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See page 428

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JOURNAL OF THE OIL & COLOUR CHEMISTS' ASSOCIATION

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1975 Increased DPP capacity, Stanlow, UK.

1976 Opening of Polymers Research Centre, Amsterdam.
New VeoVa plant, Moerdijk, Netherlands.
New DPP plant, Pernis, Netherlands.
New Versatic acid capacity, Pernis, Netherlands.

1977 Increased Epikote capacity, Stanlow, UK.
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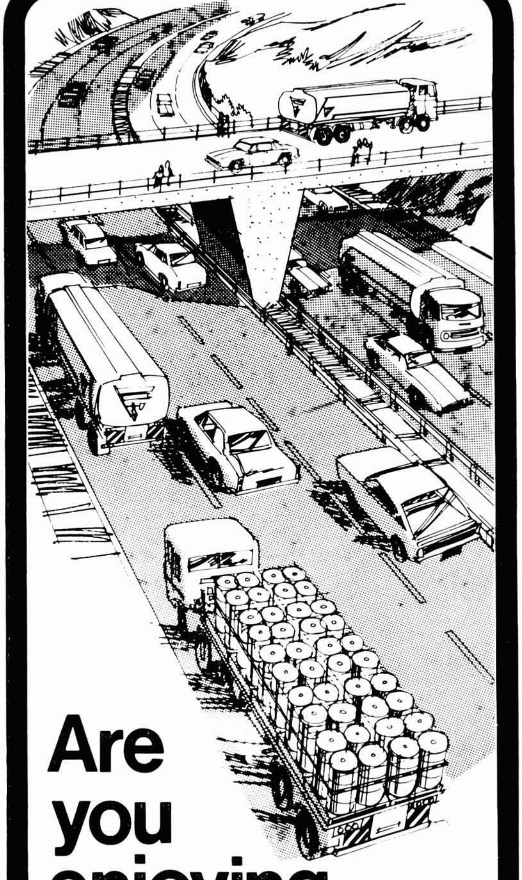

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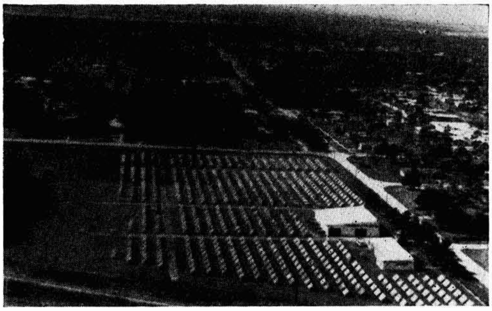

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OIL & COLOUR CHEMISTS' ASSOCIATION

TECHNICAL EXHIBITION

18-21 APRIL 1978

The motif, designed by Robert Hamblin, uses the symbol of a moving indicator on a calendar to emphasise the importance of the continuous dialogue year by year between suppliers and manufacturers. The inward-pointing letters recall the international aspect of this unique annual focal point for the surface coatings industries, which in 1977 attracted visitors from 50 countries.

TRAVEL ARRANGEMENTS FOR VISITORS TO OCCA-30

For those travelling to the Exhibition by car, ample free parking space is available in the grounds of Alexandra Palace, and recent improvements to the road system include the extension of the southbound carriageway of the M1 Motorway to the North Circular Road and the flyover on that road by the new Brent Cross Shopping Centre. By the 1978 Exhibition the extension of the Piccadilly Underground line to the Heathrow Airport Terminal will give a direct line to Turnpike Lane station from which the Association runs a free bus shuttle service to the Exhibition. The journey from central London to Turnpike Lane takes approximately 18 minutes.

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Transactions and Communications

The determination of zeta potentials as an aid to the pigmentation of water paints*

By M. Cremer

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Summary

The zeta potential, which is a measure of the electrokinetic charge on solid particles suspended in an aqueous solution, has been investigated for several titanium dioxide pigments with different surface coatings, dispersed in purely aqueous solutions and in the presence of three different water-dilutable polymeric resins, and has been considered in relation to the technological properties of correspondingly pigmented water paints. Details are given of the accuracy, the utility and the limitations of the method as a means of identifying surface-treated titanium dioxide pigments and of understanding the exchange reactions that take place on the surfaces of pigments.

Keywords

Types and classes of coatings and allied products

water based paint

Raw materials for coatings

prime pigments and dyes

titanium dioxide

Properties, characteristics and conditions primarily associated with

bulk coatings and allied products

pigment volume concentration

Processes and methods primarily associated with

analysis, measurement or testing

adsorption

manufacturing or synthesis

pigment dispersion

storage, protection or preservation

sedimentation

Miscellaneous terms

zeta potential

La détermination du potentiel zéta en vue de faciliter la pigmentation des peintures à base d'eau

Résumé

Le potentiel zéta, mesure de la charge électrokinétique sur les particules solides suspendues en mileux aqueux, a été étudié dans le cas de plusieurs pigments du dioxyde de titane ayant de différents traitements superficiels et dispersés dans des solutions exclusivement aqueuses et en présence de trois différentes résines polymères diluables par l'eau, Le potentiel zéta a été également considéré à l'égard des caractéristiques technologiques des peintures à base d'eau contenant de tels pigments. On donne des détails sur la précision, l'utilité et les contraintes de la méthode en tant que moyen de caractériser le traitement superficiel des pigments du dioxyde de titane et de comprendre les réactions d'échange qui se produisent aux surfaces de ces pigments.

Die Bestimmung des Zetapotentials als ein Hilfsmittel für das Pigmentieren wassergetragener Farben

Zusammenfassung

Das Zetapotential, ein Mass für die elektrokinetische Ladung von in wässriger Lösung suspendierten Festteilchen, wurde für verschiedene Titandioxidpigmente mit unterschiedlichen Beschichtungen untersucht, und zwar dispergiert in rein wässrigen Lösungen und in Gegenwart von drei wasserverdünnbaren Harzpolymeren. Beurteilung erfolgte in Verbindung mit den technologischen Eigenschaften entsprechend pigmentierter Wasserfarben. Einzelne Angaben über die Genauigkeit, Zweckmässigkeit und Grenzen der Methode werden gemacht als Mittel für die Identifizierung oberflächenbehandelter Titandioxidpigmente und für das Verständnis der Austauschreaktionen, welche an den Pigmentoberflächen vor sich gehen.

Introduction

The significance of the zeta potential

Refs. 1-30, 37-43

The principles and the methodology of determining the zeta potential have been stated by T. M. Riddick[1] in his monograph "Control of colloid stability through zeta potential", in which he describes its significance in the following words:

> "Zeta potential represents a basic law of Nature, and it plays a vital role in all forms of plant and animal life. It is the force that maintains the discreteness of the billions of circulating cells which nourish the organism. The stability of simple inorganic man-made systems is governed by these same laws."

In his standard work, Riddick[1] has used examples mainly drawn from the field of water treatment and other industrial applications of colloid chemistry to demonstrate the importance of zeta potential measurements for solving problems of the most varied kinds, and has introduced the Zeta-Meter®, which he developed, as a reliable, mass-produced measuring instrument*.

In addition to the extensive literature covered by Riddick in his standard work, numerous further publications have since then appeared on the same group of topics. Under the headings "electrical double layer" and "electrophoresis" alone, *Chemical Abstracts* reports over 30 papers in the period 1970 to 1975 dealing with the further development of the theory of the electrical double layer[2-14], reactions in solution at oxidic solid surfaces[2,14-20,30-33], applications[21-25] and/or

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*Manufacturer: Zeta-Meter Inc., New York

*Extended version of a paper presented at the 44th Lecture Meeting of the Paints and Pigments group of the Gesellschaft Deutscher Chemiker in Berlin on 30 March 1977, and published by permission of Farbe + Lack.

methods of measurement[26-30]. This figure does not include numerous reviews not mentioned above.

Many authors have reported zeta potential measurements on pigments in aqueous solutions. Thus, Petrova[37] has described the effect of the pH value on the zeta potential of a commercial TiO_2 pigment in water to which hydrochloric acid is added. Below pH 3, the pigment under investigation exhibited a positive zeta potential; above pH 3 it had a negative zeta potential. The isoelectric point was at an intermediate value.

Rechmann[38,39], Robinson and Tear, *et al*[40,41] have referred to the special role of the TiO_2 surface-treatment components, aluminium hydroxide and hydrated silica, in connection with investigations on the pigmentation of electro-deposited paints. At values of the ratio $Al_2O_3/SiO_2 > 1$ the number of positive charge carriers increases, while at ratios <1 the number of negative charge carriers increases. In a later paper, Robinson and Tear[42] qualify this by saying that the nature of the addition of the surface-treatment components during pigment manufacture has a more decisive influence on the value of the zeta potential than has the ratio between the inorganic oxides or the whole surface-treatment process.

As already observed by Rechmann, Franklin[43] has demonstrated with TiO_2 suspensions based on organic solvents that changes in the zeta potential can run parallel to changes in hiding power.

According to the investigations of these authors, hiding power increases when the zeta potential becomes more positive.

The aim of the present work

By posing the question "Can the measurement of zeta potentials be used for a more rapid and more exact determination of the stability of emulsion paints on storage?", Robinson and Tear[42] were successful in attempting, some years ago, to popularise the use of zeta potential measurements for technical service problems in the field of paints.

The correlation found by these authors between the stability of emulsion paints on storage and the interrelationships that can be described by zeta potential measurement between, on the one hand, the titanium dioxide pigments present in the paints and, on the other hand, the polymers, extenders, protective colloids, thickeners and other additives, has led to an investigation whether similar relationships also apply to the pigmentation of water paints.

The following questions were considered:

(1) What parameters determine the zeta potential of TiO_2 pigments dispersed in purely aqueous solutions?

(2) Does the zeta potential of pigments change in the presence of binder polymers?

(3) Which further components of a "water paint" influence the zeta potential?

(4) Is it possible to derive relationships between the zeta potential and the technological properties of water paints?

(5) Can a knowledge of the zeta potential be utilised in the selection of pigments in water paints?

In order to find an answer to these questions a large number of water paints were prepared based on different titanium pigments having varying surface-treatment and on several water-dilutable binders, in the PVC range of 10 to 50 per cent. Parallel with this, measurements of zeta potentials were made on purely aqueous suspensions of TiO_2 and on more dilute aqueous TiO_2/binder suspensions corresponding to the water paints.

The characteristics of the titanium dioxide pigments used in the investigations, such as TiO_2 content, surface-treatment, modification, Al_2O_3/SiO_2 ratio, average particle size and specific surface, are shown in Table 1.

The characteristic data of the main binders used are summarised in Table 2.

Description of tests and experimental methods

Preparation of the water paints

Ref. 44

Seven pigments, with a uniform average particle size of 0.36 ± 0.02 µm, as measured by the author's photo-sedimentation method[44], were selected from the various surface-treated pigments nos. 1 to 11 listed in Table 1, for pigmentation using each of the three binders. With binder 3, in two cases only, the pigment samples used in binders 1 and 2, no. 1 and no. 5,

Table 1

The characteristic data of the titanium dioxide pigments used

Pigment No.	% TiO_2	Surface-treatment	Modified with	Al_2O_3/SiO_2 ratio	Particle size 50.2µm	Specific surface g/m²
1	99.5	—	—		0.355	7
2	99.5	—	—		n.a.	7
3	95	Al_2O_3	—		0.35	16
4	95	Al_2O_3	—		0.29	16
5	92	Al_2O_3/SiO_2	—	1.4	0.385	16
6	92	Al_2O_3/SiO_2	—	1.4	n.a.	16
7	84	Al_2O_3/SiO_2	—	0.4	0.385	40
8	94	Al_2O_3/SiO_2	ZnO	20	n.a.	18
9	94	Al_2O_3/SiO_2, org.	ZnO	17	0.36	18
10	92	Al_2O_3/SiO_2, org.	ZnO	3.3	0.39	18
11	92	Al_2O_3/SiO_2, org.	ZnO	10	0.35	18

Table 2

The characteristic data of the water-dilutable binders used

Binder No.	Type	Solvent	Form in which supplied	Stoving residue (as supplied)	Acid Number (solid resin)	Dilutability (as supplied)	Viscosity (as supplied)	Neutralisation pH range
1	air-drying alkyd resin, medium-oil, based on drying fatty acids, isocyanate-modified	butylglycol	not neutralised	63%/110°C/1 hr.	42–48	gives clear solutions with H_2O after neutralisation	40–46P	57 parts of triethylamine/100 parts of material supplied, 10 hrs. before processing
2	air-drying epoxide resin-linseed oil/wood oil esters	ethylglycol	not neutralised	70%/110°C/1 hr.	54±4	gives opaque solutions with H_2O and organic solvents after neutralisation	3.9–8.4P (in a 50% strength solution with butylglycol)	pH: 8.4–9.2 (8.3 parts of triethylamine/100 parts of solid binder)
3	heat-curable, self-crosslinking acrylic resin	isobutanol	not neutralised	55%/110°C/1 hr.	65–75	gives opaque solutions with H_2O after neutralisation	80–110P	5.0 parts of dimethylethyl(ol)amine/100 parts of solid binder

were replaced by samples no. 2 and no. 6, respectively, which were of the same type.

The pigments were dispersed in the water-dilutable binders (which had been neutralised as recommended by the manufacturers) at a high PVC in a Cowles 'Dissolver' and grinding was then carried out in a Perl mill. The water paints, which were formulated to a viscosity of flow time of 60 seconds (4 DIN 53.211), were drawn off and stored to examine their sedimentation behaviour and the deposit formed, and, in a parallel series of tests, were applied and evaluated to determine the optical performance, gloss, brightness and hue.

Within the scope of this paper, only the results relating to the scattering power and the sedimentation behaviour of the water paints will be given.

Examination of the water paints

Refs. 35, 36, 45, 46

Determination of optical performance

The scattering power of a dried coating was determined by a method based on that of DIN 53.162 as a characteristic value for the optical performance.

Determination of the sedimentation behaviour

After the water paints had been formulated to the same viscosity and poured into calibrated measuring cylinders holding 100 cm³, the formation of a pigment-free liquid layer, as a function of the storage time, was observed by visual examination.

The divisions read off on the scale for the depth of this pigment-free zone were taken as a numerical measure of the sedimentation.

Determination of the zeta potential

Theoretical considerations

The stability, and hence also the optical performance, of TiO_2 pigments in aqueous systems depends on a number of parameters such as the character of the pigment surface, the electrical charge, the nature and concentration of the electrolyte and the extent and nature of the adsorbed layer[35,36,45].

The electrical charge of titanium dioxide particles in aqueous suspensions can have various causes:

(1) Protons or hydroxyl ions from the solution or from dissociation processes[46] can be adsorbed on the surface of the TiO_2 particles.

(2) Anions, cations or surface-active substances present in the solution are adsorbed on to the pigment surface.

Since the charged particles are in a polar medium, an electrical double layer is formed on the surface of the solids (Figure 1). According to Stern, this double layer can be divided

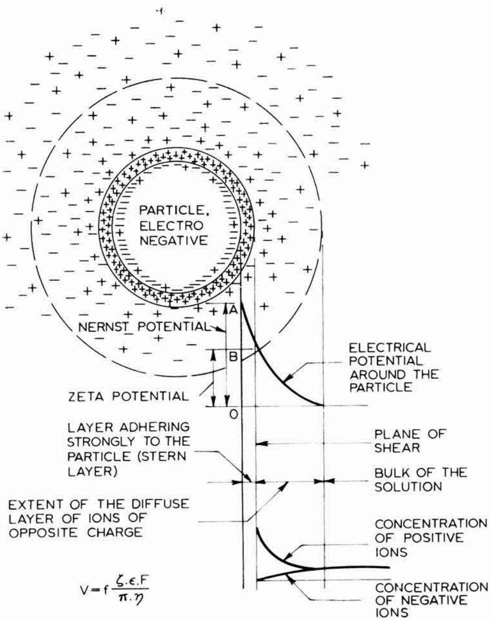


Fig. 1. Diagrammatic representation of an electronegatively charged particle in an aqueous suspension

into the two parts which are in mutual equilibrium; a compact layer, which lies on the surface of the solid and in which the potential falls off from A to B, and a diffuse layer on top of the first layer, in which the potential falls off from B to O.

Figure 1 is a diagrammatic representation of the charge of an electronegative particle.

In the so-called Stern layer positive ions predominate. The higher concentration of negative ions in the adjoining diffuse layer is responsible for the negative electrophoretic migration of the particle.

The potential difference existing between B and O is known as the zeta potential.

In the electrophoretic migration of charged particles in an electric field, a part of the adsorbed liquid layer moves jointly with the particle, its direction being given by the direction of the charge.

The migration velocity V is proportional to the zeta potential ζ, the dielectric constant ε of the solvent and the field strength F and is inversely proportional to the viscosity η of the solvent.

$$V = f.\frac{\zeta\ \varepsilon\ F}{\pi\ \eta} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The proportionality factor f is constant for a given system. It has a value between $\frac{1}{4}$ and $\frac{1}{6}$ and takes account of the change in the double layer which occurs during the movement and which is a result of the migration of ions of opposite charge in the reverse direction to the migration of the particles, and of differences in the shape of the particles.

Apparatus used for the measurement of zeta potentials

The development of the so-called Zeta-Meter® to the production stage has greatly facilitated the determination of zeta potentials. The Standard-Zeta-Meter® used consists of three basic units (Figure 2): a source of energy, an electrophoresis cell and a stereomicroscope. The energy source has a direct current voltage which can be adjusted between 0 and 300 V. The apparatus has a voltmeter, a microammeter for measuring the current in the electrophoresis cell, a pole-changing switch and a timing device with a micro-switch that can be operated by hand.

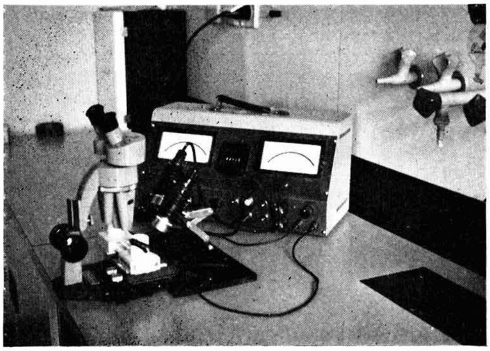


Fig. 2. The standard zeta-meter®

from the right: the energy source and in front of it the glass-Teflon cell the illumination device and stereomicroscope with a Plexiglas cell

Two differently constructed cells were used for the electrophoresis, depending on the nature of the solution under measurement; the normal cell made of Plexiglas is adequate for zeta potential measurements on purely aqueous TiO_2 suspensions, but a glass/Teflon cell must be used for investigations on TiO_2/binder suspensions.

The anode and cathode compartments of the measuring cells are connected to each other by a round, highly polished tube 10 cm long and 0.5 cm in diameter. In all the experiments the anode consisted of a molybdenum cylinder and the cathode of a platinum/iridium strip.

Preparation of suspensions for zeta potential measurement

The indirect method

(a) Purely aqueous TiO_2 suspensions

Quantities of 10 g or more of the pigment to be tested were made into a paste with fresh, completely demineralized water in a mortar, poured into a 1 litre measuring flask, made up to volume with demineralized water and dispersed under constant conditions for 20 hours by means of a shaking machine (the Hofman range, supplier: Labor-Schoeps, 41 Duisburg-Beeck).

Definite quantities of suspension, usually 1 ml of the original 1 per cent strength suspension, were withdrawn from this mixture and, at the same time, clear centrifuged products (mother-liquors) were prepared. The pigment suspension to be investigated was poured into a 100 ml measuring flask and filled up to the mark with the mother-liquor or completely demineralized water, or adjusted to a desired pH value by adding acid or base. The pH value, conductivity and zeta potential were measured in each case immediately after the preparation of a sample.

(b) Aqueous TiO_2/binder suspensions

The water-dilutable polymeric resins to be investigated and/or amine were added in varying concentrations to definite quantities of the original TiO_2 suspensions, prepared in accordance with (a), and of corresponding mother-liquors. The mixture was made up to 100 cm^3 with the particular mother-liquor and, was shaken for a period between 15 minutes and 200 hours before the pH value, the conductivity and the zeta potential were measured.

The direct method. In this method of preparation the effect of each of the components of a water paint on the zeta potential was investigated by making them into a paste, or dispersing them, directly with the pigment in a suitable concentration. A quantity of paste corresponding to 10 g of the pigment to be tested was placed in a 1 litre measuring flask, made up to volume with fresh, demineralized water and shaken for a period between 1 and 100 hours on the shaking machine. After this the indirect method (a) was used for the further preparation of the suspensions for determination (~0.01 per cent of pigment).

Determination of pH value, conductivity and zeta potential

The pH value was determined in the usual manner using a single-rod glass electrode in conjunction with a suitably calibrated millivoltmeter.

The conductivity and the zeta potential were both determined in the electrophoresis cell.

When determining the zeta potential, the measuring cell, filled with the suspension under investigation, was fixed under the stereomicroscope and the microscope focused in such a way, (by means of labelled guide-lines which are made visible by the illumination of the Plexiglas block of the measuring cell at a fixed angle of illumination) that, owing to the depth of focus, it was only possible to observe the colloidal particles that were moving at their true electrophoretic velocity in the electric field, uninfluenced by currents in the liquid. The determination was carried out by counting the sections labelled in the lens system of the stereomicroscope that were traversed by one or by several particles, in a time which was measured simultaneously.

The direct-current voltage to be applied and the period during which it is possible to count the sections, depend on the conductivity of the suspension. If the voltage selected is too high or if the determination extends over too long a period, turbulence is set up in the tubes, so that the particles no longer move in straight lines but in spirals.

The zeta potential measurements were carried out in the standard atmosphere 23/50-2 of DIN 50.014 and the electrophoretic mobility of at least 10 particles was observed for each determination.

Using tables and nomograms which are included with the operating instructions for the Zeta-Meter®, the zeta potential of pigments in purely aqueous suspensions can be calculated easily from the experimental results. In suspensions which have a viscosity and dielectric constant different from those of water, the experimental results obtained must be recalculated by the Helmholtz-Smoluchowski formulae.

Viscosity determination

The Contraves Rheomat 30 was employed to determine the viscosity of the aqueous/organic suspension liquids.

Adsorption tests

The quantities of binder solids remaining in solution in the pigment-free centrifuged fractions, described under the direct method above, that had been prepared for measuring the zeta potential of organic-aqueous TiO_2 suspensions, were determined gravimetrically in a parallel series of experiments, and the quantity, A, adsorbed per square metre of pigment surface was calculated in mg/m^2 from the decrease in concentration.

Results

Technological test data

The scattering power of water paints

Figure 3 shows the scattering power of TiO_2 pigments surface-treated with various inorganic compounds as a function of the PVC in the three water-dilutable binders 1, 2 and 3.

The influence exerted by the binder component. It is immediately evident that there is a strong similarity between the left-hand curves and the central curves. Both relate to air-drying systems. There is a distinctly lower level of scattering power in all the right-hand curves, which are based on binder 3; these are stoving paints. This fact, however, cannot account for the universally low figures of scattering power, which must be due to a flocculation of the pigments, indicated by considerable sedimentation in the water paints and by a surprisingly low pH value of 7.5. The flocculation of the pigments and, consequently, rapid sedimentation, is avoided if more amine is used in neutralising the water-dilutable binder 3 than is recommended by the manufacturer of this product. Although the resulting higher pH gives water paints of the same pigment type noticeably higher viscosity values, the level of their scattering power curves is similar to those of the two other water paint systems.

The influence exerted by the pigment. In binder 1 and in binder 2, two different types of curve can be distinguished, depending on the inorganic surface-treatment of the TiO_2 pigments employed:

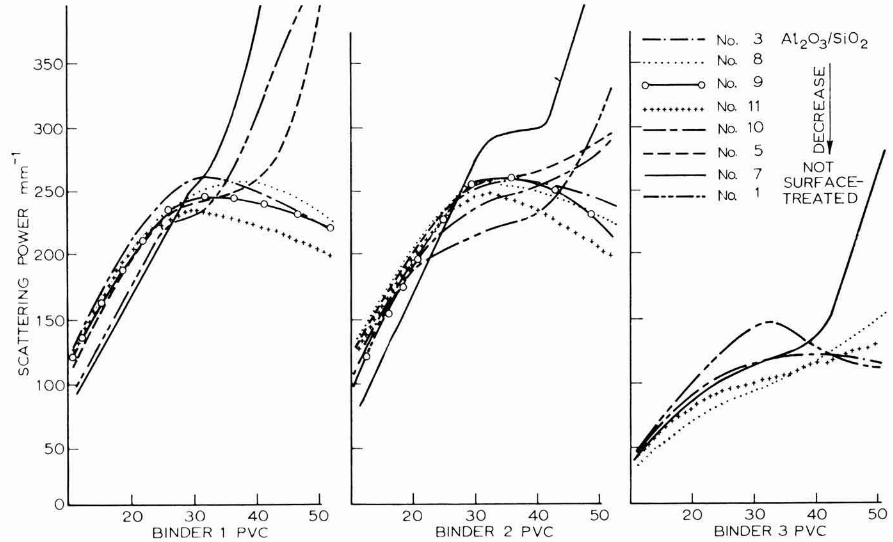


Fig. 3. The scattering power of water paints as a function of the PVC and the inorganic surface-treatment of several titanium dioxide pigments in the water-dilutable binders 1, 2 and 3

The right-hand side of the diagram shows the Al_2O_3/SiO_2 ratio of the TiO_2 pigments used.

(a) Curves that display the parabolic shape which is well known for conventional paints (TiO_2 pigments nos. 3, 8, 9 and 11) and

(b) Curves with an S-shape (TiO_2 pigments nos. 1, 7, 5 and 10).

With binder 3, at pH: 7.5, the TiO_2 pigments, with the exception of nos. 7 and 1, surprisingly exhibit an increase in scattering power, which rises without a break over the whole PVC range from 10 to 50 per cent.

Binder-pigment inter-relationships. When the individual scattering power curves are examined more closely, it becomes evident that individual titanium dioxide pigments in binders 1, 2 and 3 behave differently, both in absolute terms and in relation to one another as far as scattering power is concerned.

The sedimentation behaviour of water paints

The sedimentation of water paints exhibits a similar complexity (Figure 4).

The effect of particle size can be seen from the shape of the curves for TiO_2 pigments nos. 3 and 4. TiO_2 no. 4, which is more finely divided and surface-treated only with Al_2O_3, shows more sedimentation than sample no. 3 of the same type, which is somewhat coarser.

TiO_2-binder inter-relationships. The sedimentation of water paints is thus the result of particular inter-relationships between the pigment and the binder. In addition, at the same PVC, the same TiO_2 pigment exhibits a sedimentation which varies according to the binder. An example of this is shown by TiO_2 nos. 5 and 7. TiO_2 sample no. 5, which is surface-treated with medium quantities of Al_2O_3 and SiO_2, hardly shows any sedimentation over the whole PVC range when in binder 1, but shows a relatively high sedimentation in conjunction with binder 2.

On the other hand, the rutile sample no. 7, which is surface-treated with a large amount of silica and medium quantities of Al_2O_3, hardly shows any sedimentation in binder 2, but shows very high sedimentation in paints based on binder 1 (left-hand figure).

The most important results of the technological investigations are summarised in Table 3.

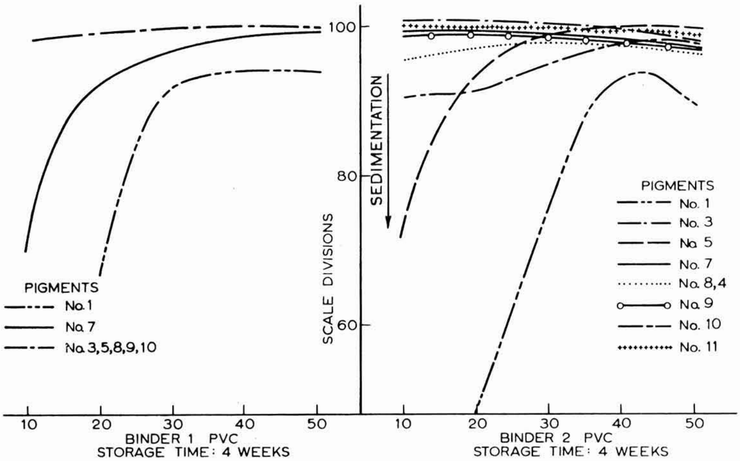


Fig. 4. The sedimentation of water paints as a function of the PVC and the inorganic surface-treatment of several titanium dioxide pigments in the water-dilutable binders 1 and 2.

(The sedimentation is quoted in scale divisions relating to the pigment-free zones formed in measuring cylinders after a storage time of 4 weeks.)

The influence exerted by the binder. Paint systems 1 and 2 are relatively stable suspensions. Depending on the particular pigment used, water paints based on binder 1 are to be preferred.

As already mentioned, sedimentation of the pigments is greatest in the systems based on binder 3.

The influence exerted by the pigment. The sedimentation behaviour depends on the concentration and type of the pigment and on its average particle size. As the PVC increases, the tendency to sedimentation decreases.

The strong influence exerted on sedimentation by pigment type can be seen, particularly in the right-hand section of Figure 4. Thus titanium dioxides no. 1 and no. 5 exhibit relatively high sedimentation, but nos. 3, 9 and 11 hardly any.

Owing to the nature of the experimental results, various ranges of scattering power have been taken for the pigment-volume-concentrations of 10 and 20 per cent and these ranges contain the TiO_2 pigments whose scattering power values fall within them—differentiated according to binders 1 to 3.

The sedimentation figures (SKt) determined for pigments nos. 1-11 in the three binders have also been entered in the Table. The Al_2O_3/SiO_2 ratios appropriate to the different TiO_2 pigments are shown in the column on the extreme left.

The experimental results shown in the Table under binder 3 also relate to water paints stabilised with a larger quantity of amine (17 g of dimethylethanolamine instead of 5.0 parts/100 parts of binder solids as indicated by the manufacturer).

The following conclusions can be drawn from Table 3:

(1) In binder 1 there is a certain correlation between, on the one hand, the scattering power and the sedimentation

Table 3

The scattering power and stability of water paints with a PVC of 10% and 20%.

		PVC 10%							PVC 20%						
			Scattering power (mm⁻¹)			Sedimentation (SKt)				Scattering power (mm⁻¹)			Sedimentation (SKt)		
			Binder			Binder				Binder			Binder		
Al_2O_3/SiO_2	TiO_2 No.	Range	1	2	3	1	2	3	Range	1	2	3	1	2	3
			Pigment No.	Pigment No.	Pigment No.					Pigment No.	Pigment No.	Pigment No.			
>3	3; 8; 9; 10; 11	130–140	3; 11	—	6	99	—	98	200–210	3; 5; 8; 9; 11	3; 8; 11	6	98–99	96–100	76
		120–129	5; 8; 9	3; 8; 11	—	99	95–100	—	190–199	—	1; 9; 10	2; 7; 8; 11	—	48–98	38–82
		105–119	—	1; 5; 9; 10	3; 7; 11	—	40–99	42–96	180–189	1; 7	5	3	67–93	94	97
1.4	5; 6	95–104	1	—	8	97	—	98	170–179	—	7	—	—	99	—
0.4	7	85–94	7	—	2	70	—	24							
		<85	—	7	—	—	99	—							
	1														

TiO_2 pigments variously surface-treated are assigned to specific ranges of scattering power and sedimentation numbers (SKt), binders 1, 2 and 3 being used.

On the extreme left: the titanium dioxide pigments used are grouped according to their Al_2O_3/SiO_2 ratio

behaviour of the TiO_2 pigments investigated, and their Al_2O_3/SiO_2 ratio on the other hand. As this ratio decreases, the scattering power of correspondingly pigmented water paints falls for PVC values of 10 and 20 per cent, whilst the tendency of the paints to sedimentation increases.

(2) In binders 2 and 3 the scattering power and sedimentation of the same TiO_2 pigments are in many cases different from the results in binder 1, both in absolute terms and as between one pigment and another. That is to say, the Al_2O_3/SiO_2 ratio of the TiO_2 pigments is, in general, inadequate for an assessment of the behaviour of the pigments in water paints.

These results led to the decision, when investigating the factors on which the zeta potential depends, not to limit the work to pure TiO_2 pigment suspensions, but to extend the experiments to the interactions between the TiO_2 pigments and the other constituents in the formulation of the water paints.

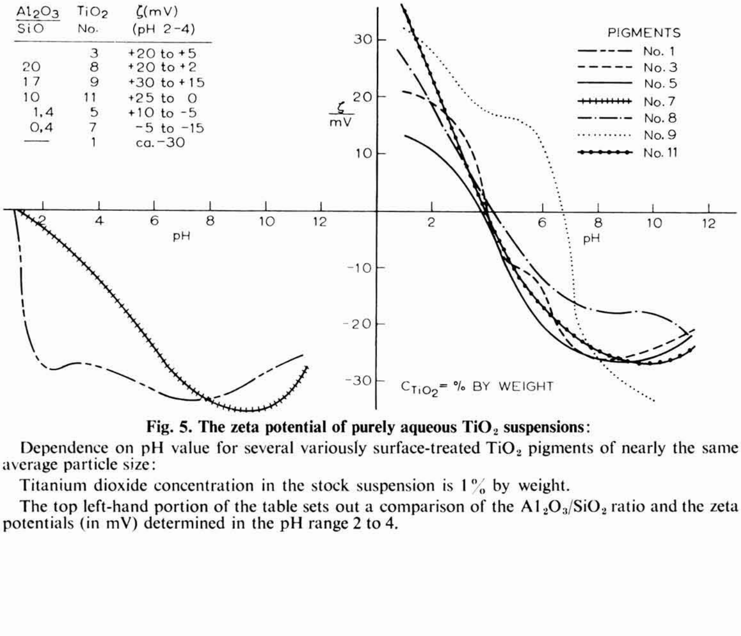
The effect of the binder components on the zeta potential was, therefore, particularly important.

Investigations into the factors on which the zeta potential depends

Refs. 31, 32, 36, 39-42, 47

The zeta potential of purely aqueous TiO_2 suspensions.

The part played by the surface-treatment of the TiO_2. Since Robinson and Tear's[42] investigations have shown that the zeta potential of pigment concentrations above 1 per cent should remain constant, the TiO_2 suspensions were uniformly made up at 1 per cent by weight (Fig. 5). The diagram shows



Al_2O_3/SiO	TiO_2 No.	ζ(mV) (pH 2-4)
	3	+20 to +5
20	8	+20 to +2
17	9	+30 to +15
10	11	+25 to 0
1,4	5	+10 to -5
0,4	7	-5 to -15
—	1	ca. -30

Fig. 5. The zeta potential of purely aqueous TiO_2 suspensions:

Dependence on pH value for several variously surface-treated TiO_2 pigments of nearly the same average particle size:

Titanium dioxide concentration in the stock suspension is 1% by weight.

The top left-hand portion of the table sets out a comparison of the Al_2O_3/SiO_2 ratio and the zeta potentials (in mV) determined in the pH range 2 to 4.

the zeta potential curves obtained for seven differently surface-treated rutile pigments with an average particle size of 0.36 ± 0.02 μm, in the pH range from 1 to approx. 12.

Within the whole pH range, more or less strongly negative values of the zeta potential are given by no. 1, untreated rutile, and no. 7, a rutile type with considerable SiO_2 surface-treatment. Pigments that have been surface-treated only with Al_2O_3 (no. 3) or pigments with a mixed Al_2O_3/SiO_2 surface-treatment (pigments nos. 5, 8, 9 and 10) show positive zeta potentials in the acid range. The position of the isoelectric points of the individual TiO_2 pigments is also markedly different. As already found by other authors[36,39-41], there is a correlation with the nature and quantity of the inorganic surface-treatment components, expressed as the Al_2O_3/SiO_2 ratio. As the Al_2O_3/SiO_2 ratio increases, the level of the positive zeta potentials rises in the acid pH range due to proton absorption at the pigment surface, whilst at the same time the isoelectric points are displaced to higher pH values. In the alkaline range, which has significance for the pigmentation of water paints, the zeta potential curves of the different TiO_2 pigments overlap each other in an uncharacteristic manner. Values of zeta potential between —20 mV and —35 mV are found.

Effect of particle size. As well as the nature of the surface-treatment, consideration must also be given to the particle size as a parameter in the determination of zeta potentials (Fig 6, upper part).

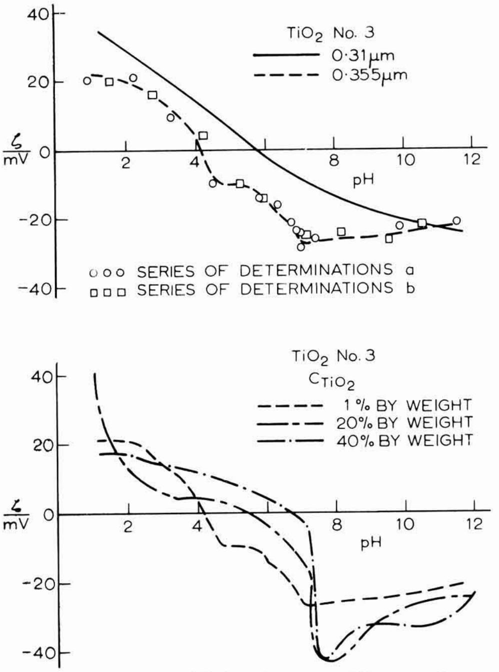


Fig. 6. The zeta potential of purely aqueous TiO_2 suspensions:

above: the dependence of the pH value on the particle size

below: the dependence of the pH value on the concentration of the stock suspension

Within the whole pH range, the more finely divided TiO_2 pigment (the upper curve) gives higher zeta potential values and its isoelectric point is displaced to a higher pH value.

It can be seen from the reproducibility of the lower zeta potential curve that there are significant differences between the two curves of zeta potential. The experimental values plotted result from two different series of determinations, separated by an interval of several weeks.

Independently, an average standard deviation σ: 1.3 mV was determined, under reproducible preparative conditions, for the measurement of zeta potentials by means of the Zeta-Meter® in aqueous TiO_2 suspensions. The accuracy of measurement is impaired if the light transmittance of the suspension liquid decreases (see also under zeta potential and scattering power later in paper).

Effect of pigment concentration. The lower part of Figure 6 shows the effect of the pigment concentration on the zeta potential as a function of the pH value. In the acid pH range, the zeta potential becomes more positive as the TiO_2 concentration increases; in the alkaline pH range, an increase in the negative surface potential can be detected as the TiO_2 concentration increases. The isoelectric point of the type of pigment which is surface-treated only with Al_2O_3 is also displaced to higher pH values as the pigment concentration increases.

Contrary to what is stated by Robinson and Tear[12], the zeta potential of TiO_2 particles can, therefore, vary as a function of the pigment concentration in the stock suspension.

Compared with pigment type no. 3, the zeta potential shows a lower dependence on the pigment concentration when a rutile pigment with a higher silica surface-treatment (no. 7) is examined.

Effect of the liquid used for suspension. Under certain circumstances, the same TiO_2 pigment gives different curves of zeta potential against pH (Fig. 7) if electrolyte-free water is used instead of the mother-liquor for the preparation of the aqueous pigment suspension used for the determination of zeta potentials. In the acid range, pigments such as nos. 3 and 8 give higher positive surface charges and higher pH values for the isoelectric point when completely demineralised water is used as the suspension liquid than when the corresponding mother-liquors are used.

On the other hand, pigments of the type of no. 1 and no. 7 exhibit comparatively low changes in zeta potential.

To account for the behaviour of pigments of the type of no. 3 and no. 8, it is assumed that the effect of the distilled water is to disturb the equilibrium in the diffuse layer around the pigment particles due to adsorbed ions being desorbed and space being made for H ions, which, in the acid range, introduce higher positive charges.

Determinations of zeta potential on aqueous-organic TiO_2 suspensions. The number of parameters that can have an effect on the zeta potential of pigment particles in aqueous systems is increased still further by the presence of binder polymers or other components of a water paint.

Effect of polymer concentration and/or reaction time. Even low concentrations of binder polymers can increase the negative surface charge of titanium dioxide pigments (Fig. 8).

This Figure shows the zeta potential curves of a pigment surface-treated with Al_2O_3 as a function of the binder concentration and the time of shaking. On the left-hand side the binder was added to the TiO_2 suspension in a concentration range of 0.001 to 1 per cent by weight with no additional triethylamine; on the right-hand side 1.35 mmols of triethylamine were added in each case.

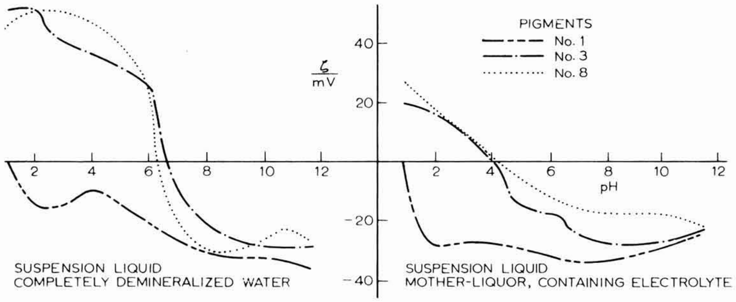


Fig. 7. The zeta potential of titanium dioxide pigments as a function of the pH value: The effect of the suspension liquid

on the left: TiO_2 suspended in completely demineralised water

on the right: TiO_2 in a "mother-liquor" containing electrolyte.

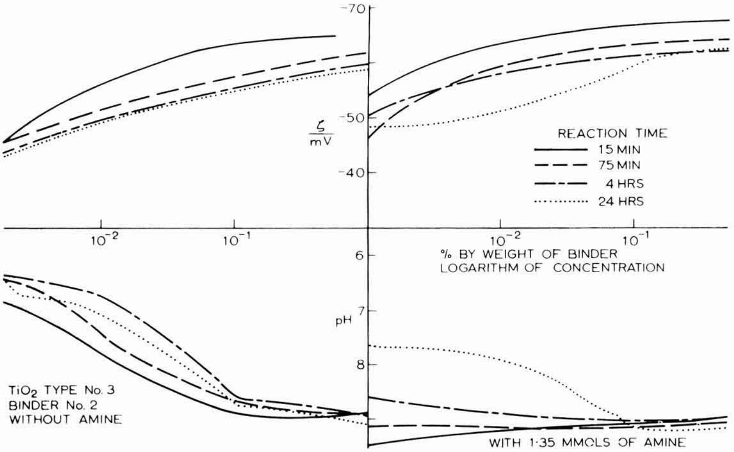


Fig. 8. The zeta potential and pH value of aqueous-organic TiO_2 suspensions:

Dependence on the binder concentration and the reaction time.

above: zeta potential curves

below: pH value curves

on the left: binder 2 without amine,

on the right: binder 2 with 1.35 mmols of triethylamine (the concentration of binder solids is plotted on a logarithmic scale)

Both with and without additional triethylamine, the level of the zeta potential curve decreases as the time of shaking increases; associated with this, as the lower Figures show, there is a reduction in the pH value of the TiO_2 suspensions.

This is particularly evident in the region of low added binder.

The supposition that, in addition to the absorption of binder polyanions, changes involving amine also take place on the surface of the pigment, is strengthened by the shape of the zeta potential and pH curves in the left-hand figures. In the presence of amine (right-hand Figures), even low concentrations of binder increase the negative zeta potential to higher values compared with those where no amine is present.

Effect of polymer concentration and of the surface-treatment of the TiO_2 pigment. Figure 9 summarises the zeta potential and pH value curves of various surface-treated TiO_2 pigments as a function of the binder concentration for a reaction time of four hours and in the presence of an excess of amine of 1.35 mmols.

The dependence of the zeta potential on binder concentration can be seen to be markedly pigment-specific.

The part played by the amine. If the level of the zeta potential of TiO_2 suspensions in the presence of water-dilutable binder polymers is higher when amine is added than in the absence of amine, it would be expected that addition of amine alone would produce a change in zeta potential. Experimental investigations have provided repeated confirmation of this.

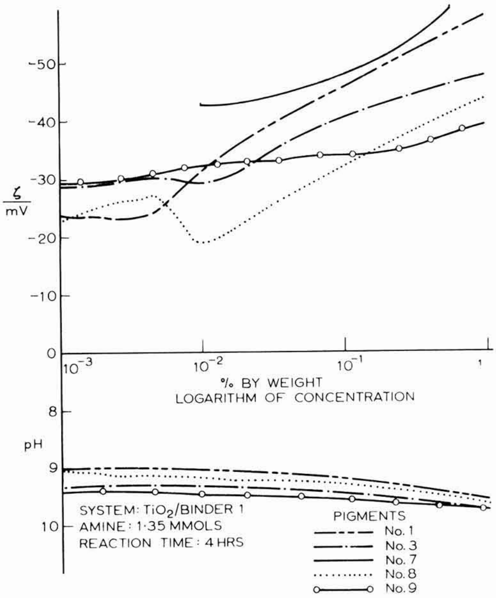


Fig. 9. The zeta potential and pH value of aqueous-organic TiO_2 suspensions as a function of the type of TiO_2 pigment and of the binder concentration.

Binder 1 with 1.35 mmols of triethylamine, direct method of preparation, reaction time 4 hours.

If, for example, the triethylamine is added as early as during the dispersion of the pigment, increasingly more negative zeta potentials are obtained as the quantities of triethylamine added are increased, and marked differences are recorded, depending on the surface-treatment of the TiO_2 type used.

How can this be explained?

TiO_2 pigments have a slight solubility in alkaline solutions (Table 4).

Table 4

The solubility of titanium dioxide pigments in solutions containing amines:

40 g of TiO_2 with 400 g of amine solutions, adjusted to various pH values and shaken for 24 hours.

	TiO_2-Type No 3	TiO_2-Type No. 7
Triethylamine		
pH: 9-		
TiO_2 (mg/l)	0	0
Al_2O_3 (mg/l)	0.55	0.3
SiO_2 (mg/l)	0	16
Triethanolamine		
pH: 9.6-		
TiO_2 (mg/l)	0	0
Al_2O_3 (mg/l)	12.5	3.2
SiO_2 (mg/l)	-1	0
Triethylamine		
pH: 11.5-		
TiO_2 (mg/l)	0	0
Al_2O_3 (mg/l)	41.3	18.1
SiO_2 (mg/l)	-1	75

This table shows the amounts of Al_2O_3 and SiO_2 that are extracted by shaking various TiO_2 pigment samples in alkaline solutions. The analytical figures indicate that the pigment surfaces that have been surface-treated with Al_2O_3 and/or SiO_2 are chemically attacked as the amine content rises.

According to Balzer and Lange[31], considerable quantities of aluminium are dissolved from γ-Al_2O_3 by oligomeric phosphates, even at pH:7, and are precipitated on the surface of the pigment as a polyanionic compound. The formation of such precipitates is also discussed by other authors[31, 32].

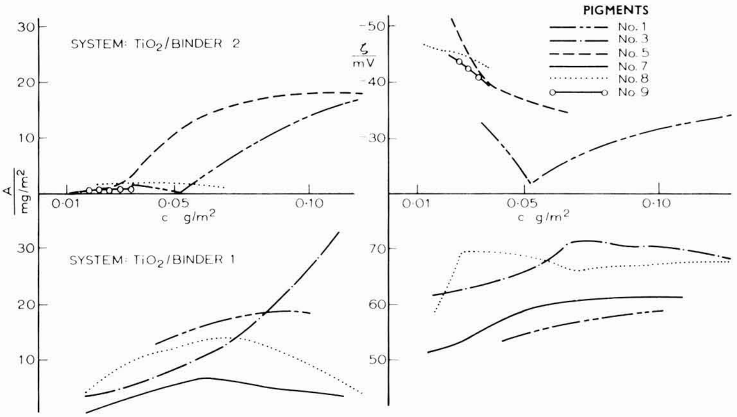


Fig. 10. The relationship between adsorption and zeta potential for aqueous-organic TiO_2 suspensions:

on the left: quantity *A* of binder solids adsorbed per square metre of pigment surface as a function of the concentration of binder solids in grammes per square metre of pigment surface (g/m²) in the TiO_2/binder suspension

above: binder 2; below; binder 1

on the right: the corresponding zeta potential curves as a function of the concentration of binder solids in g/m².

TiO_2 pigments: 1, 5, 8 and 9 (binder 2) and 1, 3, 7 and 8 (binder 1).

Similar chemical reactions at the surface of the pigment will probably also take place in water paints pigmented with TiO_2.

Some information on this point is provided by the analysis of the clear solution that was prepared for determining the zeta potential of TiO_2 no. 9 in aqueous suspension with binder 1. 1 per cent by weight of TiO_2 and 2.4 per cent by weight of binder solids were dispersed together over night and the suspension was then centrifuged and filtered (the direct method).

From 1g of TiO_2 pigment, the following constituents dissolved: 2.8 mg of Al_2O_3 and 1.2 mg of SiO_2. Soluble TiO_2 was not detected. The reactivity of the TiO_2 coating, thus demonstrated, is responsible, according to McEwan^{47}, for the generally unsatisfactory stability of water paints on storage.

Adsorption tests/zeta potentials

Adsorption tests carried out in parallel with zeta potential measurements on aqueous/organic TiO_2 suspensions strengthen the assumption that adsorption processes and chemical reactions take place side by side at the surface of the pigment (Figure 10).

Whilst the zeta potential of the rutile types nos. 1, 7, 3 and 8 in the system TiO_2/binder 1 consistently increases with the quantity of binder adsorbed within a binder concentration range up to about 0.5 g of binder solids per m^2, such a relationship between adsorption and surface charge no longer holds at higher binder concentrations.

For example, a steep increase in the quantity of adsorbate does not produce any further increase in the negative zeta potential of TiO_2 no. 3, which is surface-treated with Al_2O_3. In TiO_2/binder 2 systems, cases were established in which there is a relationship between the quantity of adsorbate and the zeta potential found, for example no. 1; and, on the other hand, examples were found in which this relationship is obviously absent, for example TiO_2 no. 5.

Exchange reactions on titanium dioxide pigments in water paints

Refs. 45, 46

The following assumptions will be made in order to explain the technological behaviour of water paints:

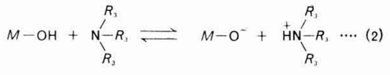
(1) Adsorption processes and chemical reactions take place side by side at the surface of the pigment.

(2) In an aqueous solution, an increasing concentration of water-dilutable binder molecules produces an increase in the negative surface potential due to adsorption of polyanions at the surface of the pigment.

(3) Apart from the nature and quantity of the individual components of the system (for example, the pigment, the binder, the amine and the organic solvent), the adsorption equilibrium is also influenced by the conditions during the preparation (for example the reaction time).

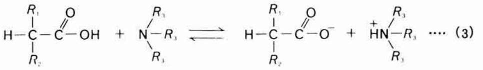
(4) The chemical reactions at the surface of the pigment^{46} are determined, *inter alia*, by the nature and quantity of the surface-treatment components, by the pH value and by the duration and intensity of the interaction between the reactants.

(5) The following chemical reactions can take place:



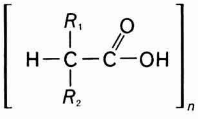
$$M{-}OH + N(R_3)_3 \rightleftharpoons M{-}O^- + H\overset{+}{N}(R_3)_3 \quad \cdots (2)$$

If an excess of amine is not present, the amine required for salt-formation^{45} in accordance with equation (3).



$$H{-}\underset{R_2}{\overset{R_1}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH + N(R_3)_3 \rightleftharpoons H{-}\underset{R_2}{\overset{R_1}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O^- + H\overset{+}{N}(R_3)_3 \quad \cdots (3)$$

can be used up, with a reduction in the pH, and the polymer acids



$$\left[H{-}\underset{R_2}{\overset{R_1}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH \right]_n$$

which are then insoluble or partly insoluble, are precipitated on the surface of the pigment.

(6) Associated with this is a reduction in the stability of the pigment, which reveals itself by a reduction of the zeta potential.

The zeta potential of TiO_2/binder suspensions and the scattering power of water paints

If a relationship exists between the zeta potential of a pigment in suspension and some technological property of a water paint incorporating this pigment, the two relevant measurable variables should, if possible, be investigated in the same system.

However, major experimental difficulties are met when determining zeta potentials in pigmented water paints:

(1) Depending on the dilutability of the polymer with water, suspension liquids containing binders are opaque, and it is difficult or impossible to recognise the migrating solid particles under the microscope.

(2) Because the zeta potential is dependent on the viscosity, the determination of which involves fairly large errors, rather inexact determinations of zeta potential must be expected in suspensions containing a high proportion of binder.

(3) The preparation of the pigment-free mother-liquors is tedious.

(4) Suspension liquids containing a high proportion of binder attack the normal measurement cell made of Plexiglas and render it unserviceable. This difficulty can, however, be surmounted by using a glass-Teflon cell.

For these reasons, in parallel with the technological investigations on water paints, the author has carried out determinations of zeta potential on correspondingly diluted TiO_2/binder suspensions prepared by the direct method. Whilst the TiO_2 suspensions containing binders 2 and 3 that correspond to a water paint of 10 per cent PVC have too small a light transmittance, zeta potential determinations can be carried out without difficulty on suspensions of lower binder content (corresponding to a PVC of 20 per cent and higher) (Fig. 11).

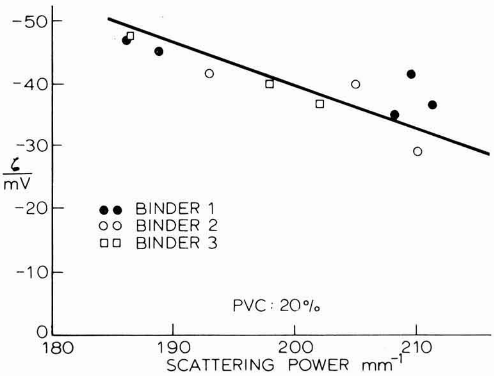


Fig. 11. The relationship between the zeta potential of aqueous-organic TiO_2 suspensions and the scattering power of water paints of a comparable pigment concentration, at a PVC of 20%.

Direct method of preparation used for the aqueous-organic TiO_2 suspensions, reaction time 1 hour.

Zeta potentials determined after a reaction time of 1 hour for TiO_2/binder suspensions corresponding to a PVC of 20 per cent are plotted against the scattering power values of the appropriate water paints of a comparable pigment concentration.

The degree of alignment of the experimental values, which relate to the various binders 1, 2 and 3, indicates that the scattering power increases, independently of the type of binder, as the negative zeta potential decreases.

Conclusions

The zeta potential of titanium dioxide pigment suspensions has been investigated, under various preparative conditions, in purely aqueous suspensions and in the presence of components which, together with the surface-treatment of the TiO_2 and the PVC, are of importance in water paints.

The accuracy and the limits of this technique of determination are discussed. From the dependence of the zeta potential on the pH value and the electrolyte content of the suspension liquid, it has been possible to indicate the effect exerted by the particular surface-treatment, the particle size and the concentration, on the magnitude of the surface charge.

It was known from the literature on surface-treated titanium dioxide pigments that a correlation exists between the ratio of hydrated aluminium oxide to hydrated silica, the zeta potential and the stability of corresponding TiO_2 suspensions. This correlation has, in part, been confirmed experimentally and has been used to provide an explanation of technological phenomena such as the scattering power and sedimentation of water paints pigmented with these products.

It is shown by means of numerous determinations of zeta potential, pH and conductivity, as well as analytical investigations, that the binder-specific behaviour of titanium dioxide pigments in the presence of binder polymers and amine can be accounted for on the basis of a complicated juxtaposition and succession of adsorption processes and chemical reactions that take place on the surface of the pigment.

However, the determination of zeta potentials can not only be employed as a sensitive and accurate method for detecting changes at the particle surface, but it can also be used to characterise titanium dioxide pigments and, under suitable conditions of preparation and determination, can provide information on scattering power in water paints.

A knowledge of the zeta potential is, however, not adequate on its own to describe the behaviour of a pigment in the system, unless the complicated relationships between the zeta potential and the numerous other parameters of the possible components in water paints are understood in detail.

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J. Oil Col. Chem. Assoc. 1977, **60**, 398-403

Binders without environmental pollution and with good penetration properties on the basis of acrylic emulsions with very fine partical sizes*

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Summary

The use of fine particle size styrene/acrylic and pure acrylic emulsions has been studied with reference to their use as sealers for porous surfaces.

The conditions under which very fine particles can be produced are discussed.

A new technique has been developed by which the depths of penetration of the emulsion particles and the aqueous phase can easily be demonstrated. Surfaces which can be successfully sealed include; concrete, masonry, plaster, lime stucco and wood.

Keywords

Types and classes of coatings and allied products

- primer
- sealer
- impregnating varnish

Types and classes of structures or surfaces to be coated

- concrete
- masonry
- brick
- wood
- plaster boards

Raw materials for coatings

binders (resins etc)

- acrylic emulsion
- styrene resin emulsion

Properties, characteristics and conditions primarily associated with

materials in general

- porosity

Processes and methods primarily associated with analysis, measurement or testing

- penetration test

Liants non polluants et de bonnes caractéristiques de pénétration à base des émulsions acryliques aux particules fines

Résumé

On a étudié les émulsions aux particules fines à base de styrolène/acrylique ou simplement d'acrylique, à l'égard de leur utilisation en tant que couches d'impression pour les surfaces poreuses.

On discute les conditions sous lesquelles peuvent être produites les émulsions aux particules très fines.

Une nouvelle technique a été mise au point pour déterminer la profondeur à laquelle les particules d'émulsion et également la phase aqueuse elle-même pénétrent dans les subjectiles poreux. Les surfaces qui peuvent être scellées avec succès comprennent le béton, la maçonnierie, le plâtre, la chaux, le stuc, et le bois.

Bindemittel ohne Einfluss auf Pollution der Umwelt und mit guten Eindringungseigenschaften auf Basis von Akrylatemulsionen sehr feiner Teilchengrössen

Zusammenfassung

Der Einsatz von Styrol-Akrylat- und reinen Akrylatemulsionen feiner Teilchengrössen wurde bezüglich ihrer Verwendbarkeit als Einlassgrund für poröse Oberflächen untersucht.

Die Bedingungen, unter welchen sehr feine Teilchengrössen erzeugt werden können, werden besprochen.

Es wurde eine neue Methode zur Bestimmung der Eindringtiefe der Emulsionsteilchen und der wässrigen Phase in die porösen Substrate entwickelt. Zu Oberflächen, deren Poren erfolgreich geschlossen werden können, gehören: Beton, Mauerwerk, Putz, Kalk, Stuck und Holz.

The growing interest in environmental problems will make the substitution of solutions of polymers, and, generally, all kinds of binders contained in organic solvents, by odourless, non-toxic, and non-inflammable emulsions a challenging task.

Additionally, as a consequence of the oil crisis, with rising prices and increasing raw material shortages, the saving of all kinds or organic solvents which are commonly used in conventional paint systems becomes mandatory.

In particular, the priming and impregnation of porous substrates usually still involve the use of great amounts of organic solvents and, therefore, the replacement of all these solvents by water is an interesting problem.

For deep priming, for example, the consolidation of old, sanding plaster, or of chalking paint coatings and the insulation of absorptive substrates such as stone, mortar, plaster, and lime stucco, the currently used products are copolymers composed of vinyl acetate and dibutyl maleate or of vinyl toluene and octyl acrylate. The vinyl acetate/dibutyl maleate-copolymers are dissolved in mixtures of aromatic and ester solvents and the copolymers of vinyl toluene and octyl acrylate are dissolved in white spirit. White spirit gives much

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better behaviour in respect of smell and skin irritation, but even this kind of solvent creates environmental problems.

Acrylic emulsions

The particle size of dispersed high polymers in acrylic emulsions is an important technological factor with respect to the properties of emulsions.

Copolymer emulsions having a specific composition and very small particle sizes will have useful application possibilities, in all cases where there is a technological demand for a thorough penetration of the latices into all kinds of absorbing substrates, as in the fields of priming and impregnating.

Most of the emulsions on the market at present have an average particle size of about 0.1 to 5.0 µm and the problem of developing new acrylic emulsions with particle sizes of about D $\leqslant$ 0.05 µm was investigated, and checks were made on some special application properties of these fine particle size emulsions.

The potential field of application calls for saponification—stable copolymer systems and, therefore, development work was done predominantly with styrene-acrylic or pure acrylic systems.

Emulsions with very fine particle sizes

After the definition of the aim, there are three fundamental problems in the synthesis of acrylic emulsions with very fine particle sizes, with regard to theoretical considerations on the mechanism of emulsion polymerisation, namely:

(1) Finding of effective emulsifiers

(2) Determination of the optimal emulsifier concentration

(3) Formulation of a suitable polymer-composition.

Increased amounts of initiator will influence particle size to a minor degree.

Emulsions with very fine particle size are produced by using, long chain alkane sulfonates and alkyl sulfates with a carbon chain in the range of C_8–C_{18} and alkali cations as emulsifiers. These anionic emulsifiers are used to produce styrene/acrylic and pure acrylic emulsions with total solid contents of 35–40 per cent and emulsifier-contents of 1–3 per cent (with respect to the emulsion).

The particle sizes of these emulsions are in the range of 0.035 to 0.06 µm.

The result is shown in Fig. 1, in which the dependence of particle size on the emulsifier content of styrene-acrylic emulsions is shown.

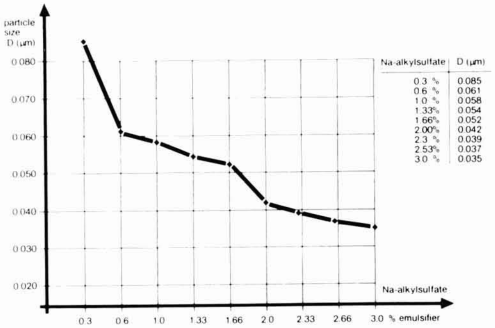


Fig. 1. Dependence of particle sizes of styrene/acrylic emulsions on emulsifier content

A photograph, taken by electron microscopy (magnification 40 000), of styrene/acrylic latices with very fine particle sizes is shown in Fig. 2. A comparison with the scale gives approximate values for the coarser particles of about 0.05 µm, so most of the latices shown on the picture have diameters of less than 0.05 µm.

Additionally it was found that the proportion of the different principal monomers used does not have any influence on the particle size, but changes important application parameters, such as the second order transition temperature of the copolymers and the minimum film forming temperature of the emulsions, as shown in Fig. 3.

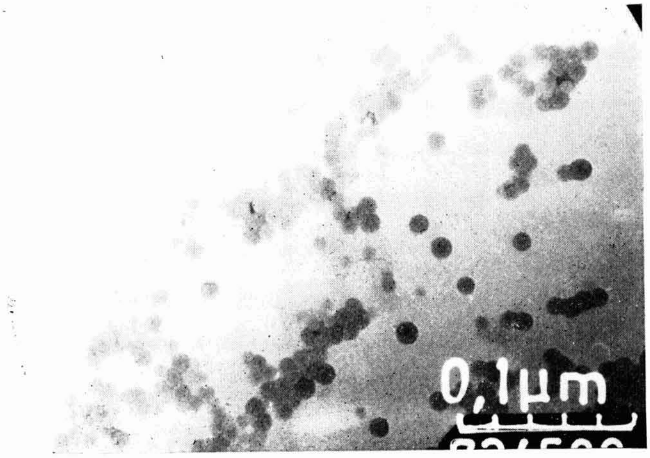


Fig. 2. Electron microscopy photograph of fine particle size latices (magnification 40 000)

Sty: BA	min.film-forming temperature [°C]	T_G [°C]
80:20	75	+ 57.5
70:30	52	+ 46.5
60:40	36	+ 35
50:50	18–19	+ 20–21
40:60	3	+ 9
30:70	<0	− 6
20:80	<0	− 16

Fig. 3. Dependence of physical film properties from the principal monomer distribution

Application of emulsions with very fine particle size

Acrylic emulsions with very fine particle sizes should, in comparison with emulsions with normal particle size, give a technical advantage in the field of impregnation and priming, where a thorough penetration of the substrate is essential. However, all the new emulsions with very fine particle sizes will replace commonly used copolymer-solutions only when all the application properties of the acrylic emulsions, at least, match the properties of the polymer solutions.

For testing the penetration of the newly developed acrylic emulsions with very fine particle size in comparison with the penetration of polymer-solutions into various absorbing substrates, a rather simple analytical device was developed for detecting the copolymer latices in various absorbing substrates.

Analytical device for fine particle size latices

Copolymerisation with various optical brighteners containing vinyl-groups in a range of 0.02 to 0.05 per cent (with reference to the monomers) resulted in optically brightened acrylic emulsions. The aqueous phase of these emulsions was tinged red by using small amounts of eosine. The colouration of the emulsions makes it possible to locate much better the overall penetration of the aqueous emulsion-serum. Additionally, an increase of the optical brightening was observed due to a synergistic effect.

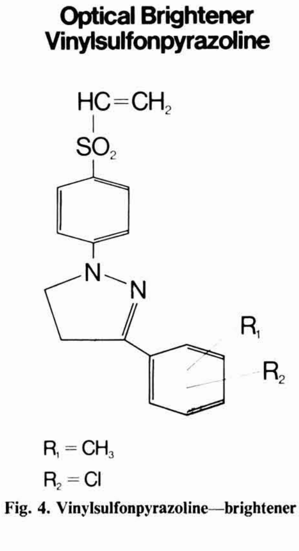


Fig. 4. Vinylsulfonpyrazoline—brightener

In the author's opinion it is remarkable that all vinyl sulfonpyrazoline derivatives, which were used as optical brighteners, did not show any regulator effect. That means, molecular weight distribution of the very small size copolymer-latices was not affected by the optical brightener.

It is possible to demonstrate by gel permeation chromatography, that all vinyl sulfonpyrazoline molecules have a random distribution in the polymer chain.

Fig. 5 shows the gel-permeation chromatograms of different copolymers containing optical brightener molecules as structural units. At the chromatographic peak the eluate has been separated into different fractions. The fractions obtained were analysed with an Aminco-Fluorometer. The results are shown in Fig. 6.

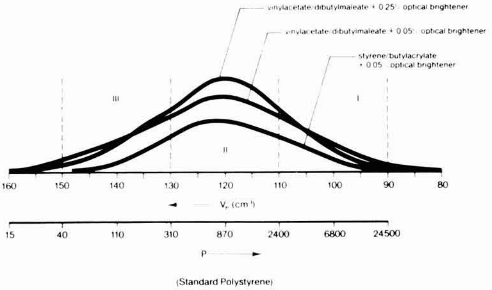


Fig. 5. Gel permeation chromatograms of optically brightened copolymers

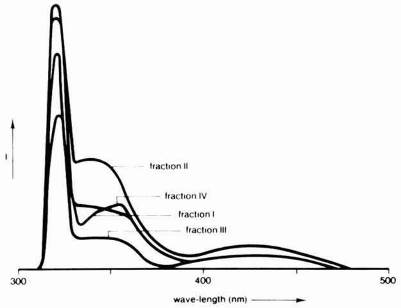


Fig. 6. Fluorescence spectra of optically brightened copolymer fractions

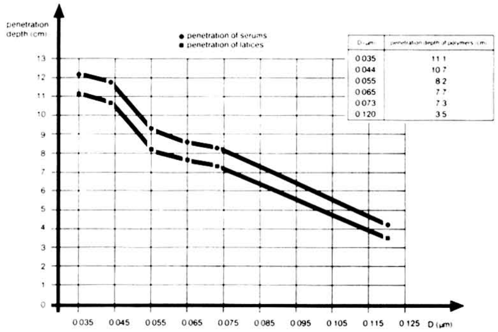
As shown in Fig. 6, all fractions of polymers contain optical brightener. The intensities of the fluorescent light correspond, as is seen from the superficial measurement of the fractions of the chromatogram, to the concentrations of the eluates.

That means that none of the optically brightened copolymer-latices contained any physically included optical brightener molecules, and that it is impossible to extract vinylsulfonpyrazoline in appreciable amounts with organic solvents. In other words, all parts of impregnated porous substrates which show a characteristic fluorescence of the optical brightener under UV-radiation contain polymeric material.

Penetration experiments with acrylic emulsions with very fine particle size

The penetration of the new acrylic emulsions was measured in various absorbing substrates, concentrating on the behaviour on mineral products, such as the pretreatment of concrete, masonry, plaster- and lime stucco before coating with emulsion-paints. From model experiments with gypsum bars it was found that the penetration of the novel acrylic emulsions for a given composition of the latex depends solely on the particle size of the copolymer-latices.

The results are shown in Fig. 7, in which the particle size *D* is plotted along the abscissa and the ordinate gives the penetration depth of the polymer particles and of the serum in centimeters.



D (μm)	penetration depth of polymers (cm)
0 035	11 1
0 044	10 7
0 055	8 2
0 065	7 7
0 073	7 3
0 120	3 5

Fig. 7. Penetration depth of very fine latices in gypsum bars

The experimental method used was ascending chromatography. An additional dependence of the penetration depth on the molecular weight (K-value of Fikentscher) of the polymer latices could not be established. Thus, for the application of the new acrylic emulsions there is the possibility of manipulating the penetration solely by varying the particle size. Extending the penetration properties of the new emulsions towards a maximum, however, should not be done because the concentration of polymeric material per unit of volume would decrease in such a way that solidification of the substrate would be incomplete.

Later the new acrylic emulsions with very fine particle sizes were used on such kinds of porous substrates, as are commonly used as construction materials: The penetration of the new emulsion on lime-sandstone, plaster-plates, mortar-bars etc. were tested.

So by testing the penetration of the new copolymer emulsions containing optical brightener on lime-sandstone, it was found that emulsions with a total solids (TS) of 30 and 40 per cent build up a closed film on the surface with filling of the uneven parts of the surface (Fig. 8).

The optically brightened molecules show a blue fluorescence under UV-light and the red tinged dispersion serum has a yellowish character due to filtration. Under normal conditions a penetration depth for the serum of about 5–6 mm was usually found.

After dilution of the new emulsions with very fine particle sizes on a TS of 20 per cent the penetration of the latices rises to 2–3 mm and the copolymer closes a small crack, which could not be observed during the treatment of the lime-sandstone (Fig. 9).

The penetration behaviour of an emulsion with a TS of 10 per cent in lime sandstone is shown in Fig. 10.

For comparison copolymers were synthesised in organic solutions on the basis of vinyl acetate/dibutyl maleate with optical brightener. Solutions of these copolymers in ester or aromatic solvents were applied on lime-sandstone. The

Fig. 8. Latex film of a new acrylic emulsion (TS 40%) containing optical brightener on lime-sandstone

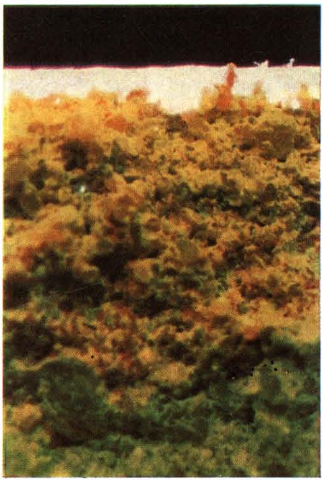
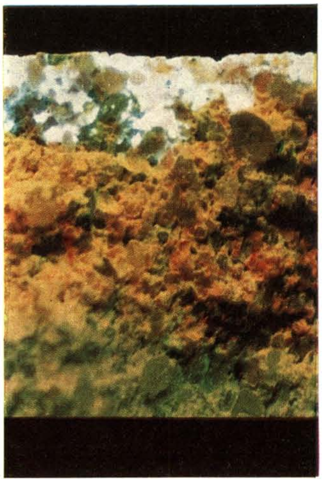


Fig. 9. Copolymer containing optical brightener in lime-sandstone (using a 20% emulsion)

Fig. 10. Copolymer containing optical brightener in lime-sandstone (using a 10% emulsion)



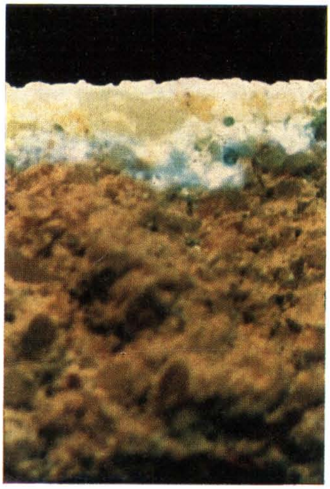


Fig. 11. Conventional primer containing optical brightener in lime-sandstone (using a 12% solution)

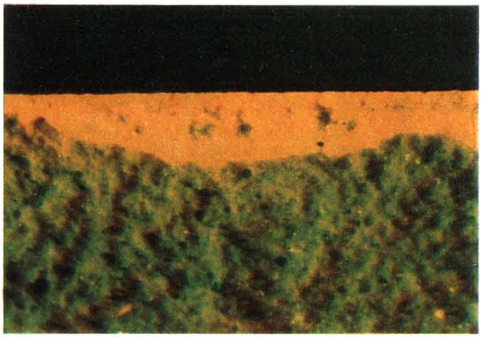


Fig. 12. Copolymer containing optical brightener in plaster (using a 17% emulsion)

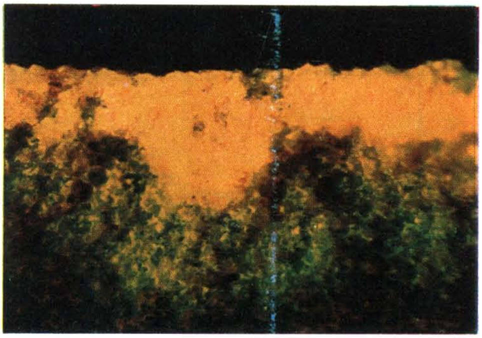


Fig. 13. Penetration behaviour of an optically brightened emulsion (TS 17%) into mortar

Fig. 15. Penetration into pine wood (detail photo)

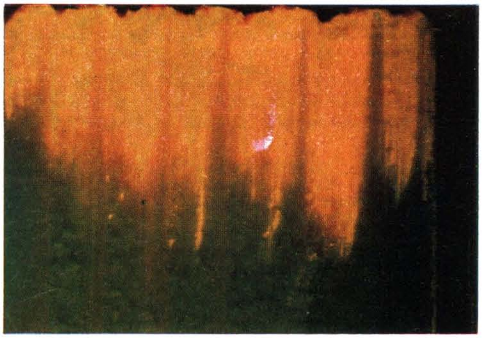


Fig. 14. Penetration depth of acrylic emulsions with very fine particle sizes containing optical brightener in pine wood

penetration behaviour of this conventional primer is shown in Fig. 11.

For completeness the penetration of acrylic emulsions with very fine particle sizes is demonstrated on various other porous substrates:

Fig. 12 shows the penetration of the new acrylic emulsion with very fine particle sizes (TS 17 per cent) into a commercial plaster plate.

Fig. 13 shows the penetration of the same emulsion into a mortar bar.

Later the behaviour of acrylic emulsions with very fine latices were tested on wood, especially on pine-wood sheets.

Fig. 14 shows the penetration of an acrylic emulsion with very fine particle size containing optical brightener into a pine-wood panel and Fig. 15 shows in detail the dependence of the penetration on the density of the substrate (pine-wood).

Conclusion

The results can be summarised as follows: aqueous acrylic emulsions with very fine particle sizes ($D < 0.05\ \mu m$) have been successfully used for priming and impregnating absorptive substrates before painting. The application properties of these new emulsions meet requirements which hitherto could be fulfilled only with polymer solutions.

There is a specific advantage in the new acrylic emulsions in their ability to replace all kinds of solvent-containing polymeric systems commonly used for priming and impregnating.

[Received 22 February 1977

Discussion at Eastbourne Conference

PROF. W. FUNKE commented that to achieve the small particle sizes a large amount of emulsifier was necessary and he asked what effects this large amount of emulsifier had on the properties of the paint film.

DR MONDT said that the major effect of the emulsifier was to cause slight foaming on application, but that this was controlled easily by the use of a suitable defoamer. He said that this eliminated all the problems in this respect and there were no problems with over-painting.

MR D. J. R. MASSY asked what was the appearance of the emulsions, commenting that with most emulsions of this type there was often a slight fluorescence or a reddish tinge, depending on the particle size. He also asked if, in common with other systems, the viscosity in relation to the solids content was high if the additional quantities of emulsifier affected the water sensitivity of the film.

DR MONDT said that the emulsions were not perfectly clear but were definitely transparent with a slight brownish tinge. The water sensitivity of the emulsion gave no particular problems and the viscosity was low in the range of 10–50 mPa.

MR I. D. LEWIS said that he thought it was commonly accepted that such systems not only had to penetrate powdery surfaces but also to bind them to a certain extent. He asked if it had been found that the particle size was the only factor operating and also if Dr Mondt had examined the effect of functional co-monomers on the ability of the system not only to penetrate but to bind loose powdery surfaces.

DR MONDT said that they had not examined this. They had only made fine particle size copolymer emulsions using styrene or acrylic systems and not any containing functional groups, such as OH, but they had found that in practice they gave very good results on powdery surfaces.

DR L. VALENTINE asked what depths of penetration into the heart wood and the sap wood of pine was obtained and whether this had been tested on other types of timber.

DR MONDT said that in the research laboratory they had only used pine wood and that in his illustrations the penetration into the soft wood was about 2mm and into the winter wood less than 0·5mm

PROF. W. Funke asked if it was possible that any residual optical brightener was not copolymerised and was contained in the liquid phase and so penetrated into the wood.

DR MONDT replied that this was not possible and they had conducted gel permeation chromatography without extracting any optical brightener by organic solvents. He said that all the optical brightener was contained within the polymer chain.

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The paint industry in a situation of diminishing availability of raw materials*

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Summary

There seems little doubt that the problems associated with the supply of chemical raw materials will intensify as the end of this century approaches. There are three main causes of the difficulties that will arise. They are treated separately in this paper, but to some extent are interdependent. They are economic pressure, the depletion of some finite resources and the effects of new legislation.

L'industrie de peintures devant la disponibilité de matières premières en voie de déclin

Résumé

Il semble quasi certain que les problèmes en ce qui concerne l'approvisionnement des matières premières des industries chimiques deviendront plus intenses vers la fin du siècle. Il y a trois causes pour les difficultés qui se présentront. Dans cet exposé on les considère separément, mais jusqu'a un certain point elles sont interdépendantes. Ce sont les influences économiques, la déplétion de certaines ressources dont les réserves sont bornées, et les effets de la nouvelle législation.

Die Lackindustrie in einer Situation wachsender Rohstoffverknappung

Zussammenfassung:

Es scheint kein Zweifel darüber zu bestehen, dass sich die mit der Verfügbarkeit von chemischen Rohstoffen verbundenen Probleme um so fühlbarer machen werden, je mehr sich das Ende dieses Jahrhunderts nähert. Für die kommenden Schwierigkeiten gibt es drei Gründe. Sie werden in dieser Abhandlung getrennt behandelt, sind aber bis zu einem gewissen Grade interdependent. Es handelt sich um wirtschaftlichen Druck, Erschöpfung einer Anzahl von begrenzten Quellen und die Auswirkung neuer Gesetze.

Economic considerations

These are not the main concern of this paper, but are of such importance that they must be mentioned, if only briefly. It would appear that the current inflationary trend will persist for some time, although the actual rate of inflation may vary and be difficult to predict. Inflationary pressure must result in higher prices for raw materials and this may be particularly evident in those which are obtained from the formerly underdeveloped countries. Countries which have gained their political and economic freedom will seek to demand what they consider to be the economic price for their exports, if only to finance their own development. This is exemplified by the recurring demand for increased prices for crude oil. As these countries develop and their standard of living improves they will compete increasingly for raw materials, not only derived from within their own boundaries, but for those coming from other countries. This increased demand must be reflected in higher costs even if the supply of raw materials is maintained at its present level.

There is evidence, however, which suggests that the availability of some chemical resources will decrease. The decrease in rate of supply will almost certainly manifest itself in an increase in cost, which will be in excess of that brought about by the political and economic pressures.

Reduced accessibility of some chemical resources

Refs. 1-4

Although the economic aspects of the supply of raw materials cannot be disregarded, it is the examination of the reasons for the decreasing availability of some chemicals with which this paper is primarily concerned and, in particular, with their likely repercussions in the paint industry.

It is suggested that there are two main causes for the progressive shortage of some chemicals. The first is the depletion of readily available stocks of some resources and the other is the possible effect of existing and proposed legislation, particularly in the fields of Health and Safety at Work, and the Control of the Environment.

Resources may be classified in two groups: infinite and finite. The infinite resources are those which are perpetuated by reproduction or photosynthesis, that is, those of animal and vegetable nature. Finite resources are the minerals and the fossil fuels. The classification is not nearly as definite as the terms "finite" and "infinite" suggest. Some minerals are present in such abundant and accessible quantities that they will be available as raw materials for many centuries; whereas some stocks of animal and vegetable products are being used up at a rate in excess of that of their reproduction. Nevertheless, in general it is the vegetable and animal products which will continue to exist, and it is the limited stocks of minerals which will eventually be exhausted.

Before the industrial revolution, the materials used in crafts and the manufacturing processes that existed were largely derived from animal or vegetable products. Since the middle of the last century, we have become increasingly dependent on mineral sources for our raw materials, and fossil fuels have replaced wood as our source of energy. When, in this country, the oil era commenced with the host of chemical raw materials derived from it, our reliance on finite resources became almost complete. Oil-based synthetics replaced a large part of the wool and cotton textiles used for clothing, furnishings, carpets *etc*. To a large extent the huge plastics industry, whose products found their way into every part of our lives, houses, transport, clothing, containers, even as replacements in our bodies, is dependent on oil. Paint which may always have used some minerals as pigments was originally largely vegetable in origin with linseed oil and natural resins as media and turpentine as solvent. Present day paint components are almost entirely derived from mineral or fossil fuel sources.

Warnings have been issued for some time and are becoming more insistent that these resources on which industry and indeed our standard and mode of life depend, are limited,

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*Paper presented at the Association's Biennial Conference held at the Grand Hotel, Eastbourne, Sussex from 16-19 June 1977 and at some time the stocks available to us will be exhausted. The facts that there are so many factors which could influence the rate of usage of these resources, and that improved technology may render accessible stocks previously considered not so, has not deterred forecasts being made of the life expectancy of the more important minerals and fuels. Table 1 represents one of many and is derived from suggestions made by Corbett, Bainbridge, Barbour and Tawn at recent conferences[1,2,3,4].

Table 1

Time of depletion of presently known sources of raw materials

Material	Year of depletion
Lead	1985
Mercury	1985
Copper	1995
Chromium	2065
Iron	2045
Cobalt	2015
Aluminium	2005
Molybdenum	1995
Tin	1985
Titanium	Well over 100 years' supply
Oil	Various estimates between 2050-2100
Coal	Several centuries supply

The term "depletion date" appearing in this table requires definition. The earth contains a store of all minerals sufficient to last for many centuries even at our present accelerating rate of consumption, but unfortunately only a small fraction is in locations suitable for mining. Most of these locations are believed to be known and the depletion dates quoted relate to the viability of mining from these known sites. It cannot take into consideration the effects of the discovery of new sites nor of possible improved mining techniques. For example, at one time it would not have been considered possible to extract, economically, oil from the North Sea.

The possibility for the discovery of reserves of lead still exists, which could significantly postpone the depletion date appearing in Table 1.

The future rate of usage is difficult to predict. All that is known is the present rate of use and the current rate of industrial growth. Thus, the date of depletion of a substance as it appears in Table 1 is defined as the year in which it is considered that economically viable stocks of it are no longer accessible in locations known to exist, assuming a future consumption which allows for the current rate (1975) of industrial growth.

Unfortunately, the rate of industrial growth and hence the rate of consumption of raw materials is affected by many factors. World depression can reduce the industrial growth rate, but an acceleration in the development of the emerging countries can increase it. The whole pattern of consumption may be influenced by world war, fashion, new technology, and restrictive legislation.

In some fields, increased recycling and recovery of materials may extend the life expectancy of a resource. At the moment, industry is discouraged for economic reasons from participating fully in recovery processes, and will only do so when the cost of freshly mined material rises to that of recovered material. Paint is not a good product from which to recover usable components. When applied, the solvent is lost by evaporation and the solid components are in the form of a thin film spread over a wide area. Even unused paint does not at the moment provide opportunity for recovering components other than the solvents, whereas, for example, in another industry, batteries, 60 per cent of the lead used is recoverable. It is anticipated that the recovery rate from batteries, old church roofs, *etc*, will grow significantly and that as a result there will be a further postponement of the depletion date of viable lead reserves.

It is likely that there will be some anticipation of depletion dates, which in the first place will take the form of increased prices, brought about by increased mining costs and scarcity. It may be that in many cases economic forces will be allowed to operate unchecked and that some materials may become unprofitable to use. In other cases, perhaps with oil, there may be some legal intervention to direct diminishing supplies to what is considered priority uses. One of the consequences could be that oil would be reserved as chemical feedstock and not used as fuel with a resultant prolongation of the life expectancy of petrochemicals. It has been suggested[4] that, by the turn of the century, electricity from nuclear sources may supply the majority of our fuel needs.

The prediction with respect to the life expectancy of mineable coal is probably even more speculative than some of the others. It is certain that the life of coal is much longer than that of the other fossil fuels and that as a result, some return to coal as a source of raw material and as fuel may occur as oil and gas become depleted. This again could mean that the lives of these latter fuels would be extended, and once more there is an implication that the data appearing in Table 1 are likely to be inaccurate. Even so, a consideration of this information is useful as it emphasises the fact that the majority of our resources are finite, and indicates where first their depletion is likely to occur.

Impact of depletion on the paint industry

There are three main components of paint: the pigment, the medium and the solvent. Tables 2, 3 and 4 indicate the present and most usual source of the)raw material used in their manufacture and the possible alternative sources. These tables

Table 2

Life expectancy of main present and possible alternative sources of pigments and extenders used in paint products

Pigments	Inorganic		Organic		
	Ti, Zn, Ba, Fe	Cu, Hg, Sn, Pb	Azo	Polynuclear	Phthalocyanine
Present source	Finite ores	Finite ores	Oil	Oil	Oil
Life expectancy	Over 50 years	Less than 25 years	50-70 years	50-70 years	Less than 25 years (Cu)
Alternative source	None	None	Coal tar	Coal tar	None, unless alternative to Cu
Life expectancy	—	—	Over 100 years	Over 100 years	Over 100 years if alternative to Cu

Table 3
Life expectancy of main present and possible alternative sources of media used in paint products

Resin	Alkyd	Phenolic	Vinyl, acrylic	Chlorinated rubber	Natural	Epoxy	Poly-urethane
Source	Oil	Coal	Oil	Vegetable	Vegetable	Oil	Oil
Life expectancy	70 years	Over 100 years	70 years	Indefinite	Indefinite	70 years	70 years
Alternative source	Coal	—	Vegetable	—	—	Vegetable	Coal
Life expectancy	Over 100 years	—	Indefinite	—	—	Indefinite	Over 100 years

Table 4
Life expectancy of main present and possible alternative sources of solvent used in paint products

Solvent	Aliphatic Hydrocarbon	Aromatic Hydrocarbon	Alcohol	Ketone	Esters	Keto ethers and esters
Source	Oil	Oil	Oil	Oil	Oil	Ether oil
Life expectancy	70 years	70 years	70 years	70 years	70 years	70 years
Alternative source	Coal/ vegetable	Coal	Vegetable	Vegetable	Vegetable	Vegetable
Life expectancy	Over 100 years/ indefinite	Over 100 years	Indefinite	Indefinite	Indefinite	Indefinite

indicate clearly the almost complete dependence of the paint industry on raw material derived from finite sources. The fact that these sources are indeed finite will first be appreciated when, probably by the end of this century, difficulty is experienced in obtaining supplies of pigments and compounds of certain metals, such as lead, tin, mercury and copper at reasonable cost. Thereafter, the gradual depletion of the world's oil reserves will have its impact on every component of paint.

Courses of action to meet the problems of resource depletion

Derivation of the present raw materials from other sources

The tables indicate that, apart from the case of some metallic pigments, alternative basic materials can be used to make practically all the raw materials used for paint from those at present in use. Solvents, now almost completely oil-dependent, were first made from other starting materials. The availability of cheap oil in abundant quantities plus the increased demand, such as that created by World War II, suggested a switch to oil as the basic resource. Alcohols, which originally were all made by the fermentation of vegetable products, present an example. The change to processes involving oil-derived olefines could be reversed when oil becomes scarce. Again, certain aromatic chemicals, which at the moment are oil-derived, could be obtained from coal tar.

Although the possibility exists for the majority of those raw materials at present derived from oil to be obtained from other sources, it may be neither economic nor sensible to do so. The chemical processes could be cumbersome, complicated, involving many steps, and thus expensive. If the new original source is vegetable, supply difficulties could arise, occasioned by harvest uncertainties, leading to wide differences in costs from year to year.

There is also the problem that no alternative basic source can replace the mineral ores from which the inorganic pigments are obtained. Recovered metals theoretically could extend the life of these for some time, but the costs may prohibit any serious exploitation of paint waste as a source of metals. A course other than the slavish adherence to the currently used raw materials just by seeking other sources is indicated, except in those cases where it has demonstrated so to do is simple and sensible.

Alternative raw materials used in conventional paints

The raw materials which are currently used to make paint were often suggested by the availability of a cheap source such as oil. Turpentine from vegetable sources was replaced by the cheaper white spirit from oil. Similarly, some alkyds were based on pentacrythritol because it was readily available from oil. When cheap oil is no longer available, the hydroxy component of alkyds may have to be obtained from some substance obtained readily from coal tar or from vegetable fermentation using, perhaps, sugar as the vegetable source.

A more profound change will be caused by the reduced availability of some inorganic pigments. It may be difficult to match them in every respect, but recourse to the organic pigments based on coal tar seems the only alternative. Since the data suggest that some mineral ores, important sources of paint pigments, may be depleted soon, the introduction of alternatives may be a matter of urgency.

As the depletion of finite resources proceeds there exists the opportunity for a more radical approach to the problems it creates, and the use of novel components in paint should be considered. Sugar and other vegetable products may be investigated anew as fermentation material, not only to produce currently used solvents, but as the source of new solvents, which this process may yield relatively easily. Perhaps media present the most likely subject for novelty. The Paint Research Association are already investigating resins derived from sugar and polymers based on silicon. Tawn[4] believes that nitrogenous polymers or those obtained from hydantoin or ferrocene may be expected to play a part in paint formulations before the end of the century.

Novel formulation

As further extension to the more radical approach to paint composition, opportunity could be taken to consider the necessity for paint to consist of the three basic components: pigment, medium and organic solvent. Of these, it is with the solvent that a change could most readily be effected, and two examples readily come to mind. The replacement of oil-based organic solvents by water has been proceeding for some time, and the emergence of emulsion paints has been the most important developments in decorative paints. As the supply of organic solvents becomes more difficult it seems reasonable to expect that advances will be made to reduce their organic solvent content and increase the scope of their applicability.

It can be expected that there will be extensions in the use of solventless or near solventless paint. At present the so-called powder coating preparations are largely based on epoxy resins and are used for painting articles or components under factory conditions with heat curing. There may be scope for the application of these preparations to be enlarged, using resins derived from sources other than oil.

Means of protection and decoration other than by paint

Paint has two main functions: to protect surfaces and to give aesthetic pleasure by means of colour. A large proportion of the production is concerned with repainting in homes, places of business, schools and hospitals. Should the problems associated with raw material supply affect the availability, quality, or price of paint, recourse may be taken to using construction materials which do not need the protection of a surface coat and in which more enduring protection and colour are included in their manufacture in the factory. These products exist already, but are largely made from plastics derived from finite resources, and are thus beset by the same problems that affect paints. Research to obtain new plastics not based on oil may produce alternatives to surface coating materials that could challenge the very existence of paint as a means of colouring and protection.

It is only within the last fifty years that oil has become so important as a source of raw materials. The plastics industry did not really emerge until after World War II, so that it is probable that within the next twenty years, some basic discovery may be made which will change the situation dramatically and render unnecessary the four courses of action suggested. However, such a discovery cannot be assumed in our calculations and in the meantime we must be prepared to take these courses of action.

The investigations to overcome the problems created by depletion of some of our resources will require the expenditure of a large amount of effort and money on research. Unless there is sufficient courage shown by seeking solutions from novel components or products, and thereby retaining the possibility of an advance in techniques and products, this effort will only be spent in maintaining the status quo.

New legislation and the supply of raw materials

Ref. 5

The new legislation to be considered is recent or proposed new laws in the fields of industrial safety and health, and environmental protection.

Whereas Man may have some control, albeit, rather small, over the economic factors affecting the supply of raw materials and has even less control over the problems associated with the depletion of finite resources, he should have complete control over the legislative processes which affect the supply of chemicals for industry. After all, the restrictions on the supply of raw materials are self-imposed with the aim of receiving the benefits of a healthier shop floor and a less polluted environment.

In a paper presented at the Golden Jubilee Conference of the Paint Research Association[5], it was observed that the industrial revolution took place with a minimum of regard to the consequences of exposure of work people to chemicals, and of their impact on the environment. Examples abound of the ill effects of uncontrolled exposure from the classical "hatters' shakes" resulting from the mercury process for felt hats, and miners' silicosis, to the more recent lung cancer from asbestos, and asthma in those sensitised to isocyanates. The gradual pollution of water courses from domestic and industrial waste, and the fouling of the atmosphere by emissions from factory and domestic chimneys were allowed to proceed almost unchecked. Some attempts were made to control the worst abuses, but it took spectacular events such as the 1953 London fog, the Torry Canyon disaster, and the tragedy of Minnemata Bay to alert the world to the hazards of chemicals to the environment. The reaction was predictable. There has followed a spate of restrictive legislation in all the major countries and directives from the EEC which will limit the freedom of use of resources and raw materials derived from them. These limitations will be in addition to those occasioned by depletion of the finite resources.

The new controls, both in being or proposed, will affect the supply of chemicals already in use, and will slow down the introduction of new materials. These two aspects are treated separately with special reference to limitations of materials used in the manufacture of paint.

Legislative control of currently used chemicals

Attention is limited in this paper to the impact of British legislation or proposals or disclosures which can lead to British legislation. Similar, though not necessarily identical, legislation exists or is being enacted in all major industrial countries. One of the benefits of our being in the European Community is that its directives tend to ensure that the controls on the member states are applied with the same order of severity.

The stimuli for legislation do not necessarily come from within this country. Concern has been world-wide, resulting in investigations being carried out in many countires, and particularly in the United States. Experience and research, irrespective of source, indicates whether control either mandatory or voluntary, should be exercised here to safeguard our workers or our environment.

Health and safety at work

Refs. 6, 7, 8, 9–12, 13

The main Acts of Parliament, government reports, EEC Directives and proposals with which we are concerned, are listed in Appendix I to this paper. Of these, it is the Health and Safety at Work Act 1974 (HASAWA)[6] which has so far made the biggest impact. This, being an enabling act, under which specific regulations can be made, is couched in general terms and its provisions are subject to some latitude in their interpretation. It could be argued that the Act does not prohibit the use of any raw material. The most relevant clause is found in Section 6 (4a) which states:

> "It shall be the duty of any person who manufactures, imports or supplies any substance for use at work, to ensure, *so far as is reasonably practicable*, that the substance is safe without risks to health *when properly used . . .*"

It contains the italicised escape phrases which suggest that the aim is not to prohibit use, but to prescribe conditions of operation which will ensure safe handling and which would be considered reasonable to introduce. The conditions of use which may limit the freedom of operation may eventually be controlled in a specific regulation (Section 15) or a Code of Practice (Section 16).

The conditions of use required may be such as to make some raw materials too expensive to use in the opinion of some manufacturers, but it may be that the sections in the Act, 6(4b and c) and 6(5) concerned with tests for safety and the provision of information which may well be considered the most likely to limit raw materials.

That there are health hazards associated with paint manufacture and its application has been realised for some time, and the necessary precautions for safe operation, such as the use of adequate ventilation to avoid the narcotic properties of solvents, or the protective measures to ensure that there is no risk of lead poisoning, are part of standard practice. The increased activity in toxicological investigation of industrial chemicals, particularly that resulting from the anti-cancer campaign begun by the Nixon Administration in the USA, has revealed that many such chemicals have health risks, which require a level of precaution much higher than that applied hitherto.

All three component classes of paint, pigment, medium and solvent, are affected. Threshold Limit Values (TLVs), the standard for safe concentrations of chemicals in factory atmospheres, are being continually reviewed and, in the majority of cases, lowered. Those for the aliphatic hydrocarbons, hexane, heptane, octane and white spirit, were all reduced in 1975.[7] Some chlorinated solvents, such as trichloroethylene, are suspected of being carcinogenic, and work is in progress to test this suspicion.[8]

With respect to limitation of media, isocyanates used in the preparation of polyurethanes are known respiratory sensitisers and limits of free isocyanates in polymer have been set.[9] It is likely that when sprayed, droplets of the polymer themselves are capable of producing these toxic effects, necessitating much more stringent control in this operation. The limitation of free vinyl chloride monomer in vinyl polymer because of its carcinogenic action[10] and the need to scrutinise all processes in which formaldehyde and hydrochloric acid occur together, to see whether toxic concentrations of the carcinogenic bischloromethyl ether are formed,[11] are further examples of the restrictions in materials for media.

Reference has already been made to the lead pigment hazard, but recently it has been suggested that the lung cancer hazard, for some time associated with the mining of chromate ores, may also be a feature of the individual chromates used in paint, such as lead, zinc, and barium. At the moment, the safe working level recommended by the US Occupational Safety and Health Authority is 0.1 mg/m^3. The National Institute for Occupational Safety and Health recommend (as CrO_3) a new limit of 0.001 mg/m^3, which can only be met by using airline breathing apparatus.

Suggestions have been made to paintmakers[12] of how they should react to evidence that important raw materials possess more serious toxic properties, particularly of a carcinogenic nature, than had hitherto been believed. After fulfilling their obligations with respect to alerting all customers and employees, manufacturers are advised to work in association with the Health and Safety Executive and manufacturers in other industries similarly affected to prepare a fresh method of safe working. Only when this is considered economically unacceptable should the raw material, product or process be abandoned.

Caution should be exercised in switching from one raw material, either because it becomes in short supply or because it is suspected of presenting a hazard, to an obvious alternative, which may have a more serious but as yet undiscovered hazard. The possible consequences are illustrated by the outbreak of peripheral neuropathy in an American factory resulting merely from the use of methyl *n*-butyl ketone in place of methyl isobutyl ketone.[13]

The legislation for the labelling of chemical substances, solvents, paints and pesticides which will result from the relevant EEC Directives may induce manufacturers to change their raw materials, with the aim of producing products that may escape hazard labelling.

Control of environmental pollution etc.

Refs. 14, 15, 16, 17, 18

The legislators have been giving attention to the ill effects of chemicals outside the factory, in the general environment, as well as to the health risks of occupation. In this country, the local authorities have had powers to intervene to prevent hazard and nuisance from omissions and effluents from factories in a relatively *ad hoc* manner, whereas the EEC would prefer specified limits for pollutants in the air or in water. Local authorities have been given powers and responsibilities to deal with industrial waste,[14] and in this there is support in the related EEC proposed Directive.[15]

The legislative activity and the investigations responsible for it have had repercussions within the paint industry, and in particular with respect to the acceptability of raw materials The continued use of a raw material which gives rise to expensive waste disposal problems should be the subject of some consideration.

The discovery of the damage to the health of young children from ingesting old lead paint film has resulted in statutory limits of lead in materials used for painting processes in and around houses being set in the United States, which correspond to a virtual ban on the use of lead in paints for these processes. The reaction in this country was for voluntary limits which in essence exclude lead pigments from such paints, but not lead driers. More recently, however, a study in Pittsburgh has shown that, whilst there was a correlation between the blood lead levels of children and the age of the houses in which they lived, there was no correlation with the lead content of the paints used in those houses.[16]

The disclosure that all mercury-containing waste in aqueous media can be converted biologically to methyl mercury, found responsible for the Minnemata Bay and other disasters, was a factor in the suggestion from the Department of the Environment (DoE)[17] that there should be a permitted list agreed between government and industry of the pesticides to be used in paint. The object is that mercury should be phased out as a biocide in both marine and emulsion paint, and DDT should be excluded from marine paint because of its accumulation in some wild life.

Resulting from complaints of the offence from fumes emitted from paint shops, particularly those in which automobile finishes are stoved, PRA, partly sponsored by the government, have carried out research which demonstrates that decomposition products from the media used are largely responsible for the offence. One remedy is to replace the medium in the offending paint, although some alleviation can be obtained by scrubbing the emissions.[18]

Thus, the preoccupation with occupational health risks and environmental pollution and the ensuing legislation will have a limiting effect on the acceptability of some raw materials.

Legislative influences on the supply of new chemicals

Refs. 19, 20, 21

The decreasing availability of many traditional raw materials for whatever reason must stimulate research to provide new alternative chemicals. There are, however, legislative impediments which could interfere with the effectiveness of such research. At one time, new chemicals were offered for sale concerning which there was little or no toxicological information. Later, the wealthier and more responsible chemical companies would submit their new products increasingly to toxicological examination in animals, either in laboratories of their own, in universities or in contract laboratories. The tests varied in degree from perfunctory dosing for acute oral toxicity to sufficient exposure by inhalation to suggest a TLV. At present, it is a fair guess that there is a majority of industrial chemicals on which no specific toxicological tests have been performed, and a large number on which the evidence is insufficient to be sure of the occupational risks. If it is considered that an opinion on the carcinogenic and teratogenic potential is desirable, then there are few compounds, indeed, for which full information exists.

The precursor of the HASAWA, the Report of the Robens Committee,[19] in Sections 322-30, calls for the notifications of all new chemicals and for manufacturers to be obliged by law to test all new chemicals adequately for safety. The testing requirement features in Section 6 (4(b and c)) and 6(5) of HASAWA and it is expected that the notification recommended will be implemented within the framework of the Act. Support for this step is to be seen in the EEC proposals which appear in Modification 6 of the Directive for the Labelling of Dangerous Substances.[20] These proposals go much further than those of the Robens' Report. They require the submission, not only of prescribed toxicological data relating to factory hazards of a new material, but of detailed information relevant to its possible impact on the environment, such as its effects on birds, fish, biochemical effects on water courses, methods of waste disposal, extent and method of distribution, type of markets, volume of sales. They would allow for an authorised body to prescribe the conditions of use after considering the evidence submitted. Thus, notification become synonymous with authorisation.

If these proposals are accepted as law, a new chemical will have to undergo a programme of toxicological and environmental investigation that could delay its appearance on the market for years, and add considerably to the cost of its development. The bill for testing all the emerging chemicals for safety at work will be very large, and when the backlog of work to be done on chemicals currently in use is added to it, it becomes enormous. In any case laboratory facilities world-wide would prove to be grossly inadequate.

An idea of the order of cost can be obtained by studying charges made by contract laboratories for various standard tests. The cost of carrying out the minimum programme suggested in the EEC proposals in the cheapest laboratory would be around £3000 per substance. The moment it is suggested that long-term tests to assess chronic toxicological, carcinogenic, mutagenic and taretogenic potential are necessary, the cost leaps to over £100 000 per substance.

Authorities are not ready to forego direct evidence in favour of behaviour suggested by that of chemical related material. Unfortunately, the knowledge of the relation between chemical structure and biological behaviour is limited. It is known, for example, that the liver will be the target organ for the toxic effects of organic materials containing substituted chlorine, that halogenated carbonyl substances will cause lachrymation, that oil dissolving solvents will cause dermatitis through defatting, that the replacement of other halogens in organic compounds by fluorine tends to reduce the toxic effect, and at one time it was believed that the classes of substances to which carcinogens were confined were known. However, the discovery of carcinogens not in these classes and the number of exceptions that have arisen to the suggested relationships between structure and toxicity has reduced confidence in the ability to forecast biological properties of any chemical with certainty. This situation will continue until more is known of the mechanism of chemical toxic action, and chemical carcinogenesis.

Attempts have been made and are proceeding to avoid the reliance on tests involving the dosing ot large numbers of animals for long periods, and thus reduce the time and cost of the experiments. Several tests have emerged of which the most commonly used is the Ames' Test.[21] This fundamentally is a test for mutagenicity in bacteria which can be used as a quick assessment of carcinogenicity. The acceptance of this test is not general, as it is known not to be 100 per cent efficient, but at least it may be used as a screen to establish priorities in chemicals for testing in animals. With the increased activity in this field, however, an acceptable quick test for carcinogenicity may be expected soon.

To all these requirements for toxicological experiments to determine the occupational health hazards of a new chemical, the EEC proposals impose on industry the burden of providing the authorities with data on the likely environmental consequences of marketing it. The supposition is made that the manufacturer can forecast the outlets for his product in advance of its promotion, for he will need to involve his potential customers in providing the required data, because they will contribute to the environmental consequences of its use.

The costs of the toxicological and environmental investigations may usually be borne by the chemical manufacturer and passed on to the customer in the cost of the product. On occasions when the advantages to the customer of the product may be large in proportion to the volume of sale from the supplier, the customer may be expected either to assist in the financing of the experiments or even to be responsible for carrying them out. Some products could be abandoned if the manufacturer considered that he could not see any returns in sales to match the high development costs resulting from the experimental requirements to show that it was safe in factory use and in the environment.

If applied without perspective, the EEC proposals could create such an impediment to research and the steady flow of new materials, that real damage could be caused to the chemical industry, all the industries which depend on it and ultimately to our standard of life. A solution will have to be found to the problem of achieving the maximum safety at work and conservation of the environment which would allow progress in research, yielding products for the betterment of our lives. The negotiations to achieve the compromise may be long and tedious.

At most, industry can expect some relaxation of the requirements of the EEC but not their removal. Bearing in mind the unfortunate occurrences on record, some control of chemical raw materials is overdue. The legislation requiring these controls must affect the continuance of some materials available to industry, including the paint industry and reduce the availability of new products and increase their cost.

Conclusion

As the end of this century approaches, the supply of raw materials to the paint trade can be expected to become increasingly difficult and costly. There are three main causes. The first is an economic one, and relates to the awakening of the previously underdeveloped country to the value of their resources, and as they develop, to their increased participation in the products resulting from their use. The second is the acceleration of the depletion of the finite resources which may result in some traditional paint components being so costly that their use is precluded before the year AD 2000, and the third is legislation in the fields of Health and Safety at Work and Control of the Environment which may require the withdrawal of some materials used in paint, and slow down the flow and increase the cost of new materials.

Demands on the industry's research facilities will increase to provide solutions to the problems created by the legislation, and the gradual depletion of some resources. The deployment of them merely to produce the same raw materials from more lasting resources, or even the same products from new raw materials, will only maintain the status quo. It is suggested that the opportunity should be taken to take a more fundamental view of the paint process and products for it, that research to prepare improved products which add protection and colour should continue, but that the freedom of the researcher be reduced to allow for the constraints introduced by legislation, and reduced availability of raw materials.

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Appendix I

(a) Health and Safety at Work *etc* Act 1974.

(b) Council Directive of 21 May 1973 amending Directive of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances. *Official Journal of the European Communities*, Vol 16, No L 167, 25 June 1973.

(c) Proposal for a Council Directive (6th Modification) of Directive of 27 June 1967 relating to the classification, packaging and labelling of dangerous substances. *Official Journal of the European Communities*, 5 Nov 1976.

(d) Council Directive of 4 June 1973 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous preparations (solvents). *Official Journal of the European Communities*, Vol 16 No L 189, 11 July 1973.

(e) Proposal for a Council Directive on the approximation of laws, regulations, and administrative provisions relating to the classification, packaging and labelling of dangerous preparations (paints, varnishes, adhesives and similar products). *Official Journal of the European Communities*, No C 166, 23 July 1975 page 2.

(f) Safety and Health at Work. Report of the Committee 1970-72, Chairman Lord Robens, HMSO, London.

(g) Deposit of Poisonous Waste Act 1972.

(h) Control of Pollution Act 1974.

(i) "The Non-Agricultural Uses of Pesticides in Great Britain" Pollution Paper 3. A Report by the Central Unit on Environmental Pollution, Department of the Environment. HMSO London.

(j) Proposal for a Council Directive on toxic and dangerous wastes, as submitted to the Council by the Commission Com (76) 385 final, 22 July 1976.

(k) "Environment Programme" 1977-1981. Bulletin of the European Communities, Supplement 6/76.

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Discussion at Eastbourne Conference

Dr F. M. Smith commented that President Carter had recently been emphasising the possible crisis situation occurring in ten years' time with respect to oil supplies, but suggested that the legislation recently proposed appeared to do nothing to help. Dr Smith said that they were continually hearing of the coming shortages of materials and about the effects of legislation, and he pointed out that this was a subject which, rather than being discussed one day and forgotten the next, was becoming of increasing importance as time went on.

Mr A. T. S. Rudram pointed out that Mr Howe had for many years served on the Health and Safety (now known

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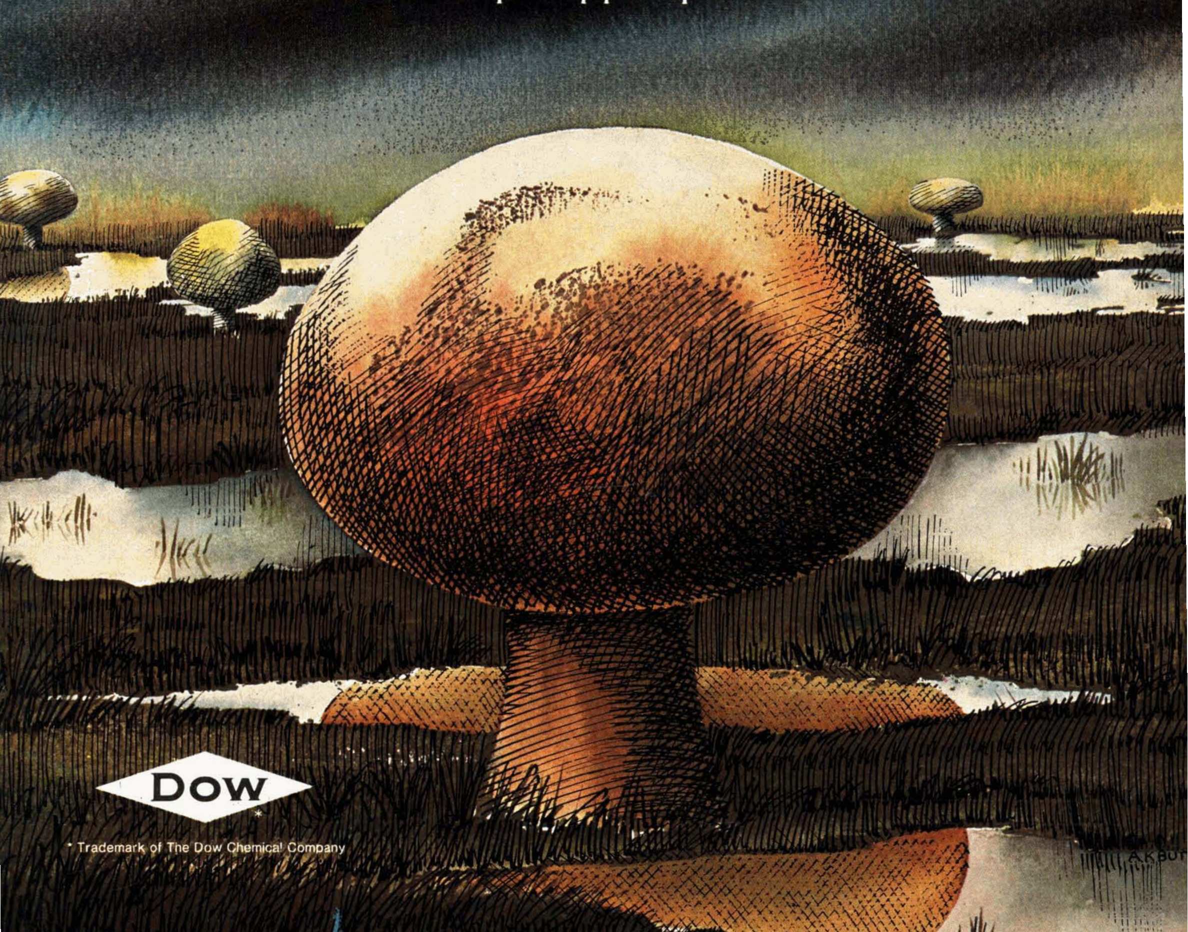

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as the Hazardous Chemicals) Committee of the Paintmakers Association. He said that he is an acknowledged expert on not only what the world is doing regarding toxicology, but of how the legislation concerning it affects the surface coatings industry. Mr Rudram asked if Mr N. Estrada could give a brief outline of the current situation in America, pointing out that although Britain was now subject to the EEC legislation, a great deal of notice was still taken of American developments.

MR HOWE said that he would not comment at length on the American situation but would leave that to some of the Americans present to deal with. He mentioned a consultative document in which the American authorities were attempting to obtain international acceptance of their proposals for implementing their Toxic Substances Control Act (TOSCA) because, of course, America imports chemicals and obviously this situation has to be looked into. He said that the European authorities, even those who were in favour of a strict notification system, were rather worried about the American proposals, because there was neither the manpower nor the material resources necessary fully to enforce it. He suggested that some sort of compromise had to be achieved, not only in Europe, but also in America to resolve the situation. He believed that, particularly in the US, there had been some over-reaction to environmental hazards as a result of emotional and political pressures. The adoption of 0·06 per cent as the permissible level of lead in household paints was an example. Mr Howe was amongst those who believed that the need to control the level of lead in such paints had been demonstrated, but considered the level of 0·06 per cent to be too low and neither necessary nor practicable.

MR N. ESTRADA said that he agreed with Mr Howe's opinions that in the American situation there was some over-emphasis of certain environmental requirements. He said that these were dealt with on a day-to-day basis and he pointed out that where legislation had been brought in to deal with a situation, the control moved over to administrators and in many cases they have pushed the matter to the limit rather than using reasonable judgment. This had made it difficult and often forced firms to stand very close to the edge of the law. He thought this was the failing of the American system because it left no room for compromise. He said that whilst he was no expert on the overall impact of the legislation in America, he could understand the feeling of the environmentalists; he was concerned with preserving the environment and was for this reason worried about the type of legislation produced. He gave as an illustration the situation in California which related closely to the paint industry where they had developed the Rule 66 philosophy which had been understood and accepted throughout the world. This philosophy recognised the relative reactivity of solvents involved in organic compounds and advised a strategy whereby the use of the more reactive types was limited, so that the less reactive types could still be used. This policy had worked out quite well but was not uniformly adopted throughout the US. However, in the last year this State had come up with a new policy of considering that all solvents are basically bad, in that if they were irradiated to a large extent by ultraviolet light they will become reactive. As a result of this it will probably become necessary to reduce all solvent emissions into the atmosphere, and the current proposal is that no coating in quantities above 0·5 litre should be allowed which contains more than a 30 per cent volatile content. This applies to architectural coatings which are defined as any coating applied to a stationary surface, thus including traffic paints etc. Industry has objected fairly strongly to many aspects of this proposed legislation, but it is certain that some such legislation will be adopted. As a result of the industries' objections, Mr Estrada said that some exceptions to the new legislation would be allowed for a limited period, such as the traffic paints, and this was a method of forcing the technological developments in this area. He commented that between 65 per cent and 70 per cent of most architectural coatings were based on water or low solvent composition at the present time due to technological developments rather than being forced by regulations.

MR J. TOOKE-KIRBY said he was pleased to see that Mr Howe had taken the conservative estimate of 70 years for the oil supply despite the multitude of figures being circulated. He pointed out that the Institute of Petroleum had recently said that figures could possibly be changed by the introduction of the new water flooding techniques for reopening fields previously considered to be worked out. The Russians have pioneered this system, and in fields where the quality of the crude oil was high this method was particularly worth while and the oil obtained was suitable for chemical use. He pointed out that against this many companies were now pulling out of new developments in the North Sea because of the local environment. Referring to the mineral/vegetable equation given in the paper, Mr Tooke-Kirby asked whether in the author's opinion the technical personnel and the technology were available to develop raw materials based on vegetable substances as replacements for mineral sources.

MR HOWE said that research into this field would, as always, be controlled by the economic factors operative at the time and that when the situation became pressing enough then obviously the necessary resources and the personnel would be put into research to find ways of developing vegetable resources and alternative sources of raw materials. He pointed out, though, that the great danger was that such development work would be left too late so that there might be a gap in between the onset of the depletion of mineral resources and their replacement by vegetable sources.

Commenting on the cost of proposals for the testing of new substances DR L. VALENTINE pointed out that £30 000, whilst it seemed a lot for many companies, especially a small one, was in reality only a very small proportion of the total turnover of each firm. He estimated that the cost of testing all new materials in this way would probably be under 0·1 per cent of the total turnover of the industry, and that this might be a small sum in relation to possible costs from damages caused by untested substances.

MR HOWE agreed that these points had to be taken into consideration.

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The structure of layers of adsorbed polymers at pigment/solution interfaces and their influence on the dispersion stability of pigments in paints*

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Summary

The paper reports experimental results of polymer adsorption studies both from aqueous and non-polar organic solutions on to pigment and filler surfaces. In aqueous systems, the pigment surfaces can become electrically charged, and examples are given of the effect of charge sign and charge density on the adsorption of electrically neutral and electrically charged polymers. Dispersions of silica, alumina, titanium dioxide, and ferric oxide in organic polyester solutions can be subjected to quantitative investigation by infrared spectroscopy. From frequency shifts of characteristic absorption bands and from the adsorbed amounts, the fractions of specifically contact-making functional groups in adsorbed polyester layers can be determined. These data allow the deduction of the formation of adsorption loop structures of polyesters on the surfaces. The sizes of loops protruding into the solutions are dependent on solid surface structure as well as the composition of the adsorbate. Sedimentation studies indicate a correlation of the loop sizes with the dispersion stability of powders in polyester solutions.

Keywords

Raw materials for coatings
binders (resins, etc)
polyester resin
prime pigments and dyes
iron oxide
titanium dioxide
extender pigments
silica
alumina

Processes and methods primarily associated with analysis, measurement or testing
adsorption
infrared spectroscopy
manufacturing or synthesis
flocculation
dispersion
storage, protection or preservation
sedimentation

La structure des couches de polymères adsorbés à l'interface pigment/solution et leur influence sur la stabilité de dispersion des pigments incorporés en peintures

Résumé

L'exposé rend compte des résultats fournis par des études expérimentales sur l'adsorption des polymêres à partir des solutions, aqueuses ou organiques et non polaires, sur la surface des pigments ou des matières de charge. Dans le cas des systêmes aqueux, la surface du pigment peut prendre une charge électrique, et les auteurs donnent les exemples de l'influence qu'exerce exercent la polarité et la densité de la charge sur l'adsorption de polymères neutres ou ayant une charge électrique. Les dispersions de silice, d'alumine, de dioxyde de titane et d'oxyde ferrique en solutions de polyesters en solvants organiques peuvent être soumises à une investigation quantitative au moyen de la spectroscopie à l'infra rouge. En raison à la fois des déplacements des bandes d'absorption caractéristiques et des teneurs en matière adsorbée, on peut déterminer les fractions des groupements fonctionnels qui se trouvent dans les couches de polyesters adsorbées, et dont le rôle spécifique est d'assurer la mise en contact des deux phases. A partir de ces données on peut déduire la formation sur les surfaces des structures bouclées composees de polyesters adsorbées. La grandeur des bandes qui font saillie dans la solution dépend de la structure de la surface du solide bien que la composition de l'adsorbat. Les études de sedimentation mettent en évidence un rapport entre la grandeur des bandes et la stabilité des dispersions de poudres en solutions de polyesters.

Die Struktur von adsorbieren Polymer Schichten an der Pigment Lösung Grenzfläche und ihr Einfluss auf die Stabilität von Pigment Dispersione in Farben

Zusammenfassung

Die Arbeit berichtet über experimentelle Ergebnisse von Studien der Polymerenadsorption sowohl aus wässrigen als auch aus unpolaren, organischen Lösungen an die Oberflächen von Pigmenten und Füllstoffen. In wässrigen Systemen können die Pigmentoberflächen elektrisch geladen vorliegen, und es werden Beispiele aufgeführt, wie das Ladungsvorzeichen und die Ladungsdichte die Adsorption elektroneutraler und elektrisch geladener Polymerer beeinflußt. Dispersionen von Siliciumdioxid, Aluminiumoxid, Titandioxid und Eisenoxid in organischen Polyesterlösungen können quantitativen Untersuchungen durch Infrarotspektroskopie unterworfen werden. Aus Frequenzverschiebungen charakteristischer Absorptionsbanden und aus den adsorbierten Mengen können die Bruchteile spezifisch an die Oberflächen gebundener funktioneller Gruppen in den adsorbierten Polyesterschichten bestimmt werden. Aus diesen Daten kann abgeleitet werden, daß sich Adsorptionsschlaufenstrukturen der Polyester and den Oberflächen ausbilden. Die Größe der in die Lösungen ragenden Schlaufen hängt von der Struktur der Feststoffoberflächen und vom Aufbau der Adsorptive ab. Sedimentationsuntersuchungen zeigen einen Zusammenhang zwischen der Schlaufengröße und der Dispersionsstabilität der Feststoffpulver in den Polyesterlösungen auf.

Introduction and object of work

Refs. 1-20

One of the most crucial stages in the production of pigmented paints and printing inks is the process of dispersion of pigment or filler powders in polymeric binder solutions. During this process, the external and internal surface of a pigment powder is wetted by the solvent, and particle agglomerates are mechanically broken up to yield separated primary particles and aggregates which are well distributed throughout the medium. The extent to which this can be achieved is of utmost technical importance as the optical properties of the final products depend upon it. However, difficulties always arise in maintaining this in most colloidal states, since it is thermodynamically unstable. The dispersions have a high tendency to flocculate due to the

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*Paper presented at the Association's Biennial Conference held at the Grand Hotel, Eastbourne, Sussex from 16–19 June 1977 van der Waals attractions between particles which are greatest when they collide.

Pigment or filler dispersions can be stabilised against flocculation by two different mechanisms, but the effect of each is the generation of strong repulsive forces between particles which overcome the van der Waals attractions and allow particles to re-separate after collisions.

In dispersions of powders in strongly polar organic solvents or in water, the particles often carry a surface charge of the same sign and are surrounded by clouds of oppositely charged counter ions thus forming electric double layers around the particle surfaces and maintaining an overall neutrality of charge (Fig. 1A, upper part). Upon the approach of two particles, the diffuse parts of their double layers begin to interpenetrate and this gives rise to strong coulombic repulsive forces which increase in magnitude as the distance between the particles decreases. The result of van der Waals attractions and coulombic repulsions is a repulsive potential maximum in the particle interaction curve (Fig. 1A, lower part), and the mathematical assessment of the resulting forces as a function of interparticle distance and other parameters is the object of the DLVO theory[1,2].

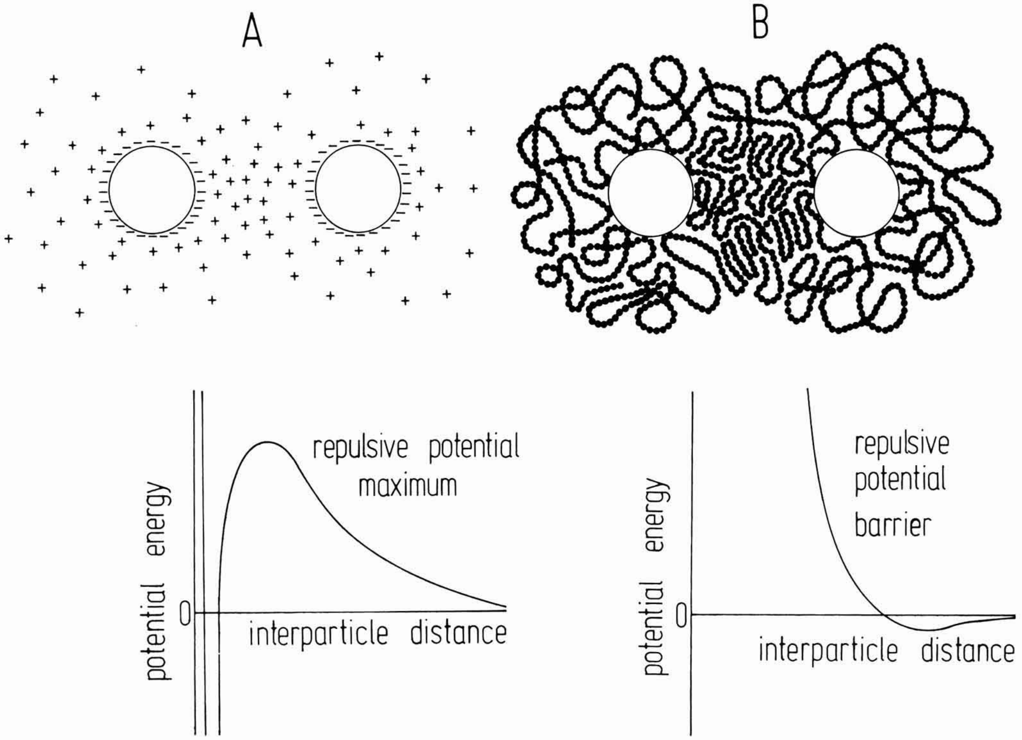

Figure 1 Simplified models describing electrostatic or steric repulsion effects between two approaching spherical particles surrounded by electric double layers (*A*) or by protective polymer adsorption layers (*B*).

The second repulsive mechanism is the more important in the field of paints and printing inks. Its origins are entropic and osmotic interactions between polymer adsorption layers which surround separated particles in a dispersion. These layers form protective steric barriers around the particles and their deformation or interpenetration upon particle collision results in strong repulsions[3-6]. A typical yet simplified model (Fig. 1B) describes the overall repulsive effect. Such polymer adsorption layers are almost always present on pigment or filler surfaces when the solids have been dispersed in polymeric binder solutions. Obviously, the steric repulsion effect must depend on the structure of these adsorption layers and on structural features such as:

(a) the thickness of the adsorbed layer

(b) the polymer segment density within a layer and its distribution function normal and perpendicular to the pigment surface

(c) the mobility of non-adsorbed segments which should be different when they form protruding loops, tails or coils

(d) the distribution of polar groups of a polymer within the adsorption layer

Consequently, a detailed knowledge of the structure of polymer adsorbed layers appears to be essential in order to provide a full understanding of their stabilising effects.

In polar organic or aqueous systems adsorbed polymer layers can alter significantly the electrostatic repulsion between particles when their presence affects the charge density on the particle surfaces or the double layer structure. Examples of such charge alteration effects will be given in a later section.

Perhaps even more important are the layer structures of adsorbed polymers on pigment and filler surfaces in non-polar dispersions, since electrostatic repulsions are inoperative in such systems and the dispersion stability depends entirely on the steric stabilisation effect.

The structure of adsorbed polymer layers cannot be determined directly, but many theoretical and indirect experimental approaches to this important problem have been undertaken in the past[7-12]. The often controversial results are discussed in terms of four limiting models of the conformation of long chain molecules attached to a surface (Fig. 2). These models clearly indicate how the conformation of the polymers at interfaces should greatly affect the thickness and stabilising effectiveness of a steric barrier and should be measurable by determination of the amount of polymer adsorbed and of the fraction of polymer functional groups in direct contact with the substrate.

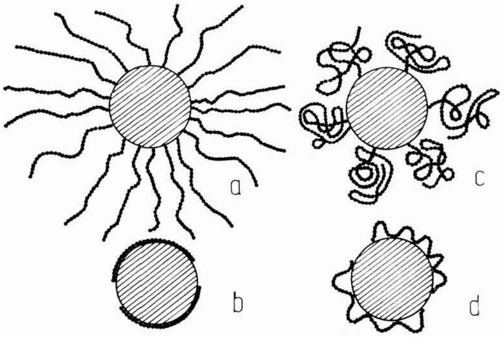

Figure 2 Limiting conformations of polymer molecules on a pigment surface adsorbed as bristles (*a*), in a flat arrangement (*b*), as coils (*c*), or loop-like (*d*).

Recently, an infrared spectroscopic method which was first applied to polymer adsorption studies by Fontana and Thomas[13] has gained some popularity. It allows determinations of the fractions of polyester carbonyl groups which upon polyester adsorption make direct contact with the surfaces of finely dispersed silica particles. The adsorption interaction of such groups with the surfaces causes shifts of their characteristic infrared adsorption bands. This method has been adopted to study the structures of adsorbed polyester layers not only on silica[14,15] but also on alumina[16], titanium dioxide, and ferric oxide surfaces. The inorganic oxides having well characterised surfaces[17,18] are either pigments or fillers, or their surface structures closely resemble those of commercial titanium dioxide pigments which are coated with protective silica or alumina layers.

It can be demonstrated experimentally that adsorbed polyesters form loop structures on the surfaces of the four oxides. Examples will be given of how these loop structures on dispersed alumina particles affect the sedimentation rates of alumina dispersions in non-polar polyester solutions.

From the results it can be deduced that it should be possible to synthesise special copolymers which on adsorption form layer structures with optimal stabilising properties. Such investigations have been undertaken at the Research Institute for Pigments and Paints, but experimental results have also been presented in recent publications[19,20]. They will be discussed together with the authors' results.

Experimental

Composition and physical data of the substrates

The substrates were four inorganic oxides of pyrogenic origin and with pore-free surfaces. Their chemical composition, suppliers, and characteristic physical data are given in Table 1.

Table 1

Composition and physical data of the substrates

Composition	Crystal modification	Supplier and name of products	Specific surface area in m^2/g	Average particle diameter in nm	Purity in %
SiO_2	amorphous	Degussa Aerosil 200	189 ± 15	12	> 99.8
Al_2O_3	γ-Al_2O_3	Degussa Al_2O_3 C	113 ± 10	20	>97
TiO_2	87% anatase 13% rutile	Degussa pyrogenic TiO_2 P 25	54 ± 5	30	> 97
Fe_2O_3	α-Fe_2O_3 hematite	BASF Eisenrot	74 ± 7	27	> 98

Prior to the adsorption experiments the pigment and filler powders were heated for 24 hours *in vacuo* at pressures of 10^{-7} bar completely to remove adsorbed molecular water from their surfaces. The baking temperatures were 100°C for Fe_2O_3, 200°C for SiO_2 and 300°C for Al_2O_3 and TiO_2. The latter was cooled to room temperature under a dry oxygen atmosphere in order to reoxidise the surface.

Polymers, low molecular weight compounds and solvents

The linear polyesters used as adsorbates throughout this work had been synthesised in the authors' laboratory by polycondensation reactions of various glycols with different dicarboxylic acids. They had been fractionated by precipitation and the average molecular weights of the fractions had either been determined by vapour pressure osmometry or had been calculated from the results of end group determinations. Molecular weights are given in the text of the result section or in the subscripts of the figures.

Poly(oxyethylene)s (*Merck*), isobutyric acid (*Merck-Schuchardt*) and carbon tetrachloride (reagent grade, *Merck*) were used without further purification. Poly(acrylic acid) was kindly presented by Röhm GmbH. The water was double distilled under nitrogen in a quartz vessel.

Potentiometric acid/base titrations

5g portions of silica were dispersed in 200ml of 0.01 N NaCl solution in a thermostatted glass vessel under dry nitrogen. These dispersions also included the dissolved polymers under investigation. Before and after addition of known volumes of 0.1 N HCl or 0.1 N NaOH standard solutions the pH of the dispersions was measured with a glass electrode, a silver/silver chloride electrode serving as the reference. The system was calibrated by the use of NBS standard buffer solutions. Precautions were taken to avoid any experimental errors due to the suspension effect.

The difference between the actual pH change after addition of acid or base and the theoretical pH change which should be observable in the absence of the solid served as the measure to calculate the surface density of potential determining ions by means of a FORTRAN computer program. Calculations were performed on the CYBER 174 computer at the University of Stuttgart Rechenzentrum.

Polymer concentrations were determined in the supernatant solutions by measurements of refractive indices with a sensitive differential refractometer.

IR investigations

Ref. 16

The infrared spectra of dispersions of the four solids in dilute polyester solutions with carbon tetrachloride as the solvent were recorded on a Perkin-Elmer double beam grating spectrometer model 257. Remountable cells with NaCl windows were used in the measuring beam, and a variable path length Leitz cell filled with polyester solutions was mounted in the reference beam for recording the differences in the spectra. Polyester concentrations in the supernatant solutions after a complete removal of the solids by centrifuging were also determined spectroscopically. The fraction p of specifically adsorbed carbonyl groups is defined as

$$p = \frac{c_b}{c_b + c_{f,a}}$$

where c_b and $c_{f,a}$ are the concentrations of bound carbonyl groups and of free carbonyl groups which are part of adsorbed polyester molecules. p was calculated from the experimental data according to the procedure described in detail elsewhere[16].

Sedimentation experiments

After 24 hours equilibration time, with occasional shaking, 10ml portions of the alumina dispersions in dilute CCl_4 solutions of polyester 6.6 or of poly(oxyethylene) 400 were filled into 10ml glass cylinders with graduations and glass stopcocks. These samples were vigorously shaken for 10 min., after which the settling rate of the visible turbidity zone between the settling dispersion and the clear supernatant solution was checked by eye at predetermined time intervals controlled by a stopwatch. Following the completion of the settling process the clear supernatant solutions were carefully removed with a syringe for concentration determinations and their volumes determined from weight differences of the cylinders on an analytical balance. The residual dispersions of high solid concentrations served for infrared determinations of p values.

Results

Adsorption interactions of polymers with electrically charged surfaces in aqueous dispersions of silica

The silica surface becomes increasingly negatively charged when the dispersion pH is gradually increased from 4 to 10 by the additions of NaOH solutions (Fig. 3a). However, there is no tendency of the silica surface to accept positive charges when the pH of the dispersion is lowered to 2 by addition of HCl solutions. The origins of negative surface charges are dissociating surface hydroxyl groups and hydroxide ions preferentially adsorbed from solution.

Poly(oxyethylene) 20 000 has a significant suppressing effect on the surface charge density when present in the dispersions at different concentrations (Fig. 3b-e). This must be due to competitive adsorption interactions of polymer segments and charge carriers with the surface. It is of particular interest to note that this suppression invariably brings about a severe reduction of coulombic repulsive forces between the separated particles.

The increase of surface charge density with increasing pH reversely affects the amount of polymer adsorbed. Whilst the plots for electroneutral poly(oxyethylene)s 20 000 and 400 level off gradually, poly(acrylic acid) and isobutyric acid are completely desorbed at higher pH values (Fig. 4). This is not unreasonable, since the two latter compounds increasingly form anions at higher pH values and should be repelled from the negatively charged surfaces.

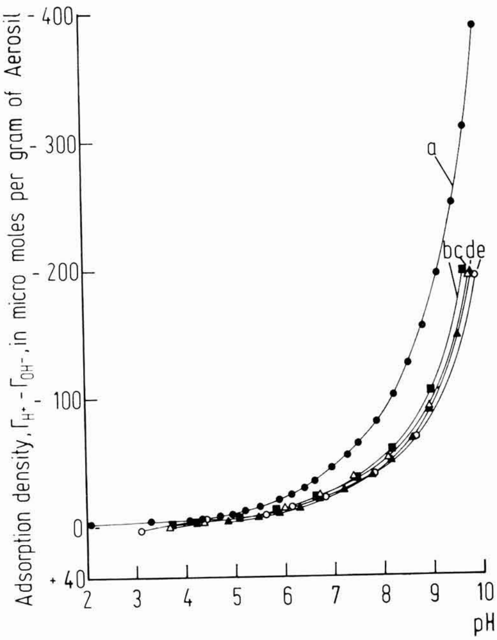

Figure 3 Adsorption densities of potential determining ions on the silica surface as a function of pH for dispersions of silica (25 g/l) in a 0.01 N NaCl solution (*a*) and in the presence of poly(oxyethylene) 20 000 at concentrations of 2.5 (*b*), 5 (*c*), 10 (*d*) and 15 (*e*) g/l.

IR investigations of polyester adsorption from solution in carbon tetrachloride on to the surfaces of dispersed silica, alumina, titanium dioxide, and ferric oxide

Polyester adsorption on silica surfaces

The sharp infrared band at 3 749cm^{-1} (Fig. 5a) due to the O—H stretching vibrations of isolated hydroxyl groups on the surface of dry, pyrogenic silica in a vacuum cell is perturbed to 3 690cm^{-1} (Fig. 5b) when the silica is dispersed in carbon tetrachloride. A further perturbation to 3 410cm^{-1} occurs in the presence of dissolved polyester 10.12 as a result of hydrogen bond formation between surface hydroxyl groups of adsorbing polyester molecules. The fraction of non-adsorbed hydroxyl groups decreases as the polyester concentration increases (Fig. 5c-e).

The hydrogen bond interaction also causes a shift of the carbonyl frequency from 1 737cm^{-1} (Fig. 5f) to 1 710cm^{-1} (Fig. 5c-e). This perturbation is almost quantitative when the polyester concentration in a sample is low (Fig. 5c), but gives rise to overlapping unperturbed and perturbed adsorption bands with two distinct maxima at higher concentrations (Fig. 5d, e). The optical density of the unperturbed carbonyl band is proportional to the concentration of non-adsorbed carbonyl groups in a sample. Its difference before and after addition of the solid to a polyester solution can be utilised to calculate the fraction p of carbonyl groups in an adsorbed polyester layer which make direct contacts with the surface.

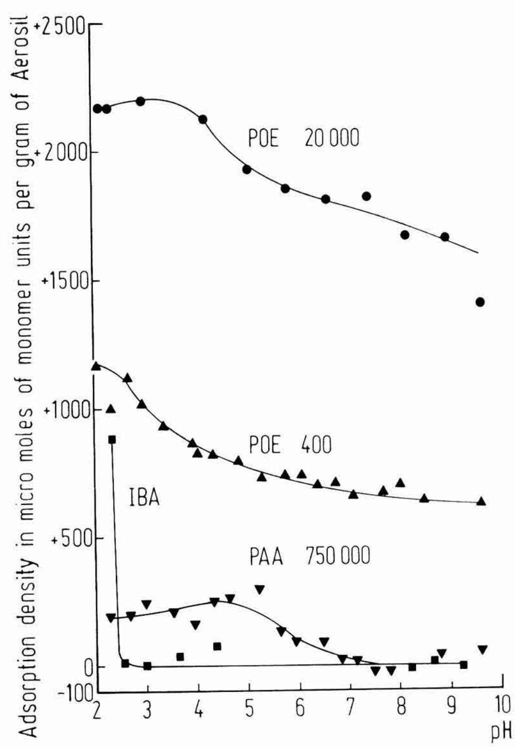

Figure 4 Adsorption densities of electroneutral and negatively charged compounds on the silica surface as a function of pH following their adsorption from aqueous 0.01 N NaCl solution at concentrations of 3 g/l (POE = poly(oxyethylene), PAA = poly(acrylic acid), IBA = isobutyric acid; numbers on plots indicate molecular weights).

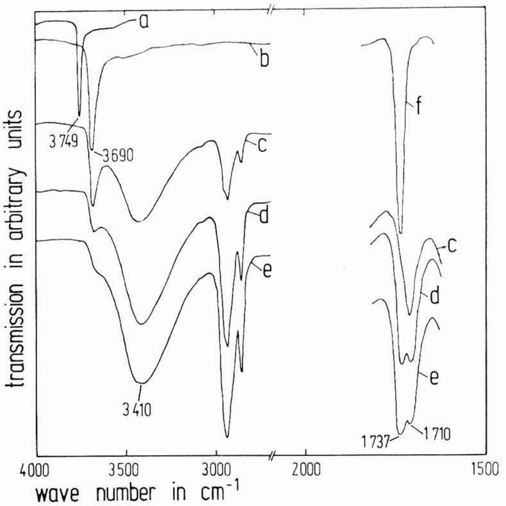

Figure 5 IR spectra of silica *in vacuo* (*a*) and of silica dispersions (50 g/l) in carbon tetrachloride (*b*) and in the presence of polyester 6.6 (MW 14 000) at concentrations of 2 (*c*), 5 (*d*) and 8 (*e*) g/l and a cell path length of 1 mm. (*f*) shows the carbonyl valence adsorption of the polyester in solution.

Such optical density determinations have to be made indirectly by application of a spectroscopic difference method described in the experimental part. Direct determinations are mostly impossible because of poor spectral resolution in the carbonyl region.

The adsorption data are indicated as p values along the adsorption isotherms of polyester 10.12 and polyester 6.6 in Fig. 6. Both isotherms display initial sharp rises of the adsorbed amounts at extremely low equilibrium concentrations of polyesters in solution, which eventually tend to change into saturation curves. The fractions p of adsorbed carbonyl groups are very high ($p = 0.9$) at low surface coverage, but gradually decrease as the amount adsorbed of both polyesters increases.

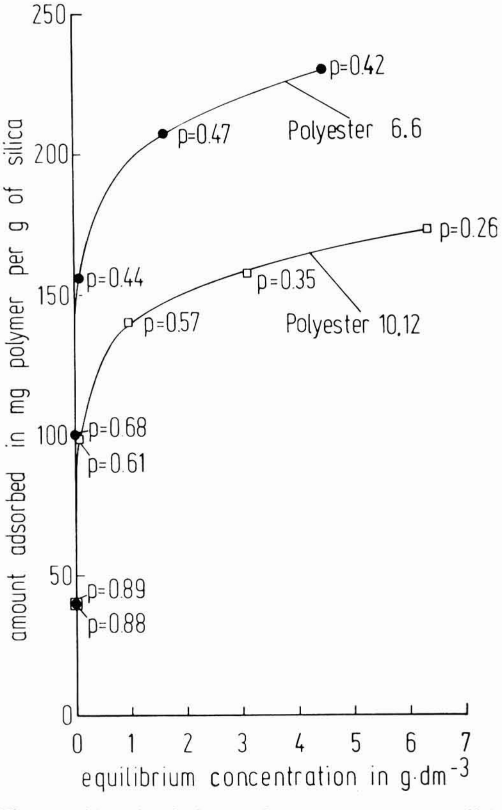

Figure 6 Adsorption isotherms of polyester 6.6 (MW 14 000) and polyester 10.12 (MW 14 000) at the silica/carbon tetrachloride interface. Numbers on curves indicate fractions p of specifically adsorbed carbonyl groups.

These results are indicative of the formation of adsorption loop structures of polyesters on silica surfaces, with high fractions of carbonyl groups attached to the surfaces and sequences mostly of methylene groups and ester oxygen atoms protruding loop-like into the adjacent solution (Fig. 7). The average lengths of these adsorption loops increase with increasing surface coverage, but the difference in monomer structure of the two polyesters has no significant effect on the overall result.

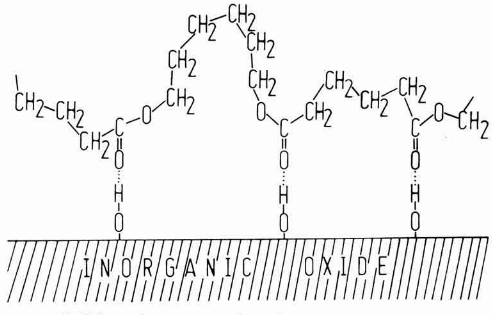

Figure 7 **Schematic representation of an adsorbed loop structure of polyester 6.6 attached to an inorganic oxide surface by hydrogen bond formation between carbonyl groups and surface hydroxyl groups.**

It can be postulated from the initial saturation behaviour of the isotherms that even at the highest surface coverages all adsorbed polyester molecules have, at least, a few direct contacts with the surface. The adsorption layer may thus be regarded as a cloudy monolayer incorporating a high proportion of solvent molecules.

Polyester adsorption on alumina surfaces

Ref. 21

Polyesters are adsorbed on to alumina surfaces by specific interactions of their carbonyl groups with surface hydroxyl groups (aluminol groups) forming hydrogen bonds. There are specific features, however, which make the adsorption process different from that on silica surfaces, provided that the alumina surfaces have been pretreated at elevated temperatures in a vacuum and do not contain any adsorbed water molecules.

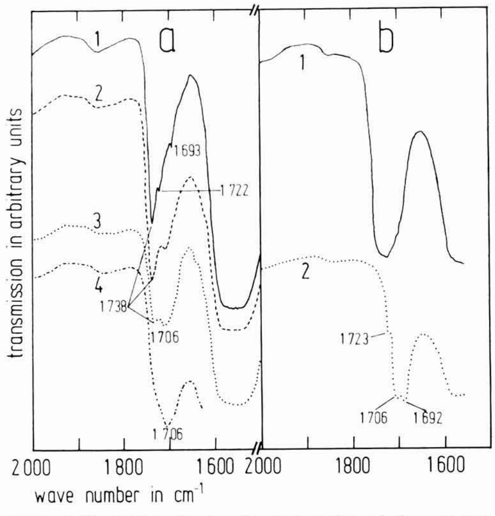

Figure 8 **IR spectra showing the perturbation of the carbonyl band due to carbonyl interactions of adsorbed polyester 6.6 with alumina surfaces carrying three different types of surface hydroxyl groups; (*a*) spectra taken after 1.5 hours (1), 67 hours (2), 168 hours (3), and 912 hours (4) following the adsorption of 28 mg PE/g Al_2O_3; (*b*) carbonyl spectra before (1) and after (2) compensation of the unperturbed carbonyl band to zero absorption.**

Fig. 8a shows infrared spectra of alumina dispersions in solutions of a polyester 6.6 registered after various adsorption times. The first spectrum taken after 1.5 hours displays the maximum of the unperturbed carbonyl band at 1 738cm^{-1} and two maxima of perturbed bands at 1 722 and 1 693cm^{-1}. After longer adsorption times a further maximum becomes visible at 1 706 cm^{-1}, its absorption increasing with time. After very long times the unperturbed band has almost disappeared, and merely a structureless shoulder remains (spectrum 4).

Due to the strong overlap of the single bands, a fine structure in the carbonyl spectrum is often invisible after long adsoption times or after adsorption of high amounts of polyester. Fig. 8b demonstrates how this fine structure reappears in a difference spectrum after compensation of the unperturbed carbonyl band to zero absorption, displaying maxima at 1 723, 1 706, and 1 692cm^{-1}.

This qualitative result can be interpreted in terms of hydrogen bond formation between polyester carbonyl groups and at least three types of surface hydroxyl groups, which have different electronic environments. Peri's computer model of a partially dehydroxylated alumina surface describes six hydroxyl species[21]. They are either arranged as pairs or multiplets when the hydroxyl concentration on the surface is high, or they are isolated from each other and have zero or as many as four adjacent oxide neighbours at much lower hydroxyl concentrations. The abundance of certain types of hydroxyl groups depends largely on the mode of temperature pretreatment. Baking temperatures of 200–300°C mainly yield hydroxyl pairs, isolated hydroxyl groups with four or three oxide neighbours, and isolated groups without any such neighbours. It is tentatively assumed that these three species are responsible for the perturbation of the carbonyl band to three distinct wavelengths.

The heterogeneity of the energy of adsorption sites on the alumina surface has a striking effect on the attainment of equilibrium structures in adsorbed polyester layers, when the distances between neighbouring carbonyl groups are relatively short. This is demonstrated in Fig. 9 where for different adsorbed amounts of polyester 6.6 the fraction of attached carbonyl groups is plotted versus the time of adsorption on a logarithmic scale.

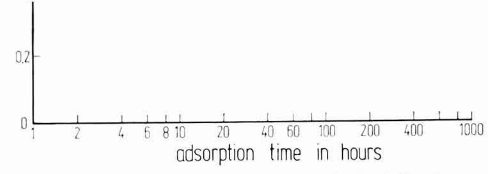

Figure 9 **Fraction *p* of carbonyl groups of adsorbed polyester 6.6 (MW 14 000) which are specifically attached to alumina surfaces, as a function of adsorbdd amount and time of adsorption; (*a*) 18.8 mg/g; (*b*) 37.5 mg/g, (*c*) 75 mg/g; (*d*) 99.6 mg/g; (*e*) 123 mg/g; (*f*) 75 mg/g; but in the presence of 150 mg co-adsorbed water per g Al_2O_3; baking temperature of alumina 300° C.**

After one hour all curves have about the same initial value of $p \approx 0.4$. For smaller adsorbed amounts p gradually increases with time (Fig. 9a-c), whereas it remains almost constant at higher surface concentrations (Fig 9d, e). Almost instantaneously a large fraction of polyester carbonyl groups is attached to a fully hydroxylated alumina surface which also contains approximately one monolayer of hydrogen bonded water (Fig. 9f).

As depicted in Fig. 10, there is a pronounced influence of molecular weight of polyesters on the orientation process, but polyester 10.12 shows a more rapid orientation at the beginning of the adsorption process. The amounts of polyester adsorbed remain constant over long periods of time following a relatively fast equilibration of the mass transfer process from the solution to the surface phase.

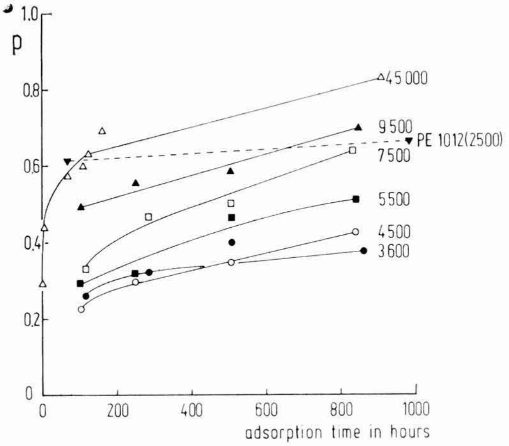

Figure 10 **Fraction p of carbonyl groups specifically attached to alumina surfaces as a function of polyester structure, molecular weight, and adsorption time for polyesters 6.6 (solid lines) and for polyester 10.12 (dashed line).**

Polyester adsorption on titanium dioxide surfaces

Ref. 17

Polyester carbonyl interactions with a temperature pretreated titanium dioxide (anatase) surface are much stronger in comparison with those on silica or alumina surfaces. This can be seen in Fig. 11 where the absorption bands of free and attached carbonyl groups are well separated. The titanium dioxide pretreated in a vacuum (10^{-7} bar) at 300°C and then cooled to room temperature under dry oxygen, does not contain significant concentrations of surface hydroxyl groups (Fig. 11, O—H region of the infrared spectra). Such a treatment is necessary to remove adsorbed water molecules completely which otherwise would be present on the surface in uncontrollable amounts and would obscure the adsorption results. As the surface tends to lose oxygen during the baking process, it has to be reoxidised.

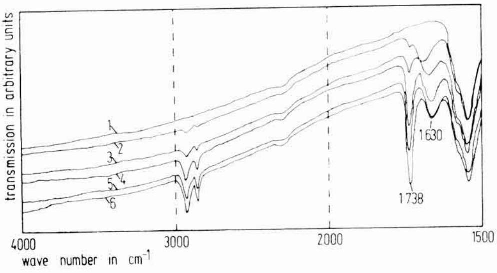

Figure 11 **IR spectra showing the perturbation of the carbonyl band due to carbonyl interactions of adsorbed polyester 10.12 (MW 2 500) with the surface of titanium dioxide. Polyester concentrations in dispersions 0 g/l (spectrum 1), 1 g/l (2), 2 g/l (3), 6 g/l (4), 8 g/l (5), 12 g/l (6). Solvent is carbon tetrachloride.**

The highly energetic sites on the surface, which cause a perturbation of the polyester carbonyl band from 1 738cm^{-1} down to 1 630cm^{-1} are Ti^{4+} ions with one of their six O^{2-} lattice coordination partners missing. These sites have a strong Lewis acidity and can form very stable coordination complexes with carbonyl groups[17].

The extremely strong adsorption interaction of polyester molecules with the titanium dioxide surface is apparently responsible for a very slow attainment of adsorption equilibria. In most of the experimental investigations the adsorbed amounts of polyesters have been found to be high at the beginning of adsorption. They did gradually decrease with time, but did not reach constant values even after several hundred hours of stirring (Fig. 12).

The fractions p of carbonyl groups specifically attached to the titanium dioxide surface could be determined from the optical densities of unperturbed carbonyl bands without the aid of difference spectroscopy. However, corrections for the loss of light intensity due to light scattering were necessary.

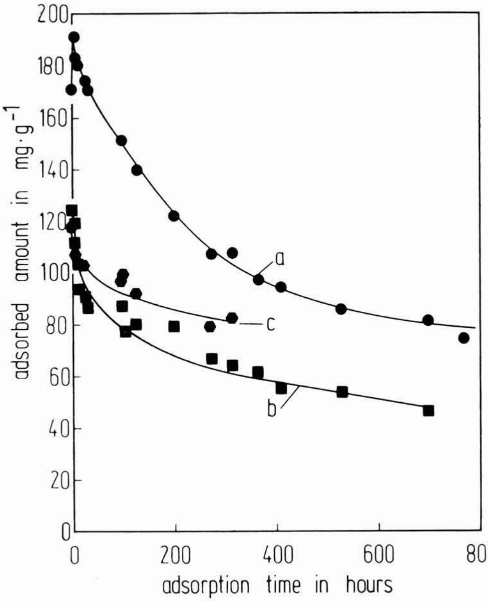

Figure 12 **Effect of adsorption time on the adsorbed amount of polyester 4.6 (MW 4 400) and polyester 10.12 (MW 2 500) adsorbed from solutions in carbon tetrachloride, and of poly(decanediol fumarate) adsorbed from trichloromethane solution on to the surface of titanium dioxide; experiments with 1 g of polymer, 5 g of solid and 200 ml of solvent.**

The *p* values of five different adsorbed polyesters 6.6 showed some severe scattering within the first several hundred hours of adsorption time. Hence, Fig. 13 includes only experimental data determined after at least 500 hours equilibration time for adsorbed polyesters having different structures and molecular weights.

The fractions of adsorbed carbonyl groups at low surface coverages are large for polyester 10.12 ($p = 0.71$), smaller for poly(decanediol fumarate) ($p = 0.51$) and smallest for five different polyesters 6.6 ($p = 0.35$–0.42). They decrease as the amounts adsorbed increase, yet the modes of decrease do not disclose any correlations with the molecular weight or with the chemical nature of the polyester end groups.

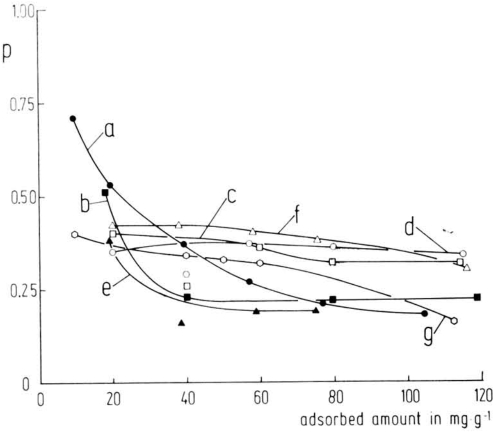

Figure 13 **Fraction *p* of carbonyl groups specifically attached to the titanium dioxide surface as a function of the adsorbed amount for polyester 10.12 (MW 2 500) (*a*), poly (decanediol fumarate) (MW 3 300) (*b*), polyester 6.6 (OH/COOH end groups, MW 2 600) (*c*), polyester 6.6 (OH/COOH end groups, MW 5 500) (*d*), polyester 6.6 (OH/COOH end groups, MW 7 500) (*e*), polyester 6.6 (OH/COOH end groups, MW 20 000) (*f*), polyester 6.6 (OH/COOCH$_3$, MW 9 500) (*g*).**

There, obviously, exists, however, a correlation between the maximum values of *p* and the maximum distances of neighbour carbonyl groups in the polyester chains. These latter distances are largest for polyester 10.12, intermediate for poly(decanediol fumarate) and smallest for the polyesters 6.6. Consequently, the statistical distances of adsorption centres on the titanium dioxide surface must be in the distance range of neighbour carbonyl groups in the chain of polyester 10.12.

There is no interference of double bonds in poly(decanediol fumarate) chains with the specific interactions of carbonyl groups with surface sites.

Polyester adsorption on ferric oxide surfaces

Ref. 18

The surface of ferric oxide undergoes severe chemical changes when treated at baking temperatures higher than 150°C. This effect has been studied by infrared spectroscopy in a heatable vacuum cell[18] and is most probably due to surface reduction. In order to avoid such alterations, ferric oxide samples for polyester adsorption experiments were mildly pretreated in a vacuum at 100°C.

Infrared spectra of ferric oxide dispersions (100g/l) in solutions of polyester 10.12 at different concentrations are given in Fig. 14a, before, and in Fig. 14b after, the compensation of the unperturbed carbonyl band to zero absorption.

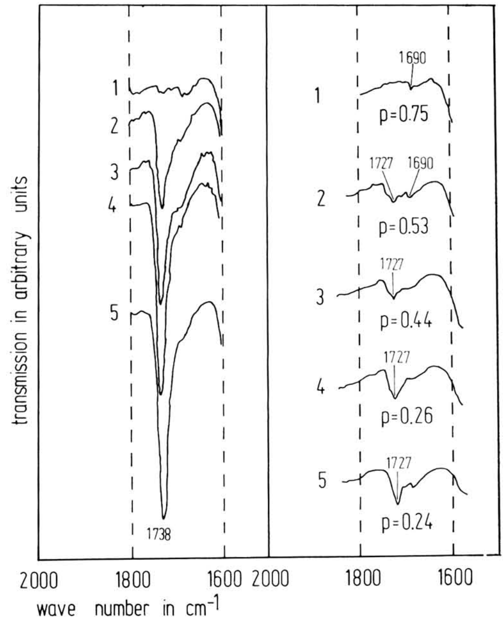

Figure 14 **IR spectra of ferric oxide dispersions (100 g/l) in CCl$_4$ solutions of polyester 10.12 (MW 2 500) before (*A*) and after (*B*) compensation of the unperturbed carbonyl band to zero absorption; concentrations 1 g/l (1), 6 g/l (2), 8 g/l (3), 12 g/l (4), 16 g/l (5).**

As reported for the other three substrates, the attachment of adsorbed polyester molecules is similarly due to specific interactions of carbonyl groups with adsorption centres at the ferric oxide surface. But the mode of interaction is distinctly different. At low surface coverage with carbonyl groups, the carbonyl band is perturbed from 1 738cm^{-1} to 1 690cm^{-1} (spectra 1 in Fig. 14a, b). Only after a complete occupation of the corresponding surface sites of highest interaction energies, a second perturbed carbonyl band becomes visible at 1 727cm^{-1} (spectra 2–5, Fig. 14b). The calculated fractions *p* of attached carbonyl groups are indicated as numbers below the spectra. Their values decrease with increasing adsorbed amounts from 0.75 to 0.24.

Infrared spectra recorded after different adsorption times did not indicate any changes of the adsorbed amounts or of the *p* values with time.

The above results may be interpreted as specific interactions of carbonyl groups with two different types of surface hydroxyl groups. In contrast to the mode of polyester adsorption on alumina surfaces with different adsorption sites, here the more energetic type of hydroxyl group is completely occupied before any carbonyl groups can interact with hydroxyl groups of the second, less electronegative type. If both types of hydroxyl groups were randomly distributed all over a polycrystalline ferric oxide surface, small molecules would first select the sites of higher energies when being adsorbed. Polyesters could hardly behave in such a way, since the specific attachment of one carbonyl group severely restricts the lateral distances of neighbouring carbonyl groups, and these neighbours would rather interact with less energetic sites than not at all. The observed phenomenon of a selective attachment of carbonyl groups could be easily understood, however, if it were assumed that at least two different crystal faces existed on the hematite surface, each of those carrying only one type of hydroxyl groups. This tentative interpretation then explains the high fraction $p = 0.75$ of carbonyl groups exclusively attached to the more electronegative hydroxyl species. The surface concentration of these groups is fairly low, and sufficiently short distances between them (allowing for high *p* values) are only imaginable for a dense local arrangement of this type of sites.

Structure effects of polyester adsorption layers on alumina surfaces on the sedimentation rate of alumina dispersions in non-polar polyester solutions

As it is possible to deduce the structures of polyester adsorption layers on silica, alumina, ferric oxide, and titanium dioxide surfaces from the amounts adsorbed and from the fractions of specifically adsorbed functional groups, structural effects on the dispersion stability can be studied to some detail. Pyrogenic alumina was chosen as substrate for the combined layer structure and sedimentation studies. The alumina samples had undergone a mild temperature pretreatment at 100°C in air before they were dispersed in carbon tetrachloride or in dilute polyester solutions. The surfaces of such alumina samples were not completely free from adsorbed water in molecular form, but this mode of pretreatment was essential for the attainment of adsorption equilibria after 24 hours dispersion with occasional shaking.

The accuracy of infrared structure studies increases with increasing solid concentration, but high solid concentrations inevitably disturb the sedimentation processes by heavy particle interactions. As a compromise, alumina concentrations of 8g/l were chosen.

Sedimentation plots of alumina dispersions in solutions of polyester 6.6 (approximately equal amounts of hydroxyl and carboxyl end groups, molecular weight 9 500) at different equilibrium concentrations (and consequently with different amounts of polyester adsorbed on the alumina surface) are given in Fig. 15.

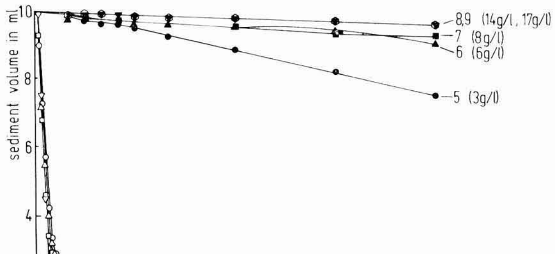

Figure 15 **Sedimentation rates of alumina dispersions in solutions of polyester 6.6 (MW 9 500) and in the pure solvent CCl_4.**

Whilst the dispersions of plots 1–4 settle quite rapidly, the rate of settling of dispersion 5 abruptly decreases by at least two orders of magnitude in the most sensitive initial part of the plot. Still smaller is the rate of settling of dispersions 6–9. Even these dispersions are not indefinitely stable, but have settled completely after two days. Thus it may be concluded that Fig. 15 illustrates the experimental observation of a transfer from complete instability to a "metastable" dispersion state.

It could be presumed that a relationship exists between the sedimentation rate and the equilibrium concentration of the polyester in solution. But the sedimentation plots of alumina dispersions in solutions of oligomeric polyethylene glycol 400 disprove this assumption (Fig. 16). The settling rates of seven dispersions in glycol solutions of different concentrations conform and are fast. Even a concentration increase of the oligomeric ether by a factor of 40 (Fig. 16, plot 7) compared with the polyester concentration (Fig. 15, plot 5) only causes a small decrease in sedimentation rate, due to the viscosity change of the solution. Likewise, the adsorbed amount of polymer cannot decisively affect the stability. This can be deduced from corresponding adsorption isotherms in Fig. 17.

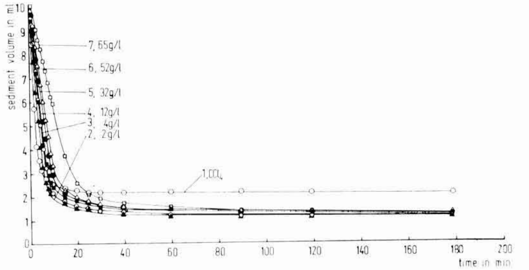

Figure 16 **Sedimentation rates of alumina dispersions in solutions of oligomeric poly(oxyethylene) (MW 400) and in the pure solvent CCl_4.**

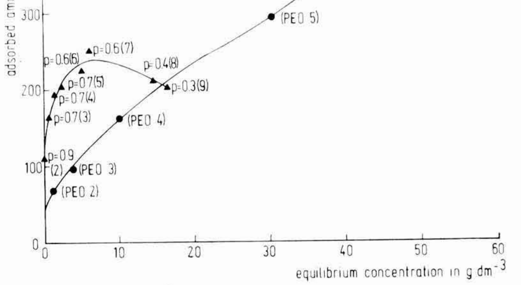

Figure 17 **Adsorption isotherms of polyester 6.6 (▲) and of poly (oxyethylene) 400 (●) on alumina surfaces; numbers in brackets indicate corresponding sedimentation rate curves in figures 15 and 16.**

The adsorbed amount of polyethylene glycol 400 exceeds that of polyester 6.6 by a factor of three, but without any stabilising effect at all. Whilst the isotherm of polyester 6.6 goes first through a maximum and then levels off slightly, this decrease of the amount adsorbed does not cause an increase in sedimentation rate.

The only parameter whose values change in the same manner as the sedimentation rate is the fraction p of specifically adsorbed carbonyl groups of the polyester. p gradually and continuously decreases from 0.9 (experiment 2) down to the lowest value of 0.3 (experiment 9). This decrease does conform with an increase in average length of the adsorption loops which protrude into the solution. Maximum loop lengths are 9 ± 2Å for a theoretical value of $p = 1$, but 26 ± 3Å for $p = 0.3$. The increase in loop length brings about an increase in layer thickness and in minimum distances between the surfaces of colliding particles. This greatly reduces the attractive van der Waals forces between particles. Polymer segments in long adsorption loops have higher degrees of freedom, and consequently the entropic repulsion effects due to restrictions of segment mobilities should be increased when particles with long adsorption loops on their surfaces begin to approach each other.

The negative influence of adsorbed poly(oxyethylene) 400 on the dispersion stability could be due to the incapability of these rather short chain molecules to form adsorption loops. On the other hand, these molecules tend to form molecular associates in carbon tetrachloride. When the molecules are adsorbed as associates, they can form a rather thin and compact adsorption layer with almost no rotational or translatory mobilities of chain segments and with negligible stabilising effects.

Discussion

A comparison of the structure results

The structure of layers of adsorbed chain polymers with specifically interacting functional groups can be deduced from the fractions p of such groups in contact with a pigment surface and from the amounts adsorbed. In particular, this is possible for layers of adsorbed polyesters on the surfaces of silica, alumina, titanium dioxide, and ferric oxide. The polyesters are attached only to these surfaces by specific interactions of their carbonyl groups, and whenever the fractions p of attached groups are high, the formation of adsorption loop structures is clearly indicated. Maximum values of $p = 0.8$–0.9 are indicative of fairly high interaction energies (in the range of hydrogen bond interactions or higher) and of sufficient concentrations of adsorbing sites available on all the four surfaces.

When the amounts adsorbed of polymer are high, loops between two attached groups must protrude into the adjacent solution, since not enough space is available on the surfaces. But a flat arrangement of loops on the surfaces at low surface concentrations seems to be unlikely because of energetic considerations. The loops mostly consist of methylene groups. These groups would need to replace solvent molecules from the surfaces when adsorbed. Flat arrangements also conform with losses of freedom of segmental motions. Both effects are energetically unfavourable.

An important parameter affecting the loop lengths is the distance between adsorbable carbonyl groups in a polyester chain molecule. It can easily be controlled by the chemical synthesis of polyesters starting from glycols and dicarboxylic acids with greater or smaller molecular dimensions.

Equally important is the average distance of adsorption centres on the pigment surfaces. Whenever such distances are larger than those of carbonyl neighbours in the chains of adsorbed polyester molecules, the fractions of attached groups will not exceed values of $p = 0.3$–0.4.

An influential parameter on the loop sizes is the adsorbed amount of polymer. Highest values of p are only found at very low surface coverages.

However, in the systems under investigation no effects of the chemical nature of polyester end groups on the adsorption results could be noticed, and the effects of molecular weight on adsorbed fractions and adsorbed amounts were always small in completely equilibrated systems.

Effects of substrates on polyester adsorption

One of the most significantly influential parameters on the adsorption process of polyester molecules is the surface structure of the solids.

A solid with energetically equivalent surface hydroxyl groups (silica surface) or covered with adsorption layers of water molecules (wet alumina surface) favours very fast equilibration processes.

In contrast to this is the extreme retardation of structure orientations on a surface with energetically inhomogeneous types of hydroxyl groups (dry alumina surface). The extent of retardation depends on the molecular weight, and maximum values of p are attained only after several hundred hours of stirring.

Even more complicated is the adsorption process on surfaces with highly energetic sites (dry titanium dioxide surface). The strong perturbation of carbonyl bands due to adsorption interactions implies that the interaction energies should be about five times higher than those typical for hydrogen bond interactions. As a result, the initially adsorbed amount exceeds the equilibrium amount which then is attained only after extremely long equilibration times.

Comparison of the stability results with literature data

Refs. 19, 20

The combined sedimentation and structure results for alumina dispersions in dilute polyester solutions provide evidence for a transition of such dispersions from complete instability to a transient state of stability when the average lengths of adsorption loops exceeded 15–20Å. This corresponds to a layer thickness of only about 10Å. Such fairly thin layers can sufficiently stabilise only very small primary particles. Commercial pigments often have particle dimensions of 1 000–10 000Å compared with a particle diameter of 200Å in the case of the pyrogenic alumina. The stability effects basically studied in the model systems of this work could be reproduced successfully only in dispersions of commercial pigments if polymers with the capabilities of forming highly extended adsorption layers were available.

Only recently Barron and Howard[19] and Thies[20] have published data on how such extended layer structures can be achieved. They synthesised random, block, and graft copolymers from the monomers styrene and methyl methacrylate[19] or from styrene and butadiene[20]. The stabilising effects of these copolymers and of the corresponding homopolymers on silica dispersions were studied in detail. The interesting outcome of these investigations is the superior stabilising effect of the block copolymers, but only when they are adsorbed in sufficiently large amounts. This can be interpreted in terms of a preferential adsorption of poly(methyl methacrylate) or poly(butadiene) blocks. The residual poly(styrene) blocks are completely displaced from the surface and form long loops or tails protruding far into the solution.

Acknowledgments

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Discussion at Eastbourne Conference

DR G. D. PARFITT remarked that the authors had conveniently removed the hydroxyl groups; whilst he appreciated the need to remove water, he questioned whether it was necessary to remove the hydroxyl groups, because in any natural TiO_2, especially in a practical application, hydroxyl groups would be present on the surface and they are very important when hydrogen bonding and interactions with the surface are considered. Dr Parfitt stated that the suggestion that the adsorption of polyester decreased with time was surprising to him and was an effect he had not encountered before. He stated that normally when a polymer and a surface are brought together, the adsorption of the polymer increases with time. If it is suggested that it decreases, this will reflect on the stability very significantly and he thought that the next stage would then be a redispersion after the adsorption had reached equilibrium, and he suggested that under these conditions very different results would be obtained when compared with those obtained after a short period of time. He asked if any such experiments that explored the changes in adsorption in relation to stability had been conducted.

DR JOPPIEN said that in their laboratory experiments they wished to achieve very pure conditions and, unfortunately, when removing the water from the titanium dioxide surface, the hydroxyl groups were also removed; at this stage of the experiments no direct comparison was possible or expected with a practical situation. With regard to the decreasing amount of adsorbed polymer on the surface of TiO_2, Dr Joppien had said that this had first been observed by a former colleague of Professor Hamann and had been published in 1965. It was something that had puzzled him also and he had conducted experiments to verify it and it seemed to be true for this particular system.

MR A. F. SHERWOOD, commenting on the decrease of adsorption, asked if the polyester used had a broad molecular weight distribution or if it was a very sharp fraction.

DR JOPPIEN said that the polyesters used had mainly been synthesised in their laboratory and during the course of their experiments they had used polyesters with molecular weights ranging from 4000 up to about 45 000, and having differing end groups, and they had used both narrow fractions as well as unfractioned samples.

Mr Sherwood said that a few years ago at the Paint Research Association they had studied the adsorption of alkyd resins on practical titanium dioxide pigments. The alkyd resins they used had very wide molecular weights spectra and it was found that in the initial adsorption the pigment surface adsorbs whatever molecules come into contact with it, but the adsorbed material is in a dynamic state (once it has been attached it can become detached again and exchanged with material in solution). After longer times it appeared that the small molecular weight material was preferentially adsorbed on to the surface and so the mass adsorbed appeared to decrease whilst the number of groups adsorbed remained the same.

Dr Joppien replied that they had carried out similar experiments, and since they wished to verify the results with the polyesters which were not obtainable in narrow fractions, they had used polyethers and found similar behaviour. They also used gel permeation chromatography on the polymers which either had contact with the solvent alone or had extended contact over varying periods of time with the titanium dioxide surface and had noted certain changes in molecular weight after contact. However, these molecular weight changes had never amounted to more than 10 per cent in the weight of the adsorbed amount because of the narrow fractions used.

Mr Sherwood said that in the case of an alkyd resin it was possible to have present short chain, highly polar material with a chain length of not more than C_{18} whilst the rest of the molecules can have molecular weights of 10 or 50 thousand. Commenting on Dr Joppien's use of dry material, Mr Sherwood queried the usefulness of this from the practical point of view, because no practical pigment would be free of water and the presence of water on the surface could cause several different interactions. He gave as an example the case of an alumina treated titanium dioxide where there is a small amount of ionic interaction between the carboxyl group and the pigment surface. He said that if the pigment was zinc modified most of the interaction of the carboxyl group is with the zinc giving a carboxylate ion.

Dr Joppien said that initially they had done their experiments on dry materials in order to have reproducible samples, but they had also performed extensive work with wet materials by adding measured amounts of water to the dried sample and they had noticed that when the surface was covered with about two monolayers of water, the adsorbed polymer was essentially separated from the surface and could interact only with the water which was itself adsorbed on to the surface. They had, of course, wished to study the interaction with the surface itself and not with the adsorbed water molecules.

PROF. W. FUNKE asked Dr Joppien if the observed decrease in the adsorption with time was in any way related to the concentration of the adsorbant and more specifically if it were more pronounced the higher the concentration of absorbant.

DR JOPPIEN said it was.

Prof. Funke suggested that there was a simple explanation for this decrease. At first, most of the polyester molecules surrounding each pigment particle have about the same chance to adsorb, and after that, due to the dynamic state of the system, there is readsorption. Some of the smaller molecules become detached, and larger ones that are already adsorbed on to the surface and kept in close proximity to it, have an increased chance of becoming attached to the surface at a second or third point. Thus, depending on its chain length, a copolymer may be attached to the surface in several places and exclude adsorption sites for smaller molecules with the result that the molecular weight of the adsorbed material increases.

Dr Joppien said that this was exactly the way they had interpreted these results.

Next month's issue

The Honorary Editor has accepted the following papers for publication, and they are expected to appear in the November 1977 isue of the *Journal:*

Save your paint, your money and your substrate *by T. R. Bullet and A. F. Sherwood*

The possible uses of reactive microgels in paint formulation *by W. Funke*

A study of the effects of thiol modification of saturated alkyd resins on their ease of cure with aminoplasts *by D. J. R. Massy, K. Winterbottom and N. S. Moss*

Labelling of dangerous substances and preparations in the EEC *by R. W. Kay*

Information Received

Ion beam etching

The Paint Research Association is developing the technique of ion beam etching to study the distribution of pigment particles in a dry paint film.

Previously, the dispersion of pigments has been measured either in the liquid paint, which has the disadvantage that the dispersion may bear little or no relationship to that of the dried film, or by cutting a cross-section of the dried film and examining it by electron microscopy. This has the disadvantage that the film is often damaged during the cutting and may not be representative of the overall state.

The new ion beam etching method uses the fact that when the paint surface is bombarded with, for example, oxygen ions, the organic binder is destroyed exposing the inorganic pigment at the surface. The pigment can then be observed with an electron microscope. Subsequent ion bombardment will expose deeper layers of the paint film, thus allowing an in-depth picture of the pigment in the paint to be built up.

The effects observed can be interpreted and used to suggest improvements in the manufacture of pigments and the formulation of paint systems to improve opacity.

Doubled "Cellosize" HEC capacity

Union Carbide Europe SA have announced that they intend to initiate an expansion programme which will more than double their present capacity at their plant in Antwerp, Belgium, to produce Cellosize hydroxyethyl cellulose. Cellosize HEC is used as a thickening agent and can also modify the properties of a wide variety of water-based chemical formulations. The expansion programme is expected to be completed by 1980.

Organic chemicals agency

TR International (Chemicals) Ltd have been appointed UK agents for organic chemicals produced by Lonza Ltd of Basle, Switzerland. The range includes intermediates and semi-finished products used in dyestuff and pigment manufacture.

Increased pressure polymerisation capacity

Vinyl Products Ltd have a new factory in Warrington which has increased their production capacity for their range of pressure polymerised emulsions including vinyl acetate-ethylene and vinyl acetate-vinyl chloride-ethylene copolymer emulsions. The new plant incorporates many new safety features and has been designed throughout by the company engineers.

Dimer acid and polyamide plant

Cray Valley Products Ltd have plans to build a new plant to increase their capacity to produce dimer acid for use in polyamides and other resins. A design study contract for the plant has been placed with Matthew Hall Norcain Ltd, and the plant is expected to be the largest of its kind in the country, capable of supplying CVP's needs and also a surplus to export to the expanding world market.

Spectral mapping of US

Desert Sunshine Exposure Tests, Inc. have announced that its Comprehensive Solar Radiation Measurements programme (COSRAM I) will be commenced on 1 October. The programme, designed to give the most complete solar data base in the US of both direct and hemispherical spectral solar radiation in the wavelength range 260-2700nm, is based on precise daily measurements at the company's main test facility in Arizona. Two mobile solar radiometry laboratories will be used in COSRAM I statistically to map the spectral characteristics of solar radiation throughout the US to give climatological variations and the effects of pollution.

Expansion of solvent vinyl resins unit

Union Carbide Corporation has announced a programme to expand and modernise their solvent vinyl resins production at the corporation's Texas complex. The increase in production, which is expected to be achieved by the end of 1978, is to supply the increased worldwide demand for the resins in the surface coatings industries.

Name change

Bush Beach & Segner Bayley Ltd have changed the name of their matting agent TK.100 to Matting Agent TS.100 to avoid confusion with another product marketed under the same name.

FMC increase Foret holdings

FMC Corporation has completed negotiations with Spanish shareholders of Foret SA, Barcelona, which has resulted in the acquisition of an additional 41 per cent of the shares of Foret to bring FMC's total holdings to 91 per cent. Foret SA is a large diversified manufacturer of inorganic chemicals with seven plants in Spain.

Degussa in Iran

Degussa, in co-operation with the Investment Bank of Iran and the Metal Containers Co., have opened the Iran Glazes and Colours Co. in Teheran, and they plan to construct a plant to produce glaze frits in Rusht in 1979.

UK agency

British Chemical Products & Colours Ltd have been appointed UK agents by La Quinoleine S.A. Paris, France, for their range of 8-hydroxy quinoline salts and derivatives. Further details on this range of products are available from British Chemical Products & Colours Ltd, 22 Buckingham Street, London WC2.

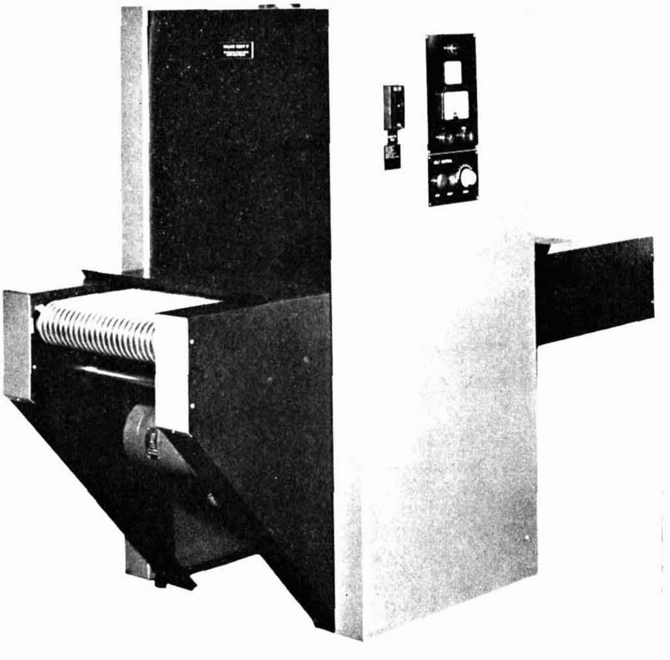
New products

Digital thermometers

Channel Electronics (Sussex) Ltd have available the new 9000 series hand held temperature indicators which are calibrated for use with a wide variety of thermocouple or platinum resistance probes. The nine portable models in the range cover from −99°C to 999°C, and are powered by batteries with a life expectancy of over 2000 operations. The illuminated digital display is operated by a single push button.

Silk screen printing using UV

Wallace Knight Ltd have announced a fully self-contained ultraviolet curing unit specifically designed for use in silk-screen printing operations on paper board and plastic. The equipment, known as Scre

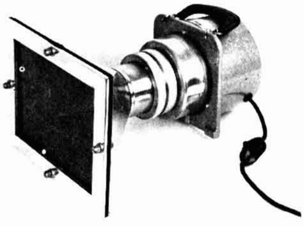


The self-contained ultraviolet curing unit from Wallace Knight Ltd

cure, eliminates the need for costly hot air driers and racking systems and is supplied with conveyors fitted.

New air sampler

Gelman Hawksley Ltd have introduced the Staplex portable hi-volume air sampler, which is equipped to take the standard Gelman range of glass fibre air sampling filters. The air flow rate is measured by means of the pressure drop across an opening in the housing, and the pump used has a 0·49 HP motor designed for 24 hour operation.



The Staplex Hi-volume air sampler

New paddle dryer range

Buss Hamilton Ltd have introduced a new range of paddle dryers, intended for heavy duty applications, such as products which pass through a highly viscous phase during drying, called the Buss SF range. The new range complements the two existing Buss ranges and operates under vacuum conditions.

Urethane coatings modified

The urethane coatings produced by Saran Protective Coatings, Detroit, used for protection against corrosion and weathering are being modified with cellulose acetate butyrate (CAB) supplied by Eastman Chemical. The new coatings are said to have excellent flow control, and the CAB esters are compatible with a wide variety of resins offering higher viscosity and better solubility in urethane solvents than other types of flow and bodying agents.

Zinfos 29

Jenolite Division of Duckhams Oils has announced the introduction of a new phosphating product, Zinfos 29 with applications in producing pure zinc phosphate coatings conforming to the requirements of DEF-29 Class II, DEF-29 Class III and BSS 3189 Class A2. It can also be used for phosphating iron and steel.

Quiet savings

The new Viscount II range of Graco hydraulic pumps from Steetly are claimed to be substantially quieter in operation than their predecessors, thus satisfying the requirements from industry for noise abatement. An added bonus of the more efficient operation is a saving of over 75 per cent in the power consumed when the hydraulic pump is compared with air motors of comparable performance.

A Viscount II 1000 hydraulically-operated fluid pump

Paliogen red 4120

BASF have introduced a new red pigment known as Paliogen red 4120 having the same chemical consitution as the Paliogen maroon pigments, 3920 and 4020. The new pigment has a high level of fastness properties, comparable with those of the Heliogen pigments.

Lift Truck Satellite attachment

Automated Container Loading Ltd have available a new drum handling attachment SDH 500 for use with the Lift Truck Satellite, developed to meet the demand from industry for a quick and economical method of loading and unloading drums in and out of containers and box cars. The attachment has a capacity of 500 Kg and can be fitted with ease.

The drum handling attachment, SDH 500, in use

Literature, courses etc.

Demco butterfly valve brochure

Loba (Industrial Products) Ltd have available a new 20 page brochure outlining the design characteristics and operational features of their Demco butterfly valves, which are available in a wide range of materials and constructions for a variety of pressure and temperature ranges.

Katharometers data

The George Kent Group has a new data sheet available on their 6517 series of katharometers, describing the principle of the katharometer, the types available, and the applications of the various types.

Kronos Titan—50th anniversary

Kronos Titan GmbH celebrated their 50th anniversary in September, this year. Originally a joint company of National Lead Co. of New York, USA, and I. G. Farbenindustrie, Germany, Titan specialised in producing titanium dioxide pigments from ilmenite titanium iron ore, which was open-mined in Norway.

After World War II, the American company had the option of purchasing the German company's interest when I. G. Farbenindustrie went into liquidation, and in June 1952 the company became fully owned by NL Industries Inc.

In 1969, Kronos Titan started up a second production plant in Nordenham, and the company now has almost 1500 employees, with the main product being Kronos titanium dioxide, used largely in paints and plastics.

Register of Members

The following elections to membership have been approved by Council. The Section to which each new Member is attached is given in italics.

Ordinary Members

Bennett, Paul, GradRIC, Crown Decorative Products Ltd, PO Box 37, Hollins Road, Darwen, Lancs. (*Manchester*)

Burke, Valance, BS, 72 Pleasant View, Bridgehill, Consett, Co. Durham. (*Newcastle*)

Charleston, Alistair, BSc, 62A Ellerton Road, Earlsfield, London SW18. (*London*)

Cromarty, Ronald Earling, BSc, 68 Juluis Jeppe St., Waterkloof 0181, Pretoria, South Africa. (*Transvaal*)

Goodwin, Ian John, BSc, Mobil Chemical (Canada) Ltd, 645 Coronation Drive, West Hill, Ontario M1E 4R6, Canada. (*Ontario*)

Jenkins, David Paul, 1330 Mississauga Valley Blvd, Unit No. 52, Mississauga, Ontario, Canada. (*Ontario*)

Jordan, Stuart Andrew, MSc, 66 Belfast St., Hillsborough, Auckland, New Zealand. (*Auckland*)

Koedyk, Wayne Gerard, MSc, W R Grace (NZ) Ltd, Box 8737, Auckland, New Zealand. (*Auckland*)

Lau, Ang Kong, 38-B Marsiling Drive, Block 9, Woodland Town, Singapore 25, Republic of Singapore. (*General Overseas*)

Makoni, George Pedzy, Vitretex Paints Ltd, Box 207, Ndola, Zambia, Central Africa. (*General Overseas*)

Purdy, Kevin Grant, Flat 4, 168 Asquith Avenue, Mt. Albert, Auckland 3, New Zealand. (*Auckland*)

Salim, Mohammed Sharif, BSc, PhD, 6 Fernview Drive, Holcombe Brook, Bury, Lancs. (*Manchester*)

Tollett, William Joseph Dennis, BSc, MSc, MRIC, 38 Bourne Court, New Wanstead, London E11 2TG. (*London*)

Weyell, David John, PhD, MRIC, Foundry Chemicals Division, Ciba-Geigy Plastics & Additives Co, Shay Lane, Halifax HX3 6SD. (*West Riding*)

Associate Members

Bartlett, Gavin William, Shell Chemicals Pty. Ltd, PO Box 2231, Cape Town 8000, South Africa. (*Cape*)

De Villiers, Cornelia Johanna, Shell Chemicals Pty. Ltd, PO Box 2231, Cape Town 8000, South Africa. (*Cape*)

Jetha, Sultan Ali, 357 Rusholme Road, Apt 1616, Toronto, Ontario M6H 2Z4, Canada. (*Ontario*)

Mason, Paul Meurig, 48 Coroglen Avenue, Birkenhead, Auckland 10, New Zealand. (*Auckland*)

Morgan, Wilfred Desmond, T & C Chemicals (Pty) Ltd, PO Box 1366, Johannesburg 2000, South Africa. (*Transvaal*)

Registered Student

McCrae, Robert John, 9 Arran Street, Avondale, Auckland 7, New Zealand. (*Auckland*)

Notes and News

News of Members

Mr W. J. D. Tollett, an Ordinary Member attached to the London Section, has been appointed as marketing manager of Burrell Colours Ltd. He comes to Burrell Colours from Albright & Wilson, where he held the position of marketing manager for service products.

Mr W. J. D. Tollett

Mr D. E. Hopper, an Ordinary Member attached to the Midlands Section and an Associate in the Professional Grade, has joined Drynamels Ltd as sales representative, West Midlands, for thermoset coating powders. Currently a Vice President, Derek Hopper is also a past Chairman of the Midlands Section.

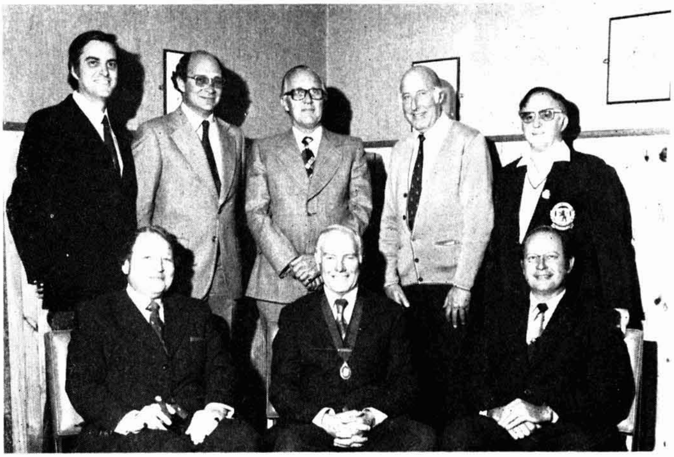
Mr R. H. E. Munn, a former Chairman of the London Section and a Fellow in the Professional Grade, has been appointed as Market Development Director to the Board of Cray Valley Products Ltd. He will be responsible for development and technical service for the paint industry both in the UK and overseas. Mr Munn is also Président Directeur Général of the company's French subsiduary.

Transvaal Section

Rhodesian Branch

Inaugural meeting

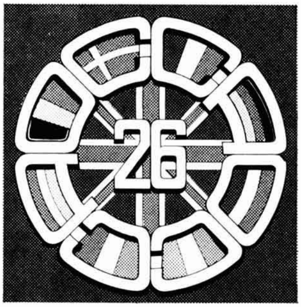
An inaugural meeting of the Rhodesian Branch of the Transvaal Section was held at the Ambassador Hotel, Union Avenue, Salisbury, Rhodesia on 23 June 1977. The speaker at the meeting was Mr D. J. Pienaar, the Vice-President of the South African Division, who is shown in the photograph with the Branch Acting Committee.



From left to right: Front row: R. E. G. Johnson (Chairman), D. J. Pienaar, L. V. Diedericks (Secretary). *Back row:* G. Ellis, T. Hayes-Jones, L. G. Preece, J. Ebdon, F. Potter.

"The OCCA"

The annual technical exhibition of the Oil and Colour Chemists' Association (known to many simply as "The OCCA") has become the world's most important event for all those connected with the paint, printing ink, polymer, adhesive colour and allied manufacturing industries. The OCCA exhibition is held every year in London, England. The symbols for the 1974-78 exhibitions were specially designed by Robert Hamblin, Director and Secretary of the Association, to emphasise the very wide coverage which all the Association's activities attract:



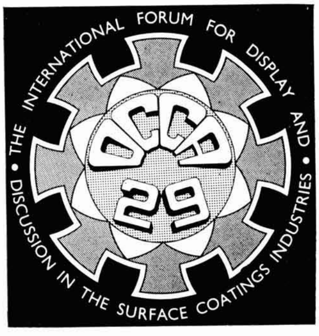
The motif for OCCA-26 used the flags of the enlarged EEC converging on the British flag to symbolise the welcome extended to visitors from overseas to the Exhibitions for more than 25 years. (1974)

The 1974 theme continued at OCCA-27 by showing the world-wide interest aroused by the Association's annual Exhibitions in London which attract visitors from all parts of the globe.

The motif for OCCA-30 uses the symbol of a moving indicator on a calendar to emphasise the importance of the continuous dialogue year by year between suppliers and manufacturers. The inward pointing letters recall the international aspect of this unique annual focal point for the surface coatings industries, which in 1977 attracted visitors from 50 countries.

The motif for OCCA-28 emphasised that the target for 1976 was London where all the Exhibitions have been held, and continued the theme of its international aspect.

In 1977 the motif for OCCA-29 used inward pointing arrows to show the many places from which people came to the Exhibition, and these arrows formed outward pointing arrows to show the subsequent spreading of knowledge.



OCCA-30 Exhibition

Alexandra Palace, London. 18-21 April 1978

Good support for OCCA-30 from organisations in many countries

The continuous dialogue between suppliers and manufacturers

Arrangements for OCCA-30

The thirtieth Annual Exhibition of raw materials, plant and equipment for the paint, printing ink, colour, adhesive, polymer and allied industries will be held at Alexandra Palace, London N.22 from 18–21 April 1978.

Whilst the Committee naturally encourages the showing of new products, it does not stipulate that a new product has to be shown each year, since it fully appreciates that there are occasions when this is not possible. Accordingly, the Committee draws attention to the fact that new technical data on existing products are regarded as acceptable subject matter.

Motif for the Exhibition

The motif, designed by Robert Hamblin, uses the symbol of a moving indicator on a calendar to emphasise the importance of the continuous dialogue year by year between suppliers and manufacturers. The inward pointing letters recall the international aspect of this unique annual focal point for the surface coatings industries which in 1977 attracted visitors from 50 countries. The colours of the motif shown on the advertisement on page viii of this issue will be carried throughout the publicity leading up to the Exhibition. The two main colours of the motif, royal blue and yellow, will be incorporated on the facias of the stands and it is intended to organise complementary flower displays in the Exhibition Hall. The use of these colours will create a pleasing contrast as visitors move from corridor to corridor at the Exhibition, as the royal blue colour will be used from east to west and the yellow colour from north to south.

Invitations to Exhibit

Invitations to Exhibit at OCCA-30 were dispatched at the end of May to organisations both in the United Kingdom and abroad and already many enquiries have been received, not only from those who exhibited at OCCA-29, but from organisations which had shown at earlier Exhibitions or are considering exhibiting for the first time.

The cost effective Exhibition

The value of showing at OCCA Exhibitions can hardly be better demonstrated than by the following quotation from an article appearing in the June issue of *Paint Manufacture*, and the Association acknowledges with thanks the kind permission of the editor to reproduce it—

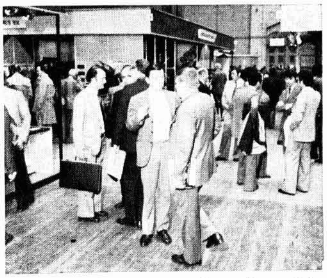
> *The encouraging conclusion which may be drawn from this experience is that visitors to exhibitions are interested in new developments and an unknown company can attract attention if it brings genuine new technology to work on tasks which are important to the industry. It is a measure of the effectiveness with which the OCCA Exhibition is conceived, promoted and administered that we at Pilamec are able to regard the considerable cost of participation as an excellent investment.*

In the May issue of the *Journal*, the following quotation appeared from another Exhibitor—

> *I think you would like to know that this was without doubt the most successful Exhibition in which we have participated; the interest was absolutely enormous . . . We have simply never known anything like it.*

Another exhibitor wrote to the Association stating

> "*. . . in the four days we had over 350 'in depth' discussions with visitors . . .* ".



Visitors to OCCA-29 came from 50 countries

The Exhibition Committee was particularly pleased to see the large number of overseas companies showing at OCCA-29, both directly and through their British associates, and this emphasises the international character of the function.

The crowd puller

Visitors at OCCA-29 are known to have come from at least 50 countries and admissions of over 10,000 were recorded at the entrance. A feature of the Exhibition is the arrangement of a seating area directly in front of the Information Centre, where exhibitors and members can arrange to meet visitors.

Official Guide

This unique publication contains descriptions of all companies and their exhibits at the Exhibition and is issued to each Member of the Association at home and abroad together with season admission tickets. As in 1977, several Sections will be organising coach parties to visit the Exhibition and any Members interested should contact their local Section Hon. Secretary. (Full Section Committee lists for 1978 were published in the August issue of the Journal.) It is also hoped that several parties will be organised from overseas to visit the Exhibition.

Advertising facilities

Advertising space is available in this important publication to both exhibitors and other organisations which are not able to show at the 1978 Exhibition. The Official Guide will be published early in 1978 so that visitors can obtain copies and plan the itinerary for their visits. Clearly, the Official Guide is a publication that will constantly be referred to both before and after the Exhibition and consequently any company wishing to advertise in the Guide should book space as soon as possible. Details of the advertising rates are available from Mr D. M. Sanders (Assistant Editor) at the address on the contents page. As in previous years the Official Guide and season admission tickets will be available several weeks in advance of the Exhibition (prepayment only) from the Association's offices but they will also be available for purchase at the entrance to the Exhibition Hall. A charge is made for both the Official Guide and the season admission tickets to the Exhibition. The policy was introduced several years ago to deter casual visitors who otherwise collected large quantities of technical literature from exhibitors stands; the policy has been welcomed by exhibitors and has in no way acted as a deterrent to bona fide visitors to the Exhibition.

The continuous dialogue

The Exhibition Committee will be meeting later this month to allocate stand space under rule 3 to those applications already received. Late applications will be considered, but any organisation which has not yet sent in its application and wishes to exhibit should contact the Director & Secretary at the address on the Contents page immediately.

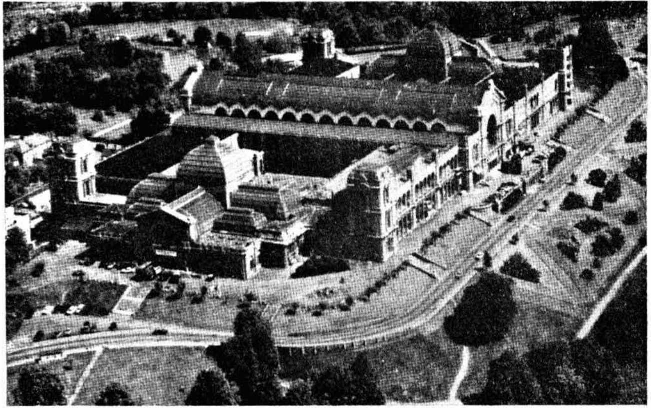
Alexandra Palace

Alexandra Palace was named after Princess Alexandra, the wife of Edward, Prince of Wales (later Edward VII). It stands high on the hills of north London giving at night time a panoramic view of the lights of the city.

The Great Hall, in which OCCA Exhibitions have been held, can be seen in the centre of the drawing above. The Palace Suite, containing the restaurants, is to the left, and at the extreme left is situated the Panorama Bar. Two bars (the West Bar and the Long Bar) in addition to a cafeteria adjoin the Great Hall and are available to visitors and exhibitors throughout the Exhibition. The Italian Gardens lie behind the Palace Suite, and in the spring time the grassy slopes in front of Alexandra Palace are gay with crocuses and daffodils. At the right of the Great Hall the British Broadcasting Corporation has for many years occupied the wing of the building and the television transmitting aerial is a landmark which can be seen for many miles. In recent years the Great Hall has been used for the degree conferment ceremony of the Open University.

For those travelling to the Exhibition by car ample free parking space is available, and recent improvements to the road system include the extension of the southbound carriagway of the M1 Motorway to the North Circular Road and the flyover on that road by the new Brent Cross Shopping Centre. By the 1978 Exhibition the extension of the Piccadilly Underground line to the Heathrow Airport Terminal will give a direct line to Turnpike Lane station from which the Association runs a free bus shuttle service to the Exhibition.

Exhibitors were allowed for the first time in 1977 to serve alcoholic refreshments on their stands and this innovation will be continued at OCCA-30. Many exhibitors expressed their appreciation of this as it allowed their personnel to remain on the stands for the whole period of the Exhibition.



All OCCA Exhibitions have been held in London, which affords excellent travel and hotel facilities for visitors from both overseas and the United Kingdom. In pursuance of the theme of the Exhibition—**The continuous dialogue**—it is felt that Exhibitors will like to know that the Exhibition Committee has also **reserved Alexandra Palace for April 1979 and will hold its annual Exhibitions there subsequently in April each year.**

It will also be appreciated that for exhibitors and visitors staying in London, the capital city offers the finest variety of entertainments for the evenings after the Exhibition.

OCCA
60th Anniversary

1918 1978
OCCA
LX
11-12 MAY

Celebrations

The May 1978 issue of the *Journal* will contain an article by Dr S. H. Bell, OBE (President 1965–67) on main Association events since the 50th Anniversary in May 1968. **Already many companies have reserved advertising space in this important issue in order to congratulate the Association on this achievement, and others wishing to do so can obtain full details from the Assistant Editor at the Association's offices at the address on the contents page.**

Full details of the two functions organised for the celebrations will appear in the *Journal* in due course and application forms will be sent to Members of the Association, either with an issue of the *Journal* or with a Section meeting notice.

In the meantime, Members wishing to participate should note the following important dates:

On the evening of Thursday 11 May it is planned to hold at the Painters' Hall a Commemorative Lecture followed by a Dinner to which Past Presidents, Past Honorary Officers of the Association and Honorary Members will be invited as guests. On Friday 12 May the Association's Dinner and Dance will be held at the Savoy Hotel, London WC2 and Presidents of other societies, together with their ladies, will be invited to attend.

Non-members who wish to receive application forms should write to the Director and Secretary at the Association's offices.

Forthcoming Events

Details are given of Association meetings in the United Kingdom and Ireland up to the end of the month following publication and in other parts of the world up to the end of the second following publication.

October

Monday 3 October

Hull Section: "Agitation—a state of the art review" by Dr Maurice F. Edwards, Senior Lecturer at Bradford University. Joint meeting arranged by the Institution of Chemical Engineers. *Venue to be announced but taking place on the South Bank.*

Tuesday 4 October

West Riding Section: "Disposal of waste solvents" by Mr A. Molyneux of Chemstar Ltd. The Mansion Hotel, Roundhay Park, Leeds 8 at 7.30 p.m.

Thursday 6 October

Newcastle Section: "Corrosion control and sensible methods of test—at last" by Mr F. D. Timmins, British Rail, Derby. St. Mary's College, University of Durham, Elvet Hill Road, Durham.

Thames Valley Section: "Offshore painting" by a speaker from BIE Anti-Corrosion Ltd. Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks at 6.30 p.m. for 7.00 p.m.

Friday 7 October

Hull Section: Annual Dinner Dance to be held at the Willerby Manor Hotel, Willerby, Nr. Hull.

Monday 10 October

Manchester Section: "Silicone protective coatings" by J. G. Price, Dow Corning Ltd. The Woodcourt Hotel, Sale, Cheshire at 6.30 p.m.

Thursday 13 October

Midlands Section—Trent Valley Branch: "Acrylamide pigments" by R. M. W. W. Wilson of Burrell Colours. Crest Hotel, Pastures Hill, Littleover, Derby at 7.00 p.m.

Scottish Section: "The use of microvoids as pigments" by Dr N. Reeves, BTP Tioxide Ltd. Bellahouston Hotel Glasgow at 6.00 p.m.

Wednesday 19 October

Ontario Section: "Novel ink resins" by L. P. Horn of Lawter Chemicals. Skyline Hotel, Toronto at 6.00 p.m.

Thursday 20 October

London Section: "Corrosion and conservation" by Mr H. Barker, Keeper of Conservation and Technical Services, British Museum. At Rubens Hotel, Buckingham Palace Road, S.W.1 commencing at 7.00 p.m.

Auckland Section: Annual Ladies' Night, in the Heidelberg Room, Harro's Hoffbrauhaus at 7.00 p.m.

Friday 21 October

Irish Section: "Printing ink lecture"—*details to be announced.*

Manchester Section: Annual Dinner Dance to be held at the Piccadilly Hotel.

Scottish Section—Eastern Branch: Annual skittles match vs Scottish Section for the Newton Cup, to be held in the Murrayfield Indoor Sports Club, Roseburn Street, Edinburgh, commencing 7.00 p.m.

Thursday 27 October

Midlands Section: "Estey dynamics tunnel coating unit, a new development in powder coating plant" by Electropaint Ltd. The Calthorpe Suite, County Ground Edgbaston, Birmingham at 6.30 p.m.

Friday 28 October

Bristol Section: Ladies' evening. *Details to be announced.*

London Section: Ladies' Night to be held at the Piccadilly Hotel.

Midlands Section—Trent Valley Branch: Hallowe'en Dance at Cross Keys Inn, Turnditch.

November

Tuesday 1 November

West Riding Section: "Wood preservatives" by Dr G. Hall of TRADA at the Mansion Hotel, Roundhay Park, Leeds 8 at 7.30 p.m.

Thursday 3 November

Newcastle Section: "External pipe line coatings" by Mr D. Grey, Gas Board at St. Mary's College, University of Durham, Elvet Hill Road, Durham.

Friday 4 November

Irish Section: Annual Dinner Dance, Clarence Hotel, Dublin 2, at 8.30 p.m.

Monday 7 November

Hull Section: "Defoamers" by Mr R. W. Harrison of Diamond Shamrock (UK) Ltd, at the George Hotel, Land of Green Ginger, Hull at 6.30 p.m.

Tuesday 8 November

Scottish Section: "Dispersion—the key factor in pigment theory", by Dr W. Carr. Joint meeting with Society of Dyers and Colourists at the North British Hotel, Glasgow, at 7.30 p.m.

Thursday 10 November

Midlands Section—Trent Valley Branch: "Production control" by Mr D. J. Murray of Crown Decorative Products at the Crest Hotel, Pastures Hill, Littleover, Derby, at 7.00 p.m.

Thames Valley Section: "Infologistics for individuals (How to cope with the information explosion)" by Dr D. Moody of OCCAM, at the Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks at 6.30 for 7.00 p.m.

Friday 11 November

Manchester Section: "Theory versus practice in vacuum pressure and centrifugal filtration" by Dr A. Rushton, UMIST, at the Manchester Literary and Philosophical Society, Manchester at 6.30 p.m.

Wednesday 16 November

London Section: "The influence of solar radiation on paint films". Day meeting in association with Thames Polytechnic, Woolwich at 10.00 a.m.

Ontario Section: "New approaches to the development of properties in paint films" by Prof. Schreiber of University-Polytechnic of Montreal at the Skyline Hotel, Toronto, at 6.00 p.m.

Thursday 17 November

Manchester Section: Student lecture "Epoxidised resins for anticorrosive coatings" by Mr A. McKay, Ciba-Geigy Plastics & Additives Co. at the Manchester Literary and Philosophical Society, Manchester at 4.30 p.m.

Wednesday 23 November

Scottish Section—Eastern Branch: "Pigment dispersion techniques—chipping" by Messrs P. J. Holland and D. Bradshaw of Foscolour Ltd, at the Alfton Hotel, 6 Grosvenor Crescent, Edinburgh 12, at 7.30 p.m.

Friday 25 November

Bristol Section: "Film for packaging" by Dr C. R. Oswin of British Cellophane Ltd at the Royal Hotel, Bristol at 7.15 p.m.

Midlands Section: Student lecture "Further education of technologists" by Mr D. Clements at the Calthorpe Suite, County Ground, Edgbaston, Birmingham at 6.30 p.m.

West Riding Section: Dinner Dance at the Crown Hotel, Harrogate.

December

Wednesday 14 December

Ontario Section: Ladies' evening. *Lecturer and topic to be advised,* at the Skyline Hotel, Toronto at 6.00 p.m.

1978

February

Friday 10 February

Scottish Section—Eastern Branch: Members are asked to note that the date for the Burns Supper has been changed to 10 February. The Supper will be held at the Commodore Hotel, Marine Drive, Edinburgh.


SYLFAT V-18
VEGETABLE OIL
FATTY ACID
sylvachem
500 ml

CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of £3.00 per cm. Advertisements for Situations Wanted are charged at 80p per line. A box number is charged at 50p. They should be sent to D. M. Sanders, Assistant Editor, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF. JOCCA is published EVERY month and Classified Advertisements can be accepted up to at least the 12th, and in exceptional circumstances the 20th of the month preceding publication. Advertisers who wish to arrange for an extension of the copy deadline should contact the Assistant Editor, D. M. Sanders, at the address given above (telephone 01-908 1086, telex 922670 OCCA Wembley).

APPOINTMENTS VACANT

RECONDITIONED EQUIPMENT FOR SALE

West Riding Section

Notice of Dinner Dance

The West Riding Section Dinner Dance will be held on Friday 25 November 1977 at the Crown Hotel, Harrogate, Yorkshire. Those wishing to obtain tickets (price £7.50 inc. VAT) should contact Mr N. Cochrane, The Coach House, Red Holt, Hainworth Wood Road, Keighley, West Yorkshire BD21 5BJ, before 4 November.

UV polymerisation

Newcastle Section Symposium 1975

The bound copies of the twelve papers presented covering many aspects of this rapidly expanding field are available from the Association offices at the address on the contents page. **Price £5.00**

BOOKS OFFERED

APPOINTMENTS VACANT

TECHNICAL MANAGER-SYNTHETIC RESINS
(Male/Female)

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