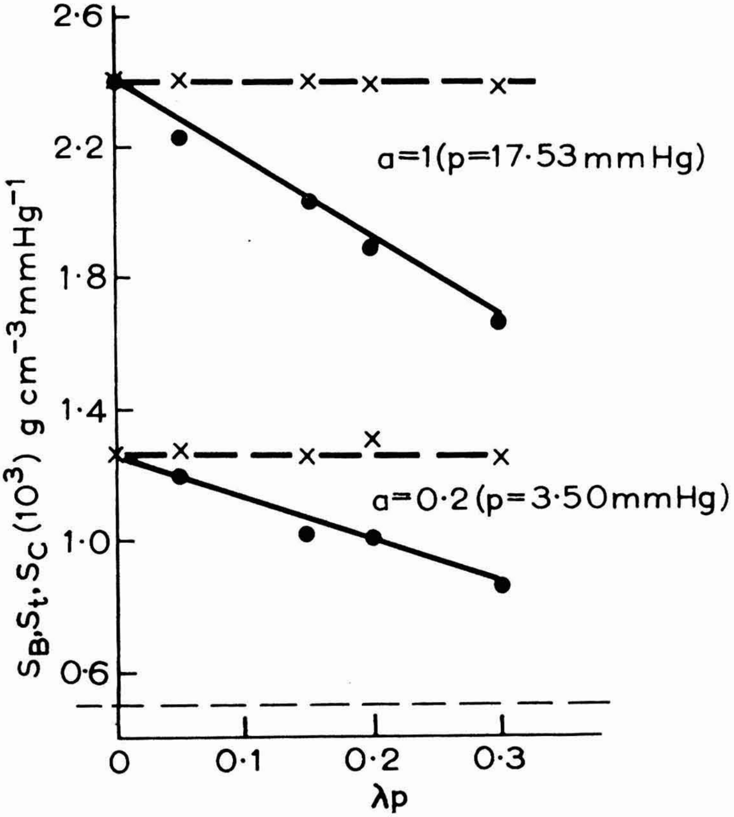

Fig. 8. Alkyd resin/TiO_2. S_B(X), S_t(●) and S_c (continuous line) versus λ_p, under two experimental conditions

Table 3

Solubility coefficients under two experimental conditions

		$S_B \times 10^3$, $S_c \times 10^3$, $S_t \times 10^3$ (g cm^{-3} mm Hg^{-1})							
		λ_p							
		0	0.05	0.10	0.15	0.20	0.25	0.30	0.40
AT–S_B	a = 1 ..	2.42	2.40	—	2.39	2.41	—	2.39	—
	a = 0.2 ..	1.24	1.28	—	1.25	1.30	—	1.25	—
S_c	a = 1 ..	2.42	2.28	—	2.04	1.93	—	1.69	—
	a = 0.2 ..	1.24	1.18	—	1.06	1.00	—	0.87	—
S_t	a = 1 ..	2.42	2.24	—	2.03	1.90	—	1.66	—
	a = 0.2 ..	1.24	1.20	—	1.04	1.02	—	0.85	—
ET–S_B	a = 1 ..	1.01	—	1.04	1.00	1.01	0.99	1.02	—
	a = 0.2 ..	1.54	—	1.50	1.48	1.48	1.46	1.56	—
S_c	a = 1 ..	1.01	—	0.91	0.85	0.81	0.75	0.71	—
	a = 0.2 ..	1.54	—	1.38	1.31	1.23	1.15	1.08	—
$S_t{}^1$	a = 1 ..	1.01	—	0.91	0.84	0.81	0.74	0.70	—
	a = 0.2 ..	1.54	—	1.36	1.28	1.18	1.12	1.04	—
AR–S_t	a = 1 ..	2.42	1.82	1.60	—	1.44	—	1.37	1.17
	a = 0.2 ..	1.20	1.07	1.04	—	0.87	—	0.78	0.66
ER–S_B	a = 1 ..	1.01	—	0.99	—	1.03	—	1.02	0.99
	a = 0.2 ..	1.54	—	1.50	—	1.58	—	1.45	1.50

S_B = experimental data as calculated per unit volume of binder; S_t = experimental data as calculated per unit volume of pigmented film; $S_t{}^1$ = after the density correction; S_c = as calculated from equation (18).

These figures show that the solubility coefficients, when calculated per unit volume of binder ($S_B = G/V_b . p$; gλ cm^{-3} mmHg^{-1}) for all the materials at constant activities of the water, do not vary with λ_p. This virtually means that the pigment in the film does not take up water, and that pigment incorporation into the binder does not affect its sorption characteristics.

From the above it also follows that:

$$S_c = (1 - \lambda_p)\, S_b + \lambda_p S_p \quad \ldots\ldots\ldots\ldots (17)$$

Since the solubility coefficient of the pigment is zero ($S_p = O$), therefore:

$$S_c = (1 - \lambda_p)\, S_b \quad \ldots\ldots\ldots\ldots (18)$$

In Figs. 8 and 9, the dependence of S_c on λ_p is represented by a continuous line, and that of the experimental data (S_t) by black circles.

For AT, a good agreement between the values of S_t and those of S_c is obtained.

For ET the agreement is also obtained, but only after the density corrections have been made. This can be explained only if the air incorporated in the film

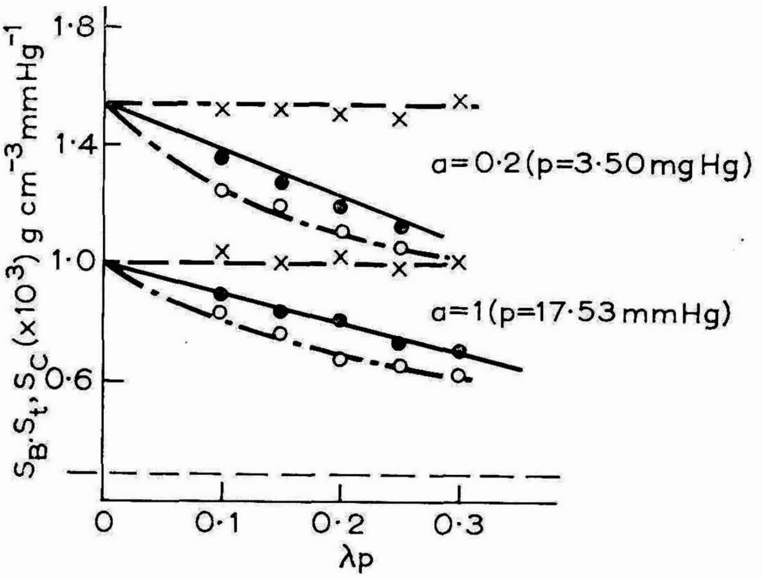

Fig. 9. Epoxy resin/TiO$_2$. S_B(X), S_c (continuous line) and S_t before (○) and after (●) the density correction, versus λ_p, under two experimental conditions

(viz. 6-8 per cent per volume) as well as the area of pigment left unwetted by binder, do not contribute noticeably to the sorption process. As already found in the literature, the solubility coefficient of the water in air S_A* ($\simeq 10^{-6}$ g cm^{-3} mmHg^{-1}) is negligible in comparison to the solubility coefficient of the water in binder ($S_b \simeq 10^{-3}$ g cm^{-3} mmHg^{-1}).

In addition, the water taken up by the pigment (e.g. 0.3 per cent at $a = 0.9$ and 20°C), under equivalent experimental conditions, is small in comparison to the water taken up by the binder (e.g. 1.4 per cent at $a = 0.9$ and 20°C).

The diffusion coefficient: From the permeability, P_t, and solubility coefficients, S_t' the mean diffusion coefficients of water in the pigmented films, can be deduced[11]:

$$\overline{D_t} = \frac{P_t}{S_t'} = \frac{qL}{\int_{a_2}^{a_1} \frac{c}{a}\, da} \; (\text{cm}^2\ \text{h}^{-1}) \ldots\ldots\ldots\ldots\ldots\ldots (19)$$

where q is the flux (g h^{-1} cm^{-2}), L the thickness of the film (cm), c the water concentration after the density correction (g cm^{-3}), and a the activity of water.

---

* S_A can also be approximated from the data of P_A and D_A (the permeability and the diffusion coefficient of the water in air), quoted in the literature[16, 17]:

$$S_A = \frac{P_A}{D_A} \simeq \frac{10^{-4}}{10^2} \simeq 10^{-6}\ (\text{g cm}^{-3}\ \text{mm Hg}^{-1})$$

For AT, D_t appears to be independent of λ_p (see Fig. 10) confirming that the mobility of water, in the range of λ_p investigated, is practically unaffected by the presence of pigment in the film. As previously shown, this is due to the fact that the pigment particles are small and well dispersed in the binder.

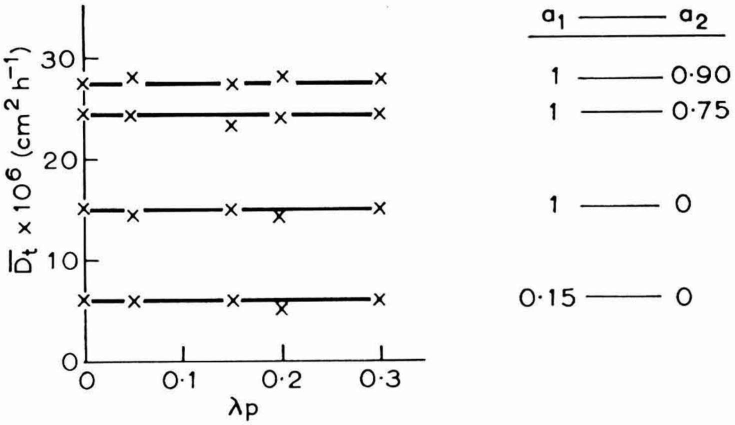

Fig. 10. Alkyd resin/TiO_2. Mean diffusion coefficient ($\bar{D}_t$) versus λ_p, under different experimental conditions

For ET, as a result of the air present in the film, $\bar{D}_t$ increases with λ_p (see Fig. 11).

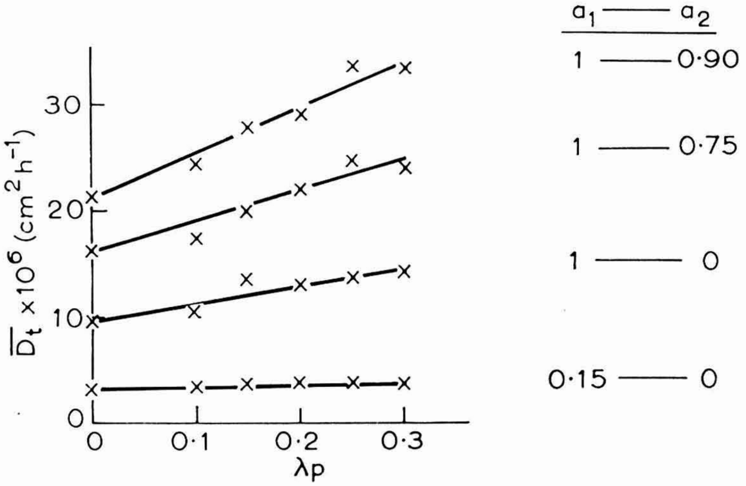

Fig. 11. Epoxy resin/TiO_2. Mean diffusion coefficient $\bar{D}_t$ (after the density correction) versus λ_p, under different experimental conditions

Films pigmented with red lead

Alkyd resin: The dependence of P_t on λ_p is characterised by a steep decrease at small values of λ_p, followed by a slower decrease with a further increase in

λ_p (see curves I and II in Fig. 12 and Table 1). The almost abrupt break in the curve indicates that the properties of the binder with respect to the transport of water are changed by pigment incorporation in the alkyd resin. Presumably, such a dependence shows that, once the pigment and the binder are in contact, a new component that is much less permeable to water is formed.

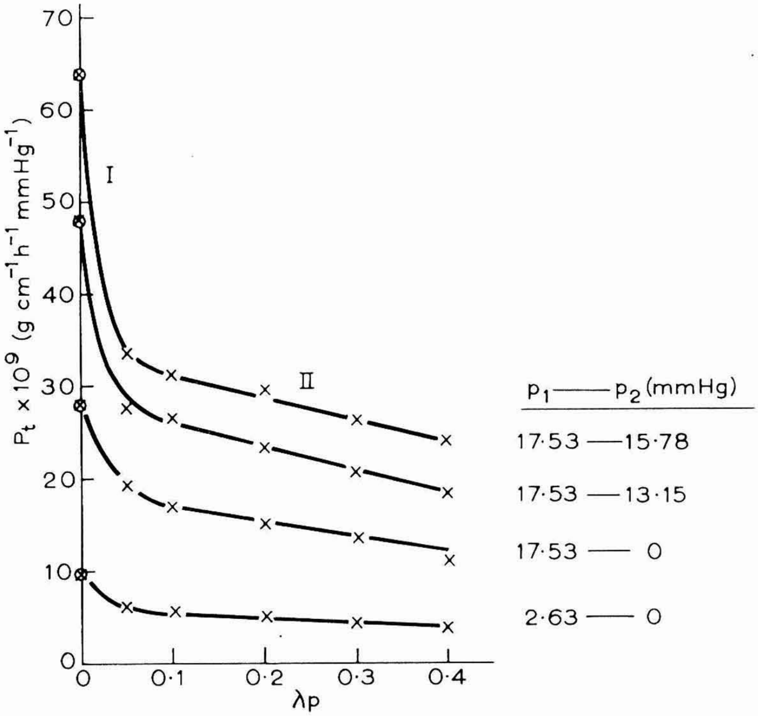

Fig. 12. Alkyd resin/red lead. Permeability coefficient (P_t) versus λ_p, under different experimental conditions

Similar conclusions could be drawn from the sorption measurements (see curve I and II in Fig. 13 and Table 3) for the water uptake in liquid water ($a=1$) and $a=0.2$. The experimental values S_t are below the values S_c calculated from equation 18, showing that red lead strongly affects the sorption properties of the binder.

The viscosity measurements of the paints and an examination of a cross-section of the films indicate that red lead interacts chemically with the alkyd resin, as already suggested in the literature[18, 19]. The increase in the paint consistency in the first days after milling (see Table 4) shows that a chemical reaction can take place, while the spots around the pigment particles (see Figs. 14 and 15) indicate the presence of lead soaps in the film.

In addition, it should be mentioned that, during the process of film formation by air drying, new compounds are formed which can also interact chemically with red lead.

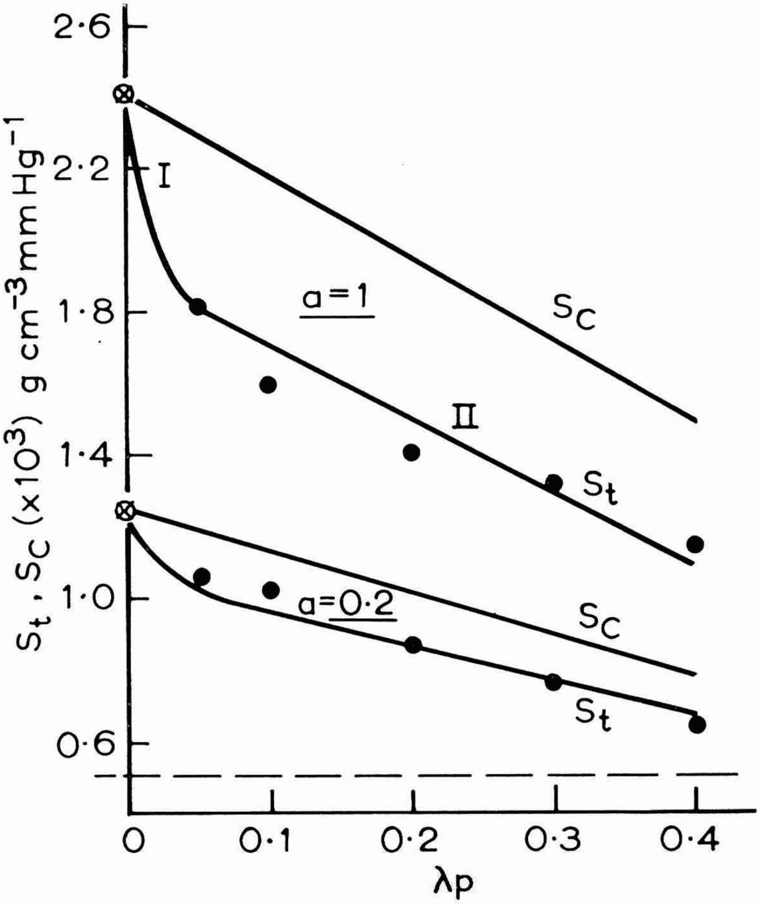

Fig. 13. Alkyd resin/red lead. S_t **(●) and** S_c **(continuous line) versus** λ_p

Table 4

Change in viscosity (cps) of red lead paints at 20°C

	Initial	After 1 day	After 10 days	After 30 days
Alkyd resin (λ_p = 0.50)	6.240	6.560	10.600	11.200
Epoxy resin (λ_p = 0.55)	3.360	3.360	3.360	3.360

Epoxy resin: The sorption measurements show that the incorporation of red lead in the epoxy resin does not affect the binder properties with respect to the water uptake. This can be seen from Table 3, where the solubility coeffi-

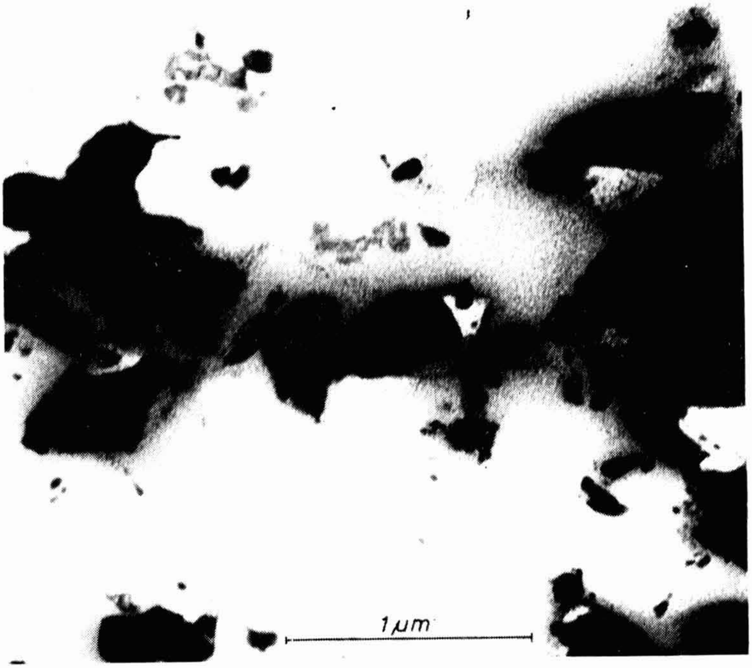

Fig. 14. Part of a cross-section (× 46,000) of an alkyd resin/red lead film (λ_p = 0.3). The spots around the pigment particles indicate the presence of lead soaps in the film

cients calculated per unit volume of binder S_B are given for different λ_p. The values of S_B appear to be independent of λ_p.

The permeability coefficients P_t, as calculated from the permeation measurements, decrease linearly with λ_p (see Fig. 16 and Table 1).

Moreover, the values of P_t are always above the curve described by the equation:

$$P_t = (1 - \lambda_p) P_b \qquad (13)$$

Such a case is in agreement with the permeation model, as described by equation 8, but for which the pigment aggregates contain air ($P_p \neq 0$). The presence of pigment aggregates and air in the films is, indeed, confirmed by an examination of a cross-section (see Fig. 17), and the density measurements (see Table 2), respectively.

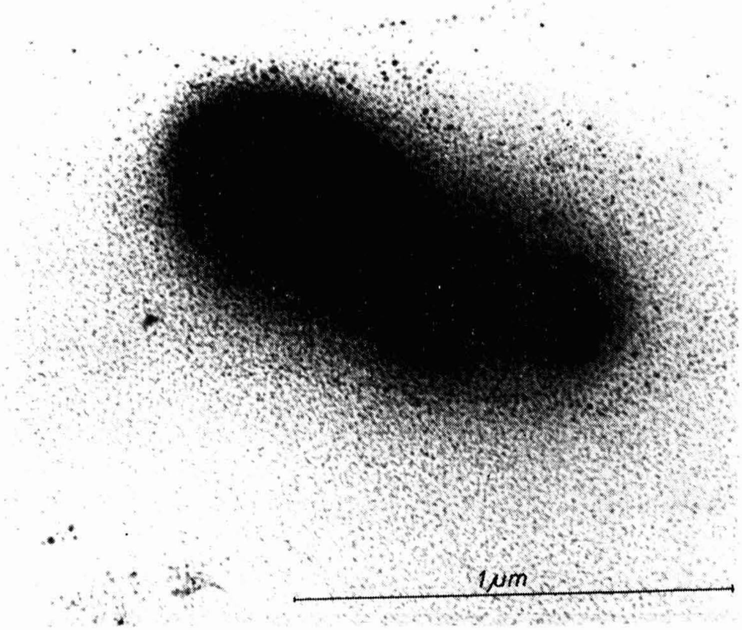

Fig. 15. An 82,500 magnification of red lead particles in alkyd resin film. The spots indicate the presence of lead soaps in the film

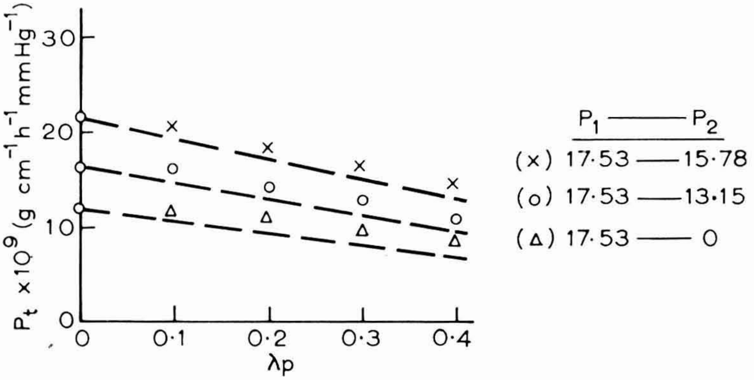

Fig. 16. Epoxy resin/red lead. Permeability coefficient (P_t) versus λ_p, under different experimental conditions

(X), (O), (Δ): experimental data
discontinuous line: $P_t = (1 - \lambda_p)P_b$ (equation 13)

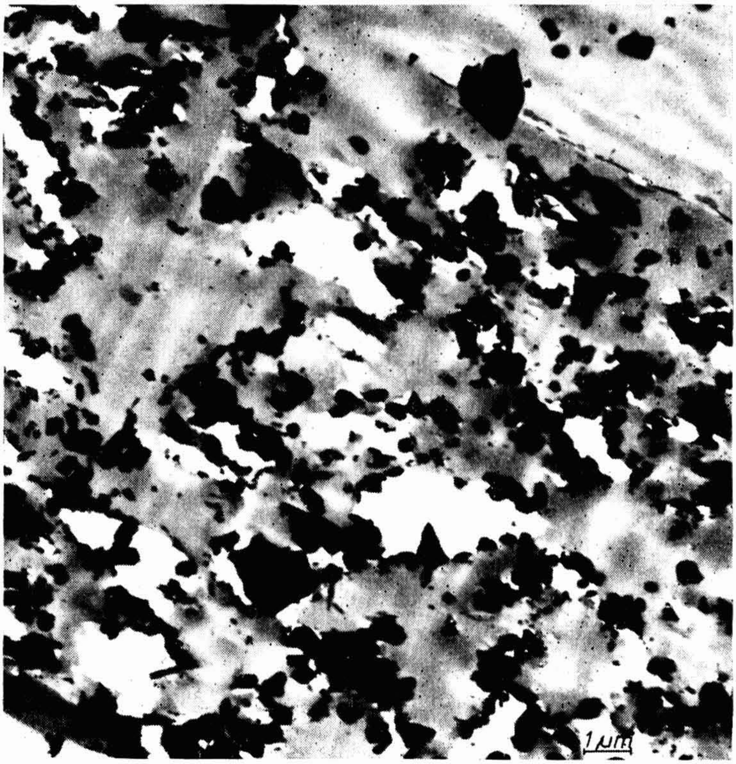

Fig. 17. Cross-section (× 9,000) of an epoxy resin/red lead film (λ_p = 0.3)

The mean diffusion coefficients, $\overline{D}_t$ as calculated from equation 19 are shown in Fig. 18. They increase smoothly with λ_p.

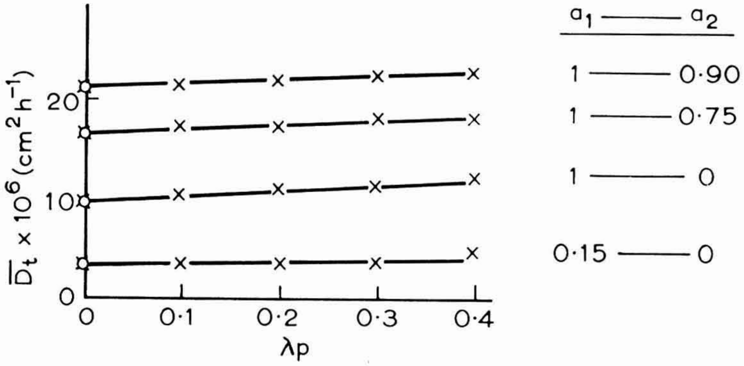

Fig. 18. Epoxy resin/red lead. Mean diffusion coefficient (after the density correction) versus λp, under different experimental conditions

From the above results, as well as from the viscosity measurement (see Table 4), it seems that the epoxy resin, in contrast to the alkyd resin, does not interact chemically with red lead.

Conclusions

The transport of water through the pigmented films is obviously affected by the nature of both pigment and binder. The different behaviour noticed experimentally could qualitatively be interpreted by a permeation model. The model predicts, for an impermeable and inert pigment which is well wetted by the binder, a linear decrease of the permeability coefficient of the pigmented films, P_t, with increase of the pigment volume fraction, λ_p. For small pigment particles, $P_t \simeq (1-\lambda_p)\ P_b$. The alkyd resin/$TiO_2$ combination investigated shows such a behaviour. When the pigment particles are incompletely wetted by the binder, pigment aggregates including air are formed in the film. As a consequence, the pigment aggregates become permeable to water.

As a function of the volume fraction of air actually involved in the water transport process, P_t may increase, decrease or be independent of λ_p. For the system epoxy resin/TiO_2, it was found that P_t is independent of λ_p, and for the system epoxy resin/red lead, it was found that P_t decreases with λ_p.

The presence of air in the pigmented films, however, does not affect the sorption measurements. This is due to the fact that the water taken up by air and by the area of pigment left unwetted is negligible in comparison with the water taken up by the binder. It also shows that the air incorporated in the film is surrounded by binder, in such a way that no direct contact (i.e. through capillaries, voids, etc.) with the exterior can be established.

If capillaries had been present through the film, a very significant increase in P_t values, as compared with the values of P_b, should have been observed, but this was not the case. It also follows that the presence of air in the film affects the permeability of water through the pigmented films, solely owing to diffusion.

The system alkyd resin/red lead represents a special case. In earlier work on red lead in media such as linseed oil, stand oil, alkyds and similar material, it was reported that a pigment/binder interaction occurred. Problems of storage, the increase in consistency, and gelation were studied[18]. Anticorrosive properties of red lead were also investigated[19], and it was concluded that lead soaps, the products of pigment/binder interaction, were the causes of these properties. The present investigation demonstrates that pigment/binder interaction causes a considerable decrease in the water solubility and permeability which, together with the inhibitive properties of lead soaps, give good anticorrosive properties for the system red lead/linseed oil alkyd.

With respect to the dependence of the permeability, solubility and diffusion coefficients on the water concentration within the film, the experimental results showed that, for all the pigmented films investigated, these were basically the same as for the non-pigmented films.

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Next month's issue

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

"Keynote Address: The changing face of paint," *by T. R. Bullett*

"Appearance and performance factors in coatings for buildings," *by P. Whiteley and G. W. Rothwell*

"Colour specification by visual means," *by K. McLaren*

"Gas chromatographic study of the interaction forces between binder and solvent in paint films," *by K.-H. Reichert*

Correspondence

Geographical distribution of Transactions and Communications

SIR,—A survey of the Transactions and Communications published in the OCCA journal during the past three years will show that some 40 per cent originated from overseas. Some 14 countries outside the UK are represented, strangely enough however, not including either Russia or France into whose languages the summaries are translated.

A figure of 40 per cent might seem to be an inordinately high proportion having regard to the numerical distribution of membership of the Association, and one is compelled to ask what are the special reasons which have led to this situation.

Do you find that papers from British sources are offered less frequently than might be expected, or do you perhaps find that the quality of these contributions is not up to the standard you require? It is noteworthy too that out of the 90 odd articles originating in the UK only about 10 per cent are from companies manufacturing paint—a sad reflection on the industry?

Yours faithfully,
F. Armitage.

195, Clarence Gate Gdns.
London NW1.
28 May 1971

Hon. Editor replies—

The statistics given by Mr Armitage are of interest, and some distinction should be made between Communications and Transactions in this connection. The Communications from home sources are of uniformly high quality and very few rejections have been made during the two years of the present Hon. Editor's service. The Transactions generally originate from Section lectures or symposia, and here the rejection rate is higher, as might be expected, because some are reviews of reasonably well known matter and are not original papers. Lectures given by visitors from overseas to Sections or at symposia account for a number of papers from overseas sources.

The papers submitted as Communications from overseas are more variable in quality, although many have been quite outstanding. Overall, the rejection rate has been higher than with indigenous papers.

It is unfortunate that so few papers have emanated from paint manufacturers; none have been rejected by the present Hon. Editor to date when submitted as Communications. The recent questionnaire carried out by the Sections resulted in several suggestions that "more practical papers should be published." Any such papers of suitable standard would be gratefully received, but they are just not forthcoming.

There is certainly a disproportion between home and overseas papers on the basis of our membership, but if the paint manufacturers, who produce few papers, are excluded, the disproportion is not so noticeable if assessed on the basis of the relative numbers of potential paper producing organisations. This is, perhaps, a more relevant comparison because our membership per organisation must be much lower overseas than in this country.

Review

EPOXIDE RESINS

BY W. G. POTTER, London, Iliffe Books (for the Plastics Institute) 1971, Pp. 239, Price £4.50.

This book is one of a series of monographs published for the Plastics Institute and is intended primarily as a textbook for those studying for the professional examinations of the Institute. Dr Potter gives a clear and concise picture of the epoxide resin field and has made the effort to include many of the more recent developments.

Although not so comprehensive as some of the well known handbooks on epoxide resins, Dr Potter has assembled his material in an orderly and logical manner which makes for easy reading. The early chapters describe in some detail the basic chemistry, synthesis and reaction possibilities of epoxide resin systems and are followed by a descriptive chapter on the various types of cross-linking agents. Next follows a short section devoted to the chemistry and properties of the newer cycloaliphatic epoxides and epoxidised olefins.

The final section of the book is more practical and describes in six chapters the current usage of epoxide resins in the various fields of application. The chapter on coatings includes the more recent developments, such as powder coatings and water soluble esters for electrodeposition. There is also a short section on the use of epoxides in flooring and as Civil Engineering materials. It is perhaps a pity that the scope of the book did not allow a more detailed treatment of this rapidly developing field.

For the student, this is a very readable and informative book and the very adequate references provide a reservoir of information for the chemist and technologist in industry.

The book is, in general, well printed but one criticism that may be levelled is that many of the chemical structures are in very small print, and would be easier to read if a bolder type had been used.

A. G. MCKAY

Information Received

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

Technical Publication No. 43, recently issued by **Joseph Crosfield & Sons Limited,** deals with the use of "*Gasil* brand micronised silica gels for matting surface coatings." The booklet recommends grades of *Gasil* for particular types of coating, and gives a few typical formulations.

A range of automatic electrostatic finishing systems which can be programmed to spray-coat products of a wide variety of shapes and sizes at maximum production speeds has been introduced by **Graco.** Made by **H. G. Fischer Co.,** the systems use automatic electrostatic spray guns mounted on a hydraulically-actuated carriage which reciprocates vertically to match the height of the article being sprayed. Even with products of mixed sizes, the reciprocators can be programmed to spray only the products, and to cut out between products. Optical sensors are used to programme the horizontal and vertical dimensions.

Mutual agreement has been reached between **Sherman Chemicals Ltd.** and **Hoechst (UK) Ltd.,** under which Hoechst will market the chemical products of **Riedel de Haen** previously handled in the UK by Sherman Chemicals. This development follows last year's acquisition by **Farbwerke Hoechst AG** of a majority holding in **Cassella Farbwerke Mainkur,** of which Riedel de Haen is a subsidiary.

A new range of *Hexacal* chemicals introduced by **ICI Ltd.,** Dyestuffs Division, will enable ICI's range of *Hexafoam* fire-resistant polyurethane foams to be made by most of the current techniques for the production of rigid polyurethane foams. Whilst having the same properties as conventional rigid foams, *Hexafoam* is claimed to have considerably increased resistance to burning and spread of flame—Class 1 or Class 2 of BS476—and the ability to withstand temperatures of up to 150°C.

The *Static Mixer,* a new development in viscous and turbulent mixing developed jointly in the USA by **Kenics Corporation** and **Arthur D. Little Inc.** and handled in Europe by **Kenics Europe,** is now available in the UK through Kenics UK representative, Mr C. D. Grace.

Said to be a new concept in fluid mixing, the *Static Mixer* has no moving parts, consisting essentially of a number of elements, each of which is a length of pipe containing a helix running along its length, each element being placed so that the helix runs in the opposite direction to that in the previous element. The fluid is pumped through the elements, which impart turbulent or laminar flow, absorbing the energy of mixing from the flowing fluid. It is claimed that the *Static Mixer* can be used with excellent results for the production of slurries, dispersions or emulsions, with a great reduction of power consumption—only sufficient power to operate the pump is required—and, since there are no moving parts, maintenance costs. It is also claimed that the controlled flow patterns produced by the elements reduce abrasion and corrosion to a point even less than that of an ordinary pipe of the same material.

Uses of the mixer in paint production in the USA are reported; in some cases it has been used in converting from batch to continuous production.

W. A. Keller Process Engineering of Zurich has been appointed general agent for the *Static Mixer* in Switzerland and Austria, and agent for the German textile and polymer industries.

Synthetic Resins Limited, the company formed recently by the amalgamation of Unilever resins companies, has issued two new publications. One covers the background to the company's formation, while the other summarises the wide product range now available.

It has recently been announced that **Pure Chemicals Limited** has changed its name to **Interstab Limited**. The company is part of the chemical division of **Akzo**, together with **Interstab GmbH, Novadel Ltd., Noury & Van der Lande NV** and **Oelwerke Noury & Van der Lande GmbH**, and the rationalisation, it is claimed, will bring many benefits in terms of new products, applications and customer service.

A new leaflet from **Allied Colloids Manufacturing Co. Ltd.** gives details of the use of *Alcopol* sulphated esters in paint and pigment applications. Two of the products, *Alcopol M Special* and *Alcopol T*, are suggested as dispersing agents for dyes and organic pigments in aqueous systems. The other, *Alcopol AH New*, has good water-carrying properties, and is thus suggested for improving pigment dispersion in non-aqueous media by solubilising surface water.

A new factory has recently been opened in Darlington by **Swale Chemicals Limited**. Although the plant was designed in 1969 to accommodate production at a rate twice that then current, demand is such that production at the old Aycliffe plant will have to be continued until extensions can be added to the new factory.

The Timber Research and Development Association has issued a new booklet dealing with wood as a building material in relation to the fire regulations. Entitled "Fire and timber in modern building design," the booklet is written by Mr L. A. Ashton, who points out that, contrary to common opinion, wood is rarely responsible for fires, and gives guide lines for the safe use of timber in buildings, tracing stages in the development of a fire, and outlining testing procedures and fire-retardant treatments. Copies of the booklet are available from TRADA, free of charge in the UK, and at a cost of 20p a copy to cover postage overseas.

Degussa has added another methacrylic ester to its range, trimethylolpropane trimethacrylate. The product is recommended as an additive to pvc-plastisols, improving their adhesion to metal.

Following the acquisition by **Vinyl Products Ltd.** of the full marketing rights for **British Oxygen Chemical's** *Vandyke* polymer emulsions, it has been announced that all production of these grades is now taking place at Vinyl Products' Carshalton works. Close co-operation between the technical staffs of the two companies is said to have accelerated the transfer; no change of quality has occurred with any of the grades concerned.

The spectrophotometric properties of an average set of the ceramic colour standards produced jointly by the **British Ceramic Research Association** and the **National Physical Laboratories**, as described previously in this *Journal*, have now been accurately determined. The colour standards, which are intended for checking and standardisation of photoelectric colour measuring instruments, are now available with this data, and also the goniophotoelectric characteristics of the various tiles.

Individually calibrated sets of the standards will also be available; 40 such sets are currently being measured at NPL.

It has recently been announced that the discussions between **Unilever Limited** and **Resinas Sinteticas SA** for the purchase of the latter's business in Barcelona have been discontinued by mutual agreement.

Allied Chemical International SA has introduced two new products from **Harmon Colors Inc**. *Indofast Brilliant Red ER-8070* is a new perylene red pigment which can be used to replace molybdate orange in automotive and industrial finishes. It is claimed to have high opacity, resistance to bleeding, alkali, and acid, and thus to be an ideal lead-free substitute for molybdate orange. *Perrindeau Violet EV-8001* is a new perylene bordeaux toner, with a deeper and more transparent shade than the existing *MV-7020*.

NL Industries, Inc. is the new corporate name for National Lead Company. It is said that the new name, while retaining the familiar NL corporate symbol, is less restrictive, and more accurately embraces the total range of the company's corporate interests.

SODAC 15th Biennial Symposium

The Society of Dyers and Colourists is to hold its 15th Biennial Symposium at the Aviemore Centre, Scotland, on 15-17 September 1971.

The title of the symposium is "Colour and processing challenges in the seventies" and 16 papers have been accepted for the technical programme. A lecture period dealing with the work of SODAC's Automation Committee is also planned. Full details are available from: The General Secretary, SODAC, PO Box 244, Bradford, Yorkshire BD1 2JB.

Solids handling course

A one-week residential course entitled "The flow and storage of bulk solids" is to be held at the University of Bradford from 20-24 September 1971.

The course is intended for engineers and scientists concerned with powder handling and storage problems; application forms may be obtained from: The Secretary, School of Powder Technology, University of Bradford, BD7 1DP.

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 Encres d'Imprimerie de l'Europe Continentale (FATIPEC). The Association also maintains cordial relations with the Scandinavian Federation of Paint and Varnish Technicians (SLF).

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

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

PUBLICATIONS

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

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

Paint Technology Manuals

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

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

OCCA-23 Technical Review

The Guest of Honour at the Exhibition Luncheon, The Rt. Hon. Margaret Thatcher, PC, MP, with (left to right) Mr F. Cooper (Chairman, Exhibition Committee), The President (Mr A. W. Blenkinsop), and Mr R. H. Hamblin (Director & Secretary)

OCCA-23 a great success in June

OCCA-23 (The Twenty Third Annual Technical Exhibition of the Oil and Colour Chemists' Association) was held at the Empire Hall, Olympia, London, from 21-25 June 1971.

For many years, the Association has held its annual Exhibitions of raw materials and equipment for the paint, printing ink, colour and allied industries in March or April but it had not proved possible to obtain such a booking for the new venue—this being the second occasion on which the Exhibition had been held at Olympia—and concern had been expressed lest the attendance at the largest Exhibition yet organised by the Association, including exhibitors from 12 overseas countries as far afield as Australia and Canada, would suffer. In the event, however, the total attendance registered at the turnstiles of 14,500 maintained that of the previous year, there being the same number of overseas countries (38), represented in the Visitors Book at the Information Centre, as in 1970. The overseas countries represented were: Argentina, Australia, Austria, Belgium, Brazil, Canada, Czechoslovakia, Denmark, Finland, France, Germany, Greece, Holland, Hungary, India, Iran, Ireland, Israel, Italy, Japan, Kenya, Malaysia, Mexico, Nigeria, Norway, Pakistan, Poland, Portugal, South Africa, Spain, Sweden, Switzerland, Syria, Trinidad, Turkey, USA, Venezuela, Yugoslavia.

Exhibition Luncheon

On the opening day, a large number of members, exhibitors and visitors attended an Exhibition Luncheon at the Savoy Hotel, London, WC2, when the Guest of Honour was the Secretary of State for Education and Science, the Rt. Hon. Margaret Thatcher, PC, MP, who replied to the Address of Welcome by the President of the Association, Mr A. W. Blenkinsop.

Mr Blenkinsop said that this occasion was one of many "firsts." It was the first time that the Exhibition had been as late in the year as June, which meant that it followed the Conference Annual General Meeting, at which, by custom, the President was elected. Thus, this was his first official appearance as President.

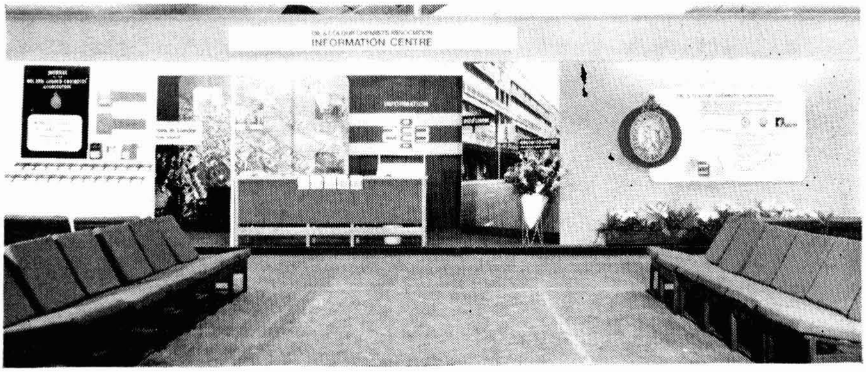
Also, this was the first time that the Guest of Honour was a lady. In welcoming the Rt. Hon. Margaret Thatcher, PC, MP, Secretary of State for Education and Science, he reminded guests that Mrs Thatcher had spent four years in chemical research in industry before being called to the Bar and, before her marriage, had replied on behalf of the ladies at a dinner held by the London Section in 1951.

The President went on to welcome the other Association guests; Dr G. de W. Anderson (Director, Paint Research Association), Mr G. H. Beeby (President, Society of Chemical Industry), Mr R. T. Bowes (President, Society of British Printing Ink Manufacturers), Mr A. O. Brantsaeter (President, Federation of Scandinavian Paint and Varnish Technologists), Mr. W. B. Cork (Chairman, British Colour Makers' Association), Mr D. Crouch, MP, (Parliamentary and Scientific Committee), Mr S. C. H. Dix (President, Paintmakers' Association), Mr K. S. Flory (Director, Paintmakers' Association), Mr J. C. Garrels (President, British Plastics Federation), Mr W. G. B. Grant (President, Society of Dyers and Colourists), Dr F. T. Hamblin, CBE (Director, British Plastics Federation), Lord Ironside (Vice-President, Parliamentary and Scientific Committee), Mr G. Isserlis (President, Institute of Metal Finishing), Professor Sir Ewart Jones (President, Royal Institute of Chemistry), Mr R. E. W. Large (Master, Worshipful Company of Painter Stainers), Mr A. P. Low, OBE (Chemical and Allied Products Training Board), Sir Harry Melville (President, Plastics Institute), Mr C. H. Morris (Chairman, British Resin Manufacturers Association), Dr E. S. Paice (President, Research Association of British Paint, Colour and Varnish Manufacturers), Mr A. H. Pangborn (Clerk, Worshipful Company of Painter Stainers), Mr H. T. Pike (Master, Worshipful Company of Wax Chandlers), Professor G. Porter (President, Chemical Society), Dr G. L. Riddell (Director, Research Association for the Paper and Board, Printing and Packaging Industries), Mr R. K. Sanders (Chairman, Research Association for the Paper and Board, Printing and Packaging Industries), Lord Sherfield, GCB, GCMG (President, Parliamentary and Scientific Committee), Mr C. Simeons, MP (Parliamentary and Scientific Committee), Sir Charles Taylor, TD, MP (Parliamentary and Scientific Committee), Professor A. G. Ward, OBE (President, Society of Leather Trades Chemists), Mr T. Wood (Clerk, Worshipful Company of Wax Chandlers) and Mr C. M. Wright (Chairman, Chemical and Allied Products Industry Training Board).

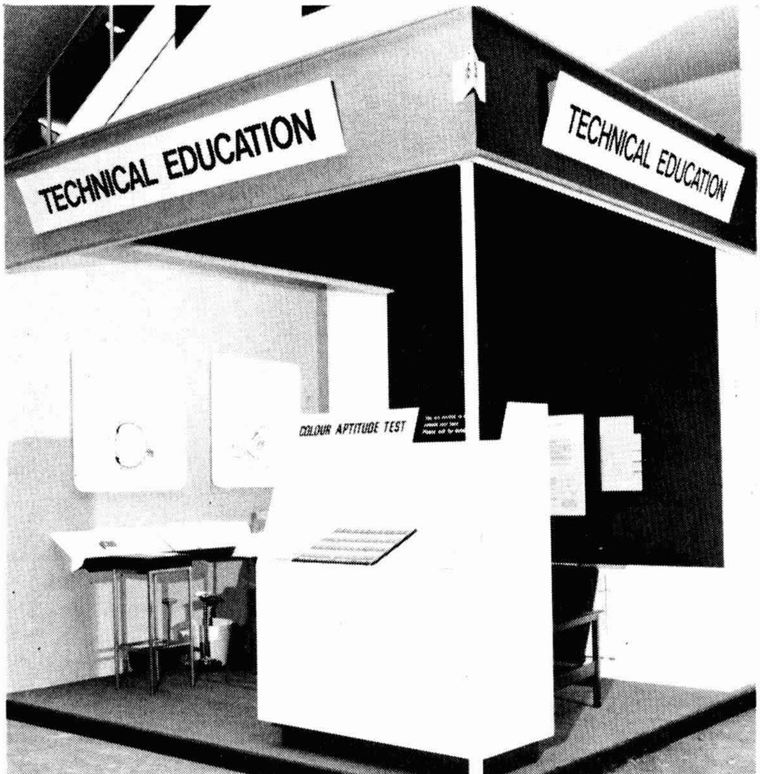
Another first was that this was the first OCCA Exhibition at which over 200 companies were mentioned in the *Official Guide;* 18 of the 120 stands were occupied by companies that had never shown at OCCA before and a further 32 did not exhibit in 1970.

Mr Blenkinsop then turned to the educational side of the Association's activities. OCCA had for many years been particularly interested in students in the industries, having published the "Introduction to paint technology," sales of which had now exceeded 15,000 copies, and the "Paint Technology Manuals," Part 7 of which, entitled "Works practice and manufacturing techniques," was to be published as a part work in the 1972 volume of the *Journal*, under Student Reviews.

In order to strengthen the technical training already being undertaken in the industries, both in the UK and Overseas, the Association was now to offer an optional professional grade to its Ordinary Members. Although it might seem a bit late in the day for the Association to introduce this scheme, there had been difficulties, the main one being that of instituting the professional grade without altering the whole concept, and perhaps even the name, of the Association. However, a way of satisfying the younger members of the Association who wished to achieve an educational identity



The Association's Information Centre, showing the large seating area provided



The theme of the Technical Education Stand was "Colour and colour matching" with their industry had now been found without amending the present constitution or name and without jeopardising the continuing success of existing courses. Full details would appear in the *Journal* in the near future.

The President felt that it was particularly apposite that he was able to mention this scheme for the first time in the presence of the Secretary of State for Education, and proceeded to propose the toast to the Association's guests, coupled with the name of the Guest of Honour, the Rt. Hon. Margaret Thatcher.

In her response, Mrs Thatcher gave an outline of her ideas on education in industry. She felt that it was important that there should be adequate research facilities available to industry; a trained "research capacity" should be maintained at the universities which could be called upon to solve problems of a fundamental nature. Of no less importance were the polytechnics, which could aid in the solution of problems which, although more practical, required academic expertise equal to that necessary in more basic studies.

At an earlier age level, children, most of whom would be average in their capabilities, should receive the best and fullest training to equip them for their working lives.

Mrs Thatcher apologised for the fact that she would not be able to open the Exhibition at Olympia, owing to an unexpected commitment in the House of Commons, but hoped that it would be as successful as previous Exhibitions.

The Exhibition

Once again the placing of the Information Centre as a focal point immediately opposite the main entrance was much appreciated by visitors. The provision of a seating area in front of the Information Centre gave those entering the Exhibition a base from which to plan their tour, having first obtained any necessary data from the Association's stand. The other seating areas on both floors were also welcomed by visitors as oases to collect their thoughts and rest feet wearied by the coverage of the largest OCCA Exhibition to date.

The cool clean greens chosen for the stand felts were echoed by many of the stand designers, and the overall level of designs was an improvement even over last year's high standard. The exhibitors are to be congratulated on their efforts, which produced a light, airy, and visually attractive show without the sacrifice of any quality in the technical content of the displays. An increasing use of visual aids—closed circuit and cassette television, and back projected film—was noted, and as has been stated before in OCCA Reviews, any such means of aiding the increasingly beleaguered visitor to gain the maximum technical information in the minimum time can only be applauded.

Technical Education

The theme of the Technical Education Stand was "Colour and colour matching," and a special leaflet was provided covering the concept of colour and how the eye sees it, and describing the basis of instrumental methods of colour measurement. Displays on the stand illustrated points from the leaflet, and included practical demonstrations of the concepts of additive and subtractive primary colours. A simple colorimeter was demonstrated on the stand, and visitors could undergo a shortened version of the colour aptitude test developed by the Inter-Society Colour Council and now handled by the Federation of Societies for Paint Technology. The latter item aroused a great deal of interest amongst visitors, a large number of whom tested their colour matching ability.

The stand also displayed literature on educational courses relevant to the surface coating industries, and staff from the technical colleges were always available to give information and advice both to the school parties invited by the Association and to any other interested visitors.

Research Associations

The PAINT RESEARCH ASSOCIATION showed aspects of their work on fungus resistant paints, demonstrating screening tests for the resistance of potential biocides to fungi that are commonly responsible for paint film breakdown. Similar procedures investigating the effectiveness of additives as agents against antifouling—brought into commercial focus by the increasingly tight schedules set for increasingly large oil tankers—were shown. Of particular interest was a number of flasks showing the effect of antifoulings on green weed; this is believed to be the first time that the weed has been grown under laboratory conditions.

The fibre optics colorimeter was also on show, and its use in continuous production, connected directly to a computer calculating quantities of tinter necessary to maintain the shade, illustrated. Several other testing instruments developed at the PRA were also exhibited.

Fungicidal and antifouling paints were also featured by the TIN RESEARCH INSTITUTE, the biocidal agent being tri-n-butyltin oxide. Particular emphasis was placed on the use of this agent in wood preservation.

Technical journals, services and publications

PAINT MANUFACTURE and PAINT TECHNOLOGY had their respective Exhibition preview issues on display, and details of the other publications produced by their two publishers. The industry's weekly publication, PAINT OIL AND COLOUR JOURNAL displayed several recent issues: the Paint Oil and Colour Yearbook was to appear within a few weeks of the Exhibition.

Appearing at OCCA for the first time, ELSEVIER SEQUOIA SA showed the new international review journal "Progress in Organic Coatings" whose stated editorial policy is to summarise and analyse the progress and correct state of knowledge in the field of organic coatings and related subjects, and in particular to concentrate on fields of activity which have undergone significant development in recent years. Other books from this publishing group which had relevance to the surface coatings industry were available on the stand.

Another new exhibitor was CRYSTAL TACK CLOTH CO. LTD., showing a hand cleanser effective against all types of paint as well as dirt, grease, etc. The cleanser is claimed to eliminate dermatological problems, without the danger of contamination of the workpiece caused by barrier creams.

A stand was sponsored by the West German Government for the CHEMICAL INDUSTRY OF THE FEDERAL REPUBLIC OF GERMANY. Attractively decorated with sample panels demonstrating methods for decorating and protecting various substrates, the stand served as a source of information on the range of chemical products offered by West German manufacturers.

Pigments

A new beta-modified, greenish blue phthalocyanine, Isol Phthalo Cyan BC3 7549, was introduced by KEMISKE VAERK KOEGE A/S. The pigment conforms to the Pantone matching system, and is intended for use as one of the four trichromatic printing inks. Good light fastness and resistance to bleeding are claimed. Isol Toluidine Red LH 2B 8507 is another new pigment, manufactured as an exact match to BS.2660-0-006 Post Office Red. This and other similar pigments were shown in various tints with white. The company's range of azo oranges was increased by the addition of two new pigments, Isol Diaryl Orange GT 7592, having high colour strength and good gloss and transparency, and Isol Fast Orange G.2519, intended for litho inks.

Several additions were made to the pigment ranges of BASF UNITED KINGDOM LIMITED. New pigments in the Fanal and Lithol series for inks showed improved colour strength and purity of shade. For coatings, new pigments with the lightfastness and cleanness of shade required for industrial finishes were introduced in the Paliogen range. The pigments were of the flavanthrone, dioxazine and perylene types. Improvements in the dispersibility and flocculation resistance of the Heliogen phthalocyanines have also been made.

Improved dispersibility on ball-milling in alkyd media was demonstrated by FRANCAIS DES MATIERES COLORANTES SA for three of its organic pigments—Lutetia Fast Emerald J (phthalocyanine green), Lutetia Fast Cyanine CS—D (solvent-stabilised phthalocyanine blue) and Lutetia Fast Red 5BO 1501. This company also exhibited Thermoplaste Yellow and Thermoplaste Orange, two pigments for use in plastics to be submitted to temperatures of up to 320°C.

Improved dispersibility was also featured by ICI LIMITED for its range of phthalocyanine green pigments for paints and plastics. VICTOR BLAGDEN LIMITED displayed easily-dispersible organic pigments from Societe des Produites Chimiques des Mulhouse. CIBA-GEIGY (UK) LIMITED showed a range of easily-dispersed organic pigments, in particular Irgalite Red LZB, a new grade for printing ink, as well as high performance and elaborated versions. Particular emphasis was given to Irgazin Yellow 3RLTN, a progression from the 3RLT and 2RLT grades, having a cleaner, brighter, slightly greener tone.

Additions to the Sandorin range of organic pigments were made by SANDOZ LTD. Organic based solvent-soluble dyestuffs in the Savinyl range, for use in flexographic and gravure printing inks, were also displayed. HARDMAN & HOLDEN LTD. exhibited a new range of five variants of Pigment Red 53, under the name Manox Lake Red C, and gave full details of their properties.

Four grades of the chloride process titanium dioxide pigments produced by LAPORTE INDUSTRIES LTD. were shown. Available last year only in sample quantities, Runa RH 472 and Runa RE 376 are now in bulk production, and Runa RE 372 and Runa RO 676 production is scheduled to go on stream in six months. Since the pigment's introduction last year, comprehensive durability tests have been carried out, and the results of these, in a variety of media, were on display.

VUORIKEMIA OY demonstrated the improved dispersibility of the Finntitan sulphate process titanium dioxide pigments using high speed mixing equipment. Properties of the pigments were compared with those of other sulphate process pigments, and also with chloride process pigments. Electron micrographs showed that the particle size distribution of Finntitan grades was as good as that of chloride process TiO_2; emphasis was placed on the importance of choosing the correct pigment for a particular application, irrespective of the pigment's manufacturing process. Two special grades of TiO_2 for emulsion paints—Finntitans RDE2 and RD1—were shown.

The TIOXIDE INTERNATIONAL LIMITED stand was centred on the use of TiO_2 pigments in powder coatings. A working demonstration of electrostatic spraying of a thermosetting powder coating formulated on Tioxide pigments was featured, and displays showed the effect of formulation on various properties of the applied coating. The use of Tioxide pigments in air-drying gloss paints was outlined, demonstrating how an adequate compromise between hiding power and pigment utilisation could be achieved.

A comparison of the gloss retention and chalk resistance of treated and highly treated TiO_2 pigments had been prepared by KRONOS TITANIUM PIGMENTS LTD., using panels exposed in Florida, Teddington and Enstenberg. The differences caused by the various pigment grades, and also the different binders, were clearly shown. The results of work on the hiding power of various pigment grades in emulsion paints was also on view, using different emulsions and several different formulations. Changes in hiding power obtained by varying overall PVC while maintaining a constant

TiO_2 PVC were demonstrated. Other exhibits showed further work on the determination of state of dispersion by measurement of the gloss haze with a goniophotometer.

Although no long-term work on the rutile TiO_2 pigments from the newly opened Scarlino factory of **MONTECATINI EDISION SPA** had been possible, information on the seven grades offered was available. These included RS 33, recommended for high gloss applications, RS 55, with superior weathering properties, and RS 99 with high hiding power and ease of dispersion in aqueous media, recommended for emulsion paints. **SACHTLEBEN AG** introduced new grades of TiO_2 pigment and gave sample formulations for several applications.

Faced with difficulties caused by the banning in the USA and other countries of the channel black process under pollution regulations, carbon black pigment manufacturers offered several alteratives. **DEGUSSA** have perfected a gas process for channel blacks which passes the stringent West German pollution control requirements. A new pre-dispersed carbon black, in free flowing powder form, was added to the company's range. Intended for emulsion paints, the new grade, Corasol A, is directly dispersible in the emulsion, giving uniform dispersion and all depths of shade. A particular advance is the high weathering resistance of the grade, the dispersing agents having little deleterious effect on the paint film.

COLUMBIAN INTERNATIONAL LTD. introduced furnace blacks to replace the existing channel grades. Suitable pigments are available for printing inks and plastics, but some grades for paints are still being developed.

Three new high and low structure furnace blacks were exhibited by **CABOT CARBON LTD.** The grades were CSX 65 and 66, with high structure and medium colour, CSX 71 and 72 with low structure and medium colour, and Regal 660, with standard colour. All these types are suitable for paints and plastics.

Pigments with anticorrosive properties were strongly represented at the Exhibition. **ALBRIGHT & WILSON LTD.** had a selection of panels demonstrating the long-term corrosion resistance of Corinac A and Corinac C, the two anticorrosive pigments introduced at OCCA 22, in various media. The National Lead Co. pigments, Oncor M50 and Oncor F31, were exhibited by **BERK LIMITED**, with examples of their corrosion protection in solvent-based and electrodeposition primers. Metallic lead primers for protection of structural steelwork were the theme of the **SPELTHORNE METALS LIMITED** stand. The Government now specifies this type of primer for steelwork and bridges on motorways, and examples of water-based primers on this substrate were shown. A display illustrated the fact that increased lead content improves the adhesion of the primer, using the torque wrench method to test adhesion.

KINGSLEY AND KEITH (CHEMICALS) LTD. showed Moly-White, a zinc molybdate pigment newly available in this country. Produced by Sherwin-Williams Chemicals, this white pigment is said to have equal corrosive resistance to basic zinc chromate while being completely non-toxic. Samples are expected to be available towards the end of the year.

The efficiency of zinc phosphate pigment in corrosion protection was demonstrated by **IMPERIAL SMELTING CORPORATION (ALLOYS) LTD.** Zinc dust in zinc rich primers, based on organic binders, was also featured, and the effect of various extenders and topcoats illustrated. **SCC COLOURS LIMITED** added zinc phosphate to its range of inhibitive pigments, and a series of tests on rusty and bright steel in various media was displayed. In the field of general purpose inorganic pigments, the company's new S range of lead chromes represents an advance in manufacturing techniques in imparting lightfastness and sulphur dioxide resistance. Four colours are available, from pale yellow chrome LEFS to pale Scalachrome LFS. The use of zinc oxide pigment in emulsion paint was demonstrated by **VVB LACKE UND FARBEN**, showing the advantages in increased shelf life and fungus resistance.

The exhibitors on the above stands cover nine of the twelve overseas countries represented at OCCA 23

A fungicidal and biocidal pigment, Busan 11-M1, was the focus of the BUCKMAN LABORATORIES INC. display. The efficiency of this barium metaborate pigment in controlling fungae and algae, and its other more general properties in coatings for external use, were outlined, and compared with the previously used organic mercury compounds. Barium metaborate does not have the harmful properties of mercury, and was shown to have a longer life span. An interesting map of the world, showing the surprisingly wide spread of areas in which fungus is a problem, was also on display. SCHERING AG demonstrated the efficacy of organo-tin compounds, particularly triphenyltin chloride, as antifoulants in marine paints.

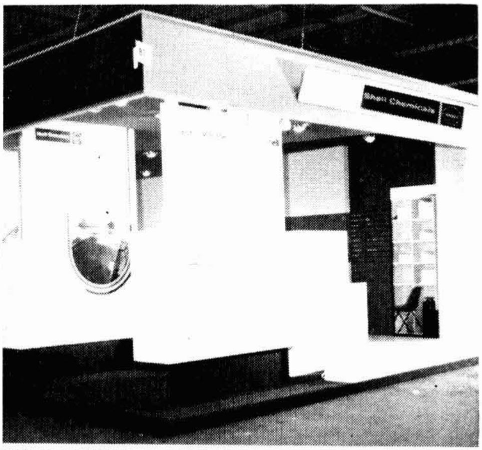
Several pigments for novelty finishes were exhibited and, of these, fluorescent types had perhaps the greatest representation. SWADA (LONDON) LTD. showed new extra strength fluorescent concentrates, the 5DE range, claimed to be 30-40 per cent stronger than the standard ZO series. Available in nine colours, the pigment is very finely dispersed, and can be incorporated in several varnish media without further milling; main uses are for litho and letterpress printing inks. A new range of solvent soluble toners was also on display, which are available in ten colours, and dissolve readily in common solvent systems. Gravure and flexographic inks are the main applications. Amongst its fluorescent pigment range, INDUSTRIAL COLOURS LTD. featured a new photographic grade, of very fine particle size, for use in photographic paper. A fluorescent "wash" is imparted to a print from an ordinary black and white negative; applications in high impact display work were demonstrated. RADIANT COLOR OF CALIFORNIA NV, a new exhibitor, showed a comprehensive range of fluorescent pigments and pastes.

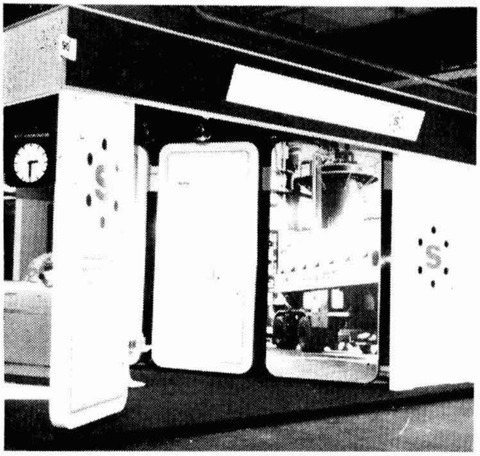
An aluminium pigment for metallic finishes, produced by Silberline Manufacturing Co., was exhibited by REX CAMPBELL & CO. LTD. Designed to give a "glitter" finish, the pigment, Sparkle Silver 3500, is of similar particle size distribution to conventional aluminium pigments, said to be much smaller than the usual "flake" pigments used for glitter effects. Midas Gold green shade hydrated iron oxide pigments from Lamont Corporation were shown by CROXTON & GARRY LTD. and examples of their use in metallic automotive finishes given. CORNELIUS CHEMICAL COMPANY LIMITED had the Murano P range of pigments for pearl finishes from the Mearl Corporation. Examples of decorative coatings and cosmetic products containing pigments from this range were on display.

A new range of the Uni-sperse Universal Tinting Pastes was featured among the range of dispersions produced by INTERNATIONAL COLLOIDS LIMITED, and its use in all types of finish was demonstrated.

COLUMBIAN INTERNATIONAL LIMITED showed the new Runnyeadem Dispersion range of dispersions, the RDX 1000 series. Supplied in solvent/wetting agent only, the dispersions are claimed to give a high degree of gloss and transparency with transparent iron oxide and phthalocyanine pigments, and drawdowns of typical formulations illustrated this; a carbon black dispersion was also on show. A range of chlorinated rubber pigment chips based on Alloprene R2D was another of the company's exhibits.

The Colourtrend Exceptionale system of tinters was the main exhibit of the CAL/INK CHEMICAL COMPANY OF CANADA LTD. The system consists of 12 lightfast, lead free, alkali resistant tinters, glycol based, and compatible with alkyd, emulsion and oleoresinous paints. Although the tinters can be applied to a manufacturer's formulations, Cal/Ink's own formulation book, which offers a total of 1,350 shades, was given emphasis. This involves four base paints—a clear and three different PVC's of TiO_2. The advantageous economics of the system were stressed, particularly when tinting took place at point of sale. BUSH, BEACH & SEGNER BAYLEY LTD. showed the Kolorit range of colourants manufactured by Henning Perrson.


Shell Chemicals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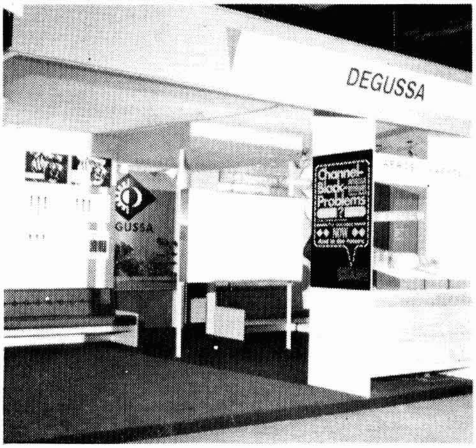
SPELTHORNE METALLIC LEAD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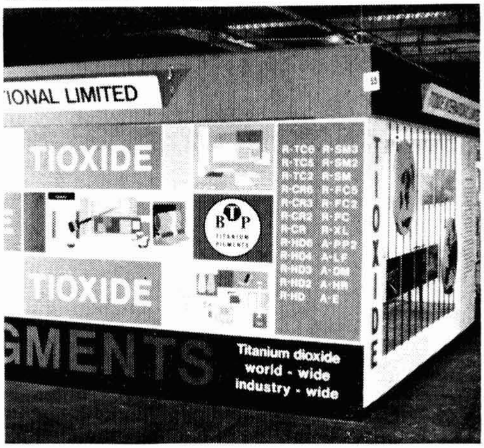
IONAL LIMITED
TIOXIDE
BTP
TITANIUM PIGMENTS
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GMENTS
Titanium dioxide world - wide industry - wide
TIOXIDE

Additions to the range of flushed colours manufactured by SCC COLOURS LIMITED included Diarylide Yellow AT. The pigment is supplied in an alkyd resin/hard resin blend in distillate solution, and shows improved tint strength, cleanliness of tone and gloss. All the pigments in this range can be supplied in media specified by the customer. Four new additions to the Diarylide Yellow range for printing inks were displayed also.

KEMISK VAERK KOEGE A/S featured two new pigment preparations for flexographic inks. Predisol C is a nitrocellulose based product for NC and polyamide inks, and Predisol V is based on a vinyl copolymer. Both products have high pigment loading. Amongst new Irgalite Blues introduced by CIBA-GEIGY (UK) LIMITED was Irgalite Blue CPV3, a paste for water-based paint systems.

Oils

Following the installation of a new plant, OULU OSAKEYHTIO have available an improved range of tall oil products, and the characteristics of alkyd varnishes based on these compounds was compared favourably with those of varnishes based on linseed and soya oils, particularly in respect of resistance to yellowing. The results of one year exposure tests were used to support the comparison. Pale grades of distilled turpentine were also displayed.

Exhibiting its wide range of processed vegetable oils, YOUNGHUSBAND STEPHENS & CO. LTD. stressed that most products could be produced and supplied to the customer's specifications.

Suggestions as to the applications for cis polybutadiene oils, Polyols 110 and 130, of low and medium viscosity respectively, were made by CHEMISCHE WERKE HUELS AG.

Modified vegetable oils were exhibited by NOURY & VAN DER LANDE NV. The Magie range of hydrocarbon oils for low odour printing inks, including deodorised grades with FDA approval for foodstuff packaging, was shown by REX CAMPBELL & CO. LTD., who also exhibited cyclopentadiene modified oils from Necof NV.

Solvents

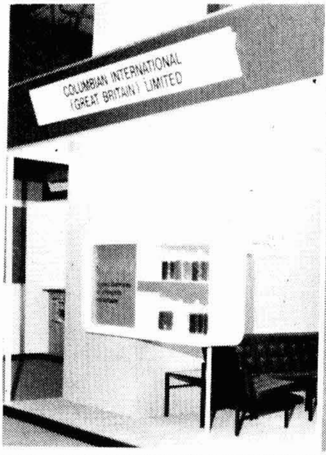
Specially featured amongst the solvents produced by ESSO CHEMICAL SA were Solvent 200, a new high flash point, high aromatic content, high boiling compound designed for use in low bake systems to reduce sagging and runs, and the Isopar range of low odour, high purity isoparaffins. The latter products are available in six basic boiling ranges, coded C, E, G, H, L and M. The G and H grades are very close fractions and can be used for electrostatic wet copying systems; the main use in the UK, however, is said to be in aerosols. Information was also available on the company's new methyl ethyl ketone plant at Southampton, said to be the largest in Europe.

The main exhibit of SOCIETE DES USINES CHIMIQUES UGINE KULMANN was the Sida range of ketone solvents. This range includes an ethyl methyl ketone recommended for polyurethanes, since it shows lower water absorption than many solvents currently used for this application.

A new solvent range from the Heavy Organic Chemicals Division of ICI LIMITED was the Ethoxol glycol ethers, and typical properties were illustrated. The Aromasol solvent range was also shown. Kel-Sol 42394, a printing ink vehicle for fast setting water-miscible letterpress inks, was introduced by CORN PRODUCTS (SALES) LTD.

The Hyvis range of polybutenes was given prominence among the wide range produced by BP CHEMICALS INTERNATIONAL LTD. Non-drying, stable, polymer oils, these solvents are available in a variety of viscosities; applications in putties, mastics and adhesives, as well as surface coatings, are recommended.

The REX CAMPBELL & CO. LTD. display included acetate solvents from Leek Chemicals Ltd.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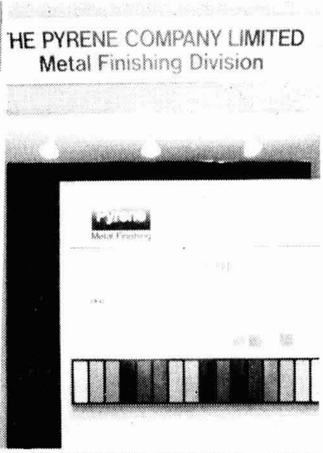
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Metal Finishing Division
Pyrene
Metal Finishing


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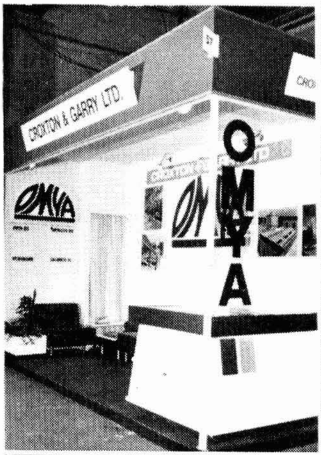
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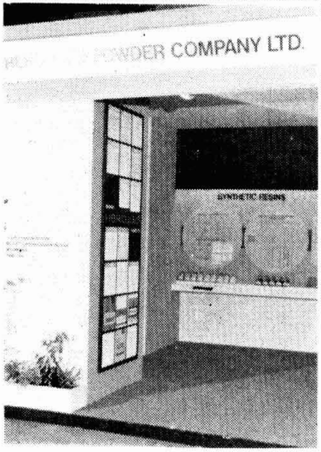
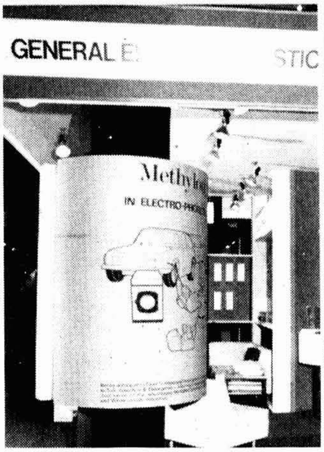
OMYA


WILLIAM SOULTON LIMITED


NOURY & van der LANDE GROUP


POWDER COMPANY LTD.
SYNTHETIC RESINS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VVB LACKE UND FARBEN DDR
VVB LACKE UND FARBEN DDR
VVB LACKE UND FARBEN DDR

Extenders

Now fully recovered from the after effects of the unfortunate fire in its factory in 1969, NORWEGIAN TALC A/S showed the familiar range of micronised Micro Minerals. A new, more complex, process for Micro Mica was announced, producing better and more varied grades. The results of investigations into the use of conventional extenders in coil and powder coatings were displayed, and a series of coarse grade Microdols for plasters and filling compounds introduced.

CROXTON & GARRY LTD. showed four products in the range of extenders from Omya that were new to OCCA. Omya D5, a fine particle size (1 — 20μ), low oil absorption, crystalline calcite was recommended for brilliant white pva and acrylic emulsion paints, acrylic sealants, undercoats, primers and eggshell finishes, showing excellent dry brightness. Hydrocarb, a crystalline brilliant white grade with top cut size of 4μ and a brightness of 96 (green filter) was demonstrated in high gloss alkyd paints, gloss and semi-gloss emulsions, and industrial finishes and primers. Advantages in reduction of chalking and the possibility of replacement of TiO_2 in typical formulations were stressed. Omyalite 90, a whiting of similar particle size to Hydrocarb, was specifically recommended for gloss and semi-gloss emulsion paints and decorative and industrial alkyds. Calibrite SL, a brilliant white grade of 15μ mean particle size, was recommended for high performance exterior masonry products. The Syloid range of silica extenders from Grace GmbH also appeared on this stand, including a new porous, amorphous grade, Syloid 165, a universal product for all finishes requiring flatting and a smooth surface.

A wide range of extenders, including lithopone from the International Lithopone Association, blanc fixe, white barytes and the Sachtoblanc series was exhibited by SACHTLEBEN AG.

A range of non-tarnishable bronze powders for metallic finishes from Claremont Polychemical Corporation was shown by VICTOR BLAGDEN & CO. LTD.

Silica extenders formed the main feature of the stand of JOSEPH CROSFIELD & SONS LTD. Particularly stressed were Gasil WP, for wallpaper and other aqueous systems, and Microcal ET, for emulsion paints.

Resins—alkyd

PLASTANOL LIMITED exhibited a new medium oil length alkyd modified with non-yellowing drying oil. The quick drying properties of the resin, Plastokyd A1, which is supplied in white spirit, were emphasised. Faster drying was also a feature of Hythane 5, a new urethane-modified alkyd following the earlier Hythane 2.

Mitchalac 4218, a novel plasticising alkyd for stoving enamels, having good colour and giving high gloss, was shown by W. A. MITCHELL & SMITH LTD., together with Mitchalac 756, a fast drying vinyl toluenated alkyd for litho inks.

Prominent amongst the resins from CHEMISCHE WERKE HUELS AG were Vestivit BL 905, a new alkyd for flexible industrial and coil coating, and Vesturit BL 901, which imparts improved compatibility with other lacquer systems in stoving finishes. A new air-drying medium oil length resin with fast surface and through dry, Alkydal F 41, intended for the motor repair trade, was introduced by FARBENFABRIKEN BAYER AG. Roskydal W9, a high build wax type polyester giving a colourless coating with good yellowing resistance, was also exhibited.

SYNTHESE KUNSTHARSFABRIEK NV had examples of alkyd/isocyanate coatings for prefabricated houses of asbestos cement or coil coated steel. These coatings were based on a new product, Setalux C1151-XX-51, an alkyd curing with aliphatic or aromatic isocyanates. Formulations for motor repair and refinishing based on this resin were also featured. For more general automobile finishes of the alkyd/melamine type, Setal 209-XX-60, a non-drying alkyd, was recommended. The


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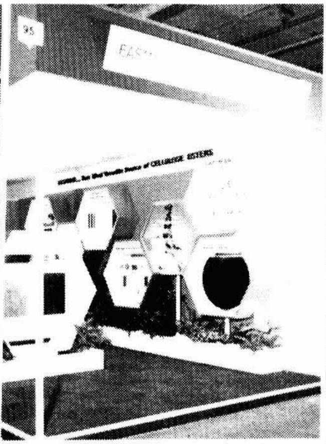
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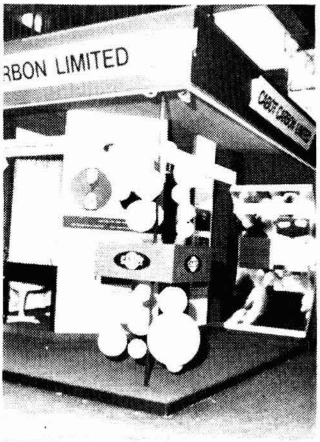
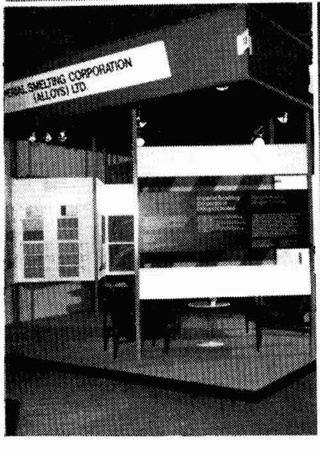

RBON LIMITED
CABOT CARBON LIMITED


RESINOUS CHEMICALS DIVISION
BRITISH PAINTS & CHEMICALS


JENAG EQUIPMENT LIMITED
LIQUID STRAINERS


LENNIG CHEMICALS LTD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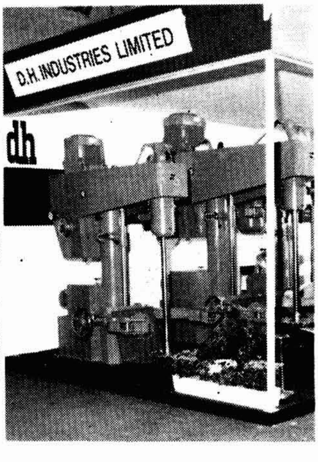
D.H. INDUSTRIES LIMITED
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good salt spray resistance of two drying oil modified alkyds, Setal 175-XX-60 and Setal 84-XX-70, in electrodeposition primers was demonstrated.

Scoplas 201SB, a silicone modified oil-free alkyd, was featured amongst the resins shown by SYNTHETIC RESINS LTD. Its use in high durability coil coating enamels was illustrated. Scoplas 101, an oil-free alkyd for cure by high functionality melamine/formaldehyde resins, was also exhibited.

AMOCO CHEMICALS EUROPE have developed an oil-free alkyd, PE-300, based on trimellitic anhydride. Flexibility and stain resistance advantages compared with resins based on trimethylol ethane were claimed. Wide strip coil coating was a suggested application. Coil coating was an application for coatings based on Dynotal FP-300, a new oil-free alkyd from NORSK SPRAENGSTOFINDUSTRI A/S, in combination with butylated or isobutylated melamines.

Alkyds were the main feature of the SCADO-ARCHER-DANIELS NV stand, and an oil-free coil coating grade, Scadonal 225, with outstanding deep-drawing properties, was shown. Scadonal 175, a recently-introduced product, was recommended for cross-linking with aliphatic isocyanates to give coatings with improved chalk resistance and gloss retention. A powder coatings formulation based on a new alkyd/melamine system, Scadonal P2001, was given prominence, excellent exterior durability and gloss retention being claimed.

DYNAMIT NOBEL AG introduced Dynapol P, an alkyd for electrostatic powder coating formulations, and also Dynapol L, a high molecular weight linear polyester with good stamping and deep drawing properties. General purpose alkyds, under the trade name Gedeglyps, based on linseed and fish oils, were amongst the resins from CDF CHIMIE and, on the same stand, silicone modified air-drying alkyds (Heydolacs SA60 and E1398) and specialist silicone alkyds (Heydolacs SA140, SA305, SA346, E905 and SA650) from Harold Heydon & Co. Ltd. were on view. SHELL INTERNATIONAL CHEMICAL CO. LTD. demonstrated a new use for Cardura E resins in low temperature bake refinishing enamels, using the resins DX-49 and DX-50 to illustrate the point.

VVB LACKE UND FARBEN displayed data on the weathering resistance of Duxalkyd S259, a drying type, in various media, and gave suggested formulations. A novel non-drying alkyd, Resenoplast F321, was introduced, and its properties in combination with polyurethanes outlined.

Resins—amino

A new isobutylated urea/formaldehyde resin, Beetle L3606, was featured by BIP CHEMICALS LTD. This is a highly reactive resin suitable for fast curing, acid catalysed wood lacquers or low temperature baking systems. The effect of various acid catalysts on hardening rate was shown. Further information on Beetle BE672, a recently-introduced isobutylated melamine with a wide range of compatibility with alkyds and acrylics, was available.

Epok U910/89, a newly developed methylated melamine/formaldehyde resin, was shown by BP CHEMICALS INTERNATIONAL LTD. High cross-linking efficiency with versatility in combination with oil-free polyesters and other plasticising resins was demonstrated, giving coatings of good hardness and flexibility, of interest for coil coating. Two new highly reactive urea/formaldehyde resins, Epok U9047, an isobutylated version, and the butylated Epok U9048, were also displayed.

NORSK SPRAENGSTOFINDUSTRI A/S introduced an acid curing isobutylated melamine resin, Dynomin FP-201, and demonstrated its combination of rapid cure, superior moisture resistance during and after cure, and good cold check resistance.


A/S NORWEGIAN TALC
Norwegian Talc


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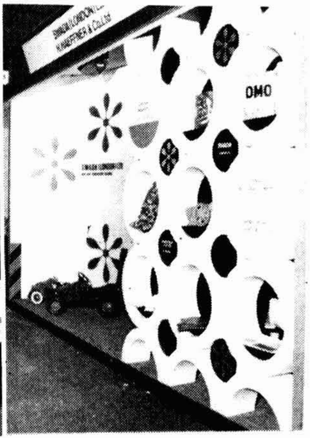
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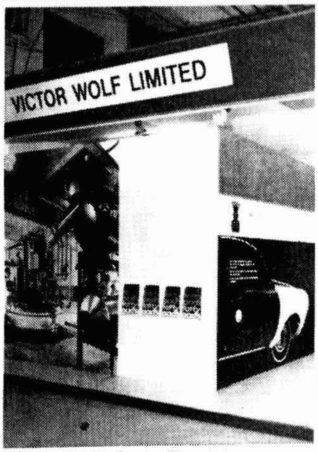
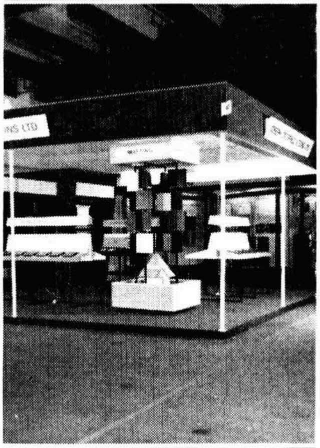
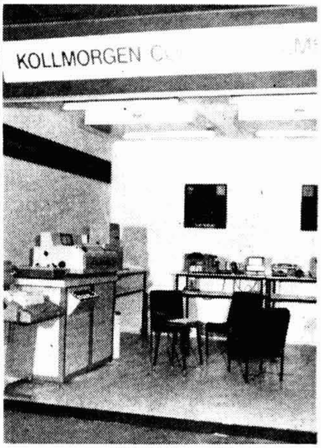

VICTOR WOLF LIMITED

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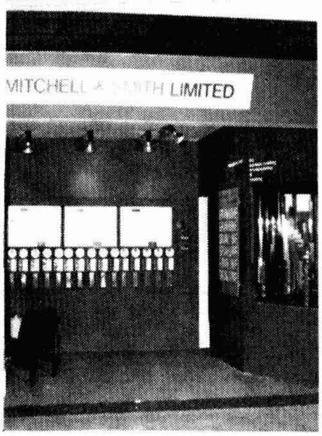

MITCHELL & SMITH LIMITED


WINKWORTH MACHINERY LTD.
WINKWORTH MACHINERY LTD
WINKWORTH MIXERS
STAINES ENGLAND


ANCHOR CHEMICAL
ANCHOR CURING AGENTS FOR EPOXIDE RESINS

It is hoped that this resin will be of interest to the wood finishing industry. Two isobutylated urea resins were also exhibited: Dynomin FP-101, with fast cure rate, long pot life, high solids and low viscosity, intended for paper coatings, and Dynomin FP-106, with particularly good compatibility with cellulose acetate butyrate and polyvinyl butyral, and giving good flexibility with long-oil alkyds in stoving finishes.

Resins—polyamide

VICTOR WOLF LIMITED exhibited a new alcohol-soluble polyamide resin, Wolfamid 19. Intended mainly for printing inks, the resin is claimed to have outstanding compatibility with nitrocellulose resins, and good grease and water resistance.

Resins—unsaturated polyester

The applications of a range of compositions based on the unsaturated polyester resins Celipal 710, 810, 830 and 850 were displayed by CHEMISCHE WERKE HUELS AG. Interesting uses included pigmented lacquers, potting compounds and fillers.

W. A. MITCHELL & SMITH LTD. gave particular emphasis to Polymaster 1209, an unsaturated polyester claimed to have excellent colour properties in castings or coating lacquers.

Coil coating was the suggested application for Ester-Diol 204, a polyester with good overbake resistance, weatherability and stain resistance offered by UNION CARBIDE EUROPE SA. Silicone modified polyesters E976, E1112 and E1135 from Harold Heydon & Co. Ltd. were shown on the CDF CHIMIE stand.

Resins—epoxy

The range of Eurepox epoxy resins, available in the UK for the first time, was the focus of the SCHERING AG stand. The resins are available in solvent-based or solventless forms, and one of the range, Eurepox 716, can be used in aqueous emulsions. The use of epoxy paints as anticorrosive coatings in modern automated construction yards and for the repair and protection of concrete was illustrated.

SHELL INTERNATIONAL CHEMICAL CO. LTD. added two resins to the Epikote range; Epikote DX216, a medium viscosity resin, and Epikote DX315, a low viscosity resin. The use of the products in solventless and high solids coatings was recommended. New decorative effects for powder coatings based on Epikote 1004, including matt and semi-metallic finishes, were demonstrated.

Iopox epoxy resins were shown by CDF CHIMIE, the particular aspects featured being self-levelling floor coatings, solventless coatings, and paints for underwater application. Floor coating applications for the Araldite range of epoxy resins, as well as general coating and civil engineering uses, were described by CIBA-GEIGY UK LIMITED.

Resins—acrylic

Four new hydroxylated resins appeared on the BP CHEMICALS INTERNATIONAL LTD. stand. Three of these, Epoks D2107, D2108 and D2109, were developed specially for metallic car body finishes including overlacquering techniques, while the fourth, Epok D2110, is intended for the low-bake domestic appliance field. A series of electron micrographs illustrated an interesting phenomenon which occurred during development work on aluminium pigmented lacquers. At certain specially-prepared formulations, an extremely regular flocculation of the pigment occurs, giving a regular pattern of evenly-spaced circular flocculates. BP Chemicals is carrying out further work in an attempt to explain this effect.

SYNTHETIC RESINS LTD. showed the Scopacron 400 series of thermosetting acrylics, and the Scopacron 800 SB range of silicone modified acrylic copolymers. The Neocryl range of thermoplastic acrylics, supplied in granular form, was exhibited by POLYVINYL CHEMIE HOLLAND NV, and printing ink applications outlined.

A new product from this company is the alcohol soluble Neocryl NJ-71 acrylic resin, displayed with special formulations for gravure and flexographic printing on plastics.

Polymethacrylate esters were featured by the Dyestuffs Division of ICI LTD. Bedacryl 200 CX was specially recommended for two-pack acrylic/urethane finishes, and Bedacryl 123 AH, for general non-convertible coatings, was also shown.

The superior stain resistance of systems based on Acrysol 110, a thermosetting acrylic, compared with three-component systems, was demonstrated by PLASTANOL LTD. Panels showing the resistance of the coatings to lipstick, boot polish and mustard were displayed.

The RESINOUS CHEMICALS DIVISION of BRITISH PAINTS & CHEMICALS LTD. exhibited two thermosetting acrylics for industrial finishes, Wresacryl R513 and Wresacryl R514. The high performance coatings—comparable with those based on acrylamide-containing acrylics—obtained by blending Wresacryl R514 with RCL's hexamethoxy methyl melamine were described. Wresinol R513 is claimed to provide tough, adherent, low bake finishes when used with amino resins.

Several new acrylics were announced by ROEHM GmbH CHEMISCHE FABRIK, including: Plexisol DV577 for coil coating; Plex 4811L, a water-soluble type for electrodeposition; Plex 5350L, for curing with isocyanates; and Plex 8675F, a methacrylate for water-free masonry paint.

BASF UNITED KINGDOM LTD's new thermosetting cross-linkable acrylic, Luprenal LR8303, was specially designed for coil coatings, and its good durability in combination with epoxies was demonstrated. For powder coatings, an improved acrylic grade, LR8259/1, has been produced.

A hydroxyl-containing polymer for use in two-pack lacquers, Synedol 2513 XF, was featured by SYNRES INTERNATIONAL NV. Use with aliphatic and aromatic polyisocyanates is intended. A display on the LENNIG CHEMICALS LTD. stand demonstrated the versatility of Primal AL388, a multipurpose acrylic binder. Various pigmented films, and also clear finishes and stains for wood, were illustrated.

Resins—emulsion polymer

Epok V8402, a new vinyl acetate/olefin/VeoVa 10 latex designed to combine the high durability of VeoVa 10 systems with the economies of olefin types, was featured by BP CHEMICALS INTERNATIONAL LTD. The high level of performance of this new product in interior and exterior coatings, including textured masonry finishes, was illustrated. Also shown was Epok V8303, a vinyl acetate/olefin latex developed from the successful Epok V8300, with higher solids than the earlier product.

CHEMISCHE WERKE HUELS AG demonstrated the applications of the Litex copolymer and terpolymer latices. In particular, the good water, alkali, dirt and scrub resistance of paints based on Litex A10 and the improved adhesion and resistance to water swelling imparted by additions of Litex 6301 to cement mortars for expanded thermoplastics tiles were emphasised.

Three acrylic emulsions with increasing film forming temperatures, Plextol D471, Plextol D541 and Plextol M600, were exhibited by ROEHM GmbH CHEMISCHE FABRIK. LENNIG CHEMICALS LTD. produced a new experimental product, acrylic emulsion E521. Comparisons with other emulsions in a water immersion test were made, and the superior resistance of E521 to water whitening when used as a glaze coat illustrated.

The display of WACKER-CHEMIE GmbH included three novel copolymer dispersions. Vinnapas Dispersion EZ 15/3 is intended for interior paints with high pigment loading and good flow. The SAF 5/37 grade of this product, based on styrene/acrylate, is for exterior coatings, having an even higher pigment loading than EZ 15/3. For use in fast setting, heat resistant pvc adhesives, Vinnapas Dispersion EV 12/46 was introduced; the improved flow on the machine of adhesives based on this dispersion was demonstrated.

Exterior finishes were the end use for two products exhibited by SYNRES INTERNATIONAL NV, Synresyls CO50 and CO56. CO56 was being shown for the first time, and panels illustrated the superior resistance of coatings based on this emulsion for testing in a humidity cabinet and in artificial weathering apparatus.

Resins—miscellaneous

The Exon range of vinyl resins produced by Firestone was introduced by KINGSLEY & KEITH (CHEMICALS) LTD. In addition to vinyl chloride/acetate types, two hydroxyl-containing polymers are offered, a maleate copolymer and a vinyl chloride/TFCE copolymer. Three carboxyl-containing "metal adhesion" types with good solubility characteristics are also included in the range.

Reactive vinyl resins with good flexibility for paper and foil coatings, VERR and VMCA, were shown by UNION CARBIDE EUROPE SA, together with a series of phenoxy resins suggested for use in can coatings in combination with phenolic or epoxy resins. A particular feature of this stand was a display showing the corrosion resistance of zinc rich primers based on ethyl and Cellosolve acetates.

SHELL INTERNATIONAL CHEMICAL CO. LTD. suggested a novel application for VeoVa 10. A water soluble polymer, DX-40, based on this monomer with styrene and acrylic monomer was exhibited in white paints for electrodeposition, exceptionally good colour and alkali resistance being demonstrated. The use of Vilit vinyl chloride/vinyl acetate/maleic acid ester copolymers in one and two-coat systems for ferrous and non-ferrous (especially hot galvanised) substrates was illustrated by CHEMISCHE WERKE HUELS AG.

Vinyl acetate/ethylene copolymers for use as stir-in additives to cement-based products were exhibited by WACKER-CHEMIE GmbH. Supplied in dispersible powder form, Vinnapas EMPZ 1 is for use in mortars and tile cements, giving improved water and alkali resistance, while the same benefits, as well as added strength, are gained by adding Vinnapas EMPZ 2 to concretes.

Urethane lacquer resin 798-8, a recent development of the Cargill Corporation, was demonstrated in leather finishes by VICTOR BLAGDEN & CO. LTD., who also had on display a moisture curing polyurethane system for seamless floorings. Polyurethanes were also prominent on the SYNTHETIC RESINS LTD. stand; Beckurane L90, L91 and DV1866 form a new series of elastomeric urethanes for non-curing coatings for leather; Beckurane 2-225 is a non-yellowing urethane prepolymer for use in two-pack coatings of good colour and durability.

A development product, Imprez 100, a petroleum resin for use in heat and UV stable finishes, was offered by ICI LIMITED, as well as the one-pack urethane prepolymers based on Suprasec 1100 and Daltolac 2200 for heavy duty finishes. Applications of the Alloprene range of chlorinated rubbers in traffic marking paints, high build marine paints and printing inks were also outlined.

Chlorinated rubbers were emphasised by FARBENFABRIKEN BAYER AG. A new range was compared favourably with existing types in respect of stability and control of viscosity from batch to batch. Bayer also showed a new condensation addition product, coded 12 70, a self cross-linking binder for coil coatings. Higher flexibility and resistance to household detergents are advantages of the product in domestic coatings. Desmodur HL, a new polyurethane intended particularly for formulations to be applied by curtain coater was announced; this product combines short drying times with long pot life and good viscosity stability.

CORN PRODUCTS (SALES) LTD., a new exhibitor at OCCA, showed latest developments in the Kelrez range of resins for printing inks. Of particular interest were Kelrez 42376, a maleic-modified penta ester of rosin, having very quick setting properties, Kelrez 42405, a rosin-modified phenolic resin imparting very high gloss, and Kelrez 40150, designed to eliminate pin-holing in alcohol based nitrocellulose or polyamide inks. Another new exhibitor, GENERAL ELECTRIC PLASTICS NV, centred its stand on Methylon, a phenolic based compound for electrophoretic primer systems. Already used in Europe, the resin was displayed as having high throwing power and good chemical resistance and mechanical film properties in electrophoretic formulations.

Coatings based on polyvinyl fluoride were indicated by DYNAMIT NOBEL AG with a binder of this type. Exceptional chemical and weathering resistance are expected for this type of paint.

An addition to the range of ketone resins from the Walter Ulbricht Leuna works was announced by VVB LACK UND FARBEN. The new resin, L, is a condensation product of cyclohexanone and formaldehyde, modified with a metal stearate. Applications in matt NC lacquers were outlined.

Amongst the wide range of resins shown by RHONE POULENC/REDIS, particular emphasis was placed on: Rhodeftal 200 polyimide resins for high temperature —up to 300°C—resistant coatings with high salt spray and weathering resistance; Rhovinal BSA, a polyvinyl butyral with less than 1 per cent acetate, applications including wash primers, shop primers, welding primers and temporary protective coatings; and a vinyl chloride copolymer for priming coats in a system designed for application to damp plaster.

Following market trends in rosin, HERCULES POWDER CO. LTD. introduced pilot plant batches of a series of hydrocarbon resins. It is hoped that these resins will find application over a very broad field, including adhesives, printing inks, floor covering, wood preservatives, rubber compounding, and hot melt applications. Two new resins for printing inks were also shown, Pentalyn 417 and Pentalyn 450, both specially designed for heat-set and quick setting offset inks.

The main feature of the EASTMAN CHEMICAL INTERNATIONAL AG stand was a large range of cellulose acetate butyrate resins, with a quick selection chart for various applications. A new development was the use of chlorinated polyolefines as media for primers for polypropylene. Although still at an early stage, excellent adhesion properties for these formulations have been shown.

Chemical intermediates

NOURY & VAN DER LANDE NV featured the Nourypol range of polyols for isocyanate-cured two-component lacquers, in particular a low viscosity version suitable for use in jointing and flooring compositions. Two polyols based on bisphenol A, Dianols 22 and 33, were given prominence; it is intended that these products will find use in the manufacture of unsaturated polyester and alkyd resins.

Examples of polyurethane foams based on the new Unem 444 series of polyols appeared on the UNILEVER-EMERY NV stand and included an impressive artificial wood. High density integral skin mouldings based on the polyols were also shown. Amongst the company's range of Empol dimeric and trimeric acids, a new product with very pale colour and high dimeric acid content, Empol 1010, was featured.

The Pamolyn range of technical grade conjugated linoleic acids was displayed by HERCULES POWDER CO. LTD. These products are produced by a precision controlled process from high grade tall oil fatty acids, and are available in three series, Pamolyn 100, based on oleic acid, Pamolyn 200, based on linoleic acid, and

Pamolyn 300, conjugated diene fatty acids. Fatty acids were also given prominence by VICTOR WOLF LTD., two dehydrated castor oil types being introduced. Dedico 80 is a DCFO containing approximately 80 per cent conjugated linoleic acid; it is hoped that this will find use in solvent- and water-based alkyds and epoxy esters where outstanding drying properties are required. Dehydrated Castor Oil Fatty Acid 55, containing a minimum of 55 per cent conjugated linoleic acid, is intended for use where the higher reactivity and better drying characteristics of Dedico 80 are not required. A pure (99 per cent) grade of isophthalic acid, produced by Arco Chemical Company, was exhibited by CORNELIUS CHEMICAL COMPANY. The range of Epiol glycidyl ethers from Nippon Oils & Fats Co. Ltd. was shown by KINGSLEY & KEITH CHEMICALS LTD.

Additives, driers, surfactants

Laromin LR8308, a new diamine hardener for curing epoxies of low molecular weight at temperatures down to 0°C was exhibited by BASF UNITED KINGDOM LTD. Epoxy curing agents formed the major exhibit of ANCHOR CHEMICAL CO. LTD.; there were two new products, Ancamine CTA, an accelerated polyamine for epoxy/coal tar systems, and Ancamine AD, of particular interest for its ability to cure films in cold, damp conditions.

THOMAS SWAN & CO. LTD., in addition to the established Casamid range of curing agents, had available a development material, coded SP258. This is a water dispersible curing agent, supplied as a 50 per cent solids solution in water. It is hoped that, using this compound with liquid epoxy resins, no solvent will be required to formulate water-thinnable coatings. This is of particular importance for paints to be applied in confined spaces; the chemical resistance of the cured film is said to be greater than that of conventional solvent-based epoxy systems. Another new product, SP232, was featured, its very rapid cure at low temperatures being emphasised, and its use as an accelerator in combination with other curing agents indicated.

VEBA-CHEMIE AG presented new uses for diamines, diisocyanates and polyamides related to isophorone. An experimental product, polyamide V208, was demonstrated as a curing agent for epoxy powder coating compositions to be applied by electrostatic methods, and an experimental blocked isophorone diisocyanate was also recommended for powder coatings. Isophorone diamine and diisocyanate were recommended as epoxy curing agents, and trimethyl hexamethylene diamine and diisocyanate as colour stabilisers in one- and two-pack lacquer systems. Trigonal 14, a UV activated curing catalyst for polyester lacquers, was given prominence by NOURY & VAN DER LANDE NV.

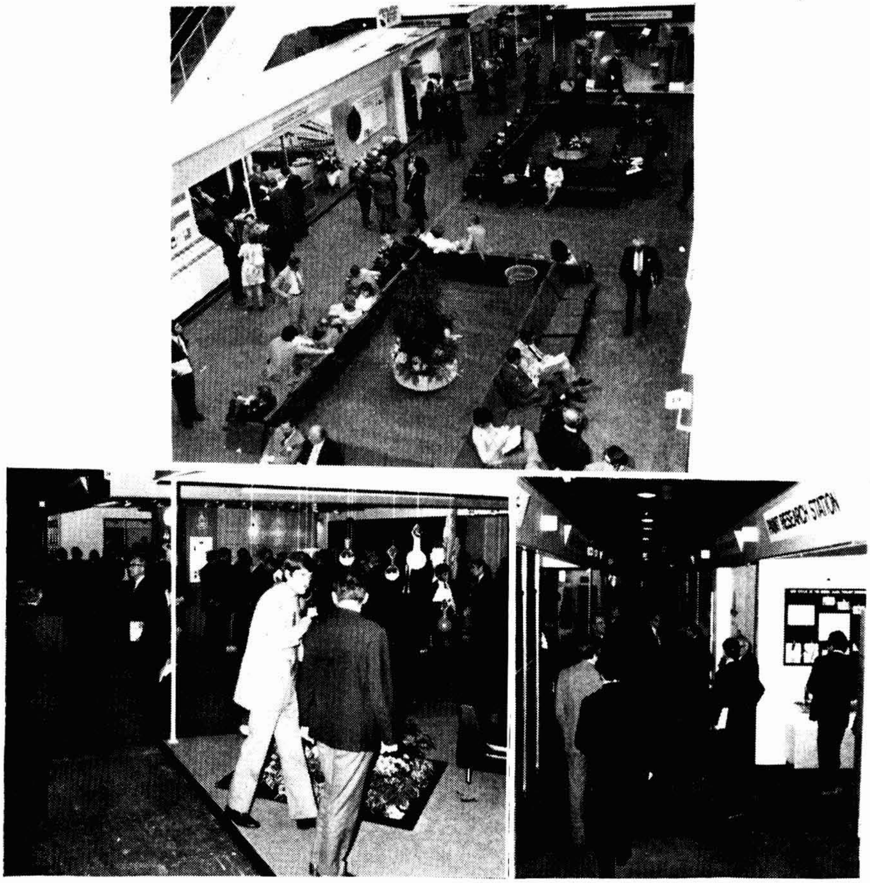
SANDOZ PRODUCTS LTD. added a whitener paste, WROL, to the Pintasol range. The improved scattering—and hence hiding power—and whiteness of paints containing the paste were demonstrated. A new product from ALBRIGHT & WILSON LTD. was Accomet C, a water-soluble concentrate based on chromium salts. Panels illustrating the excellent adhesion of coatings containing this product to metal substrates, including aluminium, mild steel, and zinc, and the improvements in corrosion resistance imparted, were displayed. Room temperature application is possible for this type of coating, and additional benefits include the lack of reaction time, the absence of sludging or effluent problems, and the fact that no rinsing is necessary.

Cutinox toxicant pastes, produced by Acima Chemical Industries in Switzerland, appeared on the KINGSLEY & KEITH (CHEMICALS) LTD. stand. For use in antifouling paints, the incorporation of these micronised pastes is intended to avoid dispersion and toxic fume problems found with other biocides.

SHELL INTERNATIONAL CHEMICAL CO. LTD. indicated novel uses for the Epikure range of curing agents.

Thixotropic emulsion paints formed the theme for TITANIUM INTERMEDIATES LTD., the use of titanium chelates in their manufacture being illustrated. Main types mentioned were triethanolamine titanate, for exterior finishes, diethanolamine titanate, recommended for glass paints, and the new Tilcom range.

Cab-O-Sil fumed silica, although introduced at OCCA 22, has only recently become available in the UK, and CABOT CARBON LTD. gave special coverage to its uses in paints, plastics, rubbers and inks, using a 20 minute film to give further emphasis. Basically a thickener and thixotropic agent, Cab-O-Sil can also be used for viscosity stability and prevention of settling. Thixotropic agents for non-aqueous systems were featured by BAKER CASTOR OIL COMPANY, including two new types. Rheox 1 is a non-hygroscopic, hydrolytically stable and chemically inert thixotrope, supplied in paste form and recommended for protective coatings where the ultimate structure for thick films is required in combination with good application properties. Thixseal is a powder-form product designed for use in polymeric sealants and recommended also for plastisols and powder coatings. In sealants, Thixseal is claimed to impart rheological characteristics such that the product is pumpable and easy to work, but maintains outstanding sag control. A new matting agent, Matt 2, an organic petroleum high polymer supplied as a fine dispersion in xylene, was also introduced, and recommended for use in clear lacquers, particularly urethane systems.



General scenes at OCCA 23: people from 38 overseas countries signed the visitors' book

BERK LIMITED demonstrated the range of applications of its Bentone gelling agents in paints, plastics and adhesives.

A broad range of additives was shown by HARDMAN & HOLDEN LTD. Particular prominence was given to the Manolox series of wetting agents. Di-alkyl sulphosuccinates, these compounds are for use in emulsion polymerisation systems, and details of the mechanisms involved were given. The results of long term durability tests on water-resistant masonry paints based on Manolox 403, a silicone-free material, were illustrated; water repellents based on this compound satisfy the requirements of BS 3826 in classes A, B and C. Amongst a variety of additives exhibited by the DANIEL PRODUCTS COMPANY, emphasis was given to Tint-Ayd opacity booster, designed to increase the hiding power of white pigments with a minimal effect on reflectance values, and Slip-Ayd, a series of low molecular weight polyolefin and polymerised wax dispersions to improve slip and mar resistance, etc. A new micronised polyethylene wax from BASF appeared on the BUSH, BEACH & SEGNER BAYLEY LTD. stand. Designed for quicker and simpler preparation of wax dispersions, the new product is intended for the paint and printing ink industries.

Maleic anhydride adducts were shown by CHEMISCHE WERKE HUELS AG to improve drying and overcoating of corrosion resistant electrodeposition primers.

Manufacturing equipment

Following the trend set in previous years towards machines for use with ready-made dispersions and easily dispersed pigments, the greatest number of machines on show were of the high-speed mixer type. As well as its range of conventional high-speed mixers, SILVERSON MACHINES LIMITED showed the new Flash Mix, in which solids and liquids are fed simultaneously through a specially designed hopper to a series of mixing heads, the homogeneous dispersion being discharged almost instantaneously. It is claimed that the machine will disperse solids at rates in excess of 1 cwt per minute, and models for batch and in-line operation are available. The company's Multishear mill, operating by multiple rotors and stators, was also exhibited in batch and continuous forms.

The Trifor H450 was featured by MOLTENI OFF. MECH, being a high-speed disperser suitable for operation under vacuum, with the facility of changing the position of the impeller without any leakage of air. A completely enclosed high-speed disperser was the WINN & COALES exhibit. Fitted with an internal temperature control jacket, the mixer is equipped with a hydraulic drive coupling, protecting the motor against jamming or solidification in the mixing vessel. A unique bearing unit is incorporated which prevents the machine charge coming into contact with the bearing by means of air trapped by the bearing assembly.

D.H. INDUSTRIES LTD. also had on display a machine with hydraulic drive, a high-speed circulation mixer in sizes up to 75 h.p., manufactured by one of the company's principals, Ateliers Sussmeyer. Another principal, Peter Kupper, provided the type VIS-D mixer, an inclined vertical helical, either single or twin, which is capable of mixing both dry and pasty materials. A twin-shaft high-speed mixer from Paul Vollrath was also shown, type VDD5, in sizes up to 200 h.p. Much reduced mixing times compared with single shaft mixers are claimed. JOHN GODRICH exhibited the Kotthoff high-speed disperser, a novel feature of which is the lack of bearings at the central disperser head.

A new series of laboratory mixers was introduced by THE MASTERMIX ENGINEERING CO. LTD. The H Drive Laboratory Heavy Duty Agitators, available with $\frac{1}{8}$, $\frac{1}{4}$ and $\frac{1}{2}$ h.p. motors, incorporate infinitely variable speed, interchangeable heads and constant speed under load. This is believed to be the first laboratory heavy duty mixer to have all these features.

A Variflow control had been added to the range of high-speed mixers produced by PETER SILVER & SONS (ENGINEERS) LTD. This is an adjustable baffle plate which can be used to regulate the flow into the machine head. This allows the processing of more viscous materials, by starting at low flow rates until the initial inertia has been overcome, and reduces strain on the motor.

The latest machines in the Rotamix and Biotomix ranges were exhibited by MILLROOM ACCESSORIES & CHEMICALS LTD. The high-speed Kreis dissolvers displayed by TECHNESSEN NV incorporated several novel safety devices, such as a pressure sensitive device to prevent the machine operating unless the mixing vessel is secure. Coupled automatic speed and power regulators prevent any overloading of the motor. Technessen also showed an agitator ball mill capable of the full dispersion process, the Netzsch Molinex for continuous operation. The patent agitator, composed of eccentrically mounted grinding rings, is claimed to give high grinding tolerances with minimum wear and temperature rise.

The Polymill was exhibited by AUGUSTS LTD. Relying on glass beads for its shearing action, the Polymill has a special disc-shaped agitator, designed to create a vortex in the bowl shaped mixing vessel. The machine is claimed to carry out the complete dispersion process in materials up to 50 poise.

Other "complete" dispersers of this type were the 255 gallon capacity 200 S Attritor from TORRANCE & SONS LTD., the Perl mill made by DRAISWERKE GmbH and the WILLIAM BOULTON LIMITED Pearlmill. The latter company also showed the Podmore Boulton Vibro-Energy Mill range, which grind dry materials by the three-dimensional vibration of a vessel containing columns of cylindrical grinding media. A very narrow range of particle sizes is obtained, owing to the "protection" of smaller particles by larger particles.

The Heidenau Power Grinder 192 B was given prominence by MASCHINENFABRIK HEIDENAU VEB. Described by the manufacturer as a spindle mill, the Power Grinder operates on the same principle as a sand mill, using silica beads as the grinding media. The mill can operate in clockwise or anticlockwise directions, equalising wear, and outputs of up to 165 gallons per hour are claimed. The company also showed a range of triple-roll mills, as did its English associate, MARCHANT BROTHERS LIMITED. BUHLER BROTHERS LIMITED exhibited what is claimed to be the largest triple-roll mill on the market, the SDV 1300/400, with roll dimensions of 16in × 51½in. The SDW 800/300, with dynamic hydraulic and automatic water cooling systems was also exhibited, as was a hydraulic laboratory mill, the SDH-300, with 6in × 12in rolls. A system of modifications by which older triple-roll mills could be updated to incorporate design developments from newer models aroused much interest on the COX'S MACHINERY LTD. stand.

A novel Z-blade mixer, claimed to be the world's smallest, was exhibited by WINKWORTH MACHINERY LTD. A ½-pint working capacity model capable of vacuum operation and fitted with an electric heating jacket, the mixer is intended for laboratory evaluation of production technique, particularly where the use of expensive materials is necessary.

The Iopor Ultrafiltration system was a new development from a new exhibitor, DORR-OLIVER COMPANY LIMITED. Based on a membrane separation process, the system separates paint components from water and undesirable ionic impurities, and can be used both for the continuous purification and dewatering of paints for electrodeposition, and recovery of paint from "drag-out" effluent. Great savings of paint in electrophoretic processes are claimed, as well as elimination of problems in effluent disposal.

A new large capacity model was added to the JENAG EQUIPMENT LIMITED range of liquid strainers. The model 3000 series has an output range of 0-2,700 gallons per hour, and has the usual Jenag feature of self-cleaning by back flushing, a gauge being fitted to show the pressure drop through the filter, which increases with increasing contamination. DIAF A/S showed a high capacity vibratory sieve, type RS450, for use with liquid or dry materials. Vibratory sieves were also featured by WILLIAM BOULTON LIMITED; in the latest model the screen is supported by a cushion of air, giving greater throughputs and allowing thixotropic materials to be handled.

STRAZDINS PTY. exhibited a dispenser for tinters to be added to white base paint at retail outlets, allowing the customer to have colours mixed "to order." Although this method is used in the UK, it has not found wide acceptance; American and Australasian manufacturers are using this technique increasingly. Strazdin's equipment is calibrated in both metric and imperial measure, so that tins of base paint in all sizes of both measures can be tinted without the need for reformulation. A colourant disperser manufactured by H. G. Fisher was displayed by CAL/INK CHEMICAL CO. OF CANADA LTD., illustrating its use with Cal/Ink's own tinting dispersions. Colour cards and books of colour samples manufactured by Colwell Colour Cards were shown in the colours of the Cal/Ink colourant systems.

Items of cleaning apparatus appeared on the stand of MARCHANT BROTHERS LIMITED, a pan cleaner handling change pans of up to 200 gallons capacity and an automatic pail washer operating at speeds of 40-120 pails per hour. This company also had a roller coating machine capable of coating strips of metal up to 13½in wide and 1in thick at speeds of 183 ft/min.

D.H. INDUSTRIES LIMITED had extended its range of volumetric filling machines by the addition of the V154 semi-automatic machine, based on the fully automatic V136. New from TORRANCE & SONS LTD. was an automatic coding machine which can print on to moving objects without smearing. Capable of being added to existing equipment, the machine can handle up to 80 operations per minute.

In the field of resin plant, HYGROTHERM ENGINEERING LTD. exhibited developments in a hard resin cooler. This machine extrudes the molten resin into rods of from $\frac{1}{16}$in to $\frac{3}{16}$in diameter, which are then water cooled, dried, and broken into ¾in lengths.

THE PYRENE COMPANY showed its range of metal test panels, available in various pretreatments.

Testing equipment

As at OCCA 22, computer-based systems for colour matching were well represented. and further development has produced instruments of greater sophistication. The Pretema 32 Filter Spectromat Spectrophotometer, shown by INSTRUMENTAL COLOUR SYSTEMS LTD., is now available for on-line use, in combination with a process control computer for formulation computation and colour correction calculation. This instrument gives automatic calculation of shade correction for production work, shade matching, tinting factors and colour difference tolerances. A new lighting cabinet conforming to BS 950 Part 2 was also displayed.

An integrated system for colour measurement and computer control of industrial processes based on the Color Eye colorimeter was demonstrated by KOLLMORGEN COLOR SYSTEMS. A selection of the other equipment supplied by Kollmorgen to the surface coatings industry, including the Macbeth range of lighting cabinets, and the new Macbeth RD505 portable lightweight solid-state densitometer for the printing ink industry, was on view.

The range of Gardner instruments exhibited by WENTWORTH INSTRUMENTS LTD. included the XL-10 digital computer, which determines automatically whether a sample is within colour tolerances, and gives a guide to the corrections needed to reach an acceptable match. This latest development of the colorimeter appeared to be a considerable advance in neatness of design and stability compared with earlier models.

FERRANTI LTD., in addition to the Ferranti-Shirley cone and plate viscometer and the coaxial cylinder viscometer, exhibited a new instrument for flow line determination of viscosity. The Unipan Ultrasonic Viscometer Type 504 A, made in Poland, consists of a probe immersed in the fluid, and measuring head. A wide range of viscosities is covered, and the instrument can be used for viscosity control of continuous processes. Given special prominence amongst the wide range of equipment from RESEARCH EQUIPMENT (LONDON) LTD. was the latest model of the ICI high temperature cone and plate viscometer. The instrument is thermostatically controlled at set temperatures between 25°C and 150°C, and is intended for the determination of melt viscosity of resins during manufacture. A paper describing this instrument has appeared in this *Journal* (1970, 53, 876).

A new sedimentometer, the Ladal X-Ray Scanning Sedimentometer, featured on the MICROSCAL LTD. stand, together with Microscal's wide angle sedimentometer, now equipped with an automatic vertical scanning facility. A new model of the flow microcalorimeter, which can be vacuum degassed to remove surface water prior to adsorption experiments, was shown. Experiments can also be performed in the presence of metered amounts of gas, and heats of degassing measured.

JOHN GODRICH exhibited test equipment for the paint and dyeing industries. The Praxitest 100 for dyestuff testing permits the application of a dye solution under controlled conditions, for subsequent examination of the uniformity of dyeing and other properties. The Xenotest range of machines for accelerated light and weather fastness testing, based on a Xenon arc, were also shown, emphasis being placed on the machines' robustness and ease of programming.

Also concerned with the dyeing industry was a laboratory sample dyeing unit introduced by DYEING SERVICES LTD. The machine has, however, a potential use for the testing of colouring techniques for non-textile substances as well as for colouring of textiles; for instance in the surface dyeing of plastic mouldings or extrusions of acrylic and urethane resins. The unit can also be used to test the sublimation fastness of pigments or dyes in a variety of media. A three-bath dyeing and testing machine was also shown.

The TORSION BALANCE CO. (GREAT BRITAIN) LTD. demonstrated its comprehensive range of weighing equipment covering the range 7 Kg to 0.1 mg, all incorporating the "no knife edge" construction. A new print-out unit was displayed.

The photosedimentometer attachment for its disc centrifuge was shown in operation by JOYCE LOEBL & CO. LTD. The particle size distribution is displayed automatically on a chart recorder from an optical/photoelectric system through the transparent disc. Automatic operation is possible.

A full range of testing equipment was exhibited by SHEEN INSTRUMENTS LTD. Of particular interest was a lever operated scratch tester combining the smooth advance of motor driven apparatus with the economy of hand operation.

Prominence amongst the instruments from ELCOMETER INSTRUMENTS LTD. was given to the Eddy Gauge 133, and eddy current type film thickness gauge, and to the Surclean 153, a surface cleanness tester operating on a reflective principle. Also featured was the Audiotester 171, a thickness gauge for routine testing which emits an audible note when the pre-set limits of thickness are exceeded.

RUDOLPH MEYER'S INC. demonstrated the Tack-o-scope for measuring the tack of printing inks. A novel feature was a print-out device for recording the tack of an ink according to a pre-set programme.

Acknowledgments

The Honorary Editor wishes to thank the following members of the Association who gave so much of their time to assist in the reporting of the exhibition:

C. Barker, R. McD. Barret, T. M. Bowerman, R. A. Brett, T. R. Bullett, C. Butler, R. A. Chappell, W. M. Collie, F. Courtman, G. P. Dee, S. Duckworth, R. N. Faulkner, H. J. Griffiths, Dr H. R. Hamburg, G. V. Hill, R. F. Hill, G. L. Holbrow, D. John, M. A. Kerr, D. H. W. Lovegrove, Dr L. A. Lowe, J. R. Lyon, W. F. McDonnell, J. N. McKean, J. E. Mitchell, I. S. Moll, Dr W. M. Morgans, R. H. E. Munn, J. L. Prosser, E. F. Redknap, F. B. Redman, D. W. Sexty, N. H. Seymour, E. Smith, F. Sowerbutts, B. Windsor and the Assistant Editor (R. Wood) who collated their reports and prepared this review.

24 OCCA

Technical Exhibition

17-21 April 1972

As announced in the July issue of the *Journal*, the Twenty-fourth Technical Exhibition will be held in the Empire Hall, Olympia, from 17-21 April 1972.

Many companies, both from the UK and overseas, have already applied for space, thus emphasising the success of the exhibition at Olympia last year. Any company, therefore, wishing to exhibit is urged to apply to the Director & Secretary immediately at the address shown on the front cover.

Olympia is easily accessible from hotels in the West End. The special extension underground service from Earls Court to Olympia will be operating at 10-15 minute intervals throughout the period of the Exhibition. The hours when the Exhibition will be open are given below:

Monday	17 April	15.30—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

As usual, information leaflets in six languages are available free of charge and these will be distributed to paint companies overseas well before the Exhibition. Any company or individual requiring copies to send to colleagues overseas should apply to the Association's office.

Interpreters for French, German, Italian and Spanish visitors will be in attendance throughout the period of the Exhibition, and all overseas visitors are asked to sign the Visitors' Book at the Information Centre.

The Association has made arrangements with several hotel groups for hotel accommodation for visitors to the Exhibition. Full information will be given in the *Official Guide* being sent overseas early in the New Year, but any person wishing to take advantage of this service should write to the Association's offices.

Report of Meeting of Council

The first meeting of the Council under the chairmanship of the Association's newly elected President, Mr A. W. Blenkinsop, was held at Wax Chandler's Hall, Gresham Street, London, on Thursday 3 June, with 27 members present.

Council received the resignation of Mr D. M. James as one of the Elective Members of Council since he was leaving the industry, and invited Mr H. R. Touchin, who had been placed fourth in the 1970 election, to fill the vacancy for the unexpired portion of Mr James's service.

The President extended a warm welcome on behalf of the Council not only to the three Elective Members—Dr V. T. Crowl, Mr D. J. Morris and Mr A. T. S. Rudram—whose election had been announced at the Annual General Meeting in Torquay, but also to other members attending for the first time and those who were serving again on Council in different capacities.

The dates of the Council meetings for the forthcoming session were agreed, together with the date of the Annual General Meeting in London on Wednesday 7 June 1972.

The Committees and Working Parties of the Council for the forthcoming session were appointed and these are listed elsewhere in this issue of the *Journal*. In accordance with the practice of previous years, the President of the Oil and Colour Chemists' Association Australia was co-opted to the Council, and the appointment of the Association's representatives on other organisations for the forthcoming session were also confirmed.

Reports were received on:

(a) Torquay Conference, 4-8 May 1971, which had been most successful and attended by representatives from 14 overseas countries—Belgium, Canada, Denmark, Finland, France, Germany, Holland, India, Italy, Japan, Norway, Sweden, Switzerland and the USA. Attendance at all the sessions throughout the Conference had been encouraging and a high standard of discussion took place not only in the technical sessions but also in the management and workshop sessions. The Conference Diary appeared in the July issue.

(b) The 1971 Exhibition, to be held at Olympia 21-25 June, the final arrangements for which were well in hand. A very late request had been received from an Australian company to exhibit and a small amount of space had been made available. This brought the number of overseas countries with direct exhibitors to 12.

(c) The 1972 Exhibition, the arrangements for which were in hand. The Invitation to Exhibit at Olympia 17-21 April 1972 would be despatched in July.

(d) Paint Technology Manual, Volume III Convertible Coatings, the revision of which was now in hand and Dr H. W. Keenan was in contact with the contributors concerned.

(e) *Chemistry in Industry in New Zealand*, in which "*OCCA* Notes and News" was now to be a regular feature.

(f) FSPT Meeting in Detroit, October 1971, at which Dr D. A. Plant had agreed that his paper entitled "Hiding power of coloured pigments" be designated as the official OCCA Paper.

In the report of the previous meeting of Council (which appeared in the April issue of the *Journal*) members will have read about the setting up of the Professional Grade Committee; at this meeting members of Council had before them the document prepared by this newly formed Committee setting out details of the optional professional grade for notification to members of the Association through the pages of the *Journal*. Considerable discussion took place and certain minor amendments were made, but in principle the document was accepted as a basis for the announcement to the Members, and it will be published in a later issue of the *Journal*.

Following the recent postal strike and in view of further increases in charges later in the year, the importance was stressed, particularly to Section Chairmen and Representatives, of sufficient time being allowed for all Section notices, etc., to be sent second class mail and for co-ordination between Section Branches and Student Groups to avoid unnecessary duplication and expenditure. Information about functions open to all Sections should be sent to the Association well in advance so that a circular could be included in an issue of the *Journal*, rather than being sent as a separate notice.

The meeting then received reports on the activities of the various Sections; Council was saddened to learn of the recent death not only of the Hon. Treasurer of the Manchester Section, Dr T. I. Kyle, but also the Section's Auditor, Mr F. A. Walker, as well as the Hon. Social Secretary of the West Riding Section, Mr D. T. Young.

Irish Section

Annual General Meeting

On the 19 March 1971, the 6th AGM of the Irish Section was held in the Clarence Hotel at 8.15 p.m.

The Chairman, Mr S. McWade, presided and 16 members attended. At the meeting the following officers were elected:

Chairman: Mr F. D. H. Sharp; Immediate past Chairman: Mr S. McWade (Ex-Officio); Hon. Secretary: Mr M. J. O'Hanlon; Hon. Treasurer: Mr J. Corrigan; Hon. Publications Secretary: Mr A. Richards; Hon. Programme Secretary: Mr D. Power; Hon. Technical Training Officer: Mr G. F. Jones. Committee: Mr R. C. Somerville, Mr K. O'Callaghan, Mr K. V. Wheatley, Miss P. A. Magee, Mr D. Berry, Mr R. Shaw.

Following the AGM, an "Open Forum" was held, the subject being the "Effects that entry into EEC would have on the paint and printing industries in Ireland." The incoming Chairman, Mr F. D. H. Sharp, presided.

Treasure Hunt

Saturday 22 May saw the Irish Section's first event in their Summer programme. This took the form of what has now become an annual event, namely, a Treasure Hunt.

Sixteen stolid crews braved the inclement weather and set out on a tour of South Co. Dublin. Having counted innumerable objects, all competitors arrived at the half-way stage where the Hon. Secretary, armed with a flagon of beer, sent them on their way. Eventually they found themselves in a car park where after a driving test which proved whether or not they could reverse, the travel worn teams made their way to the home of the Chairman and his wife, where they were enough revived by food and drink to dance until the early hours.

The Committee's thanks are due to Mrs E. O'Hanlon, Mrs B. Sharp, Mr S. Hull and Mr K. Wheatley for their efforts in ensuring the success of the event.

J.O'H.

Golf outing

What has now become known as the Irish Section's Golfing Society (as we were described by the Golf Club) held its annual outing at Clontarf Golf Club on Friday 11 June.

Once again, the weather did not favour us, nevertheless 21 enthusiasts braved the monsoon to struggle round a course which contained many natural and man-made hazards to compete for the John Kershaw Memorial Trophy.

The tournament was followed by a meal, at which the prize winners were presented with their prizes by the Chairman, who stated that he was delighted that on this occasion the trophy should go to one of the Section's new Members, Mr N. Caulwell, at his first attempt. The second Members' prize went to Mr D. Godden, who has won this event since its inception. The visitors' prize was presented through the generosity of Phillips Dufar and was won by Mr C. Day (ironically enough one of our bearded visitors), taking the form of a cordless shaver. The Chairman was pleased to present Mr A. Kershaw (son of the late Irish Section Treasurer in whose memory the trophy is named) with the runners-up prize for the visitors. Mr A. Berkley took the booby prize and Mr L. Bredin, the visitors' booby.

The Committee's thanks are extended to Mr R. Shaw and Mr D. Godden for the work they did in organising this very successful event.

J.O'H.

West Riding Section

West Riding Luncheon Lecture (left to right) Mr T. R. Smith (Hon. Treasurer, West Riding Section), Mr A. Tiley, J.P., Mrs K. Driver (Chairman, West Riding Section), Mr D. Morris (Hon. Secretary, West Riding Section)

High risk and export insurance

The third annual luncheon lecture of the West Riding Section was held at the Astoria Restaurant, Leeds, on Friday 14 May 1971.

The speaker was Mr A. Tiley, JP, who dealt with the subject "High risk and export insurance" in a lighthearted vein interspersed with anecdotes of his experiences in the House of Commons when an MP. Nevertheless, several serious points were made, particularly on methods of minimising fire risk and hence premiums, which led to a brisk discussion period.

All present heartily endorsed the vote of thanks proposed by Mr T. R. Smith.

R.A.C.

Register of Members

The following elections to membership have been approved by Council. The Sections to which new members are attached are given in italics.

Ordinary Members

BUSHILL, JOHN DAVID, BA, Shell Chemicals UK Ltd., Villiers House, Strand, London WC2. *(London)*

DAVIE, ALEXANDER KNIGHT, 19 Bollinwood Chase, Wilmslow Park, Wilmslow, Cheshire. *(Manchester)*

FRENCH, ERIC L., 39 Swakeleys Drive, Ickenham, Middlesex. *(London)*

HESTER, NIGEL LEWIS, 248 Broadway, Woodlands Estate, Featherby Road, Gillingham, Kent. *(London)*

NISBET, PETER SAMUEL, BSc, A. B. Fleming & Co. Ltd., 170 Glasgow Road, Edinburgh 12. *(Scottish—Eastern Branch)*

POBJOY, REGINALD CLAUDE, 12 Selkirk Road, Kansenji, Ndola, Zambia (PO Box 927, Ndola). *(Overseas)*

SHACKLETON, RONALD, FRIC, Downhills, Woodhill Avenue, Gerrards Cross, Buckinghamshire. *(Manchester)*

SMITH, LEONARD PERCIVAL, Willow Creek, 2 Broom Water West, Teddington, Middlesex. *(London)*

VESSEY, ERIC, 3 Princess Road, Anderton, Chorley, Lancashire. *(Manchester)*

Associate Members

GRILLO, CLEOMAR ALBRECHT, Rua Tuiuty 474, Caixa Postal 48, Indaiatuba, Est. Paulo, Brazil. *(Overseas)*

REA, ROBERT N., 8 St. Anthony's Avenue, Clondalkin, Co. Dublin, Ireland. *(Irish)*

Student Members

ALLAN, BRIAN CHARLES, 2 Muirhouse Place West, Edinburgh. *(Scottish)*

EDMOND, BRIAN, 44 Wymersley Road, Hull, Yorkshire. *(London)*

GRAHAM, RODGER WILLIAM, Wardley Chemicals Ltd., Greenhay Place, Skelmersdale, Lancashire. *(Manchester)*

Section programmes for 1971-72 session

Main Association events

1972

Monday 17-Friday 21 April

OCCA 24 Technical Exhibition. To be held at the Empire Hall, Olympia, London.

Friday 12 May

Association Dinner Dance, to be held at the Savoy Hotel, London WC2.

Wednesday 7 June

Annual General Meeting, to be held at Wax Chandlers' Hall, Gresham Street, London.

Bristol

All meetings will be held at the Royal Hotel, Bristol, at 7.15 p.m. unless otherwise stated.

1971

Friday 24 September

Chairman's Address. "Some aspects of metal pretreatment and priming" by Mr P. L. Gollop.

Thursday 7 October

"The future of plastics." Joint meeting with the Birmingham PVL Club, to be held at the Imperial Hotel, Birmingham.

Friday 29 October

Ladies' Evening. "Paint, art, colour and heraldry" by Dr S. H. Bell of the Paint Research Association.

Friday 26 November

"Quality control." Discussion evening. Panel: Mr W. S. Grainger of Berger Hall Paints, Mr D. S. Newton of British Steel Corporation, and Mr J. R. Taylor of BP Chemicals International Limited.

1972

Friday 28 January

Joint meeting with the Institute of Printing, South Western Branch. "Practical pigment dispersion" by Mr J. Groom and Mr M. Baker of Sandoz Products Ltd.

Friday 25 February

A lecture by Professor E. M. Evans of BP Chemicals International Ltd., to be held at the Angel Hotel, Cardiff.

Wednesday 15 March

Annual Dinner Dance, to be held at the Mayfair Suite, Bristol Entertainments Centre.

Friday 31 March

"Industrial relations in the surface coatings industries" by Mr J. L. Thomas of the University of Bristol, Department of Extra Mural Studies.

Friday 28 April

Annual General Meeting.

Hull

All meetings will be held in the Bullock Lecture Theatre at the Hull College of Technology, at 7.00 p.m., unless otherwise stated.

1971

Monday 4 October

"Practical pigment dispersion" by Mr J. R. Groom and Mr M. Baker of Sandoz Products Ltd.

Friday 8 October

Annual Dinner and Dance.

Monday 1 November

"Some aspects of drying oils technology" by Mr G. H. Hutchinson of A. B. Fleming & Co. Ltd.

Monday 6 December

"Emulsion polymers for exterior paints—a comparative study" by Mr K. Safe of Vinyl Products Ltd.

1972

Monday 3 January

"Current thinking on flame retardant paints" by Mr A. G. Walker of Associated Lead Manufacturers Ltd.

Monday 7 February

"Powder coatings" by a speaker from Shell Research Ltd.

Monday 6 March

Ladies' Evening. A conducted tour of the Hull Art Gallery, by the Director, Mr Bradshaw.

Irish

All meetings will be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m., unless otherwise stated.

1971

Friday 17 September

"The efficient use of titanium dioxide pigments in organic compounds" by Mr J. G. Hoogerbeets of NV Titaandioxydefabrik Tiofine.

Friday 15 October

"Factors which affect the efficiency of ball milling" by Dr W. Carr of CIBA-GEIGY (UK) Ltd.

Friday 29 October

Annual Dinner Dance at the Tara Towers Hotel, Dublin. Reception at 8.00 p.m.

Friday 19 November

"Powder coatings" by Mr Lonsdale of BJN Paints Ltd.

Friday 10 December

Ladies' Night. A talk "Reminiscences" by Dr F. W. Stoyle of Protim (Ireland) Ltd.

1972

Friday 21 January

"Magazine production by the web offset process" by C. F. Jones of Irish Printing Inks Ltd.

Friday 18 February

"The treatment of timber" by Mr P. J. Coyle of Protim (Ireland) Ltd.

Friday 24 March

"Solvents" by Dr D. H. Schärer of Shell Research Ltd.

Friday 21 April

Annual General Meeting, followed by an open forum.

Friday 20 May

Annual Treasure Hunt. Details to be announced.

Friday 16 June

Annual Golf Outing. Venue to be announced.

London

All meetings will be held at the Polytechnic of the South Bank at 7.00 p.m., unless otherwise stated.

1971

Wednesday 13 October

"Chairman's Forum: Cost effectiveness and profitability in the paint industry," by Mr D. E. Eddowes, to be held at 2.15 p.m.

Wednesday 10 November

"Changes in the physical characteristics of paint films in differing environments," by Mr R. L. J. Morris, of the Quality Assurance Directorate (Materials), to be held at the East Ham Technical College.

Friday 19 November

Ladies Night, to be held at the Strand Palace Hotel, 7.00 for 7.45 p.m.

Wednesday 8 December

"What's 'bugging' your paint?" by Catherine E. Skinner, of the Paint Research Association.

Monday 13 December

Joint Meeting with the Colloid and Surface Chemistry Group of the SCI. "Colloidal aspects of printing inks," by Dr W. Carr, of CIBA-GEIGY (UK)

Ltd., to be held at 14 Belgrave Square, London SW1, at 6.00 p.m.

1972

Wednesday 12 January

"The effects of lithographic ink ingredients," by Mr J. R. Groom and Mr K. Atkinson of Sandoz Products Ltd.

Wednesday 26 January

Symposium: "Surface coatings, their use and abuse. No. 2, Building paints," to be held at 2.15 p.m.

Wednesday 9 February

"A new approach to the preparation of alkyds based on the glycidyl ester of a branched chain acid," by Mr G. Rossa of Shell Research Ltd.

Wednesday 8 March

"Statistical evaluation of colour difference formulae," by Mr K. McLaren of ICI Ltd. Dyestuffs Division.

April

AGM, date to be arranged.

Southern Branch

All meetings will be held at the Pendragon Hotel, Southsea, at 7.00 p.m., unless otherwise stated.

1971

Tuesday 19 October

"Vinyl resins in surface coatings" by Mr D. J. Silsby of Bakelite Xylonite Ltd.

Tuesday 16 November

"Masonry finishes," by a speaker from the Cement Marketing Board.

1972

Thursday 20 January

Joint meeting with the Institute of Metal Finishing. "Electrodeposition," by Mr McKay of Berger Paints Ltd. to be held at the Lecture Theatre, Chemistry Department Portsmouth Polytechnic, Burnaby Road, Portsmouth, at 7.30 p.m.

Tuesday 15 February

"Reflections on an industry," by Mr D. E. Eddowes of Paint, Oil and Colour Journal.

Tuesday 14 March

"Zinc phosphate—its history and development," by Mr M. Rendu of Imperial Smelting Corporation (Alloys) Ltd.

Friday 26 May

Annual General Meeting and Social Evening.

Manchester

All meetings will be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester 1, at 6.30 p.m., unless otherwise stated.

1971

Friday 8 October

"The fibre optics colorimeter and its applications for industrial colour control," by Dr I. G. H. Ishak of The Paint Research Association, to be held at the Bolton Institute of Technology, Deane Road, Bolton.

Friday 22 October

Annual Dinner Dance, to be held at the Piccadilly Hotel, Piccadilly Plaza, Manchester 1.

Friday 12 November

"The management of human resources," by Mr J. Munro-Fraser of the University of Aston-in-Birmingham.

Wednesday 8 December

"Continuous production lines for paint manufacture," by a lecturer from VEB Konstruktions und Ingenieurburo Chemie, to be held at the Royal Institution, Colquitt Street, Liverpool 1, at 6.30 p.m.

1972

Friday 14 January

"Pyrolysis gas chromatography," by Mr C. E. Roland Jones of Vinyl Products Ltd.

Friday 11 February

"Chrome pigments up to date," by Dr D. A. Plant of ICI Ltd., Dyestuffs Division.

Thursday 9 March

Joint Meeting with the North Western Branch of the Institute of Printing. "Future trends in the printing and communication industries in the seventies," by Mr H. Sander of the Bonnier Group, to be held at the Royal Institution, Liverpool.

Friday 14 April (provisional date)

Annual General Meeting. Venue to be advised.

Student Lectures

1971

Wednesday 15 September

"Formulation of two-pack epoxy paints," by Mr A. McWilliam of England, Hughes, Bell & Co. Ltd., to be held at 4.30 p.m.

Wednesday 13 October

"A review of printing inks and printing processes," by Mr F. Lewis of W. P. M. Colour & Adhesives Co. Ltd., to be held at 4.30 p.m.

1972

Wednesday 12 January

"Chlorinated rubber in inks and surface coatings," by Dr D. R. Sayers of ICI Ltd. Mond Division, to be held at 4.30 p.m.

Wednesday 29 March

"Modern applications of polyurethanes," by Mr A. C. Jolly of Synthetic Resins Ltd., to be held at 4.30 p.m.

Midlands

All meetings will be held at the Birmingham Chamber of Commerce and Industry, 75 Harborne Road, Birmingham 15, at 6.30 p.m., unless otherwise stated.

1971

Friday 17 September

Ladies Evening, to be held at the Westbourne Suite, Botanical Gardens, at 7.00 p.m.

Friday 24 September

"Chlorinated rubber marine paints," by Mr C. G. Reid of ICI Ltd. General Chemicals Group.

Friday 15 October

"The importance of electrokinetics in electrodeposition," by Professor G. D. Parfitt of Tioxide International Ltd.

Friday 19 November

"Oil free alkyds," by Mr A. G. North of Cray Valley Products Ltd.

1972

Friday 21 January

Annual Dinner Lecture. "Coil coating in the seventies," by Mr P. D. Winchcombe of British Steel Corporation.

Friday 18 February

"The changing structure of the paint industry," by Mr D. E. Eddowes of Paint, Oil and Colour Journal.

Friday 17 March

Annual J. Newton Friend Lecture. "Antiques," by Mrs D. I. Bamber of J. & D. I. Bamber Ltd., to be held at 7.30 p.m.

Friday 14 April

Annual General Meeting.

Trent Valley Branch

All meetings will be held at the British Rail School of Transport, London Road, Derby, at 7.00 p.m.

1971

Thursday 14 October

Joint meeting with the East Midlands Branch of the Institute of Metal Finishing. "Corrosion and the automobile" by Mr H. L. Quick of Chrysler UK Ltd.

Thursday 11 November

"Chromate and phosphate pigments in anti-corrosive primers" by Mr H. F. Clay and Mr J. H. Cox of SCC Colours Ltd.

Thursday 9 December

"A layman's view of paint" by Mr J. R. Bourne of Mebon Ltd.

1972

Thursday 10 February

"Micronised pigments and future developments" by a speaker from Bayer Chemicals Ltd.

Thursday 9 March

"Examination of paint systems using the scanning electron microscope" by Mr H. Wells of the Quality Assurance Directorate (Materials), Ministry of Defence, Woolwich.

Thursday 6 April

Annual General Meeting, followed by "Printing banknotes" by Mr D. R. Lowther of Thomas de la Rue & Co. Ltd.

Newcastle

All meetings will be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

1971

Thursday 7 October

"The fibre optics colorimeter and its applications for industrial colour control," by Dr I. G. H. Ishak of The Paint Research Association.

Thursday 4 November

"Hazard analysis—a quantitative approach to safety," by Mr T. A. Kletz of ICI Ltd., Heavy Organic Chemicals Division.

Thursday 2 December

"Flame retardant coatings—the whys and wherefores," by Mr A. G. Walker of Associated Lead Manufacturers Ltd.

1972

Thursday 6 January

"The use of zinc oxide in photocopying techniques," by Mr P. J. Robinson of Durham Chemicals Ltd.

Thursday 3 February

"Alpha-olefins, new monomers for surface coatings," by Mr A. Laws of Resinous Chemicals Ltd.

Friday 18 February

Annual Dinner Dance.

Thursday 2 March

"Inorganic zinc rich primers," by Mr D. S. Newton and Mr M. Rendu of the Imperial Smelting Corp. Ltd.

Thursday 6 April

AGM.

Student Group

All lectures will be held at the Newcastle Polytechnic, Ellison Place, Newcastle upon Tyne at 3.00 p.m., unless otherwise stated.

1971

Wednesday 13 October

Visit to Tioxide International weathering station at Carlton.

Wednesday 10 November

"Paint formulation" by Mr H. Caddell of International Paint Co. Ltd.

Wednesday 8 December

"Instrumental colour measurement" by Mr J. Bravey of British Paints & Chemicals.

1972

Wednesday 12 January

"Marine paints" by Dr T. Banfield of British Paints Ltd.

Wednesday 9 February

To be arranged.

Wednesday 8 March

Film show.

Scottish

All meetings will be held at the St. Enoch Hotel, St. Enoch Square, Glasgow, at 6.00 p.m., unless otherwise stated.

1971

Thursday 14 October

"Personalised marketing," by Mr W. A. Coom of the International Life Assurance Co. (UK) Ltd.

Thursday 11 November

Joint Meeting with the British Paper and Board Makers' Association: "Amino resins—their use in the surface coatings and paper industries" by Mr R. McD.Barrett of BIP Chemicals Ltd., to be held at 6.45 p.m.

Thursday 9 December

"Modern trends in building and building finishes, including paints," by Mr D. K. Barron of the Building Research Station.

1972

Friday 14 January

Annual Dinner Dance.

Thursday 20 January

"Modern trends in printing inks," by Mr G. H. Hutchinson of A. B. Fleming & Co. Ltd.

Thursday 10 February

"The effect of recent changes in shipbuilding processes on ship painting," by Dr D. Atherton of Craig Hubback Ltd.

Thursday 9 March

"Some aspects of managing a new town development corporation," by Mr G. B. Young of East Kilbride Development Corporation.

Friday 7 April

AGM and Smoker.

Eastern Branch

All meetings will be held in the Carlton Hotel, North Bridge, Edinburgh, at 7.30 p.m., unless otherwise stated.

1971

Wednesday 20 October

"Developments in water-based surface coatings," by Mr A. J. Becalick of Lennig Chemicals Ltd.

Wednesday 17 November

"Pollution"—Joint meeting with BPBMA in Aberdeen, details to be arranged.

Wednesday 15 December

"Inter-personnel relationships," by Mr R. M. McKenzie of the Department of Business Studies, Edinburgh University.

1972

Tuesday 11 January

Joint meeting with BPBMA. "Development in ink technology," by Mr G. H. Hutchinson of A. B. Fleming & Co. Ltd., to be held at 6.45 p.m.

Wednesday 26 January

"Aerosols, past, present and future," by Mr D. Lake of D. H. Industries Ltd.

Wednesday 16 February

"Some problems of ink and paper performance in printing," by Mr E. W. Peacock of PIRA.

Wednesday 22 March

Film night. Film by Hoechst UK Ltd.

Wednesday 19 April

"Airless spray applications," by Mr D. I. Muirhead of Wm. Sim & Sons (Paints) Ltd.

Student Group

All meetings will be held at the St. Enoch Hotel, Glasgow, at 10.00 a.m.

1971

Friday 1 October

"The properties of anti-corrosive pigments" by Mr J. Bowden of Craig-Hubbuck Ltd.

Saturday 13 November

"Exploration of the North Sea for fuel" by Mr Junor of BP Chemicals International Ltd.

Saturday 11 December

Joint meeting. "Organic pigments for use in printing inks" by Mr D. White of Farbwerke Hoechst AG.

1972

Saturday 22 January

"The future of plastics" by Dr N. Grasse of the University of Glasgow.

Saturday 12 February

Works visit to Outram Press.

Saturday 11 March

Annual General Meeting, followed by a general knowledge quiz.

Thames Valley

All meetings will be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Buckinghamshire, at 7.00 p.m., unless otherwise stated.

1971

Thursday 23 September

"The consumers' association—the aims and achievements," by Mrs A. Williams of the Consumers' Association.

Thursday 21 October

"Pollution," by Dr R. B. Brown—Scientific Adviser to the Greater London Council.

Thursday 25 November

"The philosophy of paint testing," by Mr T. R. Bullett of The Paint Research Association.

1972

Thursday 20 January

"Painting and printing on plastics," by Mr J. R. Taylor of BP Chemicals International Ltd. and Mr R. G. Kinsman of Winstones Ltd.

Friday 4 February

Buffet Dance, to be held at "Great Fosters," Egham.

Thursday 24 February

"Training for the paint and printing ink industries," by Mr A. R. H. Tawn of Cray Valley Products Ltd.

Thursday 23 March

"Powder coatings," by Dr O. Brussman of BASF AG.

Thursday 20 April

AGM followed by a talk by Mr Compton of the Thames Conservancy.

Student Group

All meetings will be held at the Main Lecture Theatre, Slough College, at 4.00 p.m., unless otherwise stated

1971

Tuesday 5 October

"Metal pretreatment," by Mr P. Burden of Pyrene Ltd.

Tuesday 2 November

"Acrylic resins," by Mr A. R. H. Tawn of Cray Valley Products Ltd.

Tuesday 7 December

Open invitation lecture to senior members. "Microbiology and corrosion," by Dr E. Pankhurst of the Gas Council.

1972

Tuesday 11 January

"Colour," by Mr R. Jeffs of ICI Ltd. Paints Division.

Tuesday 8 February

Works visit to a furniture factory. Meeting in Slough College Car Park, at 1.00 p.m.

Tuesday 14 March

"Titanium dioxide—manufacture and treatment," by a speaker from Laporte.

Tuesday 2 May

"Analysis of paint films," by Mr N. Falla of The Paint Research Association.

West Riding

All meetings will be held at the Griffin Hotel, Boar Lane, Leeds 1, at 7.30 p.m., unless otherwise stated.

1971

Tuesday 14 September

"Microbiology in paints," Speaker to be arranged.

Tuesday 12 October

"Pigmentation of plastics," by Dr Armstrong.

Tuesday 9 November

"Silicates," by Mr K. Loftman of the Cabot Corporation.

Friday 26 November

Annual Dinner and Dance, to be held at the Crown Hotel, Harrogate.

Tuesday 14 December

"Flexographic printing inks," Speaker to be arranged.

1972

Tuesday 11 January

"Functions of the Factory Inspectorate," by Mr P. F. J. Buchanan, HM Inspector of Factories, Leeds West District, Factory Inspectorate.

Tuesday 8 February

"Industrial surface coatings and the paint industry," by Mr F. Armitage of Sherwin-Williams.

Tuesday 14 March

"Industrial espionage," Speaker to be arranged.

Tuesday 11 April

Annual General Meeting.

Forthcoming Events

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

Wednesday 15 September

Manchester Section—Student Group. "Formulation of two-pack epoxy paints" by Mr A. McWilliam (England, Hughes Bell & Co. Ltd.), to be held at the Manchester Literary and Philosophical Society at 4.30 p.m.

Friday 17 September

Irish Section. "The efficient use of TiO_2 pigments in organic compounds" by Mr J. G. Hoogerbeets of NV Titaandioxydefabriek Tiofine, to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

Midlands Section. Ladies' Evening, to be held at the Westbourne Suite, Botanical Gardens, Birmingham, at 7.00 p.m.

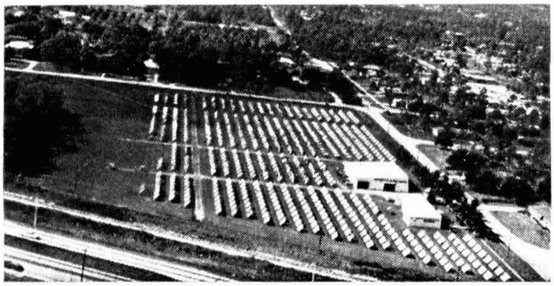
Thursday 23 September

Thames Valley Section. "The Consumers' Association—the aims and achievements" by Mrs A. Williams of the Consumers' Association, to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks, at 7.00 p.m.

Friday 24 September

Midlands Section. "Chlorinated rubber marine paints" by Mr C. G. Reid of General Chemicals Group, Imperial Chemical Industries Ltd., to be held at the Birmingham Chamber of Commerce and Industry, PO Box 30, 75 Harborne Road, Birmingham B15 3DH, at 6.30 p.m.

It is regretted that some Section Programmes were received too late for the September meetings to be included. Reference should be made to the relevant Section Programme.

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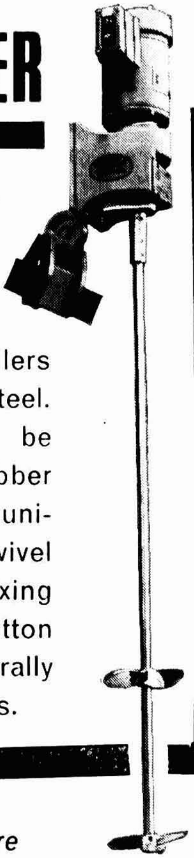

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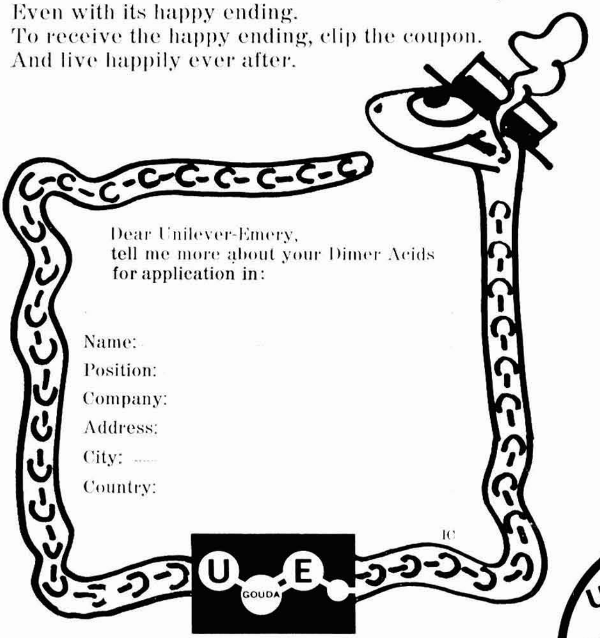
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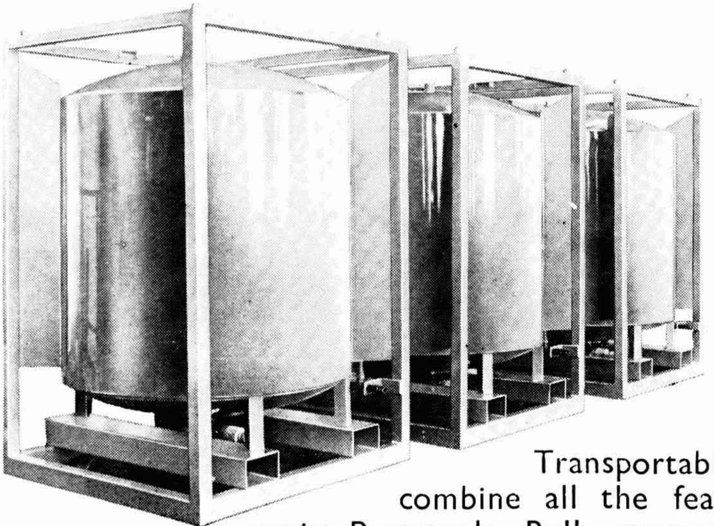

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24 OCCA

Oil and Colour Chemists' Association

Technical Exhibition 17-21 April 1972

Empire Hall - Olympia - London

Closing date for applications for stand space: 1 October 1971