

# JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION



Vol. 50 No. 10

October 1967

Corrosion inhibition by the salts of the  
long chain fatty acids

Testing of titanium dioxide pigments in paint films  
for dispersion weathering resistance and optical  
properties

On the relation between the pigment-vehicle interaction  
and the water uptake of solid paint films

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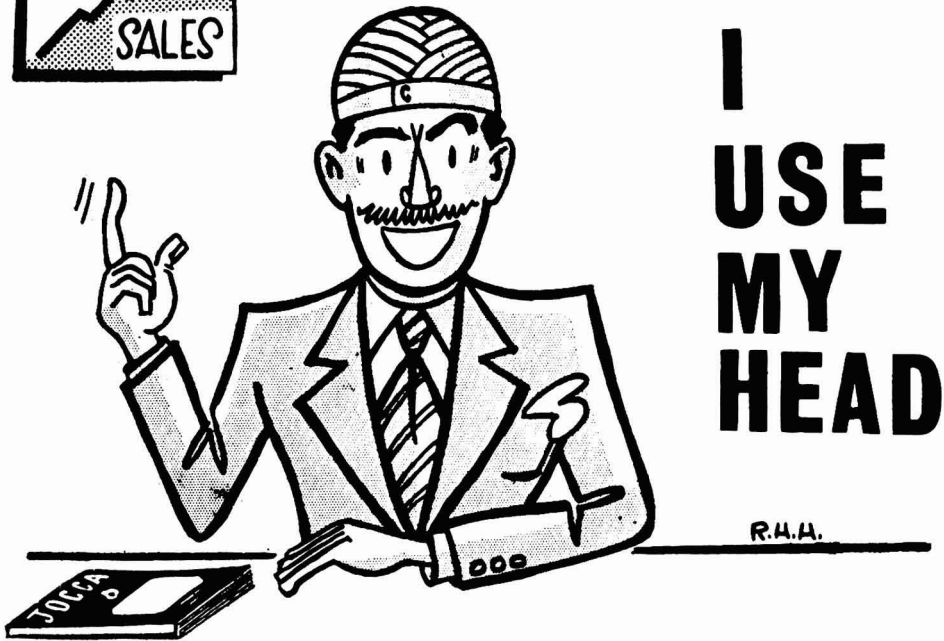
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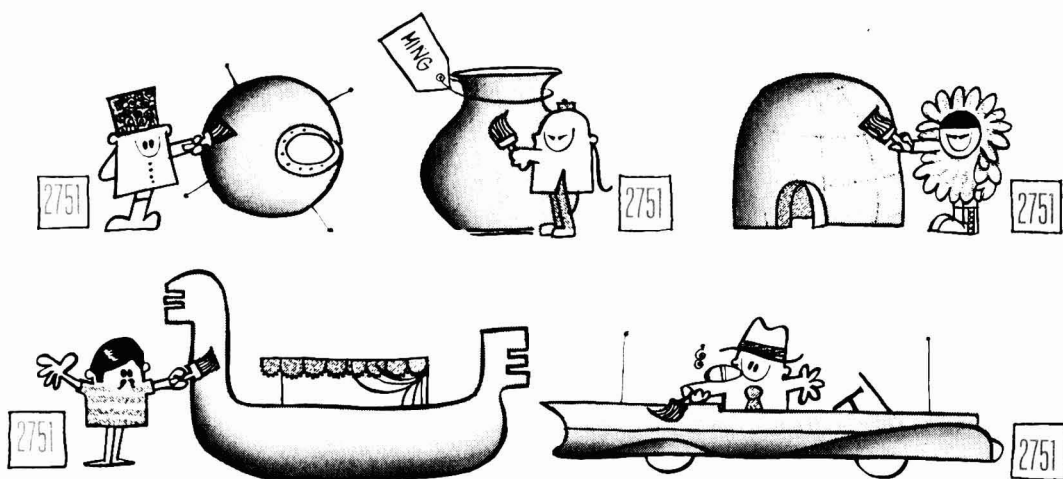
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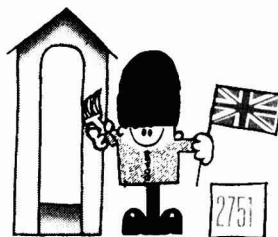


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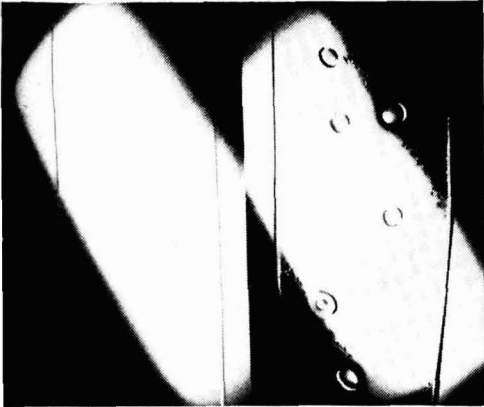
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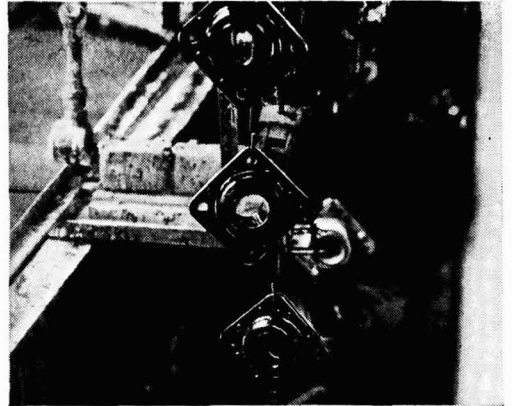
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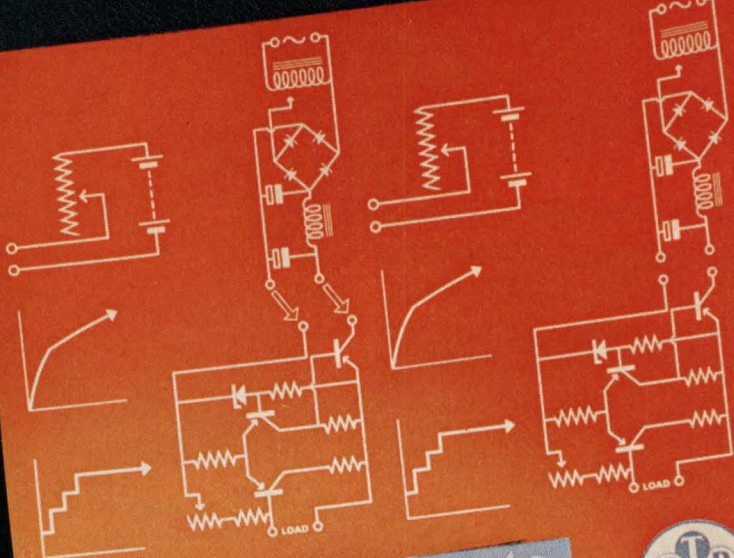
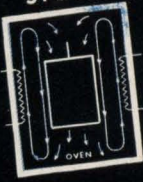
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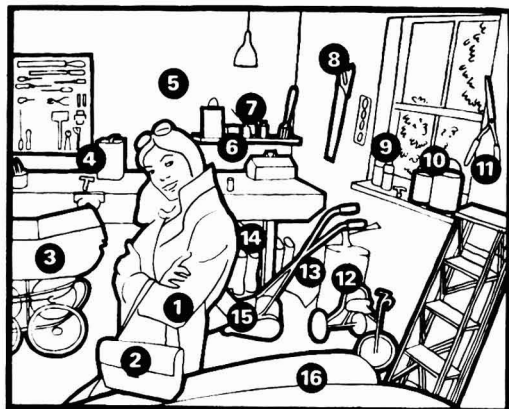
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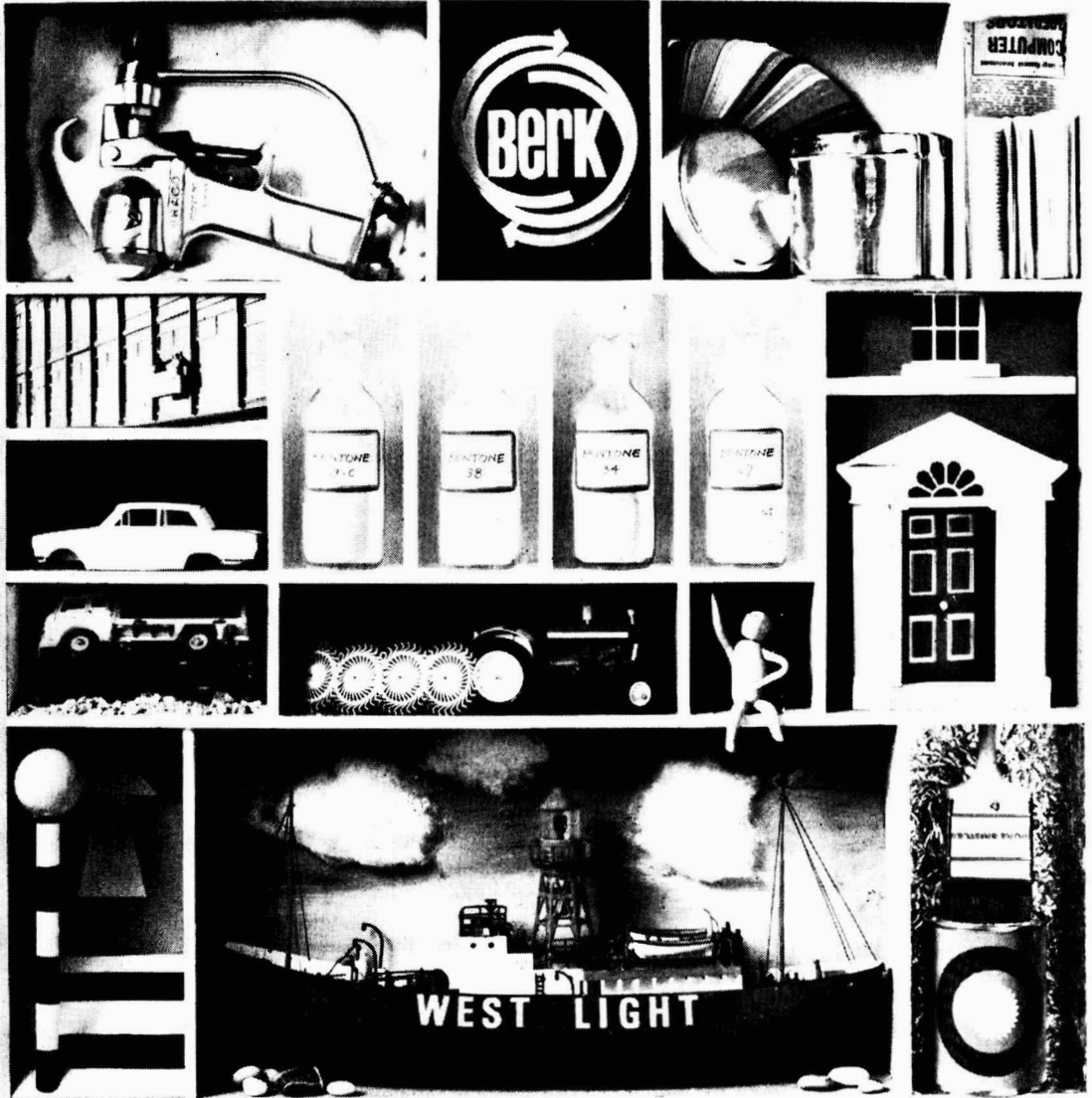
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## **Transactions and Communications**

---

# **Corrosion inhibition by the salts of the long chain fatty acids\***

By **A. J. Appleby** and **J. E. O. Mayne**

Department of Chemistry, University of Cambridge

### *Summary*

When basic pigments, such as red lead, zinc oxide and calcium carbonate, are ground in drying oils, soaps are formed. These soaps break down in the presence of water and oxygen to yield a range of salts of mono- and di-basic acids, which may inhibit the corrosion of iron at a pH as low as 4.8.

It is suggested that this inhibition is brought about by the formation of insoluble complex ferric salts, which reinforce the air-formed film until it becomes impermeable to ferrous ions. In the presence of lead ions, inhibition takes place at much lower concentrations, and a possible explanation is put forward based on modification of the cathodic reaction.

## **L'inhibition de corrosion par les sels des acides gras en chaîne longue**

### *Résumé*

Des savons se forment lors du broyage des pigments basiques tels que minium de plomb, l'oxyde de zinc, et carbonate de calcium, avec des huiles siccatives. Ces savons se décomposent en présence de l'eau et de l'oxygène et donnent une gamme de sels des acides mono et dibasique qui peuvent inhibiter la corrosion du fer, même lorsque le pH ne dépasse pas de 4,8.

On propose que cette inhibition est provoquée par la formation des complexes sels ferriques insolubles qui renforcent le feuil séché à l'air jusqu'au point qu'il devient imperméable aux ions ferreux.

En présence des ions de plomb l'inhibition se manifeste aux concentrations plus faibles, et l'on propose une explication basée sur une modification de la réaction cathodique.

## **Korrosionsverhinderung durch die Salze Langkettiger Fettsäuren**

### *Zusammenfassung*

Beim Vermahlen basischer Pigmente, wie z.B. Bleimennige, Zinkoxid und Kalziumkarbonat in trocknenden Ölen bilden sich Seifen. Bei Gegenwart von Wasser und Sauerstoff zersetzen sich diese Seifen unter Bildung einer Reihe von Salzen ein- und zweibasischer Säuren, welche die Korrosion von Eisen schon bei einem pH von 4,8 verhindern können.

Es wird angenommen, dass diese Inhibition verursacht wird durch Entstehung unlöslicher komplexer Ferrisalze, die den durch Einwirkung von Luftsauerstoff gebildeten Film solange verstärken, bis er für Ferroionen undurchdringlich wird.

Sind Bleiionen zugegen, so findet die Inhibition bei wesentlich niedrigeren Konzentrationen statt, wofür als mögliche Erklärung Modifikation der kathodischen Reaktion vorgeschlagen wird.

## **Торможение коррозии посредством солей длинноцепочных жирных кислот**

### *Резюме*

При растирании основных пигментов, как например свинцового сурика, окиси цинка и углекислого кальция в высушивающих маслах, образуются мылы. Эти мылы в присутствии воды и кислорода разлагаются в ряд солей одно- и двухосновных кислот, которые могут препятствовать коррозии железа даже при pH значении 4,8. Предполагается что причиной этого препятствия является образование нерастворимых комплексов окисных солей железа, которые усиливают воздушную пленку до тех пор пока она не становится

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\*Presented at the Scarborough Conference, 22 June 1967.

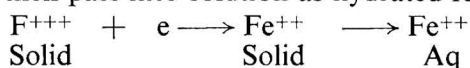
непроницаемой закисными ионами. В присутствии свинцовых ионов торможение имеет место при гораздо более низких концентрациях, и выдвигается возможное объяснение этого, основанное на видоизменении катодной реакции.

### Introduction

Inhibitive paints frequently contain basic pigments, such as red lead, zinc oxide and calcium carbonate, ground in drying oils, for example linseed oil or linseed stand oil. In a paper presented to an earlier Conference<sup>1</sup> it was shown that inhibition was associated with the formation of water soluble material derived from the metallic soaps of the linseed oil fatty acids. Van Rooyen<sup>2</sup> analysed the water soluble degradation products of a number of metallic soaps and found that they consisted of the salts of a range of mono- and di-basic aliphatic acids. He also showed that the lead and calcium salts of azelaic, suberic and pelargonic acid were inhibitors of the corrosion of iron at a pH of 4.6.

Ramshaw<sup>3</sup> examined the inhibitive properties of the sodium, calcium and lead salts of a range of mono- and di-basic acids and concluded that inhibitive efficiency increased with the length of the carbon chain up to a maximum of 8-9 carbon atoms, i.e. including that in the carboxyl group; and that the lead salts were always more efficient inhibitors than either the calcium or the sodium salts. In a later paper<sup>4</sup> he examined the degradation of the lead soaps of individual acids present in linseed oil and concluded that the inhibitive properties of their aqueous extracts were largely accounted for by the property of one of the major components of the extracts, lead azelate.

In a recent series of investigations<sup>5, 6, 7</sup>, evidence has been put forward in support of the view that, when a piece of iron, carrying its air-formed oxide film, is immersed in an aqueous solution, the oxide film breaks down by a process of reductive dissolution. Upon immersion, ferric ions in the oxide film are reduced and then pass into solution as hydrated ferrous ions thus:



Above a pH of about 9, ferrous hydroxide has such a low solubility that the second stage in the breakdown process is impeded. In the presence of oxygen, ferrous hydroxide is converted into a cubic ferric oxide, which has a similar structure to that of the air-formed oxide film. Consequently the oxide film is thickened until it becomes impermeable to ferrous ions. In the pH range 6-9, benzoate and acetate ions stimulate the oxidation of ferrous ions by dissolved oxygen and, once more, the air-formed film is repaired by material of the same composition.

The object of the following investigation was to see if these explanations of the inhibition of corrosion could be extended to solutions of sodium, calcium and lead azelate, pH 4.6, and to account for the fact that lead azelate was a more efficient inhibitor than either sodium or calcium azelate.

### The effect of azelates on the air-formed oxide film

Ramshaw obtained values of about +0.2 v., hydrogen scale, for a mild steel specimen immersed in 10<sup>-3</sup>N lead azelate<sup>8</sup>.

Hancock<sup>9</sup> measured the resting potentials of iron specimens immersed in decinormal sodium hydrogen azelate, in the pH range 3.6-4.8 and found that they were in the region of +0.25 — +0.35 v. He developed a method of estimating

by cathodic reduction<sup>10</sup> the thickness on iron of the air-formed oxide film, and used it to examine the effects of inhibitors in the pH range 7.1-12.6. He also examined the behaviour of pure iron and mild steel specimens when immersed in decinormal sodium hydrogen azelate, pH 4.8, over the period of 1-18 days, and found that, although corrosion was inhibited, the air-formed film remained unchanged in thickness. In addition he made a preliminary measurement with calcium and lead azelate solutions and found that, whereas the air-formed film was unaffected by calcium azelate solution, there was some evidence that it was thickened by lead azelate solution by about 15 per cent<sup>11</sup>.

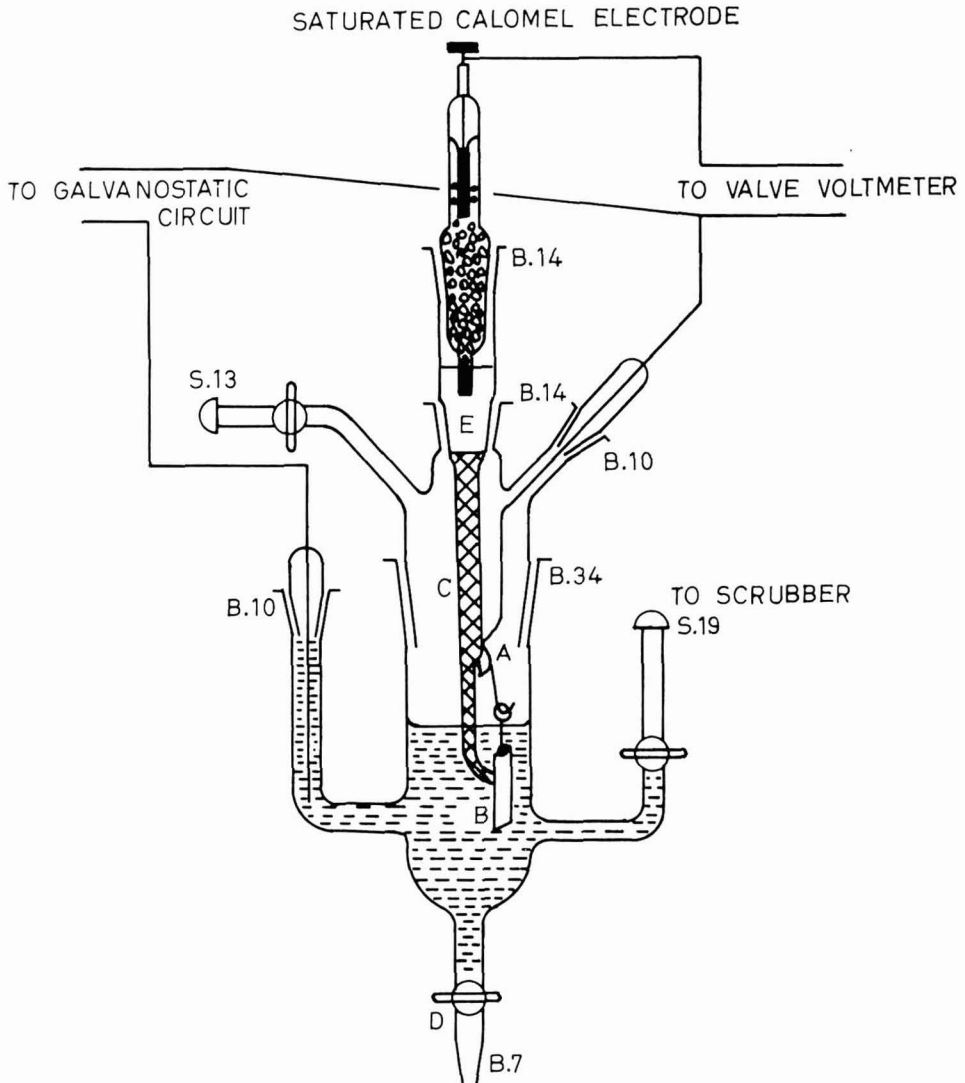


Fig. 1. Apparatus used for the measurements of the potentials of polarized and unpolarized specimens under aerobic and anaerobic conditions

In order to confirm these results, measurements were made of the changes in thickness of the oxide film brought about by solutions of calcium and lead azelate at a pH of 4.6. The apparatus used for the cathodic reduction of the oxide film is shown in Fig. 1, and the results in Table 1. The electrolyte was N/20 sodium hydroxide, which was deaerated by the method of Hersch<sup>12</sup>.

*Table 1*  
*Thickness of oxide film on pure iron*  
*Pickled under standard conditions*

Before immersion			
7.5 millicoulombs cm <sup>-2</sup> .	Thickness	41.5 Å	Average value 41.8 Å
7.6     "     "	"	42.0 Å	
7.6     "     "	"	42.0 Å	
After immersion in lead azelate solution			
8.8 millicoulombs cm <sup>-2</sup> .	Thickness	48.8 Å	% Change 16.9
8.1     "     "	"	44.8 Å	"     7.2
8.2     "     "	"	45.5 Å	"     9.0
After immersion in calcium azelate solution			
7.5 millicoulombs cm <sup>-2</sup> .	Thickness	41.5 Å	% Change 0.0
7.2     "     "	"	39.8 Å	"   -4.1
7.3     "     "	"	40.4 Å	"   -2.7

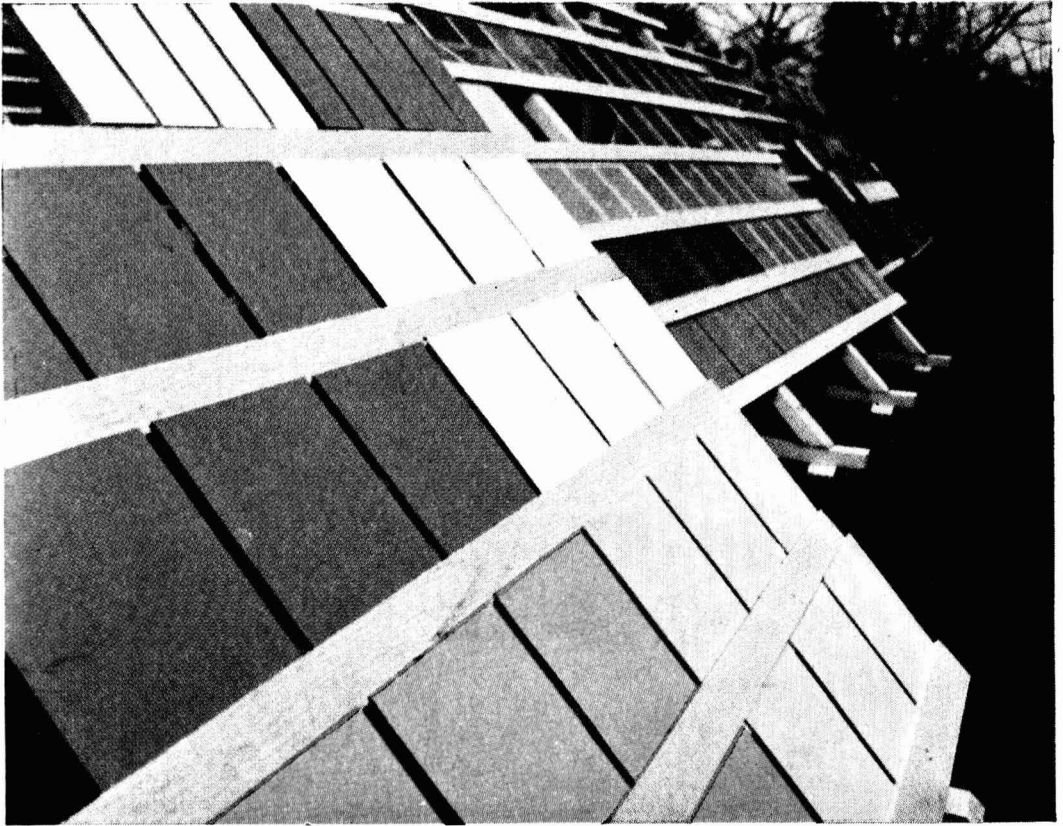
The thickness of the air-formed film was found to be 41.8 Å, a value in good agreement with that obtained earlier, 40 Å<sup>10</sup>; furthermore, Hancock's measurements were confirmed and it was concluded that, whereas inhibition in lead azelate solution was accompanied by film thickening, 0.1 N sodium and calcium azelate must inhibit by a different mechanism, since no evidence of oxide film thickening was obtained with either of these two solutions.

### **The inhibitive action of sodium and calcium azelate**

#### *Preliminary anodic polarisations*

Pickled iron specimens were aged in a desiccator over silica gel for one day and anodically polarised at a current density of 10 microamps cm<sup>-2</sup>, in the presence of air in 0.1 N sodium and calcium azelate, pH 4.84. The apparatus used is shown in Fig. 1 and the results in Fig. 2. Curve 1 refers to the anodic polarisation of a platinum electrode in 0.1 N sodium azelate and curves 2 and 3 to iron in 0.1 N sodium and calcium azelate respectively. The polarisation curves suggest that the iron specimens were being rendered passive by the formation of some surface compound, and the potential of oxygen evolution, 1.52 v., is in good agreement with the value, 1.528 v., obtained by extrapolation of the graph based on earlier work with other inhibitors of higher pH<sup>13</sup>. Curves 4 and 5 were obtained with sodium acetate and sulphate at the same pH.

In another experiment pickled specimens were anodically polarised in deaerated 0.1 N sodium and calcium azelate for about 12 hours at 50 microamps cm<sup>-2</sup> in the apparatus shown in Fig. 1 and the solutions run off and analysed for ferrous iron, by means of 4 : 7-diphenyl-1 : 10-phenanthroline<sup>14</sup>. It was found that the quantity of ferrous ions in solution corresponded, within the limits of experimental error, to the amount of electricity consumed.



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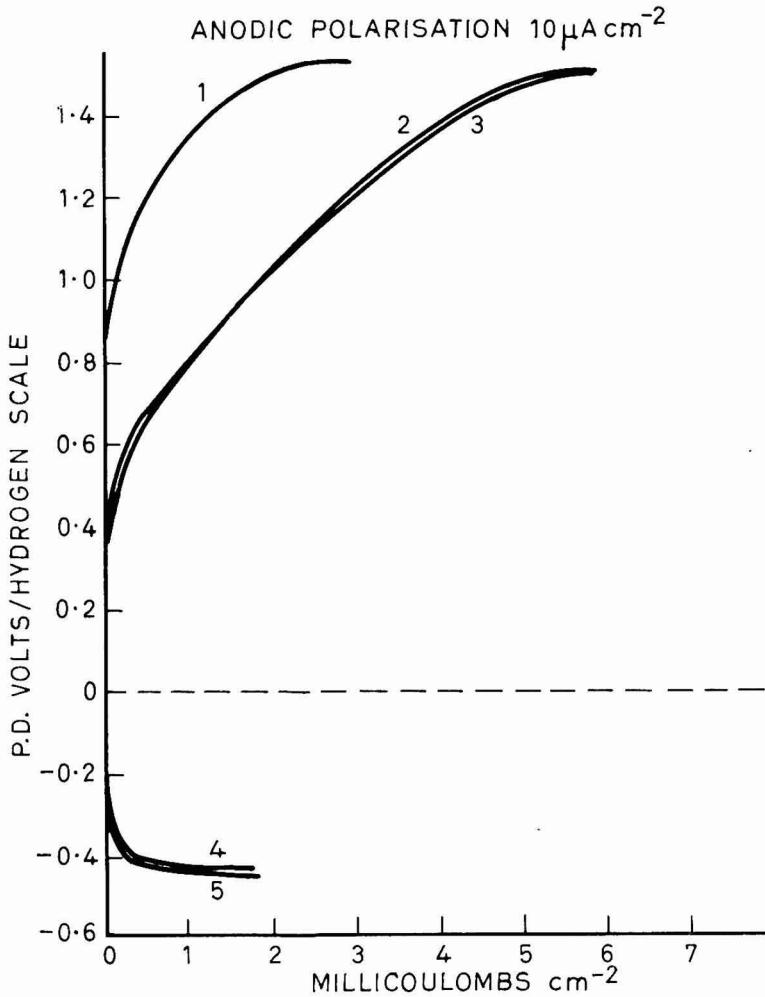


Fig. 2. The changes in potential of specimens polarised at  $10\text{ microamps cm}^{-2}$  for 10 minutes, in the presence of air in solutions pH 4.84 : 1. Platinum in sodium azelate ; 2. Iron in sodium azelate ; 3. Iron in calcium azelate ; 4. Iron in sodium acetate ; 5. Iron in sodium sulphate

#### *Potential/Time curves*

In order to obtain further information regarding the role of oxygen, potential/time curves were recorded of iron specimens immersed in various solutions containing 0.0015 p.p.m. oxygen, Fig. 3. It can be seen that in sodium azelate the specimen reduced in hydrogen broke down faster than the pickled one, probably owing to the thinner oxide film on the hydrogen reduced specimen,  $26\text{ \AA}$  compared with  $40\text{ \AA}$ ; and that the pickled specimen in sodium azelate broke down more slowly than the one in sodium benzoate, which in turn broke down more slowly than the one in sodium acetate. Similar results were obtained with solutions of calcium azelate. It was concluded that oxygen was necessary for sodium or calcium azelate to function as inhibitors of corrosion.

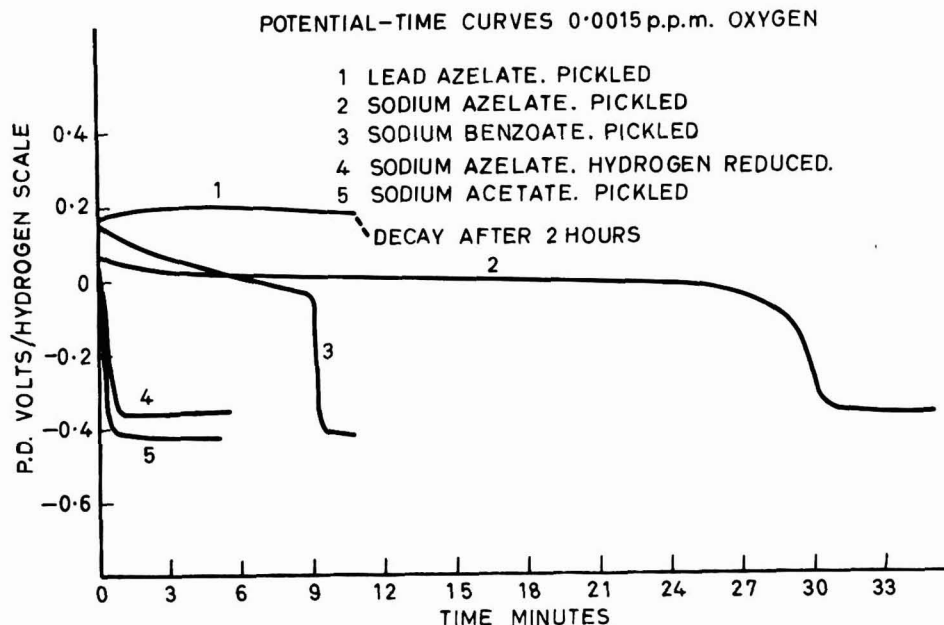


Fig. 3. Potential/Time curves for unpolarised iron specimens immersed in solutions containing 0.0015 p.p.m. oxygen: 1. Lead azelate, pickled; 2. Sodium azelate, pickled; 3. Sodium benzoate, pickled; 4. Sodium azelate, reduced in hydrogen; 5. Sodium acetate, pickled

#### *The breakdown of the air-formed oxide film*

The possibility that the air-formed oxide film broke down in solutions of pH 4.8 by a process of direct solution was next examined.

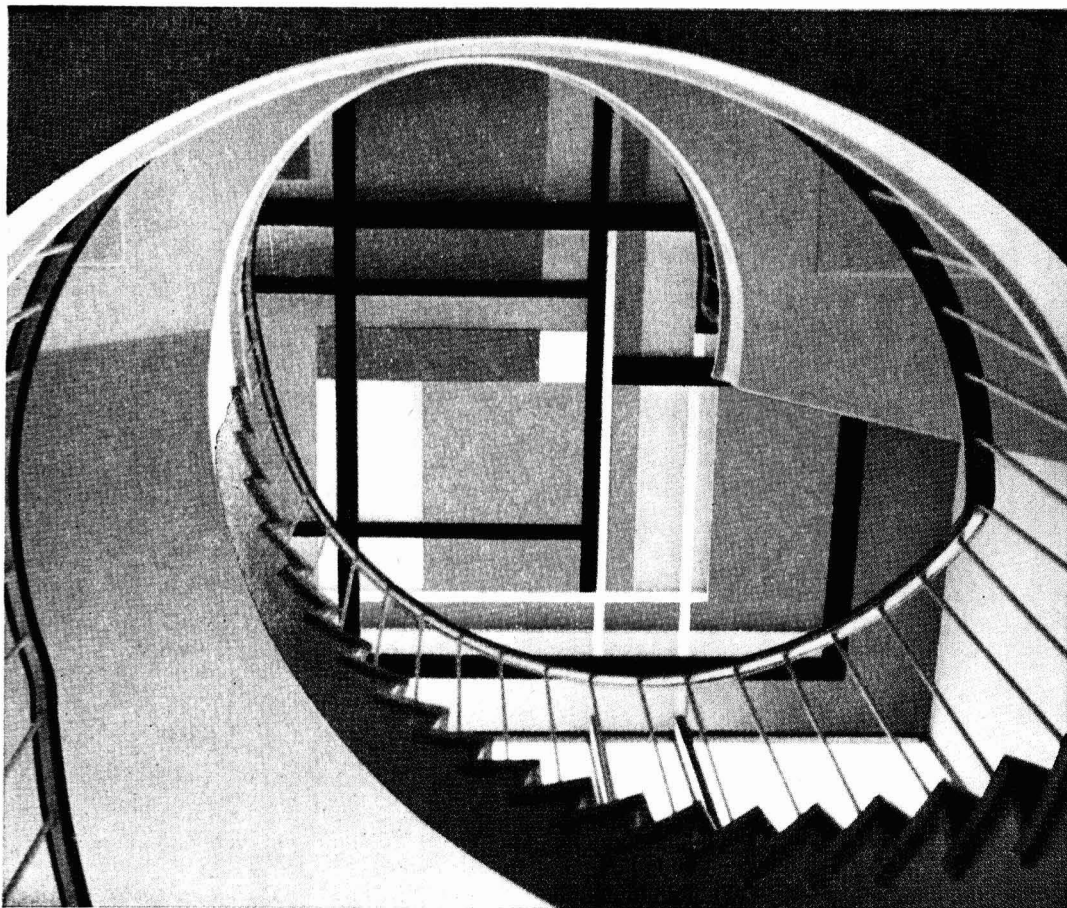
A suitable oxide, containing ferrous ions, was prepared by heating ferrous oxalate in nitrogen in the manner already described<sup>5</sup>. Analysis indicated that it was free from metallic iron. Portions of about 0.5 g., of the oxide were suspended for two hours in deaerated 0.1 N solutions of sodium acetate, benzoate and azelate, of oxygen content 0.003 p.p.m., by means of a stream of nitrogen passing through a sintered glass disc. The solutions were then removed by suction and analysed for ferrous and ferric ions. In the case of sodium benzoate and azelate, no ferrous or ferric ions could be detected in solution at the end of this period, but the sodium acetate solution contained 0.03-0.04 p.p.m. ferrous iron after 40 minutes contact with the solid oxide.

It was concluded that film breakdown in sodium azelate solutions of pH 4.8 did not proceed by direct solution, but by a process of reductive dissolution similar to that which is operative in solutions in the pH range 6-13.

#### *The oxidation of ferrous ions*

In an earlier paper<sup>6</sup> it was suggested that 0.1 N sodium benzoate and sodium acetate inhibited the corrosion of iron in the pH range 6-9 by stimulating the oxidation of ferrous ions by dissolved oxygen, and the possibility that inhibition by sodium azelate proceeded in a similar manner was next investigated.

Iron specimens were anodically polarised, after removal of the air-formed oxide film by cathodic reduction, in deaerated solutions, 0.003 p.p.m. oxygen,



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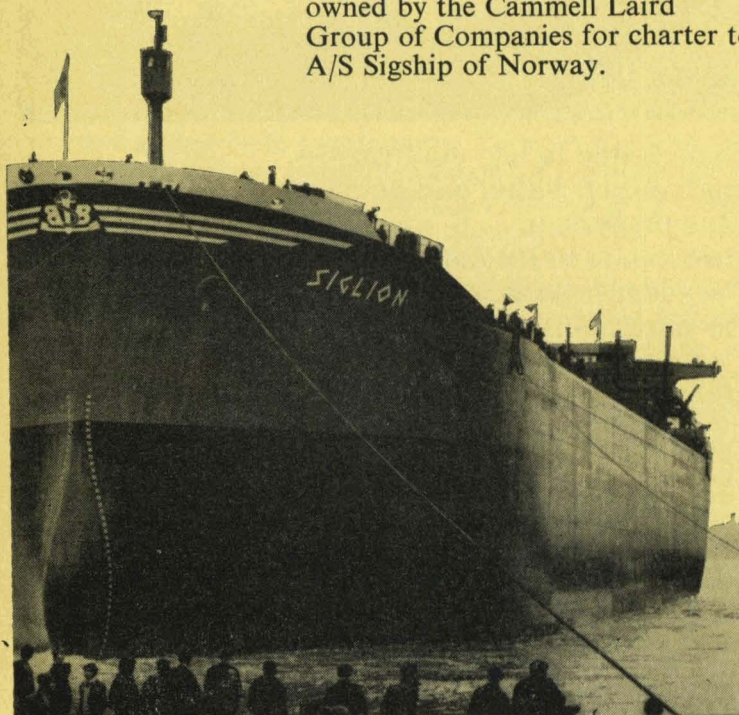
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until a concentration of about 50 p.p.m.  $\text{Fe}^{++}$  had passed into solution. Portions of the solution were run into about 200 ml of a similar solution, which was saturated with air, so that the final concentration of ferrous ions was about 2.5 p.p.m. and the rate of oxidation of the ferrous ions was measured by the analysis of samples taken over a period. It was found that in solutions of sodium benzoate, acetate and azelate, pH 4.8, the rate of oxidation was independent of the nature of the anions and was only of the order of 1 per cent after two hours, Fig. 4, curve 1.

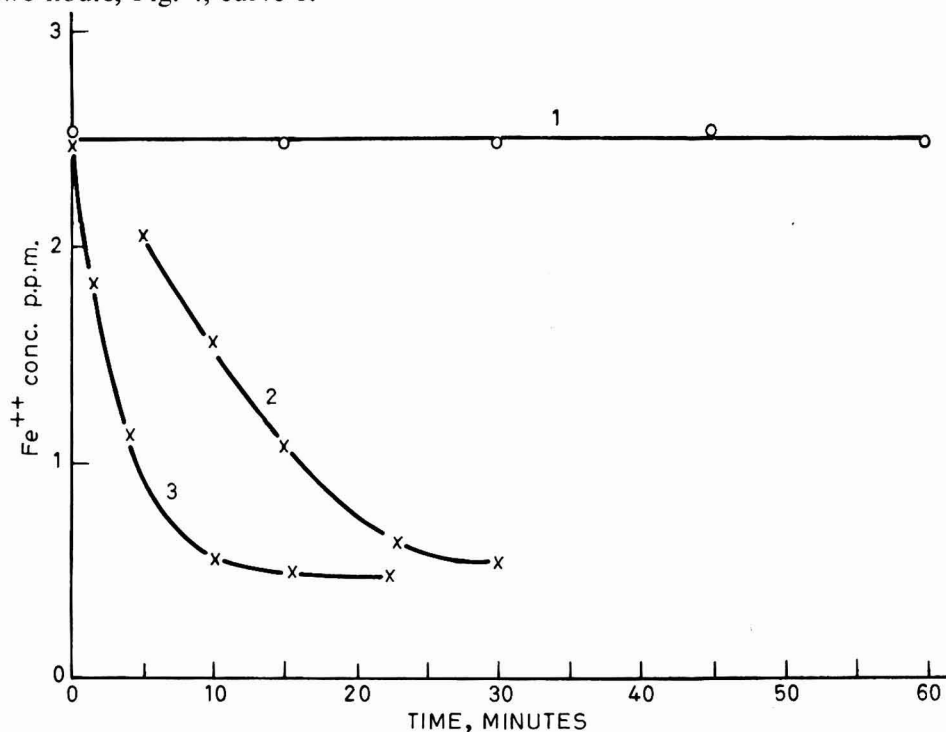


Fig. 4. Rate of oxidation of ferrous ions in the presence of : 1. Sodium benzoate and azelate ; sodium acetate alone and in the presence of lead acetate and of litharge ; 2. Sodium acetate and metallic lead ; 3. Sodium azelate and metallic lead

#### *The solubility of the ferric salts*

In order to account for the difference in behaviour of solutions of sodium azelate, benzoate and acetate at pH 4.8 there remained the possibility that their ferric salts differed in solubility. Attempts to measure the solubility of precipitated ferric azelate and ferric benzoate at pH 4.8 were unsuccessful owing to the presence of colloidal material. However, it was decided to determine the pH of precipitation of the ferric compounds ; consequently N/40 solutions of the acids were prepared where possible. (In the case of pelargonic and sebacic acids the solutions were only N/150.) To 50 ml of each solution 2 ml of N sulphuric acid was added, followed by 1 ml of saturated ferric chloride solution and this mixture was titrated against N/20 sodium hydroxide. The pH at which a stable precipitate, generally of a brick red colour, was first formed was recorded

and is shown in Table 2, together with the results obtained when the addition of the organic acid was omitted. The composition of the precipitate formed under these conditions is not known, but it is clear that the ferric compounds of the long chain aliphatic acids are less soluble than those of acetic and of benzoic acid and that there is some evidence that the solubility decreases with increase in chain length.

Table 2  
*pH values of the formation of an insoluble ferric compound*

Nature of anion				pH of formation of a precipitate
Pelargonate	N/150	1 C 9	..	1.82
Oenanthate	N/40	1 C 7	..	2.05
Sebacate	N/150	2 C 10	..	1.80
Azelate	N/40	2 C 9	..	1.79
Suberate	N/40	2 C 8	..	1.95
Pimelate	N/40	2 C 7	..	2.12
Adipate	N/40	2 C 6	..	2.20
Glutarate	N/40	2 C 5	..	2.29
Acetate	N/40	1 C 2	..	> 4.5
Benzoate	N/40		..	2.34
Blank			..	2.54

#### *Inhibition by 0.1 N sodium and calcium azelate, pH 4.8*

It had been found that when iron, carrying its air-formed film, was immersed, in the absence of air, in 0.1 N sodium or calcium azelate, pH 4.8, the air-formed film broke down. The breakdown was not due to direct solution of the oxide film, but to a process of reductive dissolution.

In the presence of oxygen, the iron surface became coated with an insoluble ferric compound, which was not a good electronic conductor, and consequently could not be readily cathodically reduced; breakdown by reductive dissolution was therefore suppressed and the original air-formed oxide film was reinforced and thickened by this ferric compound until it became impervious to ions.

#### **The inhibitive action of lead azelate**

Earlier work had indicated that the lead salts of the long chain mono- and di-basic acids were more efficient inhibitors of the corrosion of iron in the pH range 4.6-6.0 than the corresponding sodium and calcium salts<sup>3</sup>, lead azelate being one of the most effective.

The earlier observation that lead azelate brought about a thickening of the air-formed oxide film has been confirmed, Table 1, and it has been found that oxygen is necessary for inhibition to take place, since film breakdown occurred in solutions containing only 0.0015 ppm oxygen, Fig. 3, curve 1.

#### *The oxidation of ferrous ions*

It has already been shown that in 0.1 N sodium and calcium azelate, pH 4.8, the oxidation of ferrous ions by atmospheric oxygen proceeds very slowly and appears to be independent of the nature of the anion, but the possibility that lead might affect this reaction was next examined.

The experiments were carried out in a similar way to those described earlier with solutions of sodium benzoate, acetate and azelate. A 0.1 N solution of sodium acetate was used to which was added :

1. 40 ppm lead as lead acetate ;
2. 0.1 g finely ground litharge;
3. Finely divided lead, prepared by the electrolysis of lead acetate solution with a platinum cathode.
4. 0.5 g lead powder.

The solution was sufficiently well buffered to remain at pH 4.8-5.0 during the experiment and in all cases the total iron in solution was determined at the end of each experiment, to ensure that there was no loss by adsorption or exchange.

It was found that lead ions and litharge had no effect on the oxidation of ferrous ions ; however, in the presence of metallic lead the oxidation proceeded at an increased rate. In the experiments with lead powder the rates of oxidation depended on the rate of stirring the solution, but a typical set of results for both sodium acetate and sodium azelate is shown in Fig. 4, curves 2 and 3.

In order to confirm the effect of traces of metallic lead on the surface of the specimen, four pickled iron specimens were stored for two days in a desiccator over  $\text{CaCl}_2$ , and immersed in  $2 \times 10^{-4}\text{N}$  sodium azelate. A similar set of specimens was immersed in the same solution after they had been lightly rubbed with a stick of pure lead. After six weeks immersion the four specimens carrying the deposit of lead were unattacked and no lead could be detected in solution ; whereas, in the case of the untreated specimens, three out of the four were badly corroded.

#### *The cathodic reduction of oxygen*

The cathodic reduction of oxygen on iron specimens carrying their oxide films, and similar specimens, which had been lightly rubbed with a stick of " Analar " lead, was examined in 0.1 N sodium azelate, pH 4.84, in the presence and absence of 0.2 per cent hydrogen peroxide. The experiments were carried out in an open 100 ml rectangular jar and the solutions were continuously aerated, at a point remote from the specimen, by the passage of air through a sintered glass disc. The results obtained are shown in the form of a Tafel plot in Fig. 5, that is to say that the potential of the specimen has been plotted against the logarithm of the current density. Curve 1 refers to an iron electrode in sodium azelate, curve 2 to a similar specimen carrying a surface deposit of metallic lead ; whilst curves 3 and 4 were obtained with similar specimens immersed in 0.1 N sodium azelate, containing 0.2 per cent hydrogen peroxide.

It should be noted that the slope of the curve is steeper for an iron specimen than for one carrying a deposit of lead in aerated sodium azelate solution, but that the reverse is true in the presence of hydrogen peroxide. This indicates that oxygen reduction is less polarised, i.e. can take place more easily, on a lead surface than on iron oxide and that the reverse is true for the reduction of hydrogen peroxide. This behaviour in hydrogen peroxide may be due to the fact that at pH 4.84 iron oxide is a very efficient catalyst for the decomposition

of hydrogen peroxide, whereas in the presence of lead it will be relatively more stable.

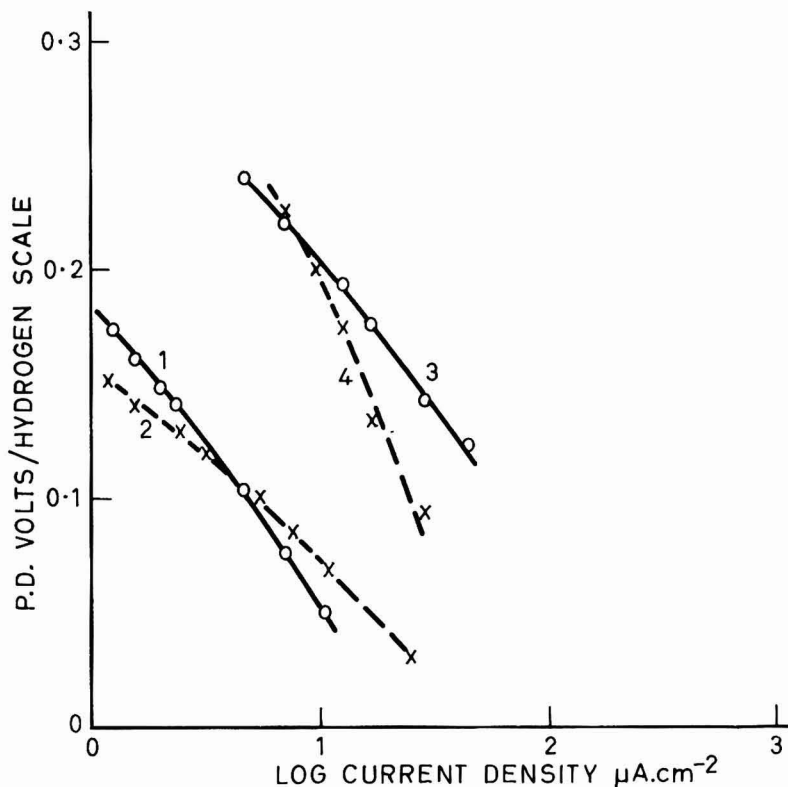


Fig. 5. Variation of the potential with the logarithm of the current density for : 1. Iron in sodium azelate ; 2. Iron with a deposit of lead in sodium azelate ; 3. Iron in sodium azelate with hydrogen peroxide ; 4. Iron with a deposit of lead in sodium azelate with hydrogen peroxide

A possible explanation of the enhanced rate of oxidation of ferrous ions by atmospheric oxygen in the presence of metallic lead may be that at pH 4.84 oxygen is reduced at a lead cathode to produce hydrogen peroxide. The anodic reaction would be lead ions passing into solution. The hydrogen peroxide could then oxidise the ferrous ions to the ferric condition.

#### *Inhibition by lead azelate*

Pure iron is not attacked when immersed in water containing 5-20 ppm lead azelate, depending on the conditions of immersion. At this concentration, inhibition cannot be attributed to the repair of the air-formed oxide film by the formation of a complex azelate, as in the case of 0.1 N sodium and calcium azelate, but it appears to be associated with the thickening of the air-formed oxide film.

It seems possible that, initially, lead ions in solution may provide an alternative cathodic reaction to oxygen reduction, and then, on being reduced to metallic lead at the cathodic areas on the iron surface, depolarise the oxygen



reduction reaction, thus keeping the current density sufficiently high to maintain ferric film formation. In addition any hydrogen peroxide so produced may assist in keeping the iron ions in the oxide film in the ferric condition, so that thickening of the air-formed film takes place until it becomes impervious to iron ions.

### Acknowledgment

The authors wish to thank Drs. U. R. Evans and J. N. Agar for their helpful comments and Mr. C. A. J. Taylor for preparing the diagrams.

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### Discussion at the Scarborough Conference

DR. J. A. W. VAN LAAR pointed out that iron oxide had been prepared from ferrous oxalate and suspended in solutions of the sodium salts or organic acids.

He could not see how the presence or absence of ferrous ions in the suspension could prove anything for the reaction of iron oxide on the steel, which was electrochemical. The experiment with the suspension would prove that the ferrous salts of the organic acids involved were more or less soluble, but not that ferrous oxide had developed in the suspension to a greater or less extent under influence of organic anions of the acids, a process which would be difficult to imagine.

DR. J. E. O. MAYNE replied that in earlier work ; (*J. Applied Chem.*, 1961, **11**, 170) it was shown that, in the case of aluminium, corrosion was associated with the initial rate of solution of the anhydrous oxide film, except in the presence of chloride ions. On the other hand the air-formed film on iron did not break down by direct solution, but in the pH range 6-13, by a process of reductive dissolution ; (*Brit. Corros. J.*, 1965, **1**, 102). The pH range in which inhibition took place had now been extended to 4.8 and it was necessary to find out whether breakdown was by a process of direct solution in this lower pH range. In short, Dr. van Laar had assumed that breakdown was electrochemical, whereas it had been felt that it was necessary to eliminate the possibility that breakdown was by direct solution, as with aluminium, before an electrochemical mechanism was considered.

DR. VAN LAAR asked if the resistance to rust by real paints could be improved by addition of some of the components indicated in the paper.

DR. MAYNE said that they had been concerned with the mechanism of inhibition and had made no efforts to exploit their conclusions. However, Evans, in "The Corrosion & Oxidation of Metals" (Edward Arnold, 1960, p. 550), had examined the possibility.

It appeared that lead azelate functions as an inhibitive pigment only in very porous vehicles. In a red lead paint the vehicle was producing inhibitive material continuously and consequently it could reach the metal surface more easily. It appeared that, if improved paints were to be made, then the lead would have to be present in the vehicle.

MR. D. M. JAMES asked whether Dr. Mayne considered that inhibition by lead azelate was the full explanation of the inhibitive powers of paints containing basic lead pigments. If this was so, and as the solubility of lead azelate was extremely small, would it lead to the conclusion that a very small concentration of basic lead pigment was needed in an oil film to give protection? In practice, a great deal was used, but it did not seem that this should be necessary.

DR. MAYNE agreed that, for inhibition, only a small quantity of lead azelate was required, but the problem was to get it in the right place at the right moment. It was well known that much of the red lead in a red lead paint was inoperative, and it followed that it should be possible to make a vehicle which gave the equivalent performance of a paint containing a large amount of red lead.

DR. L. VALENTINE (CHAIRMAN), asked if Dr. Mayne would comment on the use of lead pigments in non-oxidative drying media, and whether any of the explanations of anti-corrosive action in the case described appertained.

DR. MAYNE said that in the absence of soap formation, e.g. with chlorinated rubber, red lead inhibited by virtue of its solubility; in the absence of carbon dioxide an aqueous extract might have a pH as high as 11, which was sufficiently high to inhibit corrosion. Red lead in chlorinated rubber yielded protective films, but he had always suspected that a contributing factor might be the stabilising action of lead compounds on the decomposition of chlorinated rubber.

DR. J. B. HARRISON said that ferrous substrates normally were exposed to rainwater. What would Dr. Mayne's polarisation curves look like if they were done in rain water?

With the passage of time, red lead was being used in more and more media. He would not pick red lead/chlorinated rubber as an ideal example, but he had recently done extensive work in urethane oils. These were virtually non-hydroxylic and non-acidic. Red lead performed well in them. This supported azelate formation during drying, rather than soap formation during grinding.

Also, early theories of inhibition on steel substrates were based on very imperfectly prepared surfaces, and now, with good grit blasting on a given primer, there was such a marked improvement in performance that ideal conditions were approached.

He would like to have the lecturers' opinions on whether or not they could now translate this work to "impure" solutions, and whether it would be at all feasible to do follow-on work.

DR. A. J. APPLEBY replied, using as his basis a perfectly ordinary red lead linseed oil paint. It seemed, from further work, that this appeared to be the best system, from the point of view of the criteria established in the paper. This might not mean much in practice. However, a red lead system was not such a bad thing in practice, probably because, in an industrial atmosphere, it was capable of taking up sulphur dioxide by forming sulphates, and that lead sulphate, being very insoluble, prevented sulphate ions having any effect on what went on underneath the film; sulphate ions were extremely destructive. In an atmosphere which contained chloride ions, however, near the sea, one would not expect this paint to behave well.

As far as painting on rusty surfaces was concerned, this would trap a great deal of foreign material such as ferrous sulphate; this would not help inhibition. There must be a perfect oxide film on the surface of the specimen. If so, inhibition, and growth of a film of a complete azelate, could occur. If there were no oxide film at all, and specimens were immersed in azelate solutions at pH 4.6, they just corroded; they would

inhibit in a highly oxygenated azelate solution, but it was very difficult to get things to inhibit at pH 4.6 under any circumstances. Therefore, he stressed that a good oxide film ought to be present on the surface of the specimen, which meant an invisible oxide film, and not thick mill scale and not a rusty surface, which could trap considerable quantities of ferrous sulphate for instance, which provided an extremely good electrolytic path to allow corrosion to take place under the paint.

MR. M. SOLOMKA asked if Dr. Mayne envisaged any practical use of these compounds as corrosion inhibitors outside the coatings field—for example, in water cooling systems.

DR. MAYNE said that the lead salts of the long chain mono- and di-basic acids might be very suitable for the inhibition of corrosion in water cooling systems.

He added that this inhibition, brought about by an incomplete layer of lead, might be very similar to that obtained with a very thin layer of tin ; (S. C. Britton, *JOCCA*, 1950, 33, 125).

DR. W. FUNKE said that he had been involved in investigations on these lines many years ago, and he was interested in the mechanism of the protective action of these organic dicarboxylic acids on iron surfaces. It had been stated that complexes would be formed. He had found that carboxylic acids were not such good inhibitors as dicarboxylic acids, and perhaps this might be connected with the fact that ferrous and ferric ions were polyfunctional, whilst the dicarboxylic acids were bifunctional. Perhaps some polymer complex was formed at the iron surface. Had any indication of such an explanation for the inhibitive activity been seen ?

DR. APPLEBY replied that the complex on the surface was a polymer complex. No literature reference had been found to iron complexes of the higher di-basic acids, and it was conceivable that some kind of polymer complex was formed on the surface. This almost certainly incorporated hydroxyl ions, otherwise it could not come down into this range, and it was obviously a material of very low solubility, and the solubility decreased as one ascended the table.

DR. FUNKE said that the salts of such carboxylic acids had been found to inhibit corrosion only if the acids had dissociation constants above  $K = 10^{-4}$  to  $10^{-5}$ . The salts of stronger acids corroded instead of inhibiting.

DR. A. J. APPLEBY felt that the shorter chain acids formed complexes which were more soluble and that one or two other reactions might be associated with the inhibition. He did not believe that everything depended on the presence of the film of lead in the case of the lead soap, or that everything depended on the presence of the complex. It was often noticed that some specimens, when placed in a fairly innocuous salt solution, sometimes failed to corrode at all, and this must be due to the fact that they had a particularly resistant oxide or to some unknown causes. Possibly the azelate was acting as a second line of defence, and the lead as a third line of defence in this system.

It was important that, in an azelate, the  $pK_a$  values of azelaic acid were about 4.6 and 5.6, which meant at the pH of the experiments it was an extremely good buffer solution, and Hoar had pointed out many years ago that in a buffer solution corrosion was very much less likely. One of the contributing factors of the acid was probably the fact that it was not buffering at this pH and that would tend to make corrosion more likely.

DR. FUNKE said that the investigations reported were of considerable practical interest because the action of carboxylic acid groups at the film/substrate interface might be involved in adhesion as well as corrosion inhibition, and there were carboxylic acid groups in many paint vehicles. Not much was known about how these groups acted in contact with the iron surface, especially in the case of the new water soluble

vehicles used in electro-deposition ; some special effects of these carboxylic acid groups at the iron surface would be expected.

DR. APPLEBY thought this was probably true. Carboxylic acid groups in general, if they were attached to long chains, did certainly form complex ferric materials, and it seemed likely that the interface between a paint containing carboxylic acid groups and the ferric oxide surface probably consisted of some complex, which might explain some of the properties which were notable in these materials.

DR. R. BULT said that at Verfinstituut TNO workers had had some experience with red lead oil paints. The same type of paint was applied to freshly blasted steel, and to steel also blasted but weathered afterwards for a period of time, and finally wire brushed to remove loose rust. The corrosion resistance was then determined in both cases. It appeared that the corrosion resistance of the red lead oil paint on the rusted steel was much better than on the freshly blasted steel panels. Had this something to do with the oxide film which had been mentioned ?

He added that the red lead paint was applied—in the case of the freshly blasted steel—fairly soon after blasting.

DR. MAYNE said it was possible that the inferior behaviour of the red lead paint on the freshly sand-blasted surfaces might have been due to the fact that the air-formed oxide film was still thin or contained numerous weak points ; whereas, after the specimens had been weathered the air-formed oxide film might have attained its equilibrium thickness.

DR. VALENTINE suggested that there might have been a difference in surface roughness in the two cases, and asked if the specimens were otherwise identical.

DR. BULT said, in this case, the difference in the surface roughness was not very large. Because the weathering was in a mild atmosphere, the panel was not corroded very badly, just superficially. He did not think the degree of surface roughness was different.

DR. APPLEBY said that, as sulphur was not present, the explanation might be that it was a fairly innocuous type of rust, and it was probable that, on that particular surface, things did not wear badly, whereas on the grit-blast there was extremely thin oxide film, and this eventually did break down into rust.

# Testing of titanium dioxide pigments in paints for dispersion, weathering resistance, and optical properties\*

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## Summary

Ten rutile and two anatase pigments have been tested, each in four different degrees of dispersion, for their scattering coefficient, weathering resistance, quality of dispersion and gloss. Light stability has been determined by mandelic acid and crystal violet methods. Dispersion in paint films has been studied by means of electron photomicrographs. Weathering resistance tests have been performed in Marr apparatus and followed by gloss measurements and surface replica electron photomicrography. A new method for the determination of chalking degree using X-ray fluorescence analysis is described. It has been found that gauge readings and texture rating are of limited practical value as indicators of quality of dispersion. The development of gloss follows similar lines to the scattering coefficient in the case of easily dispersing pigments; the gloss of standard pigments seems to be less affected by the quality of dispersion than the *S* value. Gloss readings of weathered surfaces may be misleading if compared with corresponding replica photographs; more damaged surfaces have sometimes been found to give higher gloss readings.

## L'essai des pigments du dioxyde de titane en feuillets de peinture à l'égard de leur dispersibilité, résistance aux intempéries, et propriétés optiques

### Résumé

On a examiné dix pigments de type rutile et deux anatase, chacun à quatre niveaux différents de dispersion, afin d'évaluer leur coefficient de diffusion, résistance aux intempéries, qualité de dispersion et de brillant. La stabilité à la lumière a été déterminée à l'aide de l'acide mandélique et du cristal violet. La dispersion dans des feuillets de peinture a été étudiée au moyen des micrographies électroniques. Les essais de résistance aux intempéries ont été effectués avec l'appareil Marr, suivi par les mesures du brillant et la micrographie électronique des répliques superficielles. On décrit une méthode nouvelle pour déterminer le degré de farinage par l'analyse de fluorescence des rayons X. On a trouvé que les lectures de jauge et des taux de texture n'ont qu'une valeur limitée en pratique pour indiquer la qualité de dispersion. Dans le cas des pigments de bonne aptitude de dispersion, le développement de brillant présente un comportement semblable au coefficient de diffusion. Le brillant que présentent des pigments ordinaires paraît moins affecté par la qualité de dispersion que par la valeur *S*. Les lectures de brillant des surfaces vieillies peuvent être trompeuses lors on les compare des photographies de répliques correspondantes; on a trouvé, quelquefois, que des surfaces assez détériorées peuvent rendre les lectures élevées de brillant.

## Prüfung auf Dispersion, Wetterfestigkeit und Optische Eigenschaften von Titandioxyd Pigmenten in Anstrichfilmen

### Zusammenfassung

Zehn Rutil und zwei Anatas Pigmente, jedes in vier verschiedenen Dispergierungsgraden, wurden auf ihre Streuungskoeffizienten, Wetterbeständigkeit, Dispergierungsqualität und ihren Glanz geprüft. Lichtbeständigkeit wurde mittels der Mandelsäure- und Kristallviolett-

\*Presented at the Scarborough Conference, 22 June 1967.

methoden bestimmt. Die Dispersion in Anstrichfilmen wurde mit Hilfe von Elektronenmikrobildern studiert. Wetterbeständigkeitsversuche wurden im Marr Apparat vorgenommen mit anschließenden Glanzmessungen und die Oberflächen wiedergebender Elektronenmikrographie. Eine neue Methode zur Bestimmung des Abkreidungsgrades vermittels Röntgenfluoreszenzanalyse wird beschrieben. Es wurde gefunden, dass Grindometermessungen und Texturbewertung nur beschränkte Bedeutung als Indikatoren der Dispersionsgüte besitzen. Die Glanzentwicklung der leichtdispergierbaren Pigmente geht analog der des Streuungskoeffizienten vor sich ; der Glanz von Standardpigmenten wird scheinbar weniger von der Qualität der Dispersion als vom *S*-Wert beeinflusst. Glanzwerte bewitterter Oberflächen können irreführen, wenn man mit Photographien von Nachbildungen vergleicht : es wurde gefunden, dass stärker beschädigte Oberflächen in einigen Fällen höhere Glanzwerte ergaben.

### **Испытания пигментов двуокиси титана ( $TiO_2$ ) в красочных пленках на дисперсию, сопротивление к выветриванию и оптические свойства**

#### *Резюме*

Десять рутиловых и два анатазовых пигмента испытывались каждый в четырех различных стадиях дисперсии, коэффициента рассеяния, сопротивления к выветриванию, дисперсионного качества и блеска. Светоустойкость определялась методом миндальной кислоты и кристаллическим фиолетовым методом. Дисперсия в красочных пленках изучалась при помощи электронной микрофотографии. Испытания сопротивления к выветриванию производились на аппарате Марра с последующими измерениями блеска и поверхностными электронными микрофотографическими снимками. Описывается новый метод определения степени известкования применяя рентгенофлуоресцентный анализ. Обнаружено что размерные и текстурные показания не имеют большого практического значения как указатели дисперсионного качества. Развитие блеска следует тому же процессу как и коэффициент рассеяния в случае легко дисперсирующих пигментов; блеск обычных пигментов повидимому меньше подвергается влиянию качества дисперсии чем значение *S*. Показания блеска выветренных поверхностей могут быть обманчивы по сравнению с соответствующими модельными снимками; найдено что более поврежденные поверхности давали показания более высокого блеска.

#### **Introduction**

It is theoretically known and accepted that a white pigment, such as titanium dioxide, reaches its optimum relative efficiency in paints, at least so far as its optical properties are concerned, with a complete dispersion of pigment particles and without any agglomerate formation. This again depends on two factors that are inversely proportional, milling technology and the pigment itself : the more easily a pigment disperses, the less mechanical work is required for this purpose. Due to competition on the pigment market, the trend is continuously towards more and more easily dispersible pigments, thus saving the time and investments of paint manufacturers.

In this work a series of ten commercial rutile and two anatase pigments was studied ; these pigments represent a wide selection regarding manufacturing techniques, of which different methods of after-treatment are of special importance (Table 1). The pigments themselves were examined for light stability using two different methods. Test paints were prepared representing four different degrees of milling effectiveness. The quality of dispersion of all 48 samples was determined as well as scattering coefficient (hiding power) values and weathering resistance. A new method based on the use of X-ray fluorescence analysis is proposed for an exact evaluation of the chalking phenomenon.

Table 1  
Test pigments

	FINN-TITAN grade	Description; main applications	Rel. tinting strength	Modified by	Remarks
A1	AP	Uncoated anatase ; paper quality	1,300		
A2	AF	Coated anatase ; paper coatings, synthetic fibres, and indoor paints	1,300		
R1	RDI	Coated rutile ; high gloss paints, printing inks .. .. .	1,850	Al, Si	Zn-free
R2	RD	Coated rutile ; standard grade ..	1,800	Al, Zn, Si	
R3	RR	Coated rutile ; standard grade for outdoor paints .. .. .	1,700	Al, Zn, Si	
R6	RRS	Coated rutile ; improved grade of RR for, e.g. automotive enamels	1,800	Al, Zn, Si	
R8	RR2	Coated rutile for high speed dispersion, RR-type .. ..	1,750	Al, Zn, Si	
R9	RF	Coated rutile ; rubber, floor coverings .. .. .	1,750	Al, Zn, Si	
R10	RU	Uncoated rutile .. .. .	1,650	Zn	
R4	}	Pigments of type R3 .. ..	1,600	Al, Zn, Si	
R5			1,700	Al, Si	
R7		Pigment of type R6 .. ..	1,800	Al, Zn, Si	

## Methods of testing

### Light stability

Photochemical activity is commonly tested by the mandelic acid method proposed by Jacobsen<sup>1</sup>. The silver nitrate method examined, e.g. by Sbrolli and Bertotti<sup>2</sup>, is also rather popular. Weyl and Förland<sup>3</sup> developed a method based on the formation of crystal violet, a strongly coloured dye, under the influence of atomic oxygen liberated as a result of photochemical reactions. This procedure was also used by Poisson *et al.*<sup>4</sup>

In the present work the mandelic acid and crystal violet methods were selected for light stability tests.

For the mandelic acid tests the sample was prepared by mixing 5 grams of pigment and 3 ml of 0.5 M aqueous solution of mandelic acid. This mixture was worked with a spatula into a paste, which was spread on a glass plate measuring 10 cm × 10 cm. Another glass plate of equal size was pressed against the specimen to form an even paste layer between the two plates. The edges were sealed by means of adhesive tape to prevent drying of the paste and access of air. The specimen plates were exposed to radiation

from a UV-lamp (Model PL 334, Original HANAU, wavelength maximum 366 m $\mu$ , energy input 0.5 kW, distance 20 cm). Initial reflectance measurement of the specimen and further readings for discoloration were made by using a reflectance meter (Elrepho, Zeiss).

Sample preparation for the crystal violet tests was conducted as follows : a solution, 0.5 per cent in linseed oil, was prepared of the reagent, which is the leuco-base of crystal violet, 4,4', 4''-methylidynetris (N, N-dimethylaniline), having the formula  $[(\text{CH}_3)_2\text{NC}_6\text{H}_4]_3\text{CH}$  (Eastman, USA). Five grams of pigment and an amount of reagent solution corresponding to  $1.6 \times$  the oil absorption value of the respective pigment were worked into a paste on a glass plate under dark room conditions (red light). It was found that the visual evaluation of the colour formed during the exposure was best performed by using a suitable stable dye substance as an artificial standard. For the detection of the first faint appearance of colour, a stable white standard was also found useful. This was prepared from pure  $\text{TiO}_2$ -pigment and linseed oil. Colour standards were prepared by adding suitable amounts of "Permanentviolett RL Extra Pulver" (Farbwerke Hoechst) to a paste or paint pigmented with titanium dioxide. In some cases, better matching standards could be obtained by further addition of small amounts of "Heliogenblau B" (BASF). It is evident that this combination is not necessarily the best one ; for colour intensity comparisons, however, it served satisfactorily.

For testing, the pastes were drawn side by side on a glass plate. White standard was placed above these and a colour standard representing the weakest step was drawn under the test samples. Sample plates were exposed to light in two different ways :

- (a) Daylight, window facing north, at about 2 to 3 p.m. (month : August).
- (b) Exposure by means of a UV-lamp (as specified above), daylight excluded.

The development of colour was followed visually. The first sign could be detected by means of the white standard and weakest colour standard (I) on the test plate ; further increase of colour intensity was estimated by using colour standards marked II to V, the colour intensity difference between the steps being 40 per cent of the lower value. The standards I and II were only 10 per cent apart.

It was found that the colour development was dependent on the consistency of the paste ; hence, oil absorption of the pigment must be observed (Table 2). Absolute values obtained from daylight exposures varied, of course, from day to day, influenced by prevailing weather conditions, but mutual order of pigments regarding their photochemical activities remained constant.

The reaction between atomic oxygen and the reagent is a reversible one ; this must be taken into account in planning the tests. For instance, uncoated anatase with high photochemical activity showed no colour formation at all in direct sunlight, apparently because of the rate of the reversible reaction. The colour appeared first after the exposure.

The crystal violet method is more sensitive than the mandelic acid method, but less convenient in use, and is also influenced by secondary phenomena, e.g. colour formation by normal room illumination, and reversible reactions discussed above.



Table 2  
Oil absorption of test pigments

Pigment	Oil absorption ml/100 g
A1	27.8
A2	24.9
R1	20.4
R2	20.4
R3	22.2
R4	23.1
R5	22.2
R6	19.4
R7	20.4
R8	22.2
R9	24.1
R10	16.7

#### Quality of dispersion

Formulation of test paints :

60.0 grams of titanium dioxide pigment

14.3 grams of Soalkyd 3130\*

25.7 grams of white spirit

0.2 grams of Exkin 2†

were milled in a glass jar (300 ml) with 150 grams of glass ballotini (8 mm) for two, four, eight and 16 hours, respectively. Thereafter,

114.0 grams of Soalkyd 3130

6.5 ml of Drier (Pb/Co)

were added and milling was continued for an additional half-hour.

The PVC of this formulation is 15 per cent. Test paint formulation is based on a somewhat lower amount of solvent than usual, and consequently the viscosity of test paints is higher. It was found that better films for scattering coefficient (hiding power) determinations could be obtained in this way.

Thin paint films for optical microscopy and visual examination were prepared as follows : ten grams of test paint was weighed into a 50 ml beaker and 12.5 ml

\*Drying long oil soya oil modified alkyd resin by SOAB. Oil content approximately 62 per cent, phthalic anhydride content approximately 26 per cent ; 70 per cent solution in white spirit.

†ex Gebr. Borchers AG.

of white spirit added in small portions under continuous stirring to avoid pigment shock. Five ml of thinned paint was pipetted on to a glass plate (4 in  $\times$  4 in) rotated by means of a Paint Film Spinner (*ICI*). The rotation was continued for 12 seconds after the last drop of paint was applied. The film was dried at 75°C for ten minutes. A visual estimation of texture rating, i.e. the number of particles protruding through the film, was made in transmitted light using an arbitrary exponential scale from 5 (best) to 9. Test plates were further examined by taking optical photomicrographs in incident light at a small angle.

The effectiveness of grinding was followed in the usual way by taking gauge readings from different millings. A scale from 0 to 100 microns was used, the first gauge reading giving the location of the main population of particles, and the second the limit of larger particles (cf. Table 3).

**Table 3**

*Effect of grinding time on quality of dispersion, expressed as gauge reading in microns (first column), and as texture rating (second column): see text for explanation*

Pigment	Grinding time							
	2 hours		4 hours		8 hours		16 hours	
R8	0-5	7½	0-0	7+	0-0	5½	0-0	5½
R4	12-18	8-	5-9	7½	0-5	6+	0-0	5
A1	15-18	8-	10-13	7-	0-8	5	0-0	5+
R3	16-23	8	6-10	8	0-5	6+	0-0	6-
A2	18-25	>9	10-15	9	0-10	6½	0-8	5
R6	18-26	9	8-11	8+	0-5	8	0-0	5½
R9	18-26	>9	12-15	>9	0-11	5+	0-0	5+
R1	19-22	9-	9-12	9	0-0	7+	0-0	5+
R2	19-26	9-	12-17	9	0-6	7+	0-5	5½
R5	21-26	9	10-14	8+	0-10	8	0-5	5+
R7	22-32	>9	12-18	9	0-8	9-	0-0	6½
R10	28-42	n.d.	18-27	n.d.	13-18	n.d.	9-11	n.d.

(n.d.=not determined.)

#### *Scattering coefficient (hiding power)*

It has been shown by several authors that, so far as white pigments are concerned, the value of the scattering coefficient *S* alone is decisive and more characteristic of the pigment quality than hiding power, which includes light absorption phenomena as well. A detailed description of the method used by the author has been published elsewhere<sup>5</sup>; therefore the main steps of the procedure only will be listed.

Paint films were drawn on Moresst Contrast Cards (The Moresst Co. Panel Form 07P-Black on White,  $5\frac{1}{2}$  in  $\times$   $9\frac{3}{8}$  in ; thickness 0.010 in) by means of an Erichsen 25  $\mu$  applicator on a suction plate. Two cards were prepared from each sample. Reflectance measurements were made, using an Elrepho, Zeiss, remission photometer, equipped with its Y-(green) filter, of the white area of the card, of the dry paint film on white substrate, and of the film on black substrate. The thickness of paint film was measured by beta-ray absorption. Both measurements, reflectance and thickness, were made on exactly the same area of the card, circles 30 mm in diameter, very close together, separated by the black-white border only, to avoid any differences in film thickness. Scattering coefficient values were determined by using nomograms described elsewhere<sup>5, 6, 7</sup>. It has been found in practice that independent scattering coefficient determinations of one and the same paint show a maximum deviation of  $\pm 1.5$  per cent. It should be noted that the use of this method, especially the beta-ray absorption technique of film thickness measurement, results in considerable time saving ; e.g. in one particular case duplicate film thickness determinations were made of 46 cards, black and white separately, in less than two hours ; i.e. about  $2\frac{1}{2}$  minutes per card.

#### *Electron microscopy*

*Quality of dispersion* : For this study, test paints were drawn on glass plates and dried. Horizontal slices were then cut from the film using an ultramicrotome constructed by the author. The thickness of the slices was of the order of 0.5 micron. These slices were placed directly on to specimen grids of the electron microscope, and examined using an accelerating potential of 100 kV (microscope : Hitachi HU-11), and an initial electronic magnification of  $\times 4000$ .

*Surface replicas* : Surface replicas of paint films were prepared in a way already described by the author<sup>8</sup>. The following steps were involved :

- casting of the polyvinylalcohol film on to the panel,
- stripping of the dried film,
- shadowing with chromium and carbon,
- dissolving in hot water,
- catching the replicas on to specimen grids.

Thereafter the replicas were photomicrographed using an initial electronic magnification of  $\times 4000$  and an accelerating potential of 75 kV.

#### *Quantitative estimation of chalking*

There have been several attempts to develop an exact method for the determination of degree of chalking. Usually, however, this is carried out according to the well-known method by Kempf<sup>9, 10</sup>. The estimation can be made rather reliably at an early stage of chalking. To improve this method and to cover higher degrees of chalking, Ghanem<sup>11</sup> developed a technique based on successive "prints" to be taken from the surface. Garmsen<sup>12</sup>, and later Boers<sup>13</sup>, weighed the amount of loosened pigment, the former as matter washed away and separated, the latter as the weight loss of the test panel, hence providing a numerical expression for the phenomenon.

A rapid and reliable quantitative determination of most elements can be made using an X-ray fluorescence spectrometer. The sample holder of this instrument is constructed in a way that already suggests its possible application for an analytical study of chalking. A short description of the procedure only will be given together with some typical results.

Because the method is based on the determination of loosened  $\text{TiO}_2$ , no material containing titanium, e.g. photographic paper (Kempf), can be used in sample preparation. The following technique was found to be useful :

A solution of polyvinyl alcohol in water was spread on to the paint surface to be examined and allowed to dry. To protect the resulting film, it was covered with ordinary adhesive tape and stripped from the surface.

For the analysis, a circle of 25 mm diameter was placed into the specimen holder of the X-ray fluorescence apparatus (*Philips* all-vacuum spectrograph Model 1540). The intensity of the  $\text{TiK}_\alpha$ -radiation resulting from  $\text{TiO}_2$ -particles present was registered by electronic counters (as cps, counts per second).

Typical results from two experimental series are presented in Figs. 14a and b. It is to be noted that it is not necessary to express the absolute content of Ti in the film ; the cps-value itself is sufficient to enable one to follow the degree of chalking. A detailed description and analysis of the procedure will be published elsewhere.

#### *Weathering tests*

All tests were carried out in a Marr artificial weathering apparatus. For this test, stainless steel panels of 3 in  $\times$  6 in each were prepared from each of the test paints as follows : The viscosity of paints seven days old was adjusted, by adding white spirit, to  $140 \pm 5$  seconds as measured with Ford Cup No. 4. The paint diluted in this way was poured on to the panel in a paint film spinner and the panel was rotated for 45 seconds. On the next day another layer of paint was applied in the same way, whereafter the panel was allowed to dry for four days.

Gloss measurements were made from washed panels by means of a *Lange* gloss meter (type 259/II) at an angle of  $45^\circ$ , a polished black glass plate serving as a standard (=100). Each gloss value represents the mean of ten separate measurements. Test panels were further examined by means of surface replicas, and, where applicable, by absolute X-ray chalking determinations.

## **Results**

### *Light stability of pigments*

The results obtained by the mandelic acid method are presented in Figs. 1 and 2, where reflectance readings after one, two and three hours of exposure have been plotted against time. Initial reflectance of each pigment paste has been set to 100 per cent to facilitate the comparison. It can be seen that uncoated anatase (A1), due to its great photochemical activity, darkens rapidly and shows by far the lowest reading after three hours' exposure. Coated anatase, however, shows a remarkable stability, comparable with that of uncoated rutile ; both these pigments, of course, are weaker than most coated rutile grades. As expected, rutile pigments R3 and R6, also R5, R7 and R8, and

not quite expectedly, R9, show the highest light stability. The first-named ones are typical outdoor paint pigments with maximum weathering resistance ; R9, on the other hand, is not a typical paint pigment at all.

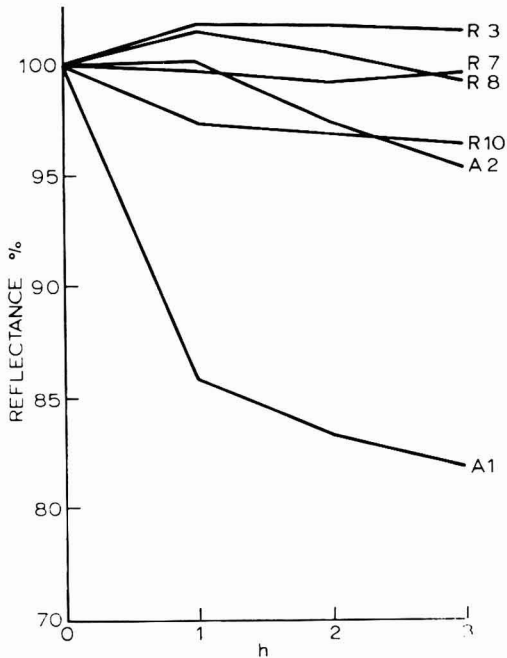


Fig. 1. Mandelic acid test results on pigments A1, A2, R3, R7 and R10. Initial reflectance value of each specimen has been set to 100 per cent

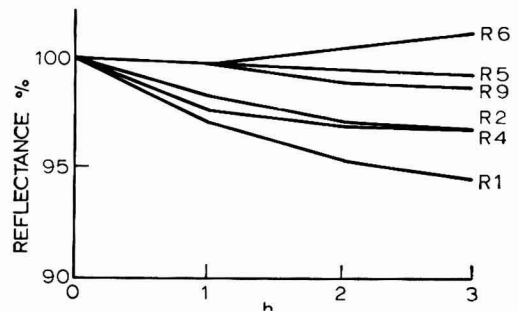


Fig. 2. Mandelic acid test results on pigments R1, R2, R4, R5, R6 and R9 (cf. Fig. 1)

Figs. 3 and 4 show the results of photochemical activity tests using the crystal violet (C) method. Representing in this case activity rather than stability, the curves run reversed if compared with the former figures, lower graphs corresponding to higher stability values. In these tests, uncoated anatase holds its position as the most light sensitive pigment both in daylight (d) and in artificial light (without subscript). Coated anatase A2 and uncoated rutile R10 follow, but the difference is more distinct than in the mandelic acid (M) test. As far as other grades are concerned, the order is not throughout the same if compared with the M-test, as can be seen from the following arrangement, where the pigments are listed according to improving light stability (a dash between pigment symbols means that grades are practically equal) :  
 M-test : A1, R1-A2, R10, R4-R2, R7-R9, R8-R5, R3-R6.  
 C-test : A1, A2, R1-R9, R10, R2-R3, R6, R8-R4-R5, R7.  
 (Daylight)

If these results are compared with each other, it can be seen that certain differences occur. Most interesting in this case, however, is to find out which one of these tests more closely predicts the weathering resistance achieved by using the same pigments in paints. The comparison is shown in Table 5.

The results obtained using artificial light exposure differ to some extent from those resulting from daylight exposures, but the order of pigments remains the same with one slight exception (R4 and R5 are equal when exposed to daylight, R4 being somewhat better than R5 in UV-light).

### Scattering coefficient

As stated above, hiding power of a pigment is determined, *inter alia*, by the quality of dispersion, and this in turn can be improved either by more effective milling or by improving the pigment itself. The values obtained for the scattering coefficient  $S$  as a function of grinding time are presented in Table 4. The most definite absolute as well as relative increase of the  $S$  value can be observed in the cases of R3, R5 and R4, which all represent standard rutile grades. The pigments R8 and R7, with improved dispersion properties, show the highest values after two hours' grinding, and these will not be definitely

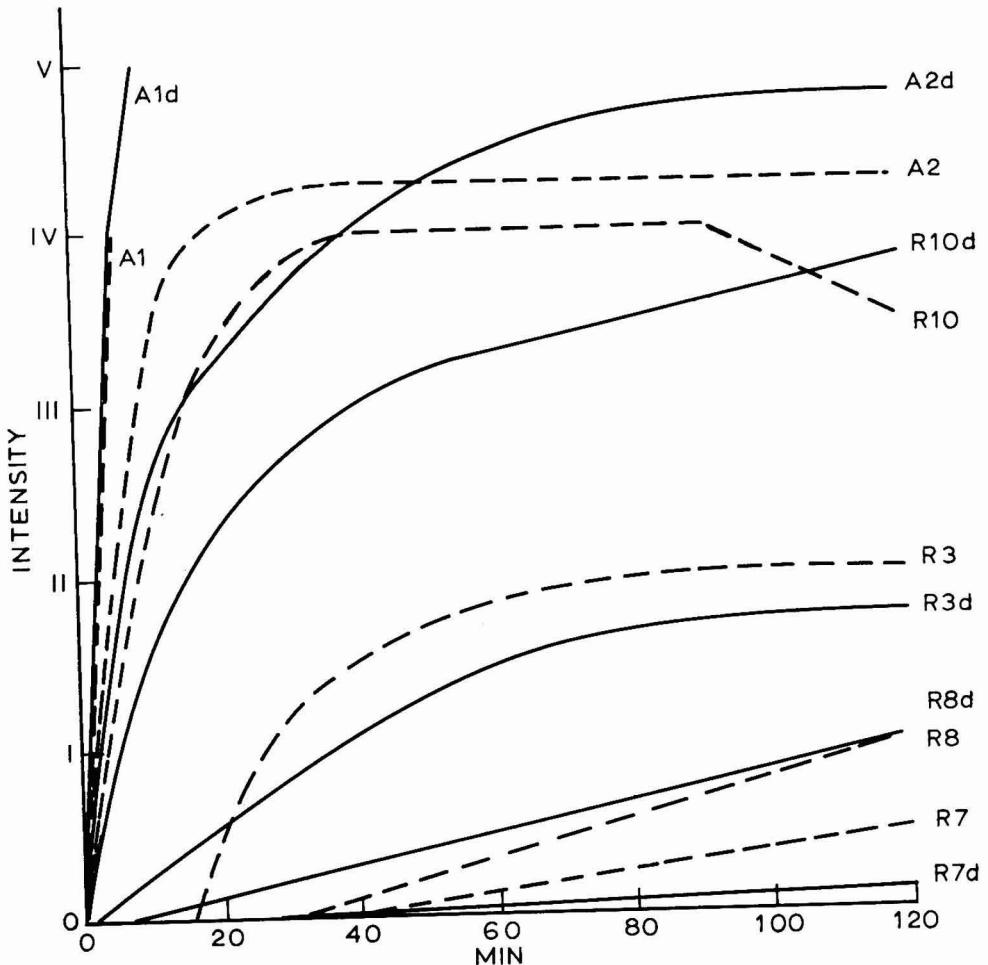


Fig. 3. Crystal violet test results on pigments A1, A2, R3, R7, R8 and R10 in UV light and daylight (marked with d)

improved by more effective milling. The pigment R6, a special grade, has a high initial value, and this situation is improved by milling, giving the second highest value for this pigment. In the author's opinion, these results are very informative so far as the interaction of pigment properties and effectiveness of grinding on the scattering coefficient are concerned. Finally, it should be noted that the averages of all *S* values also show a steady improvement with more effective milling.

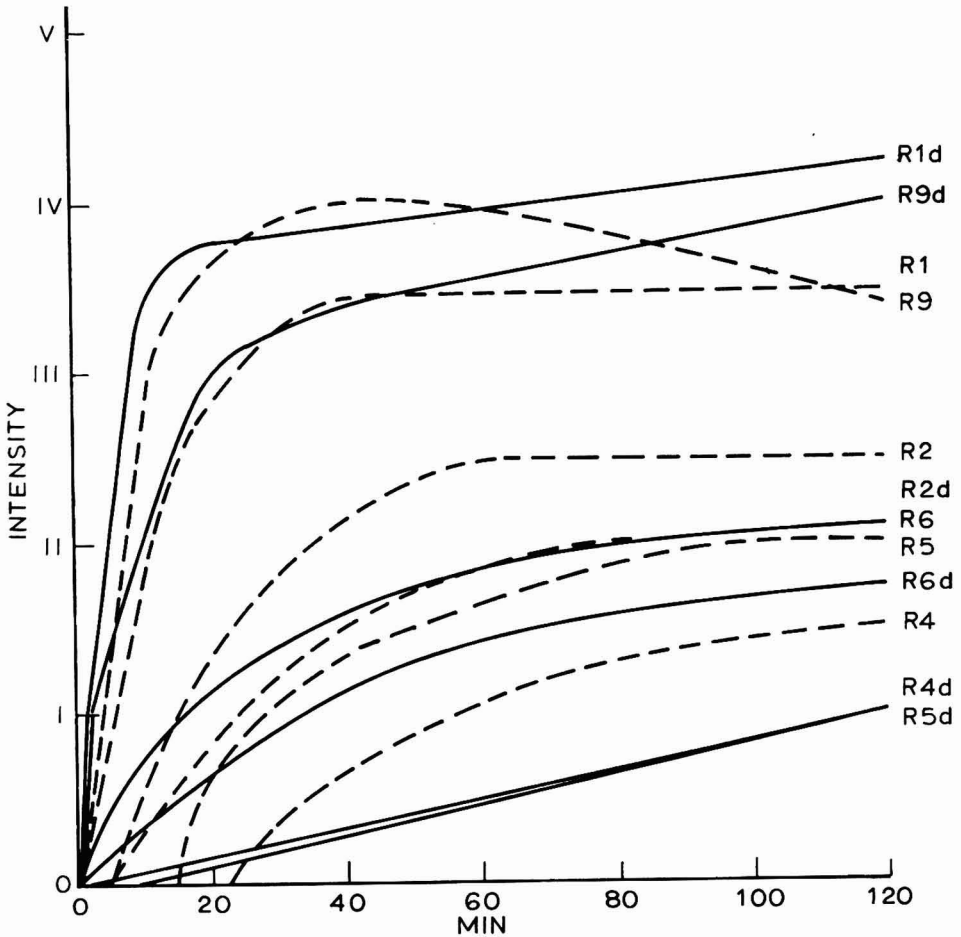


Fig. 4. Crystal violet test results on pigments R1, R2, R4, R5, R6 and R9 (cf. Fig. 3)

Table 4  
Effect of grinding time on scattering coefficient *S* of test pigments

Pigment	Grinding time			
	2 hours	4 hours	8 hours	16 hours
R1	235	236	239	245
R6	225	227	234	240
R7	233	233	234	236
R8	235	228	234	233
R2	218	222	222	225
R3	203	208	220	225
R5	199	199	208	219
R4	190	194	198	208
R9	190	197	200	204
A2	157	164	165	165
A1	153	154	157	156
R10	140	146	149	146
Mean value	198	201	205	209

Table 5

Test pigments arranged according to decreasing weathering resistance based on gloss readings. Deviation (*d*) from this order is given for corresponding mandelic acid (*M*) and crystal violet (*C*) test results

Pigment	Order (gloss)	Order ( <i>M</i> )	<i>d</i>	Order ( <i>C</i> )	<i>d</i>
R7	1	6	5	1	—
R5	2	3	1	2	—
R6	3	2	1	5	2
R8	4	4	—	3	1
R3	5	1	4	6	1
R1	6	11	5	9	3
R4	7	7	—	4	3
R2	8	8	—	7	1
R10	9	9	—	8	1
R9	10	5	5	10	—
A2	11	10	1	11	—
A1	12	12	—	12	—
			22		12

### Quality of dispersion

*Gauge readings* : Gauge readings and visual estimation of texture rating can be seen in Table 3 ; Fig. 5 shows mean values of all gauge readings as a function of grinding time. It is to be noted that the results from two hours' milling do not show the same tendency as Table 4 for scattering coefficients ; moreover, the pigments are almost equal with only one exception, R8, which showed a high initial *S* value. The results from further millings are not very clear either, and it is to be concluded that the development of hiding power is far more



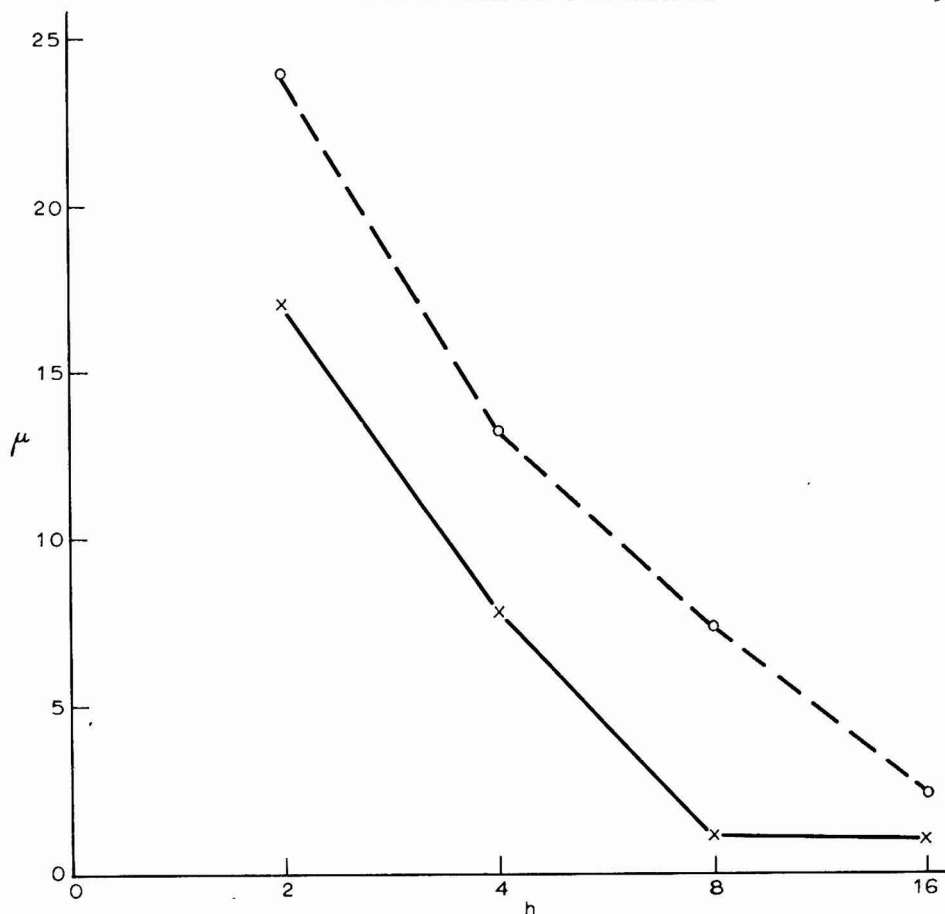
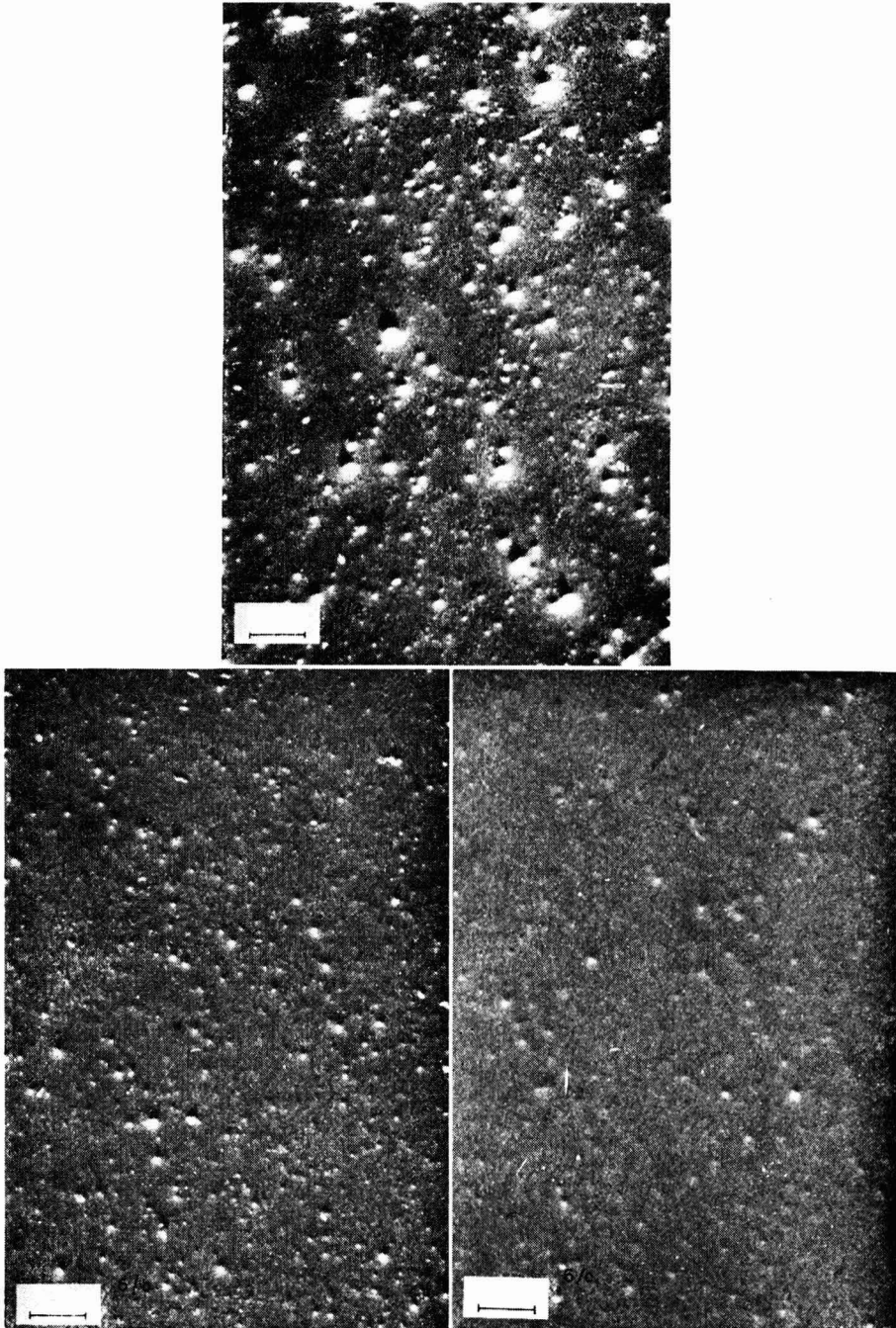


Fig. 5. Gauge readings at different degrees of grinding (mean values of all samples) : x main readings, o stragglers

informative than gauge readings and texture rating. Of course, both improve during continued milling (Fig. 5), but differences between test pigments are not easily detected (with the one exception already mentioned). It is clear that the number of protruding oversize agglomerates does not tell the whole story about the equality of dispersion. The improvement of texture rating can be seen from Fig. 6, which presents optical photomicrographs of panels after two, eight and 16 hours of milling respectively (grade R5 also required an effective milling for developing its hiding power). Protruding oversize particles are easily detected (film thickness *ca.* 6  $\mu$ ). Fig. 7 shows three photographs representing pigments R7, R1 and R8 respectively after two hours' milling. That of R8 is completely in line with other dispersion quality determinations; it is an easily dispersible pigment. Surface photographs of the latter pigments confirm the gauge readings and texture ratings presented in Table 3; on the other hand these pigments have high hiding power and gloss values. This suggests that quality of dispersion, as estimated using gauge readings or texture ratings, is of limited practical value only.



**Fig. 6.** Development of a paint film texture : (a) after two hours, (b) after eight hours, (c) after 16 hours of milling (R5). It is to be noted that the thickness of the film is approximately 6 microns only. Scale line is  $180\mu$  in length.

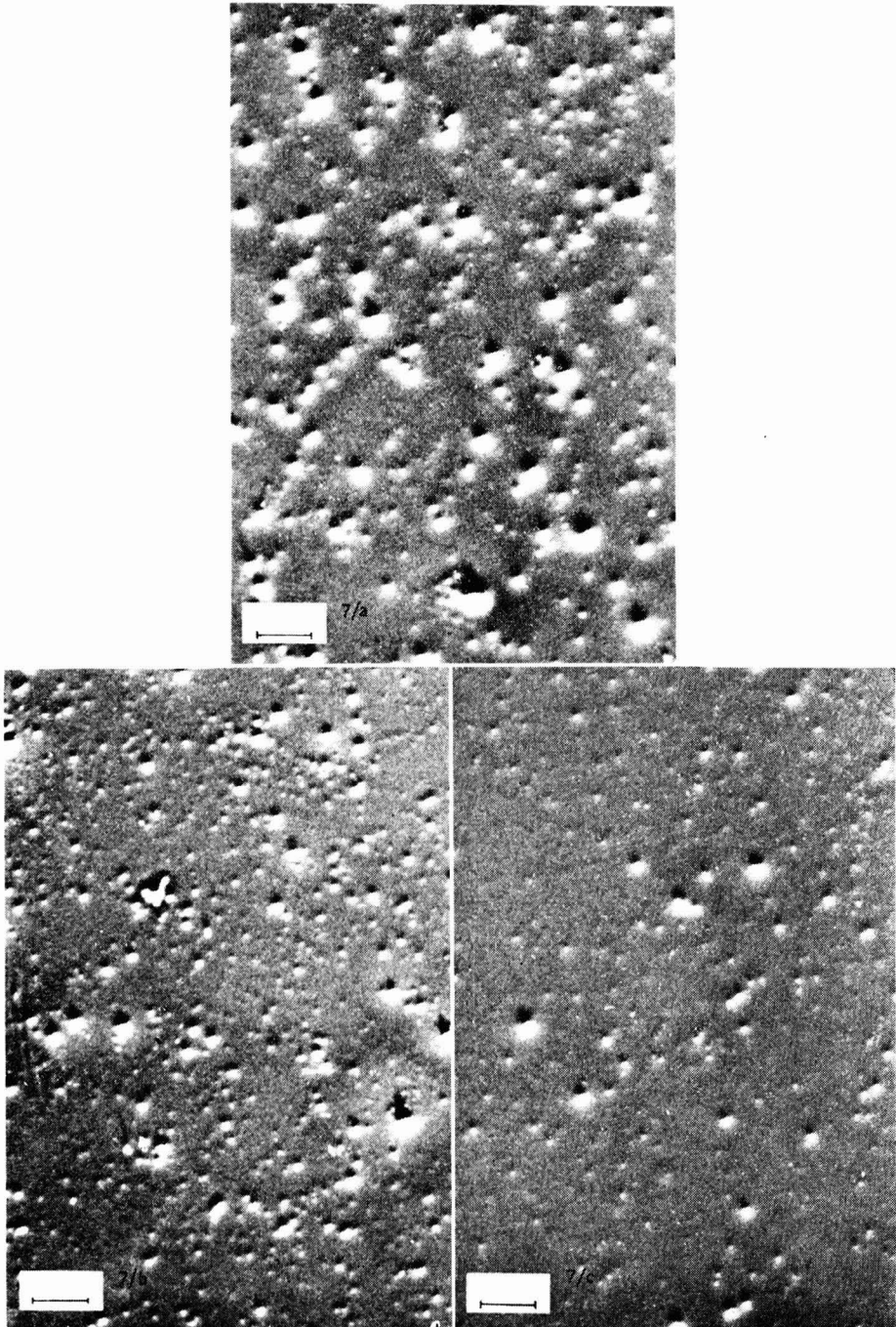


Fig. 7. Comparison of three paint film textures after two hours' milling : (a) R7, (b) R1, (c) R8 (cf. Fig. 6)

*Initial gloss*

Gloss measurements of panels were made before inserting them into the Marr apparatus, and these readings are referred to here as initial gloss values. The

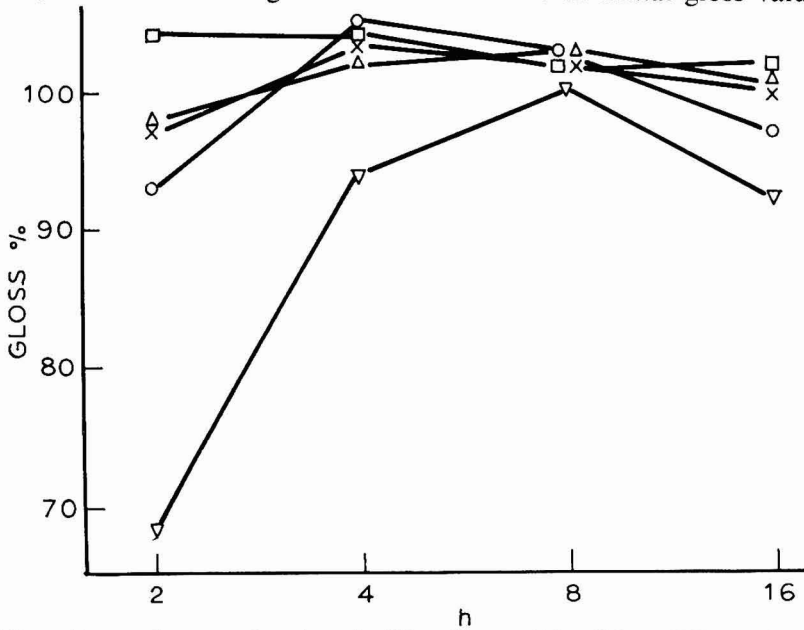


Fig. 8. Gloss of test points as a function of milling time : x R1, o R2, Δ R7, □ R8, ▽ R9

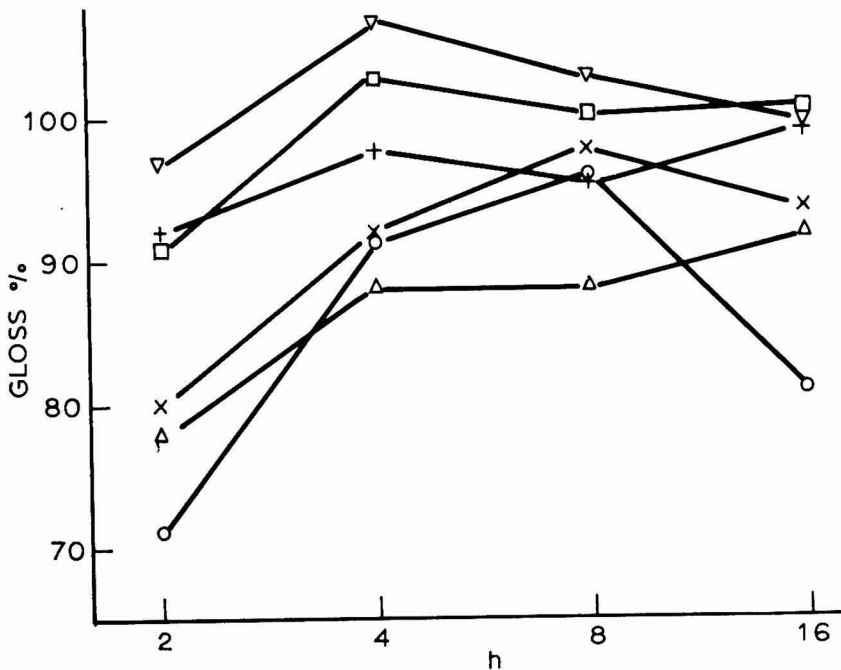


Fig. 9. Gloss of test points as a function of milling time : x A1, o A2, □ R3, Δ R4, + R5, ▽ R6

gloss of a paint is certainly affected by the quality of dispersion : it should be borne in mind that only one pigment grade may be considered at a time, because pigment properties other than dispersion contribute to gloss. It can be seen from Figs. 8 and 9 that the pigments showing best initial *S* values in Table 4 also present highest gloss readings after two hours of milling : R8, R7, R1, R6. Further development is similar : the gloss of R8 does not improve during continued milling, nor does its *S*-value ; the highest increase in *S*-value occurs in the case of R3, which also showed a definite increase of gloss during milling. This now appears sooner after a milling time of four hours. Exceptions also occur : both anatase pigments, R9, and, to a lesser extent, certain others, show a gloss maximum at about eight hours, not convincingly detectable as a *S* maximum in Table 4. R5, having the next highest *S* increase, does not show corresponding gloss improvement between four and 16 hours, the value at 16 hours being only slightly higher than that at four hours.

It is to be stated that, while certain easily dispersing pigments show good correlation between the development of scattering coefficient and that of gloss, the former is more dependent on the quality of dispersion than the latter if standard grades are considered. On the other hand, it is evident that new special grades develop both properties to a maximum using a moderate degree of mechanical dispersion, established standard grades (R3) require more energy to reach maximum hiding power, but the gloss is nevertheless not adversely

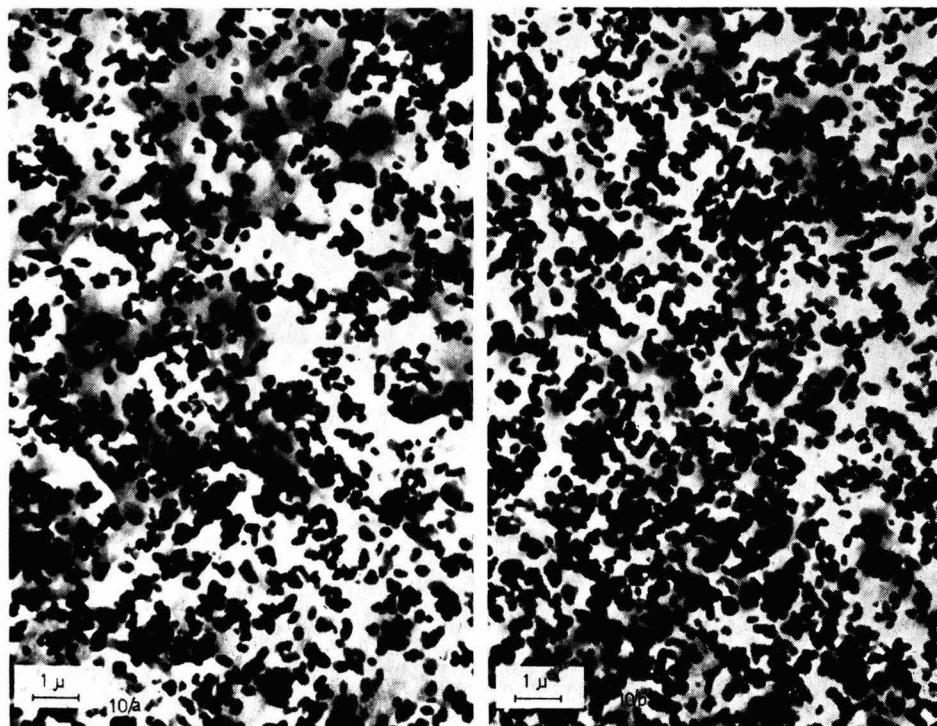


Fig. 10. Quality of dispersion in paint film (R8) : (a) milling two hours, (b) milling 16 hours

affected, whilst grades not representing modern paint pigment standard (anatase) or not being paint pigments at all (R9), show a disadvantageous behaviour in both respects.

#### *Dispersion of pigment in paint film*

To study the actual quality of dispersion of different pigment grades, electron photomicrographs were made of paint film slices, only a few of which can be included in this presentation. Fig. 10 shows an example of an easily dispersed pigment (R8) that, together with R1, had the highest  $S$  value after two hours' grinding. As can be seen, there is not much difference between these two dispersions, and, as already stated, the scattering coefficient did not improve during further milling. The scattering coefficient of R1 (Fig. 11) improved from 235 to 245 by grinding, and this improvement can also be seen from the photographs, although the dispersion was not very bad even in the two hours' case. Fig. 12 shows two examples of poor dispersion, R9 and R10, both of which have low  $S$  values even after 16 hours' grinding, R10 being far lower than R9 as can be expected from the dispersion.

Paint film microscopy is an effective tool for actual dispersion studies, but it has two drawbacks: the estimation is visual and requires a large number of pictures of both standards and the paint itself; in a printed report the presentation of all necessary material is not feasible. Therefore the photographs shown here serve as examples only.

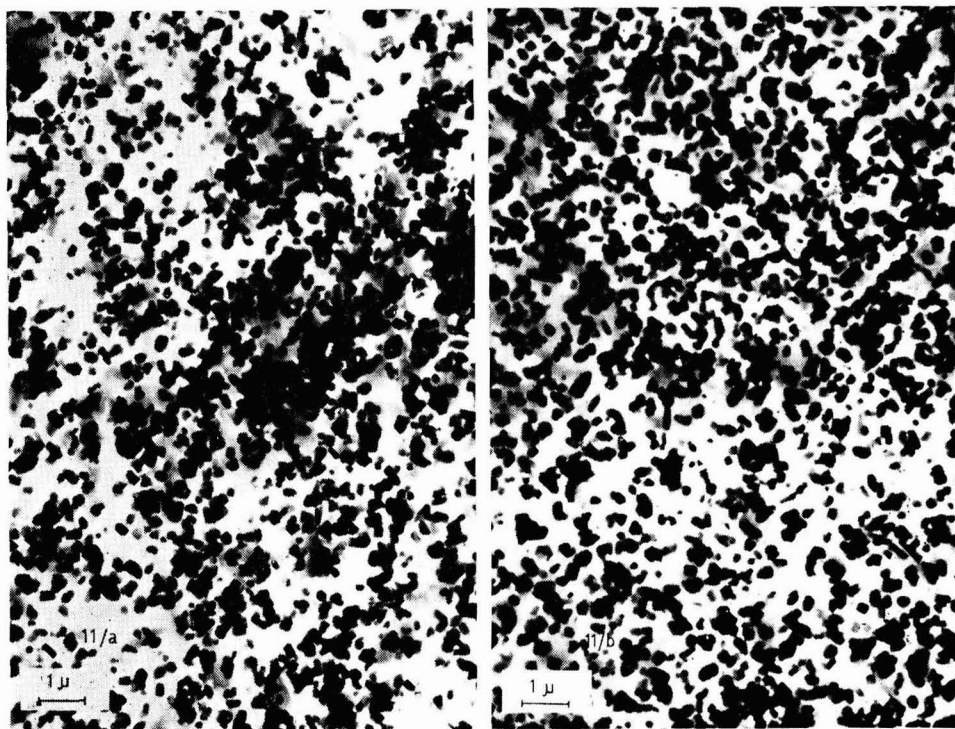


Fig. 11. Quality of dispersion in paint film (R1) : (a) milling two hours, (b) milling 16 hours

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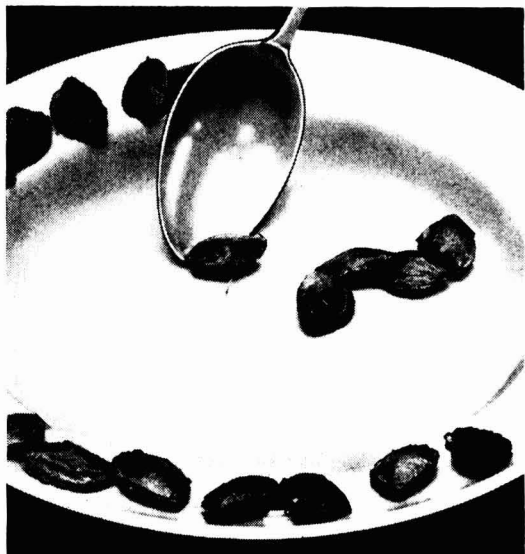
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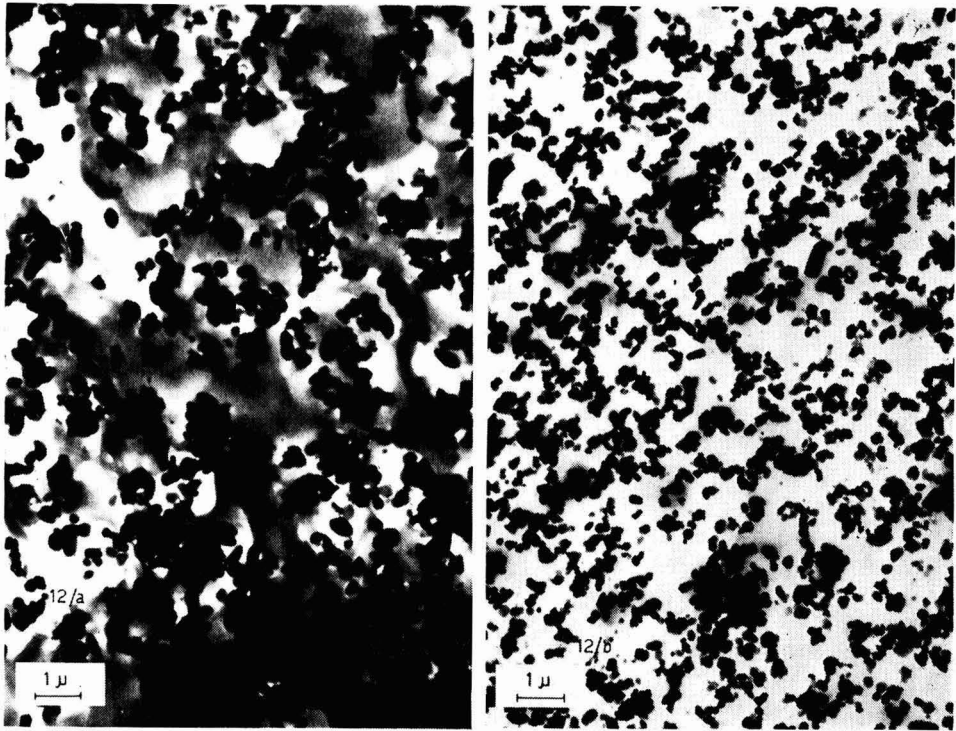


Fig. 12. Example of poor dispersion in paint film : (a) R10, (b) R9 (16 hours) ; these pigments are not intended for paints

### *Weathering resistance*

*Chalking* : Chalking, in the real sense of the word, was detectable even after 1,008 Marr hours only in the case of anatase pigments, as can be seen from surface replica photographs. A typical series of anatase (A1) pigmented paint panels can be seen in Fig. 13, which presents the replicas made after 0, 45 and 492 Marr hours. It is interesting to note that pigment particles are just starting to protrude through the film at 45 hours ; after 492 hours the phenomenon is nearly complete. The replicas were not made on one and the same spot of the panel.

A separate series was made to serve as material for the X-ray fluorescence study of the chalking phenomenon. The results are presented in Figs. 14a and b. In both graphs the left hand ordinate indicates the X-ray fluorescence response expressed in counts per second ; corresponding gloss readings appear on the right, lowest gloss readings corresponding to highest cps values. It can be seen that, if time is presented on a logarithmic scale as the abscissa, the graphs representing cps values are linear ; an initial slow period is followed by a more rapid development of chalking. Corresponding gloss values follow about the same path, but do not yield distinct graphs.

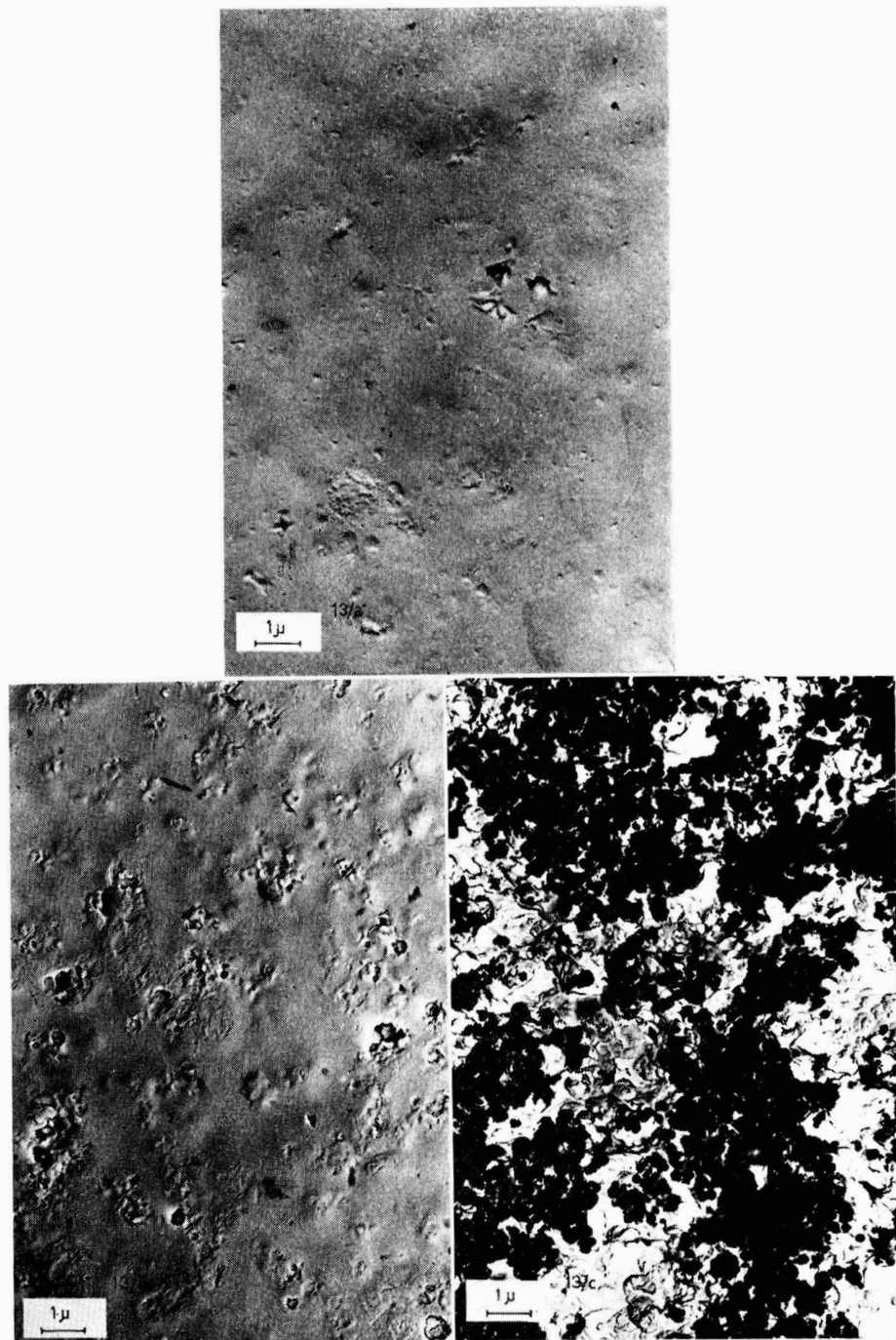


Fig. 13. Surface replica series of a freely chalking test paint (A1) : (a) 0 hours, (b) 45 hours, (c) 492 hours in Marr

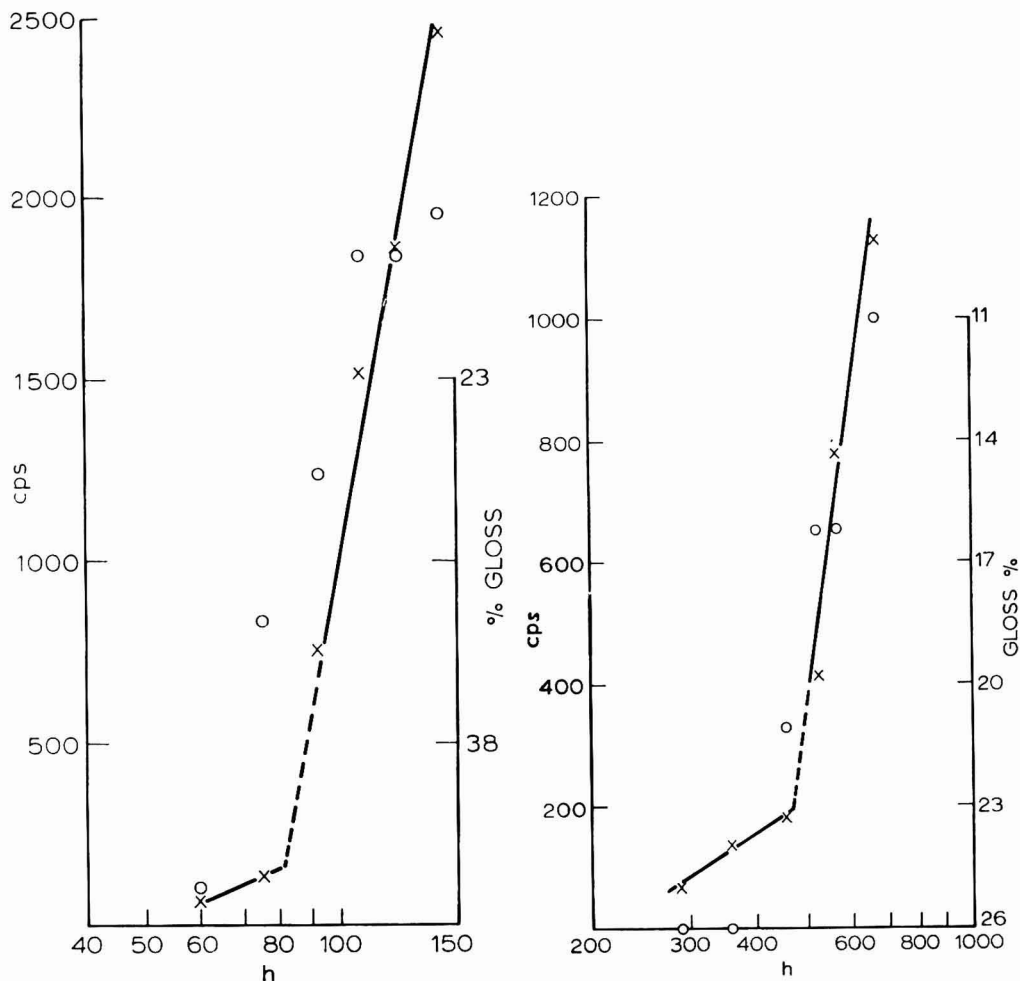


Fig. 14. Chalking of test paints as determined by the X-ray fluorescence method (left axis) and gloss readings (right axis) Marr hours appearing on the abscissa : (a) A1, (b) A2, x X-ray, o gloss

It is apparent that X-ray analysis is a useful tool, provided that chalking occurs in a sufficient amount to allow an analytical determination of loosened pigment particles.

*Gloss retention* : Weathering of test panels was followed by gloss measurements. The results are presented graphically in Figs. 15 to 17. It was observed that, if gloss readings are plotted against exposure time on semilogarithmic paper, the latter on the log axis, graphs roughly approaching straight lines result. This trend can best be seen from Fig. 15, which presents average gloss values of all samples. It can be seen from this figure that a higher gloss at 45 hours, obtained by more effective milling, is preserved towards the end of the experiment ; the values of medium milling (four, eight hours) show somewhat

irregular behaviour at the end. As a whole, it seems that the quality of dispersion does not have a remarkable influence upon artificial weathering resistance; in Figs. 16a and b, compared to 17a and b, individual pigments appear in the same order (uncoated rutile R10 being the only exception); the whole group of graphs is only moved upwards in the case of 16 hours as compared with two hours. It is to be noted that in these figures relative gloss is given rather than absolute, i.e. the initial gloss value of each pigment has been set to 100 per cent, and others calculated accordingly.

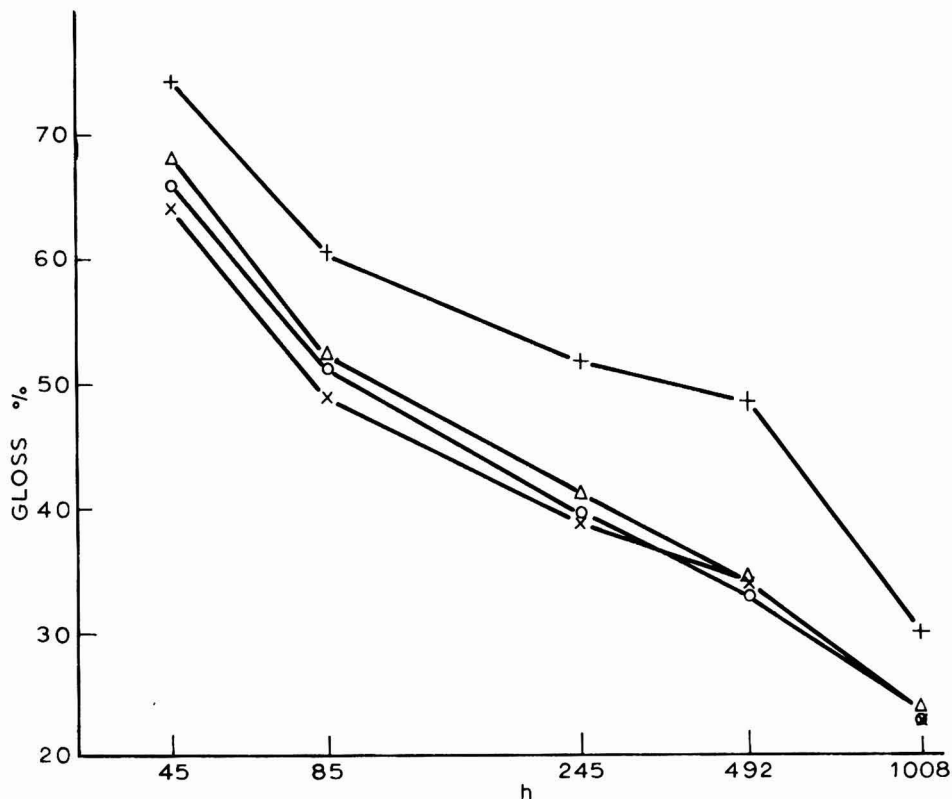


Fig. 15. Weathering resistance tests (Marr), initial gloss of each specimen set to 100 per cent. Mean values of all samples, milling time: x two hours, o four hours, Δ eight hours, + 16 hours

As to the weathering resistance of individual test pigments, the graphs are self-explanatory. It remains only to compare the development of gloss with methods of predicting weathering resistance, i.e. light sensitivity determinations, and to discuss some typical surface replicas selected from the great number representing different degrees of weathering of 48 test panels.

The relationship between (relative) gloss readings after 1,008 Marr hours (milling time 16 hours), reflectance readings using the mandelic acid test method and arrangement according to crystal violet test (daylight) values, is shown in Table 5, where test pigments appear, best rated first, and least resistant taking the last places.

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FW 2 V*	64	0.78	700	Very deep black standard pigment for high-quality lacquers, disperses readily	Carbon Black 30*	90	0.91	400	For rotary inks and cement mixes
FW 200*	64	0.73	540	For deep black thermosetting acrylics	Carbon Black 300	94	0.94	360	For rotary inks and gravure printing inks with good flow, for cheaper letterpress and offset inks, for carbon papers
S 170	71	0.98	650	Medium black giving high degree of opacity	Carbon Black A*	94	0.73	300	For multi-colour shading and newspaper inks
Special Black 4*	80	0.86	300	Medium black, disperses readily, high opacity, for letterpress, offset and gravure printing inks, high-quality industrial lacquers	Carbon Black G*	98	0.64	250	Blue-tinted, for multi-colour shading and newspaper inks
Special Black 4 A	80	0.86	730	Black pigment for high-quality modern illustration inks, carbon papers, ink ribbons and duplicating inks	Lamp Black 700	93	0.66	400	Tinting pigment for the lacquer industry, as for printing inks with good flow characteristics especially gravure inks
1000 V	83	0.95	400	Pigment for black industrial lacquers, and gray lacquers with brown tint. Standard quality for rotary, offset and gravure inks	Lamp Black 101	102	0.21	280	For tinting with blue shade, in combination with Printex or Printex 140 for newspaper inks

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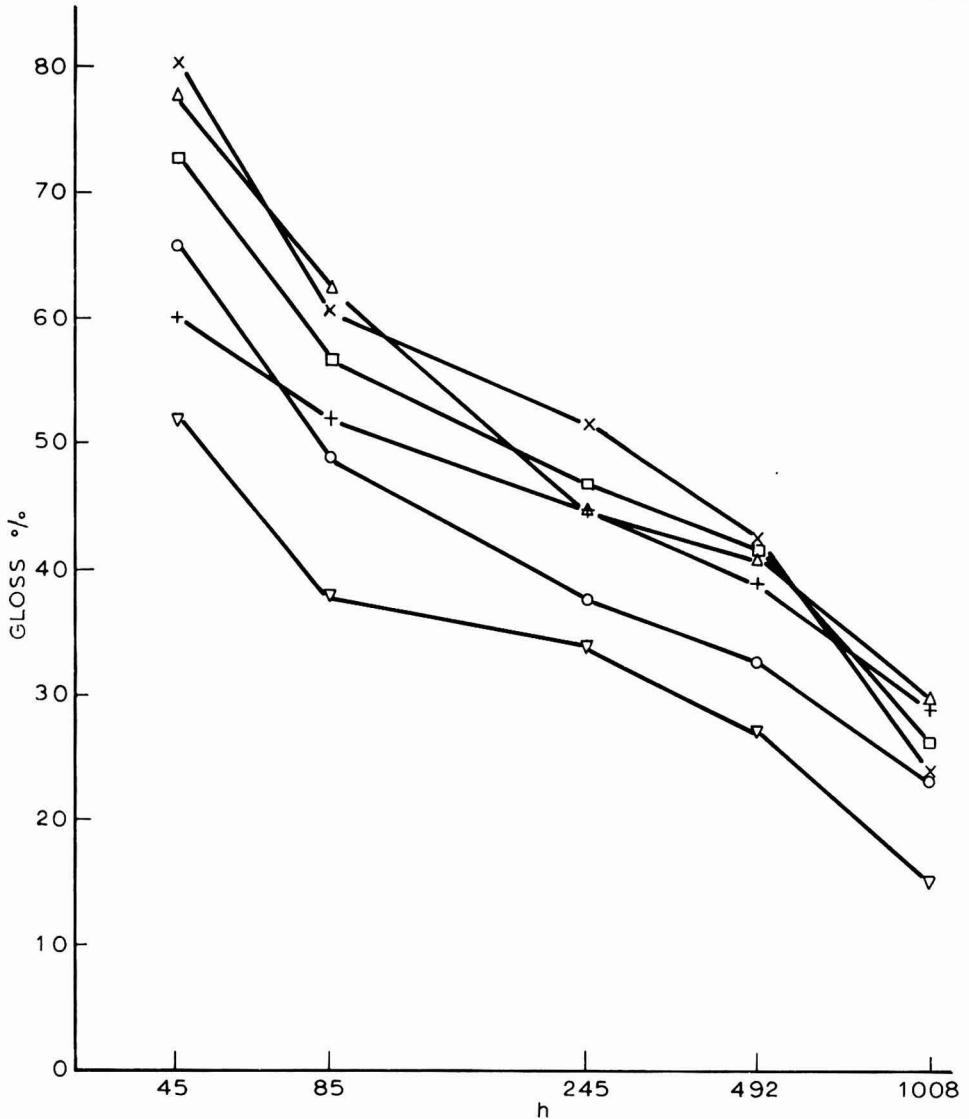


Fig. 16a. Weathering resistance tests (Marr) (cf. Fig. 15). Milling two hours : x R1, o R2, Δ R7, □ R8, ∇ R9, + R10

To obtain a rough numerical expression for the "reliability" of light stability test methods, the weathering resistance order of test pigments as determined by gloss measurements has been assumed correct; a deviation from this order (marked d) is registered as a difference between the figures indicating the rating. E.g. the mandelic acid method places the pigment R3 at the first place, gloss measurement at the fifth, hence a deviation of 4. It can be seen that, at least in this experiment, the crystal violet method more closely matches the results obtained in the actual weathering test (sum of deviations 12 compared with 22 in the mandelic acid method).

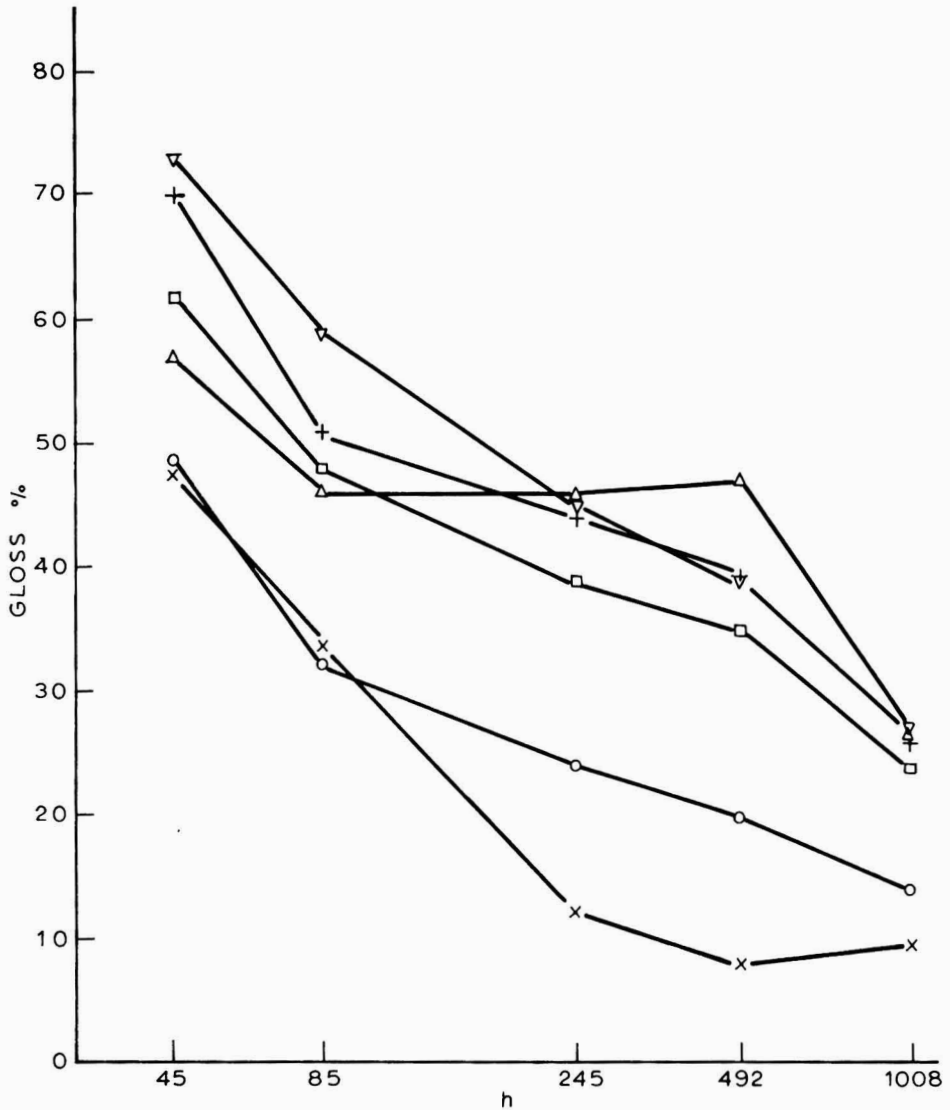


Fig. 16b. Weathering resistance tests (Marr) (cf. Fig. 15). Milling two hours : x A1, o A2, □ R3, Δ R4, + R5, ▽ R6



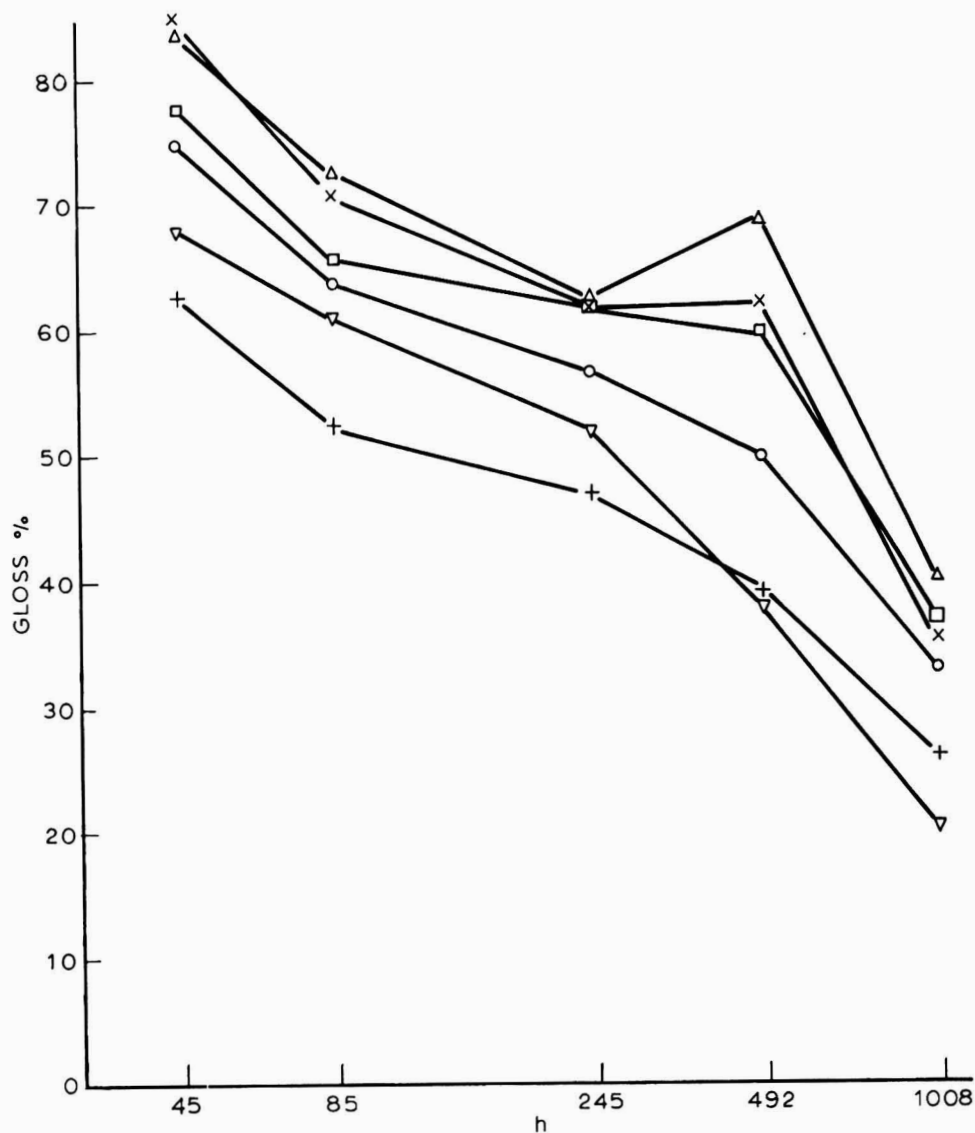


Fig. 17a. Weathering resistance tests (Marr) (cf. Fig. 15). Milling 16 hours : x R1, o R2, Δ R7  
□ R8, ∇ R9, + R10

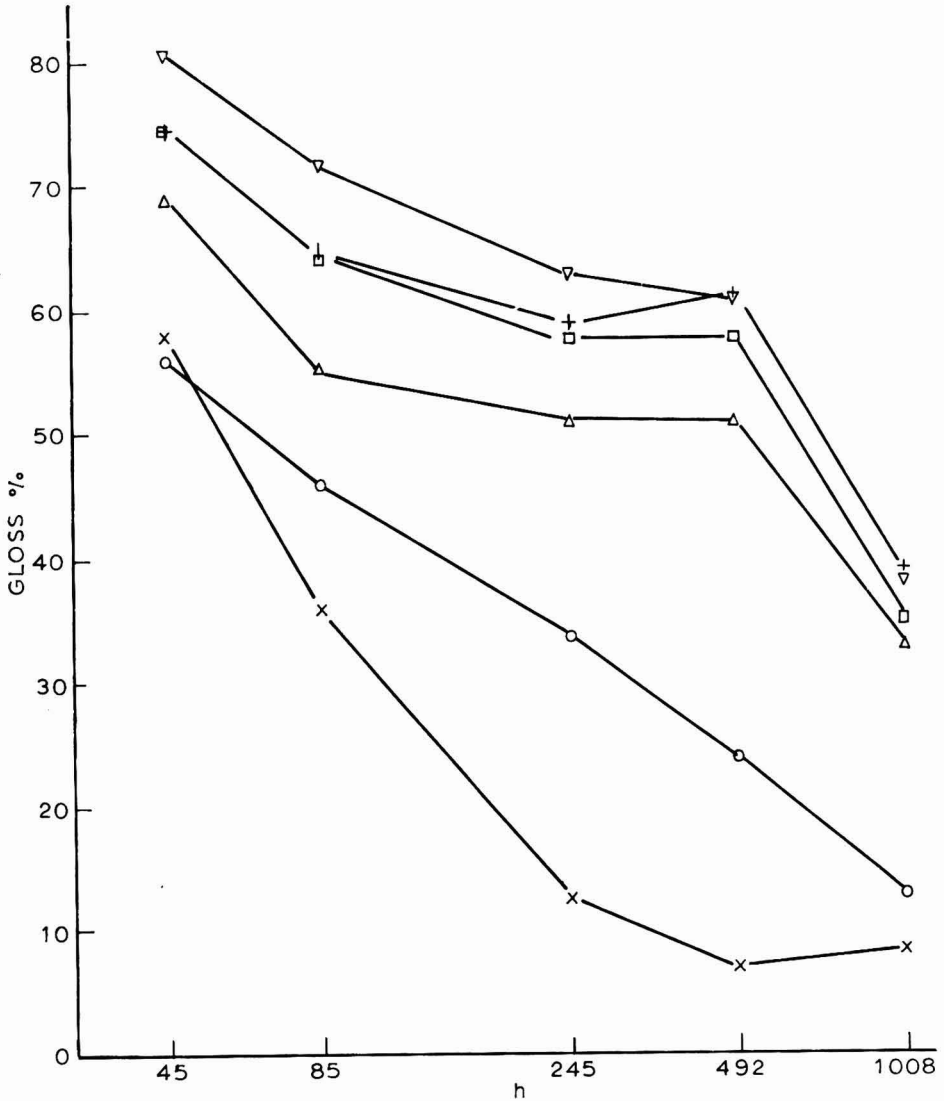


Fig. 17b. Weathering resistance tests (Marr) (cf. Fig. 15). Milling 16 hours : x A1, o A2, □ R3, Δ R4, + R5, ∇ R6

On the other hand, small differences in gloss readings do not have very great significance because of uncertainties always involved in a method like the artificial weathering test. Fig. 18 shows surface replicas of test panels of R5, R7, R6 and R2. Of these, the surfaces of R6 and R2 are apparently the least affected, others being approximately equal.

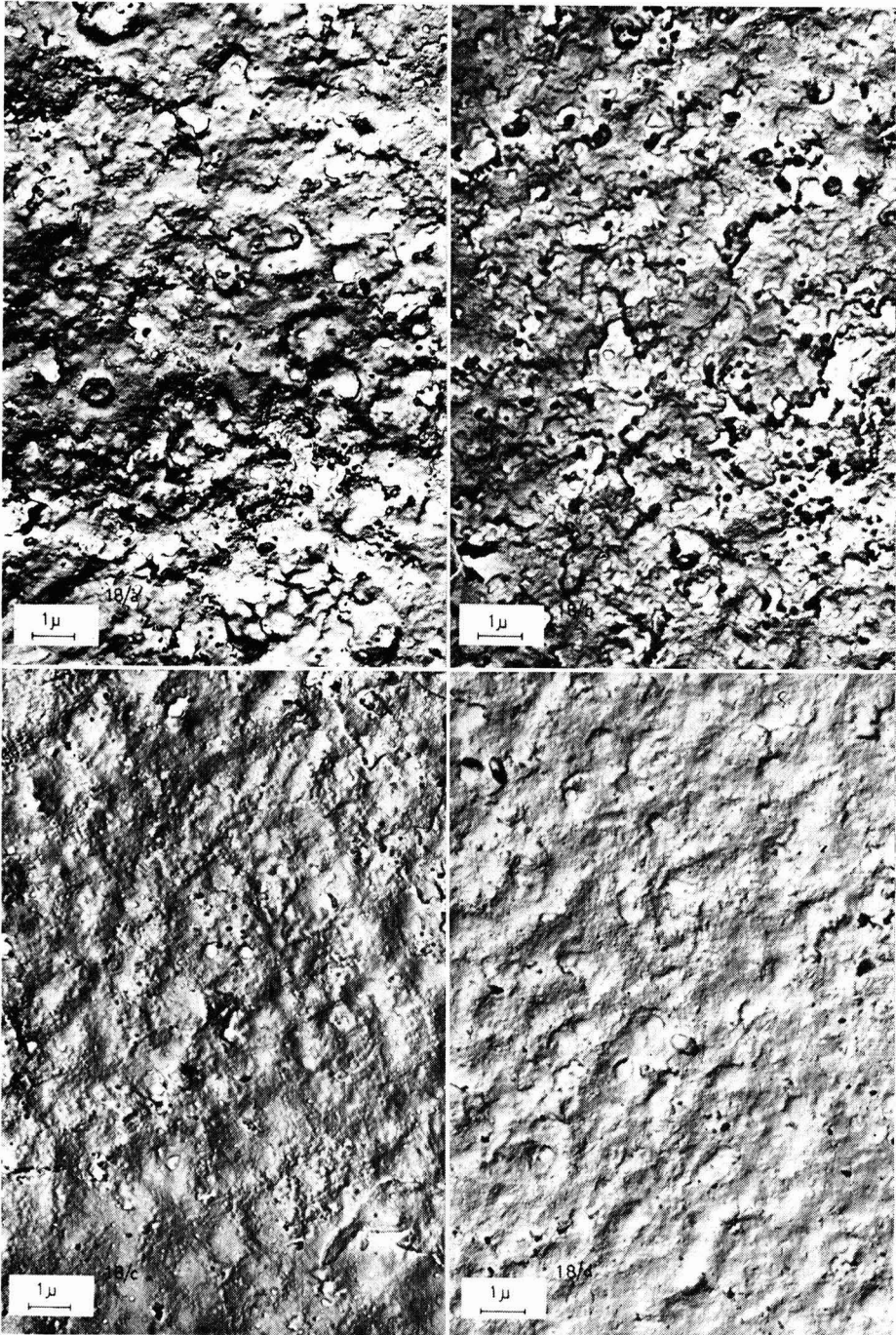


Fig. 18. Surface replicas of test panels after 1,008 Marr hours : (a) R5, (b) R7, (c) R6, (d) R2

### Conclusions

If the two light stability tests, the mandelic acid method and the crystal violet method, are compared, the former is easier to perform and gives the results as numerical readings. On the other hand, the crystal violet test is more sensitive and therefore better applicable to coated rutile grades. Results obtained during this work suggest that the latter method would give somewhat better correlation with actual weathering resistance; the material, however, is not extensive enough to allow any definite conclusions.

Scattering coefficient (hiding power) develops easily, using only moderate milling in the case of special pigments developed for easy dispersion. An equal level can be achieved using standard pigments, but more effective milling is required. Here, as in all cases of this work, it must be kept in mind that the results represent one paint formula with a fixed PVC value only.

It has been observed that gauge readings and texture ratings are of limited practical value as an indicator of quality of dispersion; hiding power and gloss values may be high in spite of poor gauge and texture readings.

The development of gloss has been found to follow similar lines to the scattering coefficient in the case of easily dispersing pigments. As far as standard pigments are concerned, the development of  $S$  seems to be more dependent on the quality of dispersion than the development of gloss.

The degree and development of quality of dispersion as described above has also been ascertained by means of electron micrographs of paint films.

A new method based on the use of X-ray fluorescence analysis has been developed for an exact determination of the degree of chalking.

Weathering was followed mainly by gloss measurements. It was found that the quality of dispersion did not have a notable influence on artificial weathering resistance. Surface replica electron photomicrographs reveal that gloss measurements may be in some cases misleading, giving, for instance, higher gloss values for more damaged surfaces.

### Acknowledgment

The author gratefully acknowledges the co-operation and invaluable help of all research staff members of Vuorikemia Oy. Especially the contributions of Miss Maija Rantakallio, M.Sc. (CHEM. ENG.), Mr. M. Alatalo, ENG., research chemist, and Mr. I. Mäki, M.Sc., head of the physical laboratory, are to be mentioned. He also thanks the management of Vuorikemia Oy (FINNTITAN) for permission to publish this work.

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### Discussion at the Scarborough Conference

DR. H. W. TALEN congratulated Dr. Wilska and his colleagues on the paper and said that there was one question that had intrigued him for many years. When the rutile type of titanium dioxide was first marketed, special emphasis had been laid by the suppliers on the improved resistance to chalking compared with that of the anatase type. This was attributed to the crystal type of the rutile. Since then, however, the quality of the rutile had been progressively improved by the manufacturers, mainly by modification with zinc oxide and surface treatment with alumina and silica. By comparison with Dr. Wilska's work, it would seem that the greater part of the improvement was due to the modification and after-treatment, and not to the rutile crystal as such.

He asked what results would be obtained for anatase pigment treated in the same way. Was it possible to differentiate between the improvements due to the crystal-formation and those due to modification and after-treatment? Could the results of the mandelic acid and crystal violet tests be attributed to the crystal form (Theory of Jacobsen), and the improved dispersibility, etc., to the modification and after-treatment?

DR. S. WILSKA replied that it was true that anatase grades could be improved by coating, but not so much that they could be used as outdoor pigments.

Uncoated rutile pigments were not weather-resistant, as had been shown. Uncoated rutile behaved almost in the same way as coated anatase. So, to improve weather resistance, two techniques must be used; first, it must be possible to make rutile particles where crystal form and primary particle size were absolutely correct. Then after-treatment techniques must be used to get maximum possible weather resistance from this rutile particle.

However, weather resistance was not the only thing to be considered. Many other properties of this rutile pigment particle could be improved by after-treatment, and it was very difficult to produce a pigment that had the best possible properties in all respects. This was one reason why nowadays there were so many different grades, because customers required special pigments for a special purpose.

In the mandelic acid and crystal violet tests photochemical activity was caused by the catalytic activity of titanium dioxide, and the catalytic activity was greater in the case of anatase type than in the case of rutile type. The mechanism of the coating influence was not yet fully known. Roughly, he would say that in this case, to improve the light stability, the function of the after-treatment was to isolate the titanium dioxide core and surroundings, hence decreasing its photo-chemical activity.

MR. M. HESS commented on the observation that the surface roughness did not have the relationship to gloss which had previously been believed. Continuing Dr. Talen's remarks, was the surface treatment of titanium dioxide in some cases responsible for the difference in gloss? That was to say that the scattering was different, according to the materials used for surface treatment and this compensated in some cases for the greater surface roughness of  $\text{TiO}_2$ .

DR. WILSKA replied that, in the tests for texture ratings, a film was used, the thickness of which was only about six microns, and if the pigment was ground to ten microns, it was apparent that a rough surface would be obtained, but particles of ten microns or 15 microns behaved well in actual paint films which were about 40 microns thick. This might be an explanation for this behaviour.

With regard to the influence of surface treatment on the optical properties of the pigments referred to in the paper, these coatings were so thin that they did not have much effect upon the scattering properties or other optical properties.

DR. V. T. CROWL asked about the initial gloss of the films shown in Figs. 8 and 9. Some of these curves passed through a maximum and then decreased on further milling. Was it possible that the presence of the residual agglomerates in films prepared in the early stages of milling had a favourable effect on the pigment packing in the film, giving high gloss, and that, on further milling, with the breakdown of these agglomerates, this structure was lost?

DR. WILSKA felt that the fact that the figures sometimes had a maximum might be caused partly by scattering in instrumental values but in some cases there must be some other reason for it. He agreed with Dr. Crowl's explanation; it might be that there was some breaking of agglomerates that improved the gloss in the early stages of milling.

DR. L. VALENTINE (CHAIRMAN) asked whether microtome cross-sections of these films had been examined. Was there any difference in the thickness of the clear pigment-free layer with variations in milling time?

DR. WILSKA replied that no microtome sections had been taken.

DR. T. DOORGEEST commented on the colour scale imitated by the two pigments mentioned, Permanentviolett RL Extra Pulver and Heliogenblau B. The colour difference between steps 2 and 3 was very small, but there was a marked difference between steps 1 and 2, 3 and 4 and 4 and 5. How was this scale made, and why was the difference in colour between steps 2 and 3 so small?

Secondly, methods of determining the light stability had been mentioned (the mandelic acid test in particular) where the paste was covered with a plate of glass: would it not be better to use a plate made of quartz, which had better light transmission?

DR. WILSKA said that, as far as the colour standard scale was concerned, the intensity difference between each two steps was 50 per cent.

Quartz was a good material for the purpose Dr. Doorgeest suggested. However, it was rather expensive, and quartz plates broke easily, and as results obtained using glass plates were reasonable, there was no reason to use more expensive ones.

MR. M. SOLOMKA referred to the mandelic acid test, and asked if Dr. Wilska could explain the apparent anomaly that the reflectance of several pastes increased upon exposure to ultra-violet rays.

Secondly, referring to the scattering coefficient, this coefficient was usually determined by the reflectance of paint films which were practically infinitely thick. In this case an applicator which was 25 microns had been used; it seemed this would leave a dry film thickness of perhaps 12 microns; would Dr. Wilska comment on this?

DR. WILSKA replied that, in the mandelic acid test, some higher readings were obtained, in some cases during prolonged exposure. The reason for this was not known. It only showed that there was no photochemical activity, because the sample did not darken. There must be some secondary phenomenon that caused this apparent increase of reflectance.

With regard to the scattering coefficient, the "S" value had been determined, using the technique described before, without actually having an infinitely thick paint film.

MR. SOLOMKA observed that there were a number of these pigments—for example, there were seven pigments which were merely described as alumina, zinc and silica treated pigments. The paper was a very interesting one ; nevertheless, the interest would be further enhanced if there could be some further characterisation between these different pigment types. Actually, the only difference indicated was a small difference in tinting strength for the different grades. Would Dr. Wilska elaborate on this ?

DR. WILSKA said that he would like to describe in detail all these coatings but, for obvious reasons, the discussion must be confined to what was printed in the paper, or published elsewhere. In the present work the samples had been identified by giving their commercial names and corresponding types ; this was sufficient information for a pigment expert.

He added that it was a pity that the properties and structure of  $\text{TiO}_2$  pigments were not known to people who work in the independent research institutions. It could often be observed that they did not work on material that was not fully characterised, and the results obtained from such work could always be a little bit questionable.

DR. VALENTINE followed up Dr. Talen's questions by asking if the photochemical difference between the anatase and rutile crystal forms was transmitted at a distance through the coating, or whether it was due to incomplete coverage of the pigment surface by the coating.

DR. WILSKA said it was very important to have the coating very even, and to have no holes in it, but it was very hard to detect holes in the particles. A technique for photographing these layers had been developed, and, to some extent, the evenness of the coatings could be seen ; but considering that there were 6,000 million titanium dioxide pigment particles in one milligram of pigment, then it was obvious that each particle could not be photographed to see whether it was completely covered. His opinion was that small differences in photochemical activity might depend on the evenness and the thickness of the coating.

MR. H. F. CLAY pointed out that in the paper the basic mechanism was attributed to the release of atomic oxygen. Was this the result of Dr. Wilska's own observations, or was he perpetuating the earlier statement by Jacobsen ?

DR. WILSKA said that there were many different opinions about the mechanism of photochemical activity. He had not studied this mechanism theoretically, and could only say that the presence of atomic oxygen was one natural explanation for the phenomenon, but there might be other possible explanations.

DR. J. A. W. VAN LAAR pointed out that it was possible, by use of an electron beam, to examine particles of less than one micron in size. On metal surfaces it was possible, if the pigment was not too small, to examine the surface of a single pigment. It could be done in two ways ; by measurement of the electric conductivity of the electron beam, or by measurement of the reflected ray, and subsequent analysis would show which crystals were present.

DR. H. RECHMANN asked what test, in Dr. Wilska's opinion, was really good for forecasting the outdoor behaviour of a pigment, bearing in mind the differences shown in the three tests examined.

DR. WILSKA replied that this question had not been investigated. Outdoor tests were going on, with the same material, and the results would be compared with the mandelic acid and crystal violet methods.

DR. RECHMANN commented that, for forecasting weathering resistance, incorrect results were sometimes obtained in the mandelic acid test, in the presence of, for example, phosphates ; there were some manufacturers who added magnesium phosphate and others who added titanium sulphate to pigments, and it had often been seen that this gave quite a different picture in the mandelic acid tests. It would be better if the crystal violet test gave better correlation.

# On the relation between the pigment-vehicle interaction and liquid water absorption of paint films\*

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## *Summary*

Water absorption is usually considered as a property which may be important for the protective function of a paint film. The present investigations have given some evidence that, apart from this more practical aspect, liquid water absorption of paint films is also related to the interaction between the pigment and the vehicle in the solid state. If the liquid water absorption is calculated on the vehicle content of the film, three different dependencies on the PVC may be encountered :

- (1) The water absorption is independent of PVC or even decreases with rise of PVC. This relation indicates that the adhesion between the pigment and the vehicle is strong enough to resist the invading water.
- (2) The water absorption increases steadily with increasing PVC. This indicates a lack of adhesion between pigment and vehicle.
- (3) The water absorption has a maximum at relatively low PVC. This maximum is caused by osmotic processes occurring at the inner interfaces of the film as a consequence of water soluble substances present there. The decrease in water absorption after the  $PVC_{max}$  has been reached may be attributed to the close approach of the pigment particles.

The specific dependence of the liquid water absorption on the PVC thus provides a simple and sensitive indication of the interaction between pigment and vehicle in solid paint films, at least in the presence of water. Work is continuing to extend these investigations also to organic solvents as swelling agents. It is hoped that an interaction scale may be set up, which will permit comparison of the strengths of the interactions between pigment and vehicle in presence of different swelling agents. Moreover if certain solvents are found readily to displace the vehicle adsorbed at the pigment surface, it may be possible that such solvents would entirely prevent interaction between pigment and vehicle, if they are used in paint formulation.

The height of the maxima of liquid water absorption depends on the concentration of water solubles at the inner interfaces of the paint films, on the chemical and morphological structure of the films, and on the duration of the water immersion.

The range of PVC and the breadth of these maxima are influenced by the dispersion of the pigment in the solid film. Experimental evidence exists that the absorption maximum is the more extended the better the pigment is dispersed in the film.

It has been shown that absorption maxima may only appear if the temperature is definitely above the glass transition point of the paint film. This is somewhat analogous to the temperature conditions most favourable for the blistering of paint films on a substrate when exposed to humid air or to liquid water.

It is generally known that, at the critical PVC as formulated by Wolff, Asbeck and van Loo, the packing density of the pigment particles attains its maximum. Obviously a second, lower critical PVC may exist where the pigment particles, flocculates or agglomerates touch each other with a rather low co-ordination number. This is equivalent to a bad dispersion of the pigment in the paint film. Perhaps this lower critical PVC accounts also for the discontinuous or even abrupt change which is sometimes observed with other paint properties such as diffusion coefficient, hiding power or glass transition, at low PVC values.

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\*Presented at the Scarborough Conference, 1967.



These aspects indicate that the liquid water absorption of paint films, commonly designated as swelling, may become much more informative as a criterion for the characterisation of paint films than it has been in the past.

## Sur le rapport de l'interaction pigment-véhicule à l'absorption d'eau de feuillets de peinture

### Résumé

Bien qu'en général on considère l'absorption d'eau au point de vue de son influence sur les fonctions protectrices de feuillets de peintures, les investigations actuelles fournissent de l'évidence sur le rapport de l'absorption d'eau à l'interaction pigment-véhicule dans l'état solide. Où l'on calcule l'absorption d'eau comme pourcentage de la teneur en véhicule du feuillet, l'influence de la CVP peut se témoigner par les trois possibilités suivantes :

- (1) L'absorption d'eau est indépendante de la CVP, ou même diminue-t-elle lors de l'augmentation de la CVP. Cet effet indique que l'affinité pigment-véhicule est assez forte pour résister à l'entrée d'eau.
- (2) L'absorption d'eau s'accroît régulièrement suivant l'augmentation de la CVP. Ceci indique une manque d'affinité pigment-véhicule.
- (3) L'absorption d'eau maximale se présente à une CVP assez faible, à cause des processus osmotiques qui se produisent par conséquent des matières solubles dans l'eau aux interfaces pigment-véhicule du feuillet. La diminution d'absorption d'eau qui se met en évidence à la CVP maximale, peut être attribuable au tassement serré des particules pigmentaires.

Ainsi le rapport spécifique de l'absorption d'eau à la CVP peut rendre une indication exacte et facile, au moins en présence d'eau, de l'interaction pigment-véhicule dans des feuillets solides de peinture. On est en train de faire étendre ces études afin de renfermer des solvants organiques en tant qu'agents de gonflement. On espère établir une échelle d'interaction qui permettra la comparaison des forces d'interaction pigment-véhicule en présence de différents agents de gonflement. D'ailleurs, si l'on trouvera certains solvants qui peuvent déplacer facilement la véhicule adsorbée à la surface pigmentaire, il y aurait la possibilité que tels solvants, lors de leur utilisation en peinture, empêchent-ils complètement l'interaction pigment-véhicule.

La grandeur de l'absorption d'eau maximale se dépend ; de la concentration de matière soluble dans l'eau aux interfaces pigment-véhicule des feuillets de peinture ; des structures chimique et physique des feuillets ; de la durée d'immersion dans l'eau.

La gamme de CVP et l'amplitude de ces valeurs maximales sont également influencées par l'état de dispersion du pigment dans le feuillet sec. L'évidence expérimentale suggère que l'étendue de l'absorption maximale se dépend du degré de dispersion du pigment dans le feuillet.

On a démontré que l'absorption maximale ne peut se présenter que la température dépasse, d'une manière déterminée, le point de transition à l'état vitreux du feuillet de peinture. Ceci est assez analogue aux conditions de température qui favorisent fortement la formation de soufflures lors de l'exposition à l'air humide ou à l'eau.

Il est bien compris, en général, qu'à la CVP critique calculée selon la méthode de Wolf, Ansbeck, et van Loo, le tassement des particules pigmentaires est maximal. Évidemment il peut exister une autre CVP critique de valeur inférieure, ou le tassement des particules, floculats ou agglomérats de pigment démontrent une coordination assez faible, qui répond au pigment mal dispersé. Peut-être cette alternative CVP critique explique-t-elle également la discontinuité ou même la change subite que l'on remarque quelque fois aux CVP faibles en ce qui concerne d'autres propriétés de peinture comme coefficient de diffusion, pouvoir couvrant, et point de transition à l'état vitreux.

Ces aspects témoignent que l'absorption d'eau de feuillets de peinture, que l'on désigne souvent par gonflement, peut-elle devenir beaucoup plus intéressante qu'auparavant en tant que critérium pour caractériser les feuillets de peinture.

## Über die Beziehung der Wechselwirkung zwischen Pigment und Bindemittel zur Wasserabsorption von Anstrichfilmen

### Zusammenfassung

Wasserabsorption wird gewöhnlich als eine Eigenschaft angesehen, die für die Schutzwirkung einer Farbschicht wichtig sein kann. Abgesehen von diesem mehr praktischen Gesichtspunkt haben die vorliegenden Untersuchungen den Beweis geliefert, dass die Wasserabsorption

von Austrichfilmen auch zur Wechselwirkung zwischen Pigment und Bindemittel im Festzustand in Beziehung steht. Berechnet man die Wasserabsorption auf Grundlage des Bindemittelgehalts der Film, so ergeben sich drei verschiedene Abhängigkeitsverhältnisse vom Film :

1. Die Wasserabsorption ist unabhängig vom PVC oder nimmt mit zunehmendem PVC ab. Diese Beziehung deutet darauf hin, dass die Adhäsion zwischen Pigment und Bindemittel stark genug ist, um einfallendem Wasser zu widerstehen.
2. Die Wasserabsorption nimmt mit zunehmendem PVC beständig zu. Dies deutet auf Mangel an Adhäsion zwischen Pigment und Bindemittel hin.
3. Die Wasserabsorption zeigt ein Maximum bei relativ niedrigem PVC. Dieses Maximum wird durch osmotische Prozesse verursacht, die infolge des Vorhandenseins wasserlöslicher Substanzen an den inneren Grenzflächen der Schicht vor sich gehen. Der Rückgang der Wasserabsorption nach Erreichen des PVC-Maximums lässt sich auf die enge Annäherung der Pigmentpartikel zurückführen.

Die spezifische Abhängigkeit der Wasserabsorption vom PVC bildet also einen einfachen, empfindlichen Hinweis auf die Wechselwirkung zwischen Pigment und Bindemittel in festen Farbschichten, zumindest bei Vorhandensein von Wasser. Es ist beabsichtigt, diese Untersuchungen auch auf organische Lösemittel als Quellungsmittel auszudehnen und eine Wechselwirkungsskala aufzustellen, die einen Vergleich der Stärke der Wechselwirkung zwischen Pigment und Bindemittel bei Vorhandensein verschiedener Quellungsmittel ermöglichen wird. Wenn darüber hinaus bestimmte Lösemittel gedundet werden, die das an der Pigmentoberfläche adsorbierte Bindemittel leicht verdrängen, so dürfte es möglich sein, bei Verwendung dieser Lösemittel im Ansatz der Farbe die Wechselwirkung zwischen Pigment und Bindemittel überhaupt zu verhindern.

Die Höhe der maximalen Wasserabsorption ist von der Konzentration wasserlöslicher Stoffe an den inneren Grenzflächen der Farbfilm, von der chemischen und morphologischen Struktur der Schichten und von der Dauer der Eintauchung abhängig.

Der PVC-Bereich und die Breite dieser Maxima sind von der Verteilung des Pigments in der festen Schicht abhängig. Experimente lassen darauf schließen, dass das Absorptionmaximum eine umso größere Breite hat, je besser das Pigment in der Schicht verteilt ist.

Es ist gezeigt worden, dass Absorptionsmaxima nur eintreten können, wenn die Temperatur definitiv über dem Glasübergangspunkt des Farbfilms liegt. Dies ist mit den Temperaturbedingungen vergleichbar, die Blasenbildung bei Farbschichten auf einem Substrat bei Feuchtluft— oder Wassereinflüssen begünstigen.

Es ist allgemein bekannt, dass nach Wolff, Asbeck und van Loo die Packungsdichte der Pigmentpartikel bei kritischem PVC ihr Maximum erreicht. Offenbar gibt es eine zweite niedrigere kritische PVC, bei welcher die Pigmentpartikel, Flocken oder Agglomerate sich gegenseitig mit einer ziemlich niedrigen Koordinationszahl berühren. Dies entspräche einer schlechten Pigmentverteilung in dem Farbfilm. Vielleicht ist diese kritische PVC auch die Ursache für die diskontinuierliche oder selbst plötzliche Änderung, die zuweilen bei anderen Eigenschaften, wie Diffusions-Koeffizient, Deckfähigkeit und Glasübergang bei niedrigen PVC-Werten zu beobachten ist.

Diese Gesichtspunkte deuten darauf hin, dass die gewöhnlich als Quellung bezeichnete Wasserabsorption von Farbschichten sehr viel aufschlussreicher als Kriterium für die Charakterisierung von Farbfilm werden dürfte, als dies es in der Vergangenheit war.

### **Зависимость между взаимодействием пигмента с растворителем и абсорбцией жидкой воды красочными пленками**

#### *Резюме*

Абсорбция воды обычно считается свойством которое может играть важную роль в защитной функции красочной пленки. Настоящие исследования показали до некоторой степени что кроме вышеупомянутой практической точки зрения, абсорбция жидкой воды красочными пленками также связана с взаимодействием между пигментом и растворителем в твердом состоянии. Если абсорбция жидкой воды рассчитывается на основании содержания растворителя в пленке, то встречаются три различные зависимости от значения PVC:

- 1) Абсорбция воды не зависит от PVC или даже уменьшается с повышением PVC. Это соотношение показывает что сцепление между пигментом и растворителем достаточно сильно чтобы оказать сопротивление вторгающей воде.

- 2) Абсорбция воды равномерно увеличивается с повышением PVC. Это показывает недостаток сцепления между пигментом и растворителем.
- 3) Абсорбция воды достигает максимума при сравнительно низких значениях PVC. Этот максимум обусловлен осмотическими процессами на внутренних поверхностях раздела пленки, по причине присутствия веществ растворимых в воде. Уменьшение абсорбции воды после достижения PVC макс может быть приписано непосредственному приближению пигментных частиц.

Специфическая зависимость абсорбции жидкой воды от значения PVC, таким образом, может служить простым и чувствительным показателем взаимодействия между пигментом и растворителем в твердых красочных пленках, по крайней мере в присутствии воды. В данный момент продолжается работа чтобы распространить эти исследования на органические растворители, как средства набухания. Выражается надежда что будет разработана шкала взаимодействия, которая предоставит возможность сравнения интенсивностей взаимодействий между пигментом и растворителем в присутствии различных набухающих средств. Кроме того, если некоторые растворители окажутся способными вытеснить растворитель адсорбированный на поверхности пигмента, то может оказаться возможным что такие растворители полностью предотвратят взаимодействие между пигментом и растворителем, при применении в формуляции красок.

Предел максимумов абсорбции жидкой воды зависит от концентрации растворимых в воде веществ на внутренних поверхностях раздела красочных пленок, от химической и морфологической структуры пленок и от продолжительности погружения в воду.

Диапазон значений PVC и протяженность этих максимумов зависят от дисперсии пигмента в твердой пленке. Существуют экспериментальные доказательства что максимум абсорбции тем более распространен, чем лучше пигмент дисперсируется в пленке. Показано что максимумы абсорбции обнаруживаются только если температура определено выше точки стеклования красочной пленки. Это более или менее аналогично температурным условиям на более благоприятным для образования пузырей на подслое красочных пленок, подверженных действию влажного воздуха или жидкой воды.

Общезвестно что уплотнение пигментных частиц достигает максимума при критическом значении PVC согласно формуляции Вольфа Азбека и Ван Лоо. Ясно что может существовать второе более низкое критическое значение PVC при котором пигментные частицы, флокулаты или агломераты прикасаются друг друга с довольно низким числом координации. Это эквивалентно плохой дисперсии пигмента в красочной пленке. Возможно что это более низкое значение PVC объясняет также те прерывистые или даже внезапные изменения, которые иногда наблюдаются в других свойствах красок как например в коэффициенте рассеяния, скрывающей способности или стекловании, при низких значениях PVC.

Вышеупомянутые соображения показывают что абсорбция жидкой воды красочными пленками, обычно определяемая как набухание, может оказаться значительно более информативной как критерий для характеристики красочных пленок, чем это было в прошлом.

## Introduction

In paint films the pigments have to fulfil various functions such as endowing the substrate with colour, protecting it from corrosion, or contributing to the physical and mechanical strength of the organic film material. A very impressive example of the properties last mentioned, from a different field of polymer application, is the reinforcing action of carbon black in rubber. Such an active filler may strongly enhance the tensile strength and decrease the extensibility of polymeric materials, whereas inert fillers exert scarcely any influence. Similarly the pigmentation of paint films may either effect reinforcement or be inactive, depending on the strength of interaction between the pigment particles and the surrounding vehicle.

The reinforcement of rubber by fillers manifests itself in the swelling properties, as several authors<sup>1-4</sup> have recently emphasised. Assuming that the

adhesion between filler and rubber matrix is either lost or retained during the absorption of the swelling agent, Kraus<sup>5</sup> calculated the swelling of filled rubber. By comparing the actual solvent absorption of rubber filled with carbon black with the values to be expected theoretically, it could be deduced that even under these conditions carbon black strongly adheres to the rubber matrix.

Similar considerations led the author to estimate the adhesion between the vehicle and the pigment particles according to the amount of the swelling agent absorbed by the paint film in relation to the pigment volume concentration (PVC). Because water is the most important swelling agent for paint films, pigment-vehicle interaction in the presence of liquid water was first investigated.

### **Liquid water absorption by paint films**

It is reasonable to assume that, in general, pigments do not swell in water to a significant degree. Therefore it is convenient to relate the water absorption of the film to its vehicle content ( $Q_B$ ). Earlier investigations with unpigmented films showed that the amount of water absorbed by the supported film was in no case less than by the corresponding free film. Moreover, supported films frequently absorbed considerably more water than free ones and tended to blister formation after sufficiently prolonged immersion<sup>6</sup>. It could be stated that, generally, an increased water absorption of supported films indicated loss of adhesion to the substrate and finally resulted in blister formation or even film detachment. In other words, a comparison between the water absorption of free and of supported films enables one to judge whether the interaction between the film and the substrate is strong enough to resist the penetration of water into the interface.

The water absorption of paint films may depend markedly on the pigmentation used in the formulation. Moreover, it could be established<sup>7</sup> that the water absorption is related to the PVC in a rather characteristic way, and that this dependency of  $Q_B$  on PVC is well reproducible.

At least three different relations have been found (Fig. 1) :

#### *Case I :*

The water absorption is independent of the PVC, provided that the swelling equilibrium is attained. It is logical to assume that, in this case, only the vehicle absorbs water and no loss of adhesion between pigment particles and vehicle occurs. Because the pigment particles may be considered as multivalent cross-linking sites in this case, one might expect that the water absorption would even decrease with an increase in PVC. It is only because the water absorption of most paint films is quite low that, generally, it was found to be independent of the PVC. If strong organic swelling agents are used instead of water, the reinforcement by the pigment may be revealed very significantly by a decreased swelling with rising PVC (Fig. 1, Ib).

#### *Case II :*

The water absorption increases continuously with increasing PVC. This relation has been explained by the loss of adhesion between the pigment and the vehicle, followed by penetration of water into the interfacial space arising from the expansion of the vehicle by swelling. In principle this dependence of water absorption on the PVC could also be explained by the entry of water into the empty interstices of pigment agglomerates or flocculates. There are however

two arguments against this explanation. First, case II mostly proved to be temperature dependent, changing to case III at sufficiently high temperature. As will be shown later, case II therefore needs some modified explanation. Secondly, no influence of the method and duration of the milling or grinding process on the characteristic shape of the curve could be found.

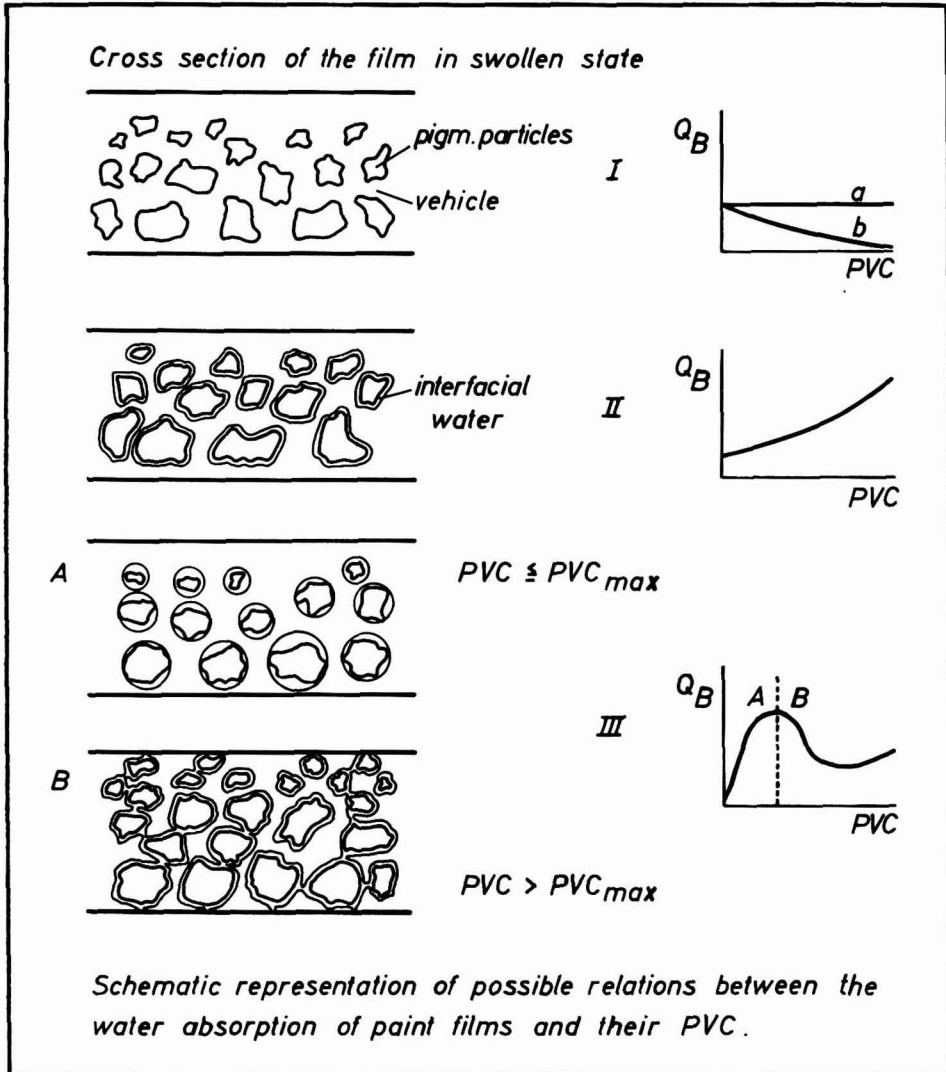


Fig. 1. Schematic representation of possible relations between the water absorption of paint films and their PVC

*Case III :*

The water absorption of the paint film first increases with rising PVC to a maximum and then decreases until the critical PVC is reached. Then water absorption increases again due to capillary water in the porous film.

The existence of a maximal water absorption at a certain PVC, far below the critical value, has already been mentioned by Hintze<sup>8</sup>, who gave no satisfactory explanation. Experimental evidence has been presented<sup>7</sup> that these absorption maxima must be explained by osmotic processes taking place at the interfaces between pigment particles and vehicle during the exposure of the films to liquid water. These osmotic processes depend on the presence of low molecular weight water soluble substances at the surface of the pigment particles. The source of these substances may be the vehicle or the pigment itself. Furthermore, for osmosis to take place, it is necessary that the vehicle surrounding each pigment particle be permeable to water, but sufficiently impermeable to the soluble substances present at the interfaces.

It is known that low molecular weight, polar substances are absorbed in particular on the surface of oxidic pigments<sup>12-14</sup>. Moreover, preliminary experiments with membranes made from usual paint vehicles showed that considerable osmotic pressures may develop. If paint films pigmented with soluble inorganic salts like NaCl<sup>7</sup>, or with a water soluble azo dye such as Acilanponceau RR®<sup>9</sup>, were immersed in distilled water, similar maxima of water absorption can be observed at low PVC. Furthermore, maxima, which appeared with the swelling of certain paint films, could be completely suppressed by using solutions of salts in an adequate concentration instead of distilled water (Fig. 2). No significant influence was exerted on the water absorption of salt-free films immersed in salt solutions.

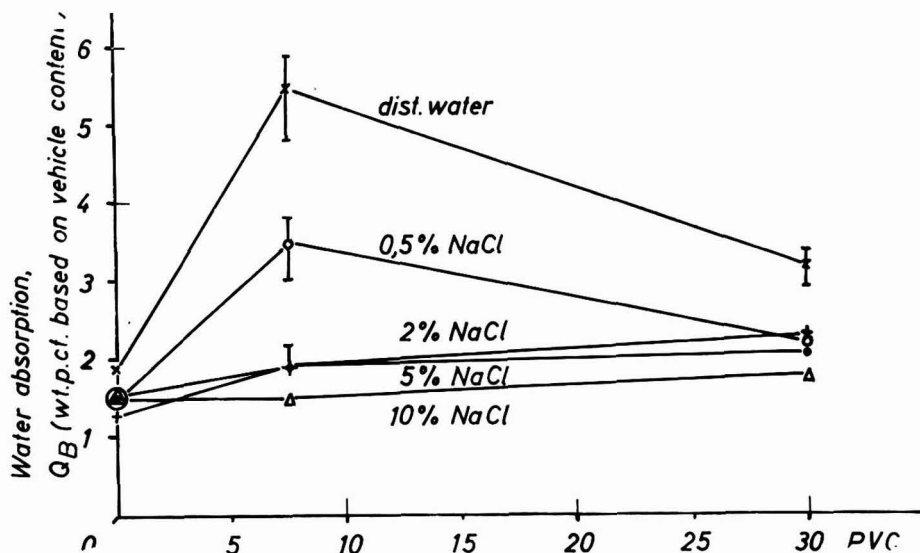


Fig. 2. Water absorption of linseed oil alkyd resin films pigmented with titanium dioxide (rutile) in distilled water and aqueous solutions of NaCl, after seven days (dry film thickness 35-40  $\mu\text{m}$ )

The decrease of water absorption at  $\text{PVC} > \text{PVC}_{\text{max}}$ , can be explained by the close approach, or even contact, of the pigment particles at sufficiently high PVC values. Then, not enough vehicle is present between the particles to ensure semipermeability. Therefore, the soluble substances at the interfaces may easily be drained off by water, and osmosis ceases to proceed (Fig. 1, IIIB).

If this explanation is correct, one has to expect that the value of  $PVC_{max}$  is dependent on the size and dispersion of the pigment particles in the solid paint film. As will be shown later, there is some experimental evidence that a relation exists between the degree and structure of pigment agglomeration or flocculation and the value of  $PVC_{max}$ , as well as the shape of the swelling maximum.

The occurrence of water absorption/PVC relations corresponding to case II or III gives evidence of low interaction between the pigment and the vehicle surrounding it, at least in the presence of water. It may be questioned whether this statement may also be applicable to corresponding films in a dry condition. Electron microscopic inspection of cross section fractures of paint films indicated that, in some cases at least, a relation seems to exist.

In some cases, the efficiency of water to invade the pigment-vehicle interfaces was compared with white spirit as a swelling agent (Fig. 4). Work is continuing to include other organic swelling agents of different physical and chemical properties. Preliminary results have shown that, by determining the absorption of different swelling agents, it might be possible to set up a similar concept for the interaction between pigment and vehicle as the solubility parameter for the interaction between vehicle and solvent.

#### **Extractable substances in paint films**

After swelling of paint films in water or in organic solvents, some loss of weight is usually observed, due to extraction of soluble substances from the vehicle or the pigment. If this weight loss ( $L_B$ ) is based on the weight of the vehicle component of the film before swelling took place, the relation between the amount of extracted substances and the PVC indicates where the extracted substances originate.

As is shown in the diagrams of Fig. 3, several characteristic  $L_B$ /PVC curves may be found. If  $L_B$  is independent of the PVC, the extractable substances originate only from the vehicle (I). If the soluble substances are solely due to the pigment,  $L_B$  will increase with the rise in PVC (II).

Frequently, both the pigment and the vehicle will contain some extractable material. Then the curve will intersect the  $L_B$  scale as in III. Finally, it is possible that  $L_B$  decreases as PVC increases (IV). Provided the adhesion between the pigment particles and the vehicle is strong enough to resist the attack of the swelling agent, the length of the diffusion pathways, which also increases with PVC, may be responsible for the decrease of the  $L_B$  values. Some doubt arises about this last interpretation, because even with good organic swelling agents, generally no significant time-dependent change in the tendency of the  $L_B$  curves could be observed.

#### **Experimental determination of the absorption of swelling agents by paint films**

The absorption of water or other swelling agents was measured gravimetrically. In order to avoid inclusions between film and substrate, free films were used. They were prepared by using either tin foils, which were dissolved by mercury after film formation, or films of polytetrafluorethylene, as a substrate. The films had a circular area of  $11\text{cm}^2$ . After weighing, the films were immersed in distilled water at  $23^\circ\text{C}$  for different lengths of time. For each immersion time 5-6 separate samples were used. After immersion the films

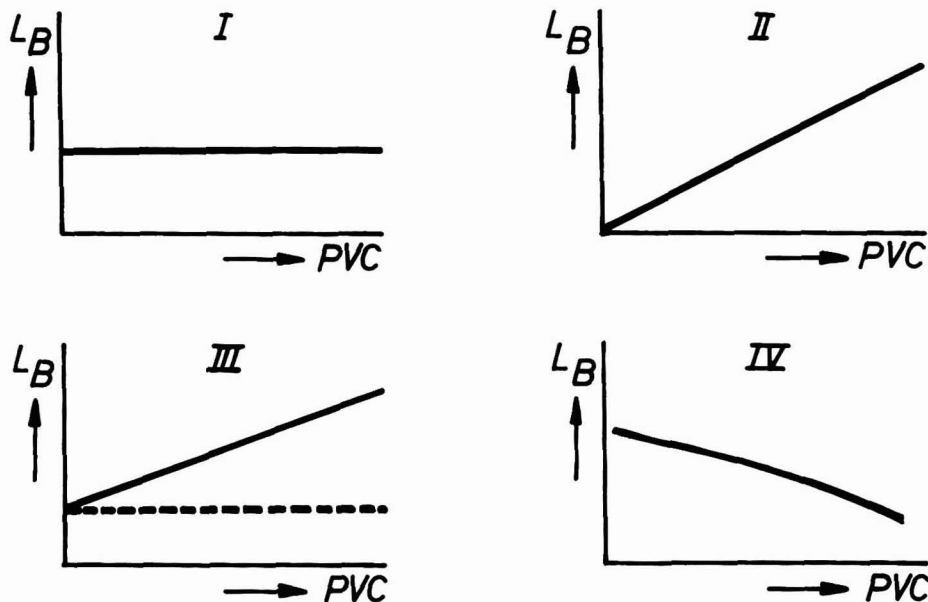


Fig. 3. Schematic representation of possible relations between the weight loss involved in swelling of paint films and the PVC

were blotted in a definite way with filter paper and weighed immediately afterwards. Normally the whole procedure between removing the films from the water bath and reading off the weight lasted not longer than about 30 seconds. After drying to constant weight at 23°C and 45 per cent rel. humidity, the films were weighed again. The degree of swelling,  $Q_B$ , is given as the weight percentage difference between the film in swollen and in dry state after swelling, based on the weight of the vehicle present in the film.

It may be true that, in spite of the precautions taken in determining the water absorption, a little water may have evaporated before weighing the swollen film. Nevertheless the values for  $Q_B$  obtained in this way were sufficiently reproducible to allow a good distinction between different paint systems. The points of the  $Q_B$ /PVC plots in the following figures represent mean values, and the vertical lines above and below each point indicate the maximum deviations of single values from the mean value.

Strictly speaking, swelling means a homogeneous solvation of the vehicle molecules by the swelling agent. Most paint vehicles, however, besides swelling, also take up water heterogeneously, which finally may lead to cluster formation or similar infiltrations. For convenience the water absorption of paint films will be referred to as swelling throughout this paper, irrespective of the distribution of the absorbate in the film.

The weight loss of paint films due to the extraction of soluble substances was determined from the film weight before swelling and after drying to constant weight. This weight loss ( $L_B$ ) was based on the vehicle content of the solid film.

#### Swelling of paint films containing reinforcing pigments (case I)

In this connection reinforcement simply means some interaction between



pigment particles and vehicle by physical or chemical bonds, which persists during adsorption of the swelling agent. If the absorption of swelling agents by paint films is independent of or even decreases with PVC, it must be concluded that neither the pigment nor its interface with the vehicle is involved in the swelling process. Paint films from urea formaldehyde resin (UF) or from epoxide polyamide resin (EA) pigmented with titanium dioxide, absorbed water proportional to the vehicle content of the film, i.e. independently of its PVC (Fig. 4). The water absorption of linseed oil alkyd resin films (LA) and of urea formaldehyde resin films even decreased with PVC, when carbon black (CB) was used as pigment<sup>10</sup>. This effect of carbon black, in contrast to titanium dioxide, may be explained by the higher functionality of this pigment as a crosslinking site. The average particle size of the carbon black was only  $0.013\mu\text{m}$ , compared with  $0.18\mu\text{m}$  for the titanium dioxide used. Even if both pigments had similar absorptivity for vehicle molecules, carbon black would expose much more surface area to the vehicle surrounding it at the same PVC.

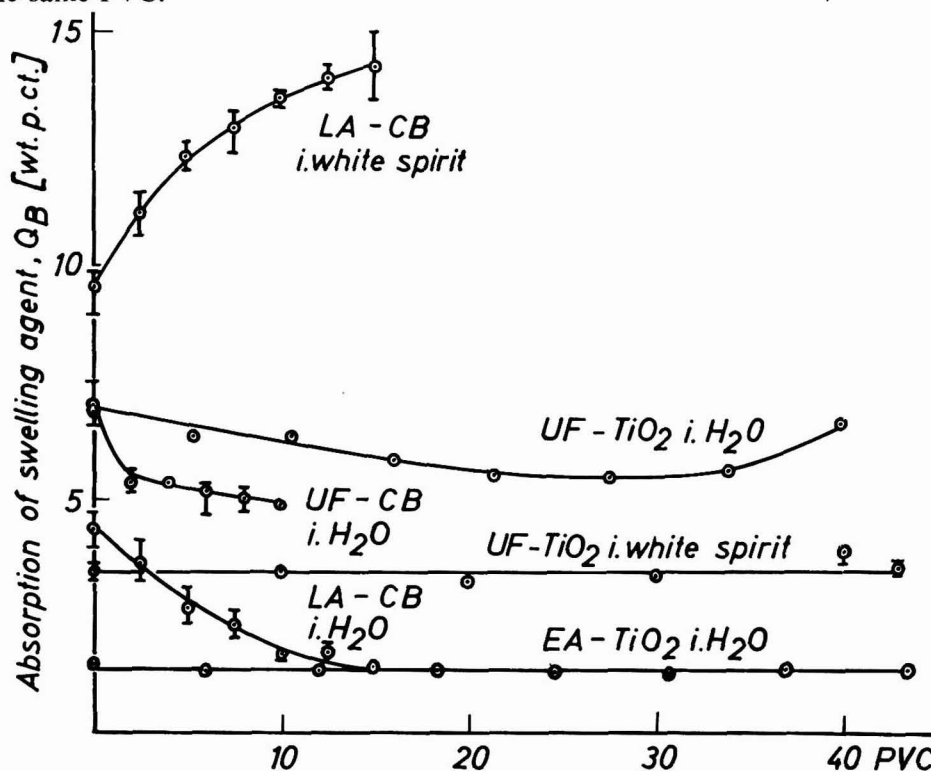


Fig. 4. Absorption of swelling agent by paint films with reinforcing pigments (except LA-CB in white spirit)

Paint system	Film thickness ( $\mu\text{m}$ )	Immersion time
LA-CB white spirit	29-45	24 hours
LA-CB water	29-45	14 days
UF-TiO <sub>2</sub> water	50-80	7 days
UF-TiO <sub>2</sub> white spirit	65-85	2 days
UF-CB water	40-55	14 days
EA-TiO <sub>2</sub> water	45-70	7 days

A further explanation for the decrease of  $Q_B$  when carbon black is used as pigment may be its ability to adsorb low molecular weight soluble substances rather strongly while the paint is still in the liquid state. By this adsorption the content of water soluble material in the vehicle would be diminished and so also would the swelling.

Such pronounced absorptivity of carbon black would be consistent with the fact that with this pigment the amount of water extractable substances from the vehicle significantly decreased with increasing PVC (Fig. 5). On the other hand, the  $L_B$  values of linseed oil alkyd films pigmented with phthalocyanine blue (PB) (average particle size  $0.07\mu\text{m}$ ) did not depend on the PVC if water was used as swelling agent. Just as with films pigmented with carbon black, the water soluble substances were derived from the vehicle, but phthalocyanine blue may not be able to free the vehicle from soluble substances by strong adsorption.

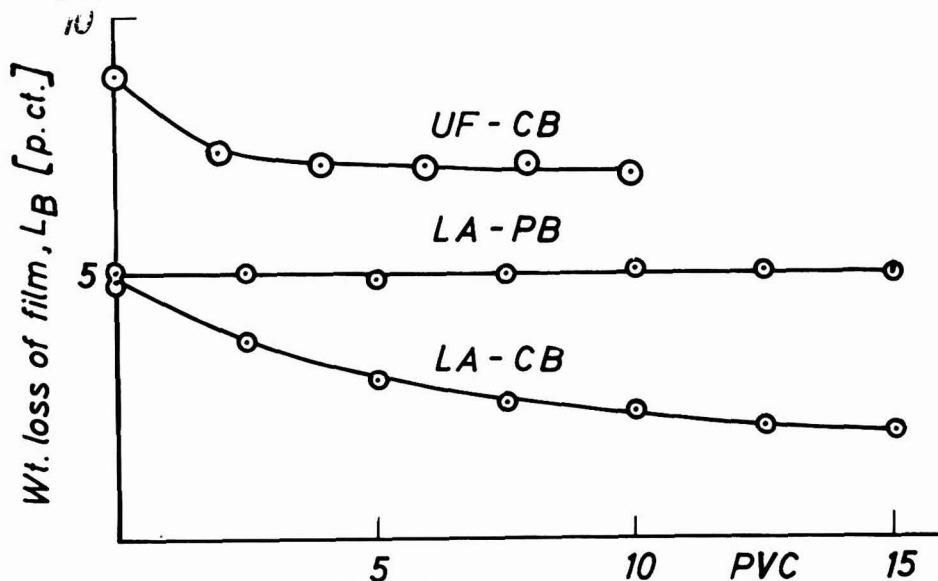


Fig. 5. Weight loss,  $L_B$ , of paint films with carbon black (CB) and phthalocyanine blue (PB) after swelling (14 days) in water, related to the PVC. Film thickness ( $\mu\text{m}$ ): LA-CB 29-45, LA-PB 35-55, UF-CB 40-55

When white spirit was used as a swelling agent instead of water,  $Q_B$  was independent of PVC in the case of urea formaldehyde resin films pigmented with titanium dioxide (Fig. 4), even after prolonged immersion<sup>10</sup>. Accordingly, white spirit is not able to invade the pigment vehicle interfaces, just as with water as a swelling agent. On the other hand, carbon black obviously does not reinforce linseed oil alkyd films swollen in white spirit, whereas reinforcement takes place with water as a swelling agent.

### Swelling of paint films exhibiting an absorption maximum (case III)

In earlier investigations of some paint films containing inorganic oxide pigments, maxima of water absorption were found at PVC values well below the critical point<sup>7</sup>. Since then, further experimental evidence has been obtained that these maxima are caused by osmotic processes<sup>9</sup>. Thereby, an increased

accumulation of water takes place at the interfaces between the pigment particles and the vehicle surrounding them. Such swelling experiments have now been extended to some organic pigments.

Linseed oil alkyd films with phthalocyanine blue (PB) or with quinacridone red (CR), after 14 days of immersion, had maxima of water absorption at PVC of 10 and 15 respectively (Fig. 6)<sup>10</sup>. This is in contrast to the same films with carbon black as a pigment (Fig. 4), where the water absorption steadily decreased with rising PVC.

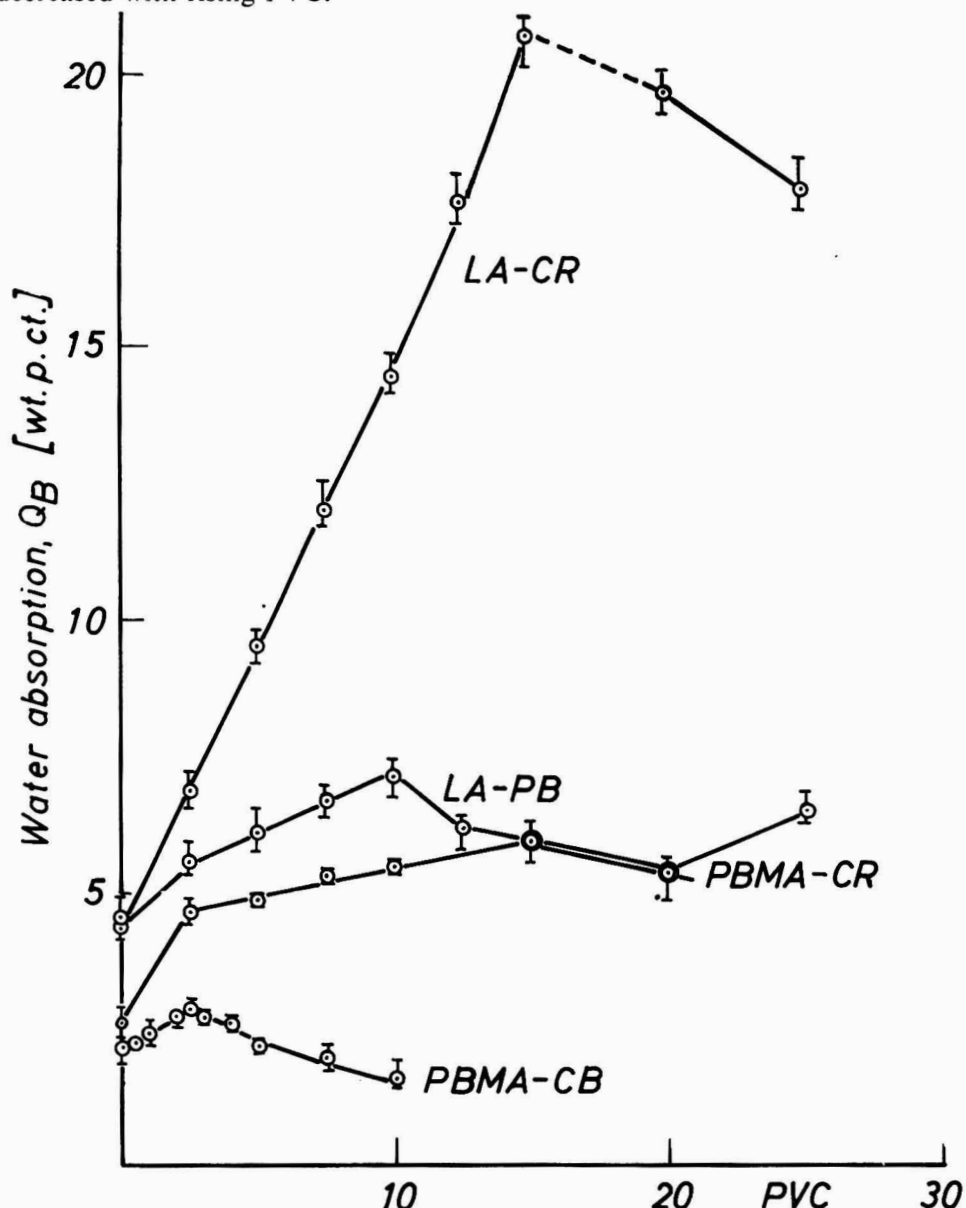


Fig. 6. Water absorption of paint films with an absorption maximum, after 14 days. Film thickness ( $\mu\text{m}$ ): LA-CR 35-55, LA-PB 35-55, PBMA-CR 55-74, PBMA-CB 55-74

It must be concluded from the increased water absorption that not only does water displace the vehicle from the pigment surface, but also that low molecular weight water soluble substances are present at the interface. The source of the soluble substances responsible for the strongly increased water absorption of films with quinacridone red still remains somewhat obscure. Both pigments, quinacridone red and phthalocyanine blue, have about the same conductivities in 10 per cent aqueous dispersions ( $264 \cdot 10^{-6}$  and  $296 \cdot 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  respectively), scarcely any water soluble impurities (0.25 per cent and 0.35 per cent respectively), and also similar average particle sizes ( $0.06 \mu\text{m}$  and  $0.07 \mu\text{m}$  respectively); but films with phthalocyanine blue have only a weak absorption maximum and a much lower water absorption. Perhaps quinacridone red absorbs low molecular weight substances more strongly from the vehicle in the liquid state. In contrast to carbon black, these substances are displaced relatively easily when water invades the interface (compare with Figs. 4 and 5). Admittedly, this explanation is still somewhat speculative until more is known about absorption and displacement processes at the surface of these pigments.

Films from plasticised polybutyl methacrylate (PBMA), when swollen in water, tended to give absorption maxima with all pigments investigated<sup>7</sup>. The soluble substances responsible for the osmotic processes involved in the water absorption of these films are derived from the plasticiser used. Because the content of plasticiser varied according to the vehicle content of the film, the weight loss,  $L_B$ , was expected to be independent of PVC, as is confirmed in Fig. 7. When dimethylglycolphthalate was replaced by dimethylthianthrene as plasticiser, no maximum was observed in the swelling of PBMA-films with titanium dioxide as a pigment<sup>7</sup>.

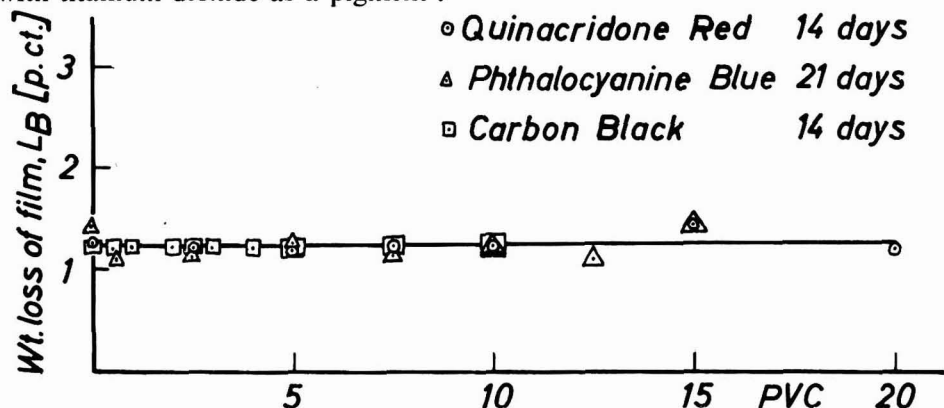


Fig. 7. Weight loss,  $L_B$ , of pigmented polybutyl methacrylate films in water, related to PVC; dry film thickness ( $\mu\text{m}$ ): PBMA-CR 55-74, PBMA-PB 66-82, PBMA 55-74

If osmosis is involved in the swelling of paint films, it must be expected that the end point of the water absorption, which corresponds to the equilibrium state, will be attained only slowly. In fact, when absorption maxima were observed, it was rather difficult to arrive at constant values of the water absorption. When plasticised films of polybutyl methacrylate pigmented with an azo pigment (CI Pigment Red 48) were swollen in water, no constant values of water absorption could be obtained even after 42 days of immersion. The

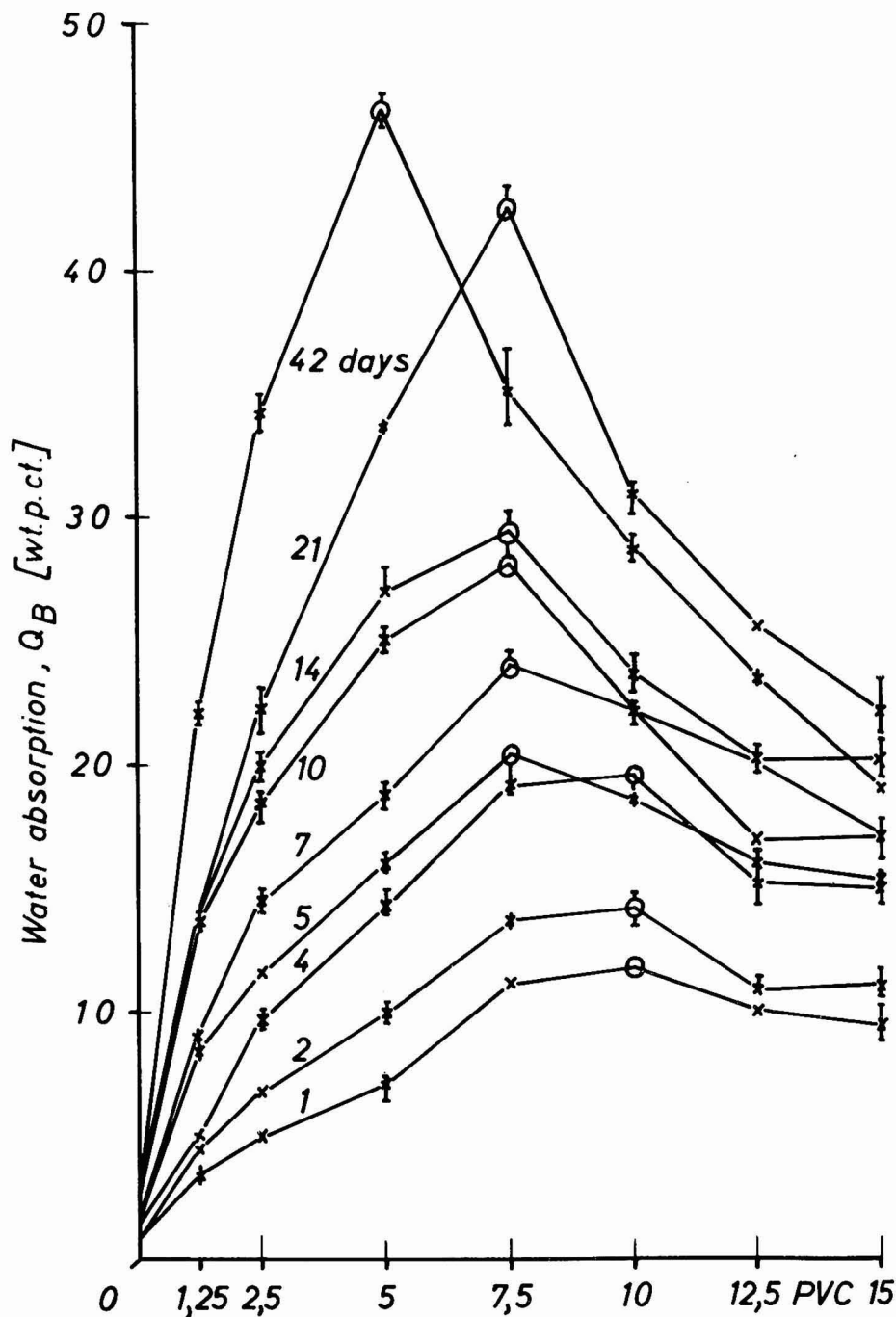


Fig. 8. Shift of the absorption maxima of plasticised polybutyl methacrylate films with CI-Pigment Red 48 during water immersion (dry film thickness 67-83  $\mu\text{m}$ )

pigment used is known to be sensitive to water. After some time the water used for the swelling experiment showed a reddish coloration. Presumably the pigment gradually hydrolyses during swelling to give manganous hydroxide and water soluble azo acid, thus explaining the extraordinarily high water absorption of these films (Fig. 8). It is important to note the shift of the absorption maximum to lower PVC as swelling is continued. This shift may be explained by defects arising in the vehicle layer surrounding the pigment particles as a result of the expansion by the increasing osmotic pressure within the interfacial spaces. Such defects will occur sooner the higher the PVC of the film is. Because the vehicle layers between the pigment particles decrease in thickness with increasing PVC, osmosis will cease as a consequence of the rupture of the vehicle surrounding the pigment, and first of all in films with the highest PVC. In the course of swelling, the rupture of the vehicle then gradually proceeds also to films of lower PVC, whereas films whose vehicle layers are still intact continue to absorb water. According to this mechanism the weight loss due to the loss of water soluble material from the film increases markedly at  $PVC > PVC_{max}$  (Fig. 9). Moreover, the PVC values, where the

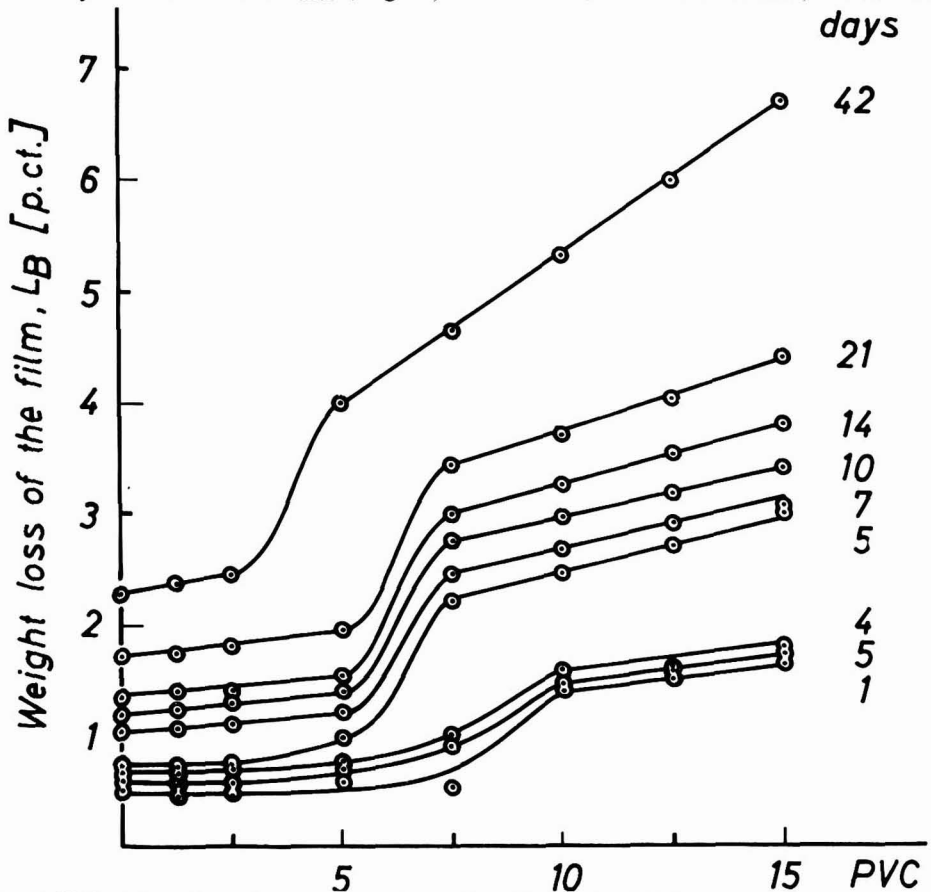
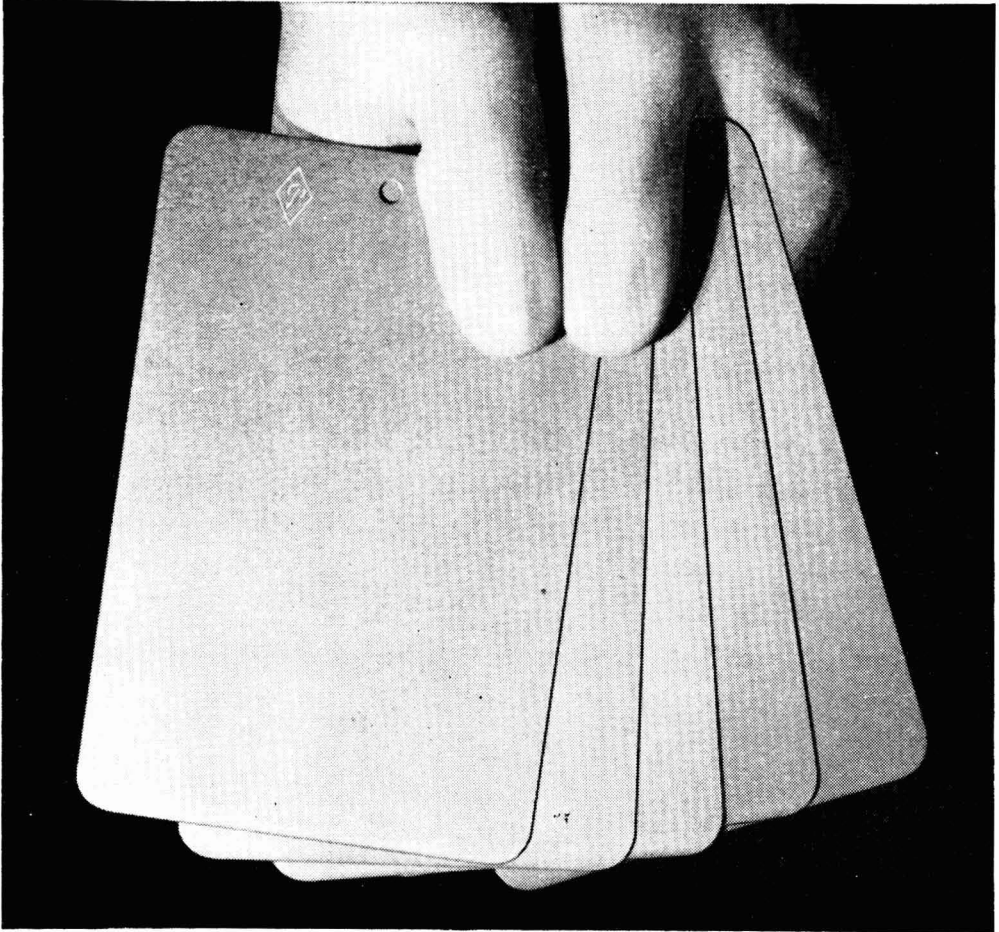


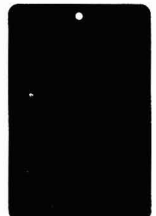
Fig. 9. Weight loss, LB, of polybutyl methacrylate films with CI-Pigment Red 48 at different times of water immersion, related to PVC (dry film thickness 70-85 μm)



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jump to higher  $L_B$  values takes place, agree perfectly with the PVC of the absorption maxima.

### Influence of the swelling temperature on the absorption characteristics of paint films

Expansion of the vehicle layers surrounding the pigment particles by osmotic pressure arising in the interfaces is only possible if the vehicle responds to this pressure by elastic or plastic deformation, to a certain extent at least, without losing its semipermeable or permeation-retarding property. When the water absorption takes place at temperatures ( $T_s$ ) below the glass transition temperature ( $T_g$ ) of the film, it must be supposed that the vehicle is no longer able to yield to the rising osmotic pressure at the interfaces, and consequently ruptures. With water as a swelling agent it is rather probable that the critical temperature, where such a rupture occurs, will be within the range of the glass transition point of the vehicle. It has been found by Kumins and co-workers<sup>11</sup> that glass transition temperature is affected markedly by pigments, so it might be the  $T_g$  of the pigmented film which has to be considered in this connection. The special mechanism of water absorption involved in this case, however, provides that interfacial adhesion is already lost at the beginning of the swelling. Therefore, in such a case no reinforcing effect of the pigment is to be expected in the swollen state of the film. Furthermore it has to be considered that  $T_g$  may continuously decrease during swelling as a result of the plasticising action of the swelling agent. Yet for most vehicles used in

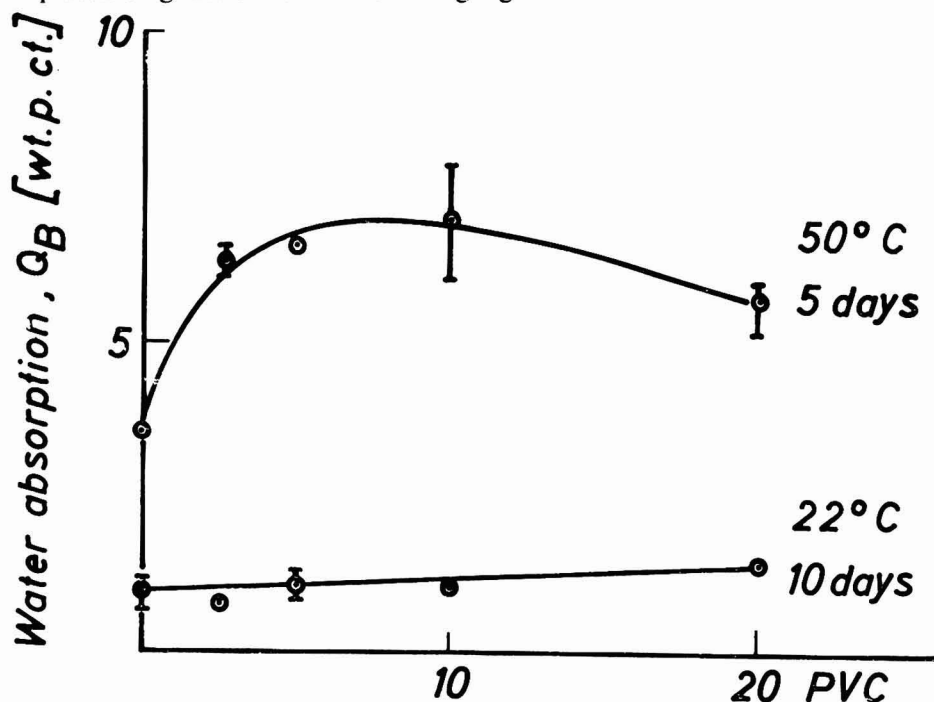


Fig. 10. Water absorption of films from nitrocellulose + coconut oil alkyd resin + dibutylphthalate + titanium dioxide (rutile) at different temperatures. ( $T_g$  of unpigmented film, dilat. 17-19°C; dry film thickness 40-60  $\mu\text{m}$ )

paint films, water is an ineffective swelling agent. Its plasticising action, therefore, will not be of much influence on the  $T_g$  of the vehicle.

With films from plasticised polybutylmethacrylate "pigmented" with lead nitrate, as well as with an epoxide-polyamide resin film pigmented with zinc

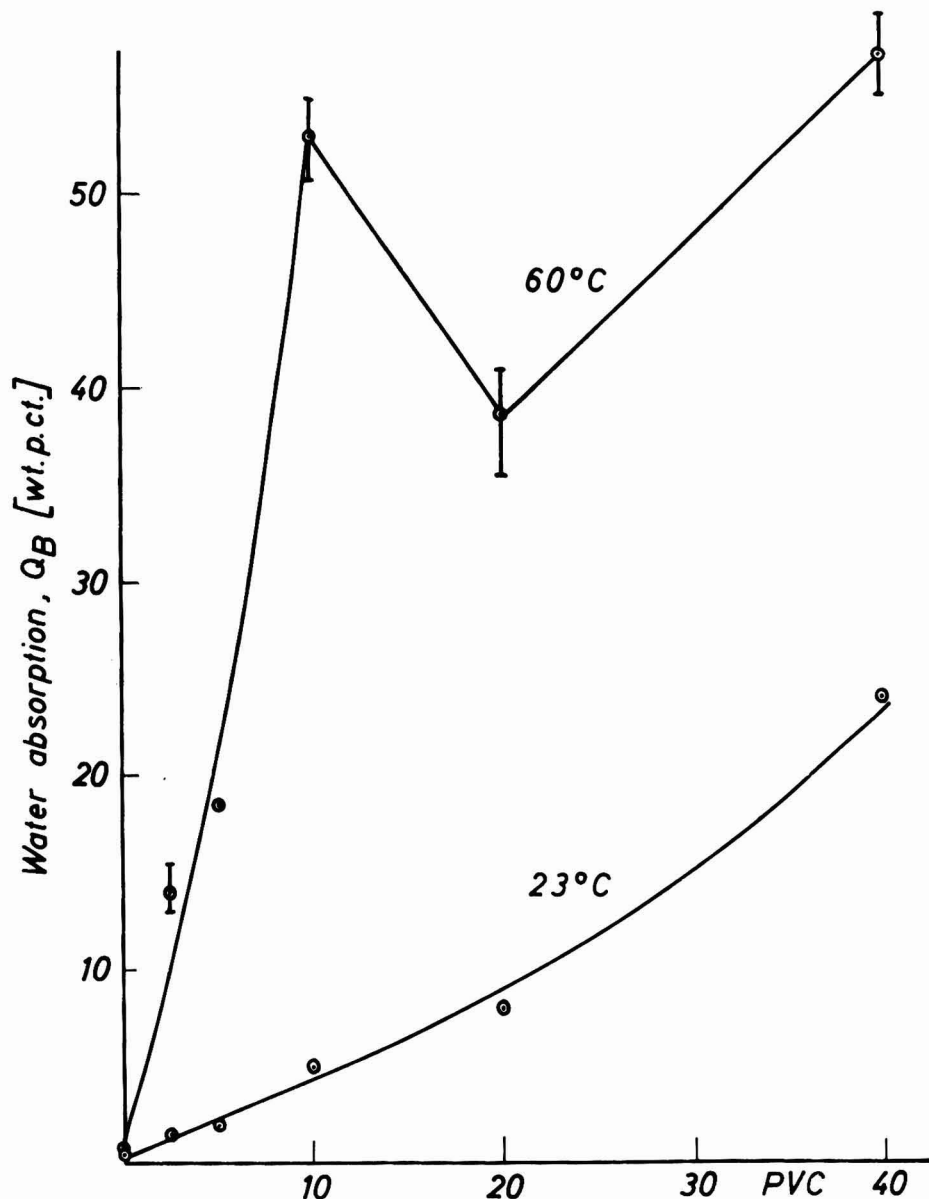


Fig. 11. Water absorption of coconut oil alkyd-urea formaldehyde films with zinc yellow at different temperatures after six days. ( $T_g$  of unpigmented film, dilatom. ca.  $55^\circ\text{C}$ ; dry film thickness 40-60  $\mu\text{m}$ )

oxide, the water absorption was shown to change from case II to III by increasing the swelling temperature above the transition range of the vehicle<sup>9</sup>.

Films from nitrocellulose/alkyd resin plasticised with dibutylphthalate and pigmented with titanium dioxide (Fig. 10), from alkyd-urea formaldehyde resin with zinc yellow (Fig. 11), and from linseed oil alkyd with zinc oxide (Fig. 12), now provide additional experimental evidence that it is the swelling temperature relative to the  $T_g$  of the resin used which decides whether an absorption maximum is to be expected or whether the water absorption will increase continuously. A mixture of water and glycol was used as swelling agent for

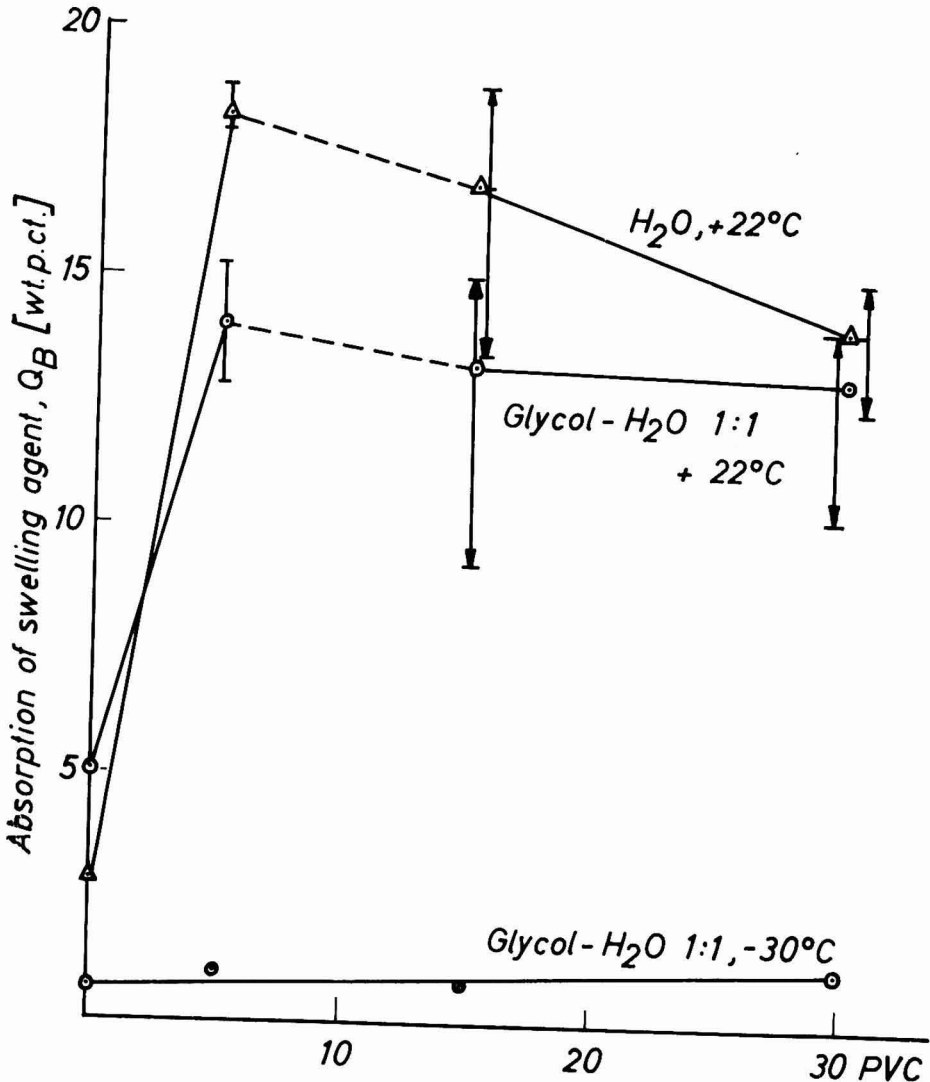


Fig. 12. Absorption of swelling agent by linseed oil alkyd resin films with zinc oxide after eight days at different temperatures. ( $T_g$  of unpigmented film, dilatometer,  $-22^\circ C$ , torsion pendulum  $-5$  to  $-15^\circ C$ ; dry film thickness  $35-50 \mu m$ )

the linseed oil alkyd films because the  $T_g$  of this resin was below the freezing point of water. In spite of the relatively wide fluctuation of the individual values, the absorption characteristic was not influenced too much. The absorption characteristic for case II therefore needs some modified explanation. In fact so far no paint film has been found in which an absorption characteristic corresponding to case II has not proved to be temperature dependent.

If CI Pigment Red 48, which tends to hydrolyse under the influence of water, was used, this temperature-dependent transition is demonstrated impressively,

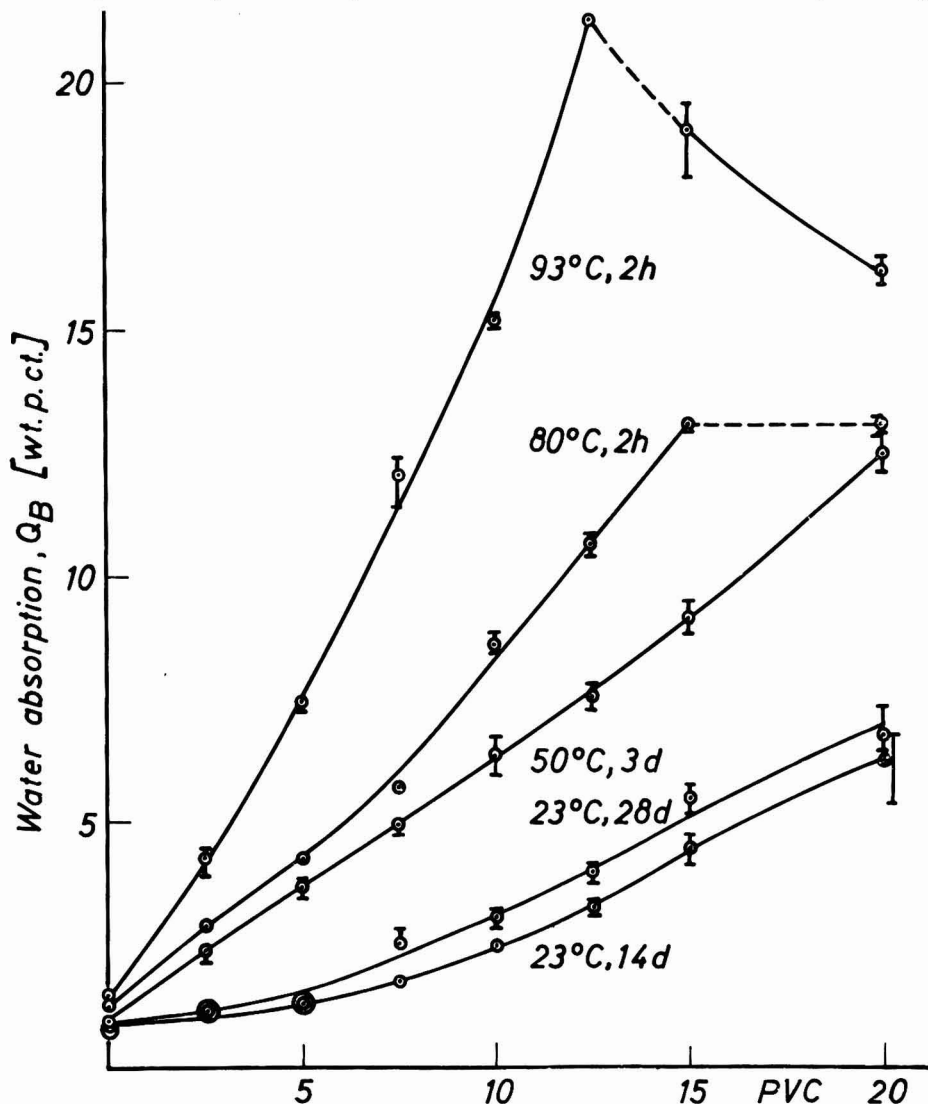
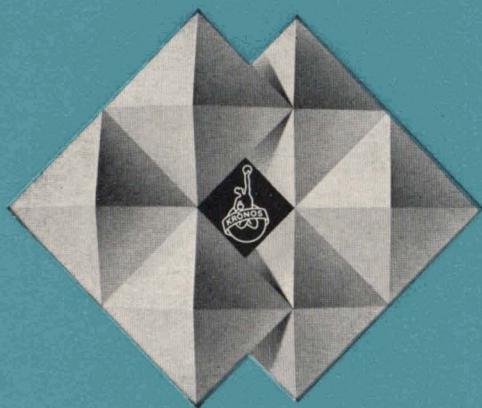


Fig. 13. Water absorption of films from coconut oil alkyd-melamine formaldehyde resin with CI-Pigment Red 48 at different temperatures. ( $T_g$  of unpigmented film, dilatom. ca.  $70^\circ\text{C}$ ; dry film thickness 50-70  $\mu\text{m}$ )

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and is in accord with the  $T_g$  of the vehicle (Fig. 13). The loss of the semi-permeable property of the film at swelling temperatures above  $T_g$  is reflected in a steeper increase of the weight loss curve beyond  $PVC_{max}$  (Fig. 14). At 23°C the weight loss of the film remains fairly constant up to a PVC of 15 and then steadily increases at higher PVC values. This increase may be attributed to voids in the film produced by internal rupture of the vehicle.

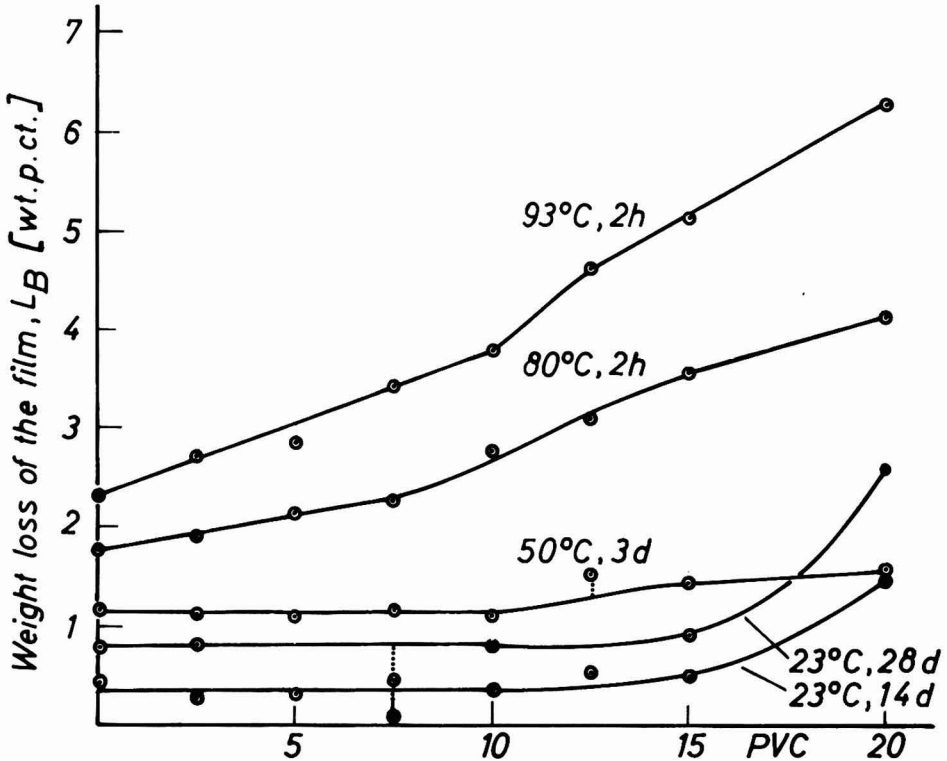


Fig. 14. Weight loss,  $L_B$ , of films from coconut oil alkyd-melamine formaldehyde resin with CI-Pigment Red 48 at different temperatures and times of water immersion (dry film thickness 50-70  $\mu m$ )

With regard to the glass transition temperature of the film it must be assumed that some relation exists between the appearance of the maxima of liquid water absorption and the blistering tendency of supported paint films in a humid atmosphere. It is well known that blistering is greatly accelerated at elevated temperatures. Because many vehicles have a  $T_g$  somewhat above room temperature, blistering caused by osmotic processes at the interface between film and substrate, if it occurs at all, is expected to become pronounced only at temperatures sufficiently above the  $T_g$  of the film. At temperatures below  $T_g$ , paint systems, which are liable to blistering by osmosis, will not be able to yield to the osmotic pressure arising at the interface and therefore will crack or fissure. In the case of ferrous substrates, rust will finally bleed out at the surface of the film without damage of the film necessarily being visible.

**Inspection of fracture cross-sections of paint films by the electron microscope**

The strength of interaction between pigment and vehicle can be expressed by the adhesion between both phases at their interfaces. This adhesion may be estimated by inspecting the cross-sections obtained by fracturing the paint films after embedding them in a rigid resinous material such as an epoxide resin.



Fig. 15. Fracture surface of an urea formaldehyde resin film pigmented with zinc oxide (PVC=15)



It must be expected that the fracture surface mainly runs through the vehicle if the adhesion between the pigment and the vehicle exceeds the cohesion of the vehicle. In the case of an urea formaldehyde resin film with zinc oxide as a pigment (PVC=15) scarcely any pigment particle can be observed in the

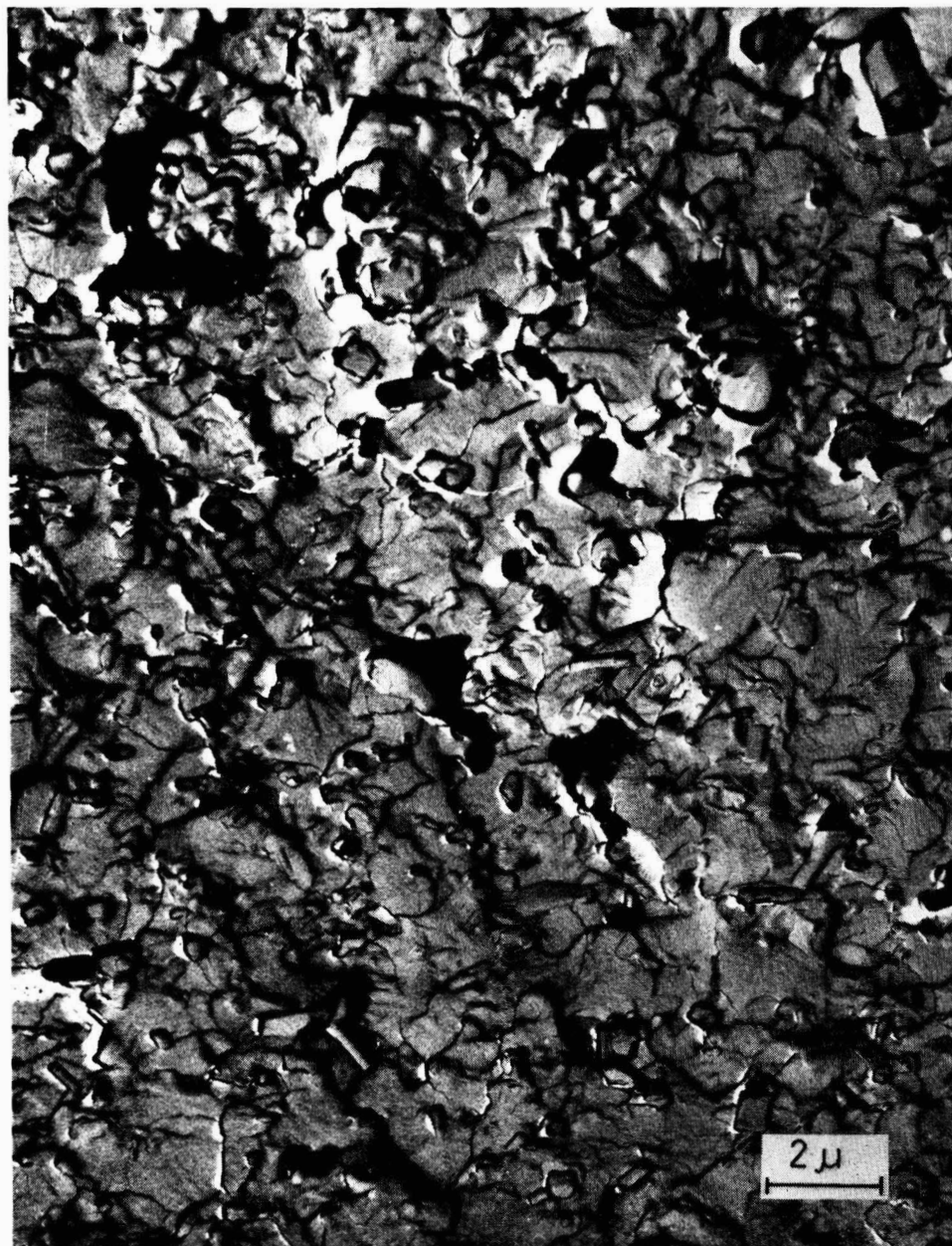


Fig. 16. Fracture surface of a linseed oil alkyd resin film pigmented with zinc oxide (PVC=15)

electron micrograph of the fracture surface (Fig. 15). Accordingly it may be concluded that the vehicle is reinforced by the pigment. Obviously this reinforcement is maintained when these films are exposed to water, for the water absorption was shown to be independent of PVC<sup>7</sup>. In the case of a linseed

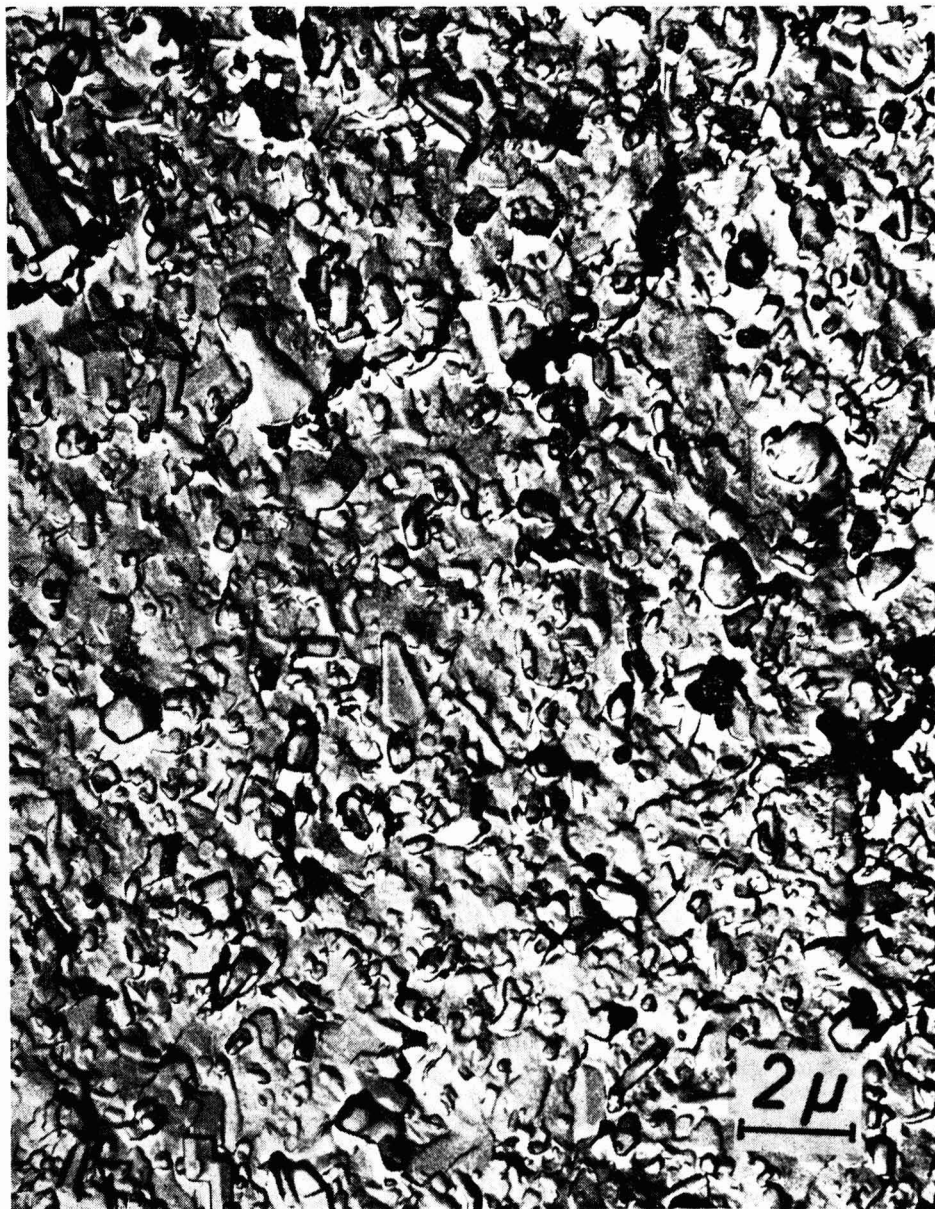


Fig. 17. Fracture surface of an epoxide-polyamide resin film pigmented with zinc oxide (PVC=15)

oil alkyd resin film and an epoxide polyamide resin film, both pigmented with the same amount of zinc oxide, the appearance of the fracture surfaces was quite different (Figs. 16 and 17). In contrast to the urea formaldehyde films, the fracture proceeded along the pigments which were encountered by the advancing fracture front. Therefore the single pigment particles can easily be distinguished from the vehicle. It may be concluded, therefore, that the adhesion between the pigment and the vehicle is weaker than the cohesion of the vehicle. Correspondingly the water absorption was found to increase with rising PVC<sup>7</sup>. In spite of this correspondence, some doubt remains whether it is generally permissible to draw conclusions, from the structure of the fracture surface of dry films, about the interfacial condition present in swollen films when immersed in water. One may assume that water is already absorbed at the pigment surface during the preparation of the paint films, if it is absorbed preferentially at all, and that this condition does not change significantly when the film is exposed to liquid water. Nevertheless it must be borne in mind that the concentration of the water present and its state of aggregation may have an important influence on interfacial behaviour.

An interesting case of rather bad adhesion between pigment and vehicle was encountered in films of plasticised polybutyl methacrylate pigmented with titanium dioxide. The pigment flocculates present in the fracture surface can easily be distinguished in Fig. 18. The dark spots visible in the picture indicate pigment particles which have been displaced from their original position during the preparation of the replica. Probably there is no adhesion at all between pigment and vehicle, and the flocculates are embedded in the dimethylglycol phthalate which was used as plasticiser. Some support for this view is provided by the permeability of this film to liquid water, which was found to increase with rising PVC<sup>9</sup>. This relation is understandable if the water penetrating the film has pathways at its disposal which offer much less resistance than the vehicle itself. These pathways must be situated at the surface of the flocculates or in their interior. The presence of vehicle-free spaces in the flocculates of this film is very improbable, because then there is no reason why the liquid water absorption should strongly decrease again with rising PVC after the swelling maximum has been passed<sup>7</sup>. The appearance of a maximum of water absorption is consistent with bad adhesion between pigment and vehicle, which is evident in Fig. 18.

#### **Relations between pigment dispersion and the shape and position of the maximum of water absorption**

As has been mentioned before, the decrease in water absorption with rising PVC after the maximum has been passed may be explained by the close proximity of the pigment particles or flocculates in a paint film below the critical PVC. As a consequence of this, the osmotic processes will gradually cease with rising PVC, because the vehicle layers between the pigment particles no longer retain their permeation-retarding property. If the lower water absorption at PVC values beyond the maximum is caused by the close approach, or even contact, of the pigment particles, it must be supposed that the PVC range of the absorption maximum in some way depends on the size of the pigment as well as on its degree of dispersion in the vehicle.



Fig. 18. Fracture surface of a plasticised polybutyl methacrylate film pigmented with titanium dioxide (rutile) (PVC=20)

In Fig. 19 the complete fracture cross-section through the film made from plasticised polybutyl methacrylate (PBMA) with a PVC of 20 ( $>PVC_{max}$ ) is shown. It can be seen that the titanium dioxide particles are not uniformly

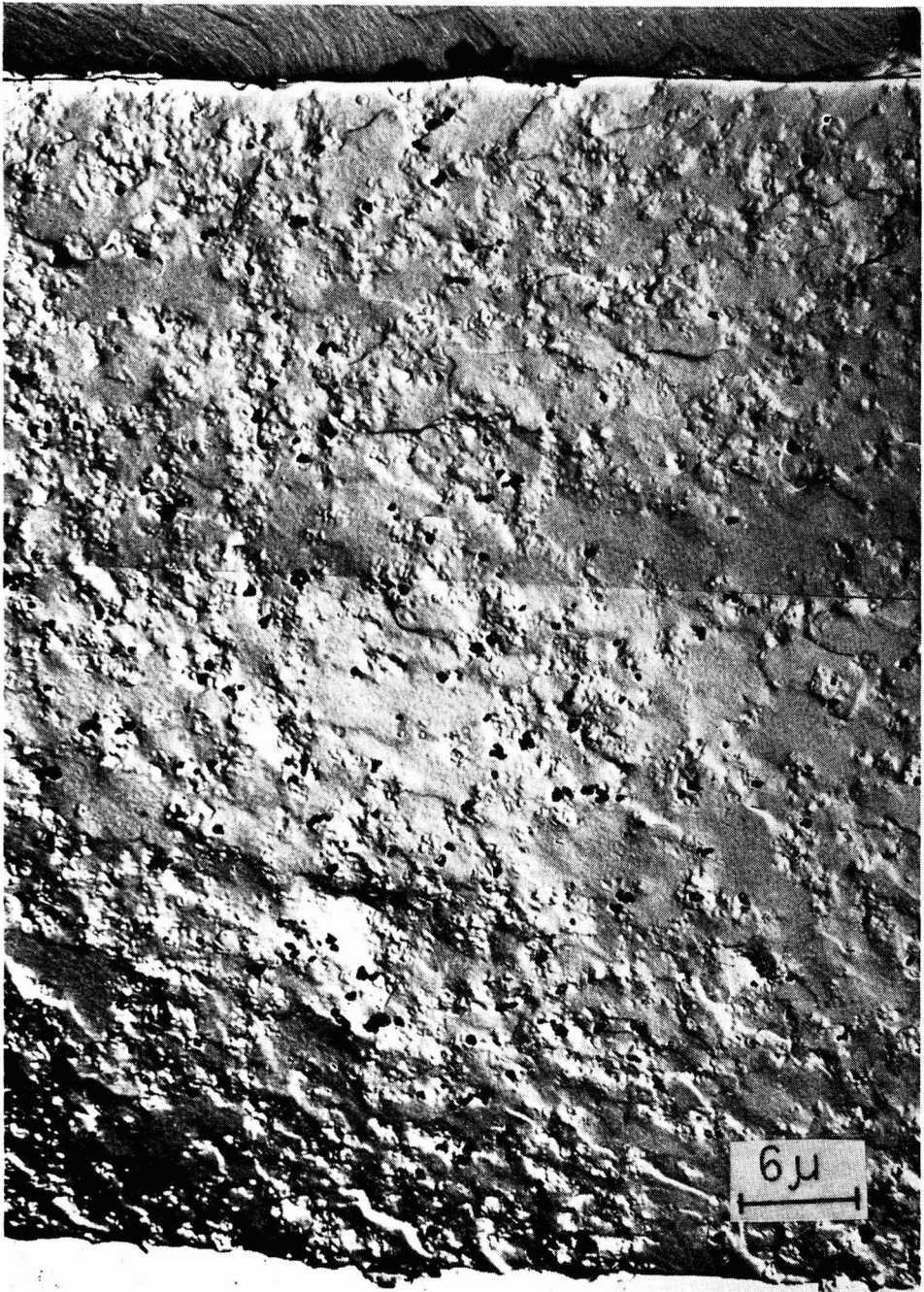


Fig. 19. Complete cross-section of the fracture surface of a plasticised polybutyl methacrylate film pigmented with titanium dioxide (rutile) (PVC = 20)

distributed throughout the film, but are arranged as chain-like flocculates which extend through the whole fracture surface of the film. When  $PVC < PVC_{max}$ , the flocculates of the pigment are still mostly isolated in the vehicle.

If single pigment particles of a definite size are uniformly distant from one another in a film, one can expect that they will not touch each other until the CPVC is reached at a high packing density. However, when the distribution is more random, some of the pigment particles will be in contact at a lower PVC (Fig. 20, II).

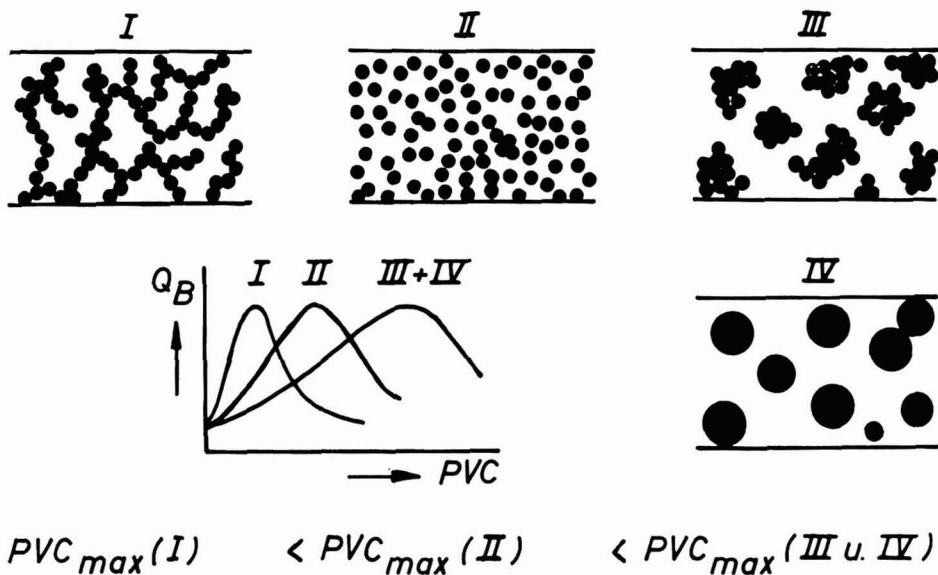


Fig. 20. Schematic demonstration of the relations between pigment particle size, degree of dispersion (flocculation or agglomeration), structure of flocculates or agglomerates and the pigment volume concentration ( $PVC_{max}$ ), where the absorption of swelling agent attains a maximum

In the case of a very unequal distribution, the pigment particles (or flocculates) will come into contact at a rather low co-ordination number at still lower values of PVC (Fig. 20, I) and give such chain-like structures as are seen in plasticised PBMA/titanium dioxide films (Fig. 19). Therefore, if osmotic processes occur, the absorption maximum will appear at a relatively low PVC and be relatively sharp (Fig. 21).

On the other hand, if the pigment particles are highly co-ordinated in the flocculates, but these flocculates are equally distributed through the paint film, the absorption maximum would be expected to shift to higher PVC values (Fig. 20, III). The same will be true for agglomerates or for pigment particles of a correspondingly larger size. For the latter alternative some experimental evidence was given earlier with titanium dioxide pigments of different average particle size but similar degree of dispersion in plasticised PBMA films<sup>9</sup>.

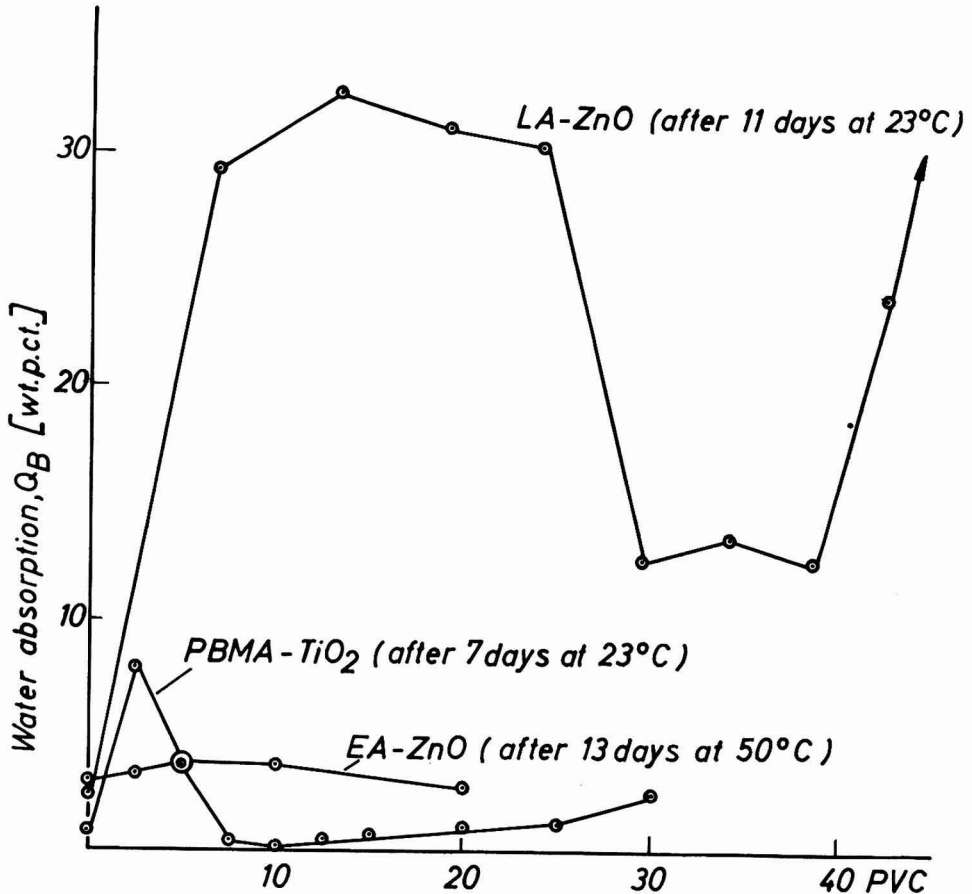


Fig. 21. Shape of absorption maximum related to pigment dispersion. Zinc oxide is well dispersed in LA and EA, but badly in PBMA; dry film thickness ( $\mu\text{m}$ ): LA—ZnO 30-50, PBMA—TiO<sub>2</sub> 28-45, EA—ZnO 50-70

With a more random distribution of pigment particles and a low tendency for flocculation (see Figs. 16 and 17), pigment chains extending through the whole film will be formed only gradually with rise of PVC. Accordingly the absorption maximum will be broad, as shown in Fig. 21, by a linseed oil alkyd resin film (LA) and an epoxide polyamide resin film (EA), both with zinc oxide as a pigment.

Generally it may be stated that, if the same pigment was used in different paint films and if a maximum appeared, the more it was shifted to higher PVC values and became extended, the better the pigment was dispersed in the film.

The height of the absorption maximum depends not only on the amount of soluble substance present at the interface but also on the rates of the water absorption and leaching processes. It is necessary, therefore, to prolong the swelling for a sufficient time in order to decide unequivocally whether an absorption maximum occurs.

Table 1  
Vehicles used for swelling experiments

Vehicles	Abbrev.	Trade name <sup>®</sup>	Drying or stoving conditions
Epoxy-polyamide resin	EA	Epikote 1001	24 hours/23°C; 1 hour/120°C; 28 days/23°C, 45% (rel. hum.)
		Versamid 100	
Urea formaldehyde resin, plasticised	UF	Plastopal AT	40 hours/23°C; 2 hours/140°C (TiO <sub>2</sub> ); 28 days/23°C, 45% 40 hours/23°C; 2 hours/120°C (CB); 28 days/23°C, 45%
		Plastopal AW	
Linseed oil—alkyd resin	LA	Alkydal L 67	14 days/23°C; 1 hour/70°C; 25 days/23°C, 45%
Polybutyl methacrylate, plasticised	PBMA	Plexigum P 24	3 days/23°C; 2 hours/70°C; 7 days/23°C, 45%
		Palatinol 0	
Nitrocell.-coconut oil alkyd resin, dibutylphthalate	—	Wolle E 510	7 days/23°C; 1 hour/70°C
		Alkydal C 25	
		Palatinol C	
Coconut oil alkyd resin urea formaldehyde resin	—	Alkydal C 25 Plastopal EBS 400	½ hour/130°C

Table 2  
Pigments used in paint films

Pigments	Abbrev.	Trade name <sup>®</sup>
Titanium dioxide (rutile) .. .. .	TiO <sub>2</sub>	Kronos Titandioxid RN 56
Zinc oxide .. .. .	ZnO	Zinkweiss Grünsiegel
Phthalocyanine blue (stab. α-mod.) .. ..	PB	Siegle echtblau BSN
CI-Pigment Red 48 .. .. .	—	Sicoechscharlach 22 M
Quinacridone red .. .. .	CR	Permanentrot E 5 B extra
Carbon black .. .. .	CB	Farbruss FW 1
Zinc yellow .. .. .	—	Zinkgelb KSH (Siegle)

[Received 2 December 1967]



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## Discussion at the Scarborough Conference

MR. J. D. SCANTLEBURY, in a written communication, asked what evidence there was to show that the glass transition temperature of the system did not change with PVC? Also, was there evidence to show that the glass transition temperature was not influenced by the plasticising action of water?

DR. W. FUNKE replied that since the submission of the paper, the dependence of glass transition temperature on PVC in paint systems based on alkyd/melamine resin/TiO<sub>2</sub>, vinylacetate copolymer/TiO<sub>2</sub> and thermosetting acrylic resin/Cr<sub>2</sub>O<sub>3</sub> or ZnO, had been carried out, and there was not much difference in the range of PVC below 20 per cent. On the other hand, it was known that Kumins had found a considerable change in the glass transition temperature with PVC in a film based on vinylchloride-vinylacetate copolymer. This dependence would probably differ from system to system, but this would not affect the explanations given for the influence of glass transition temperature on swelling behaviour.

As for the second question, it could not be stated generally that water did not plasticise a paint film, yet most paint vehicles had a rather low water absorption. Furthermore, if the amount of water distributed heterogeneously in the paint film was allowed for, then only a small amount of water was left for solution of the resin molecules. This was not proof, however; therefore, at the present time work was going on to determine the influence of different degrees of humidity on glass transition points by measuring the torsion modulus of the paint films.

DR. L. VALENTINE (CHAIRMAN) said that other factors, e.g., strain in a film, could influence the glass transition temperature, generally to lower it. Was it possible that the osmotic pressure action which had been shown to occur could lead to a condition of strain that would, over a long time, lower the T<sub>g</sub> value of the film itself?

DR. FUNKE said this was possible. If pigments were not reinforcing in the presence of water, then there might be some influence, but, the exact influence of the pigmentation on glass transition had not been studied in great enough detail. There had been very little published until recently.

DR. J. A. W. VAN LAAR said that Dr. Funke had stated that water was an ineffective swelling agent. It had been found that hard urea-alkyd baking enamels, which had a glass transition point above room temperature, when pigmented with about 15 per cent PVC, softened in pure water at 40°C after a few hours if the aluminium was not pretreated. Was not this because the glass temperature was then under room temperature due to the plasticising action of the water? This had also been observed with clear films.

Secondly, Dr. Van Laar referred to the lecture to the FATIPEC Congress of 1966 by Van Westrennen, who had found that blistering could be avoided, even in boiling water, in certain paints by adding quartz powder to raise the glass temperature. This was in agreement with the work of Kumins et al., quoted by Dr. Funke.

DR. FUNKE replied that he maintained that water was a poor swelling agent. The data in the figures did not refer only to swelling, but was the total water absorption. This must not be confused with swelling, where the single molecules of the vehicle were solvated. Such solvation did not take place in most paint films. With regard to the first point, it was generally agreed that to effect plasticisation, the polymer chains of a vehicle must interact with or at least be separated from each other by the plasticiser. It was reasonable to assume that solvents, like water, which didn't swell most paint vehicles significantly, were also bad plasticisers. Therefore, little influence on the glass transition temperature would be expected.

As to the second question, mechanical properties of a film might be affected by quartz powder, but it was doubtful whether this influence would be maintained in boiling water. The prevention of blistering might be explained by the porosity of films highly filled with quartz powder, which was not necessarily related to the behaviour of the pigment/vehicle interface.

DR. E. SUNDERLAND said that Dr. Funke had postulated that the binder acted as a semi-permeable membrane. How was it possible, therefore, to leach out from an unpigmented film large quantities of highly osmotic active substances?

DR. FUNKE answered that he had described vehicles as being semi-permeable, but this semi-permeability must not be considered as a constant property. If water was absorbed, the permeability might change. Moreover it was not maintained that such vehicle layers must be semi-permeable in a strict sense. It would be sufficient if the film layers surrounding the pigment particles were simply permeation retarding, thus allowing the water to go into the paint film more quickly than soluble substances would diffuse out of it. Therefore osmotic processes might occur for some time. This could be demonstrated in some model experiments with soluble pigments, e.g. with sodium chloride or lead nitrate. These substances were leached out very rapidly, but before all soluble substance left the film an absorption maximum developed. In Fig. 8, the maximum appeared at first at high PVC values, and drifted to lower PVC values, after some time had passed. Simultaneously the water absorption at higher PVC values decreased because films had become leaky and correspondingly the leaching rate increased. This showed that, during water absorption, the permeability of the vehicle layers surrounding the pigment particles might be subject to considerable changes.

MR. R. R. DAVIDSON said that some recent work at Welwyn Hall Research Association tended to confirm the existence of a permeability critical pigment concentration at a value lower than the normal critical packing pigment volume concentration (CPVC). Films had been made of chalk whiting in polybutadiene, a water-resistant binder, in a PVC ladder. Films were tested for water permeability simply by immersing them in dilute hydrochloric acid. Below about 20 per cent PVC the rate of reaction between the acid and the calcium carbonate was negligible, and above it reaction was rapid.

The critical value obtained was higher than most of those quoted by Dr. Funke, which seems quite reasonable for a material with particles which packed well together and which had a high CPVC.

MR. P. FINK-JENSEN said that the explanation had been advanced that, below the glass temperature, there might be breaks and fissures in the film, while above that temperature there was no break, which would explain a maximum at a certain PVC.

All the examples shown indicated that, above the glass temperature, type 3 kind of curve was obtained, while below the glass temperature the type 2 was obtained.

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According to the explanation about breaks in the film, the opposite effect would be expected.

Had Dr. Funke any support for the idea that breaks do occur in the film?

DR. FUNKE said that vehicle layers surrounding the pigment particles might rupture by rising internal osmotic pressure below, as well as above, the glass transition temperature of the film. In the first case these layers could not yield sufficiently to the osmotic strain and in the second case they were forced to yield too much, provided a sufficient amount of soluble material was present at the internal interfaces. That the vehicle layers might become permeable was supported by the change in the leaching rates at PVC-values below and above the absorption maximum and by the shift of the absorption maximum to lower PVC-values as absorption proceeded.

MR. FINK-JENSEN said that there should still be leakage below the glass temperature, but not above the glass temperature.

DR. FUNKE said that the water absorption and leaching of non-plasticised polybutylmethacrylate films pigmented with sodium chloride or lead nitrate powder had been studied at temperatures definitely below the glass transition range. As expected no absorption maximum appeared, but there was, apart from at low PVC, as little NaCl left in the films after a few days of immersion as in films immersed above their glass transition temperature (Fig. below). It was concluded, therefore, that besides the relative slow diffusion process,  $\text{Pb}(\text{NO}_3)_2$  found pathways for getting out of the film much more quickly. It could be assumed from the results of the PVC-dependence of the leaching above and below the glass transition temperature of the films that this was due to fissures and breaks in the film. It was reasonable to assume that above the glass transition temperature the vehicle layers surrounding the pigment particles would mature under the increasing osmotic pressure.

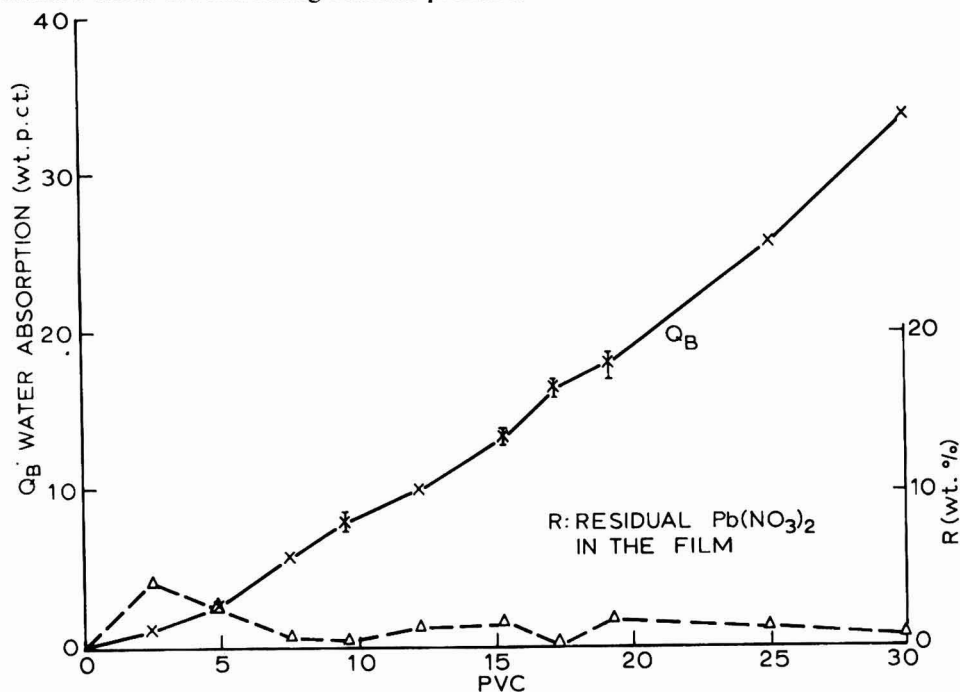


Fig. 1. Water absorption,  $Q_B$ , and residual salt content of films from unplasticised polybutylmethacrylate with  $\text{Pb}(\text{NO}_3)_2$  powder as pigment after three days of water immersion at 23°C. Glass transition temperature 30°C

MR. FINK-JENSEN asked if Dr. Funke had been able to observe the breaks in the film or the position of the water? Would the technique of breaking a film, which was used to see whether or not the pigment was at the surface, be applicable? Had Dr. Funke tried this with wet paint?

DR. FUNKE answered that it had not been possible to make the breaks visible, because replicas had not been obtained from wet-film cross-sections for the electron microscope.

MR. FINK-JENSEN said in all these cases the film was put in water. If they were kept at 100 per cent humidity, without condensation, would a Type 2 kind of curve always be found?

DR. FUNKE said that the water absorption/PVC relation with polybutylmethacrylate films immersed in water and exposed to 98 and about 100 per cent relative humidity had been compared<sup>9</sup>. With 98 per cent humidity Type 2 absorption characteristics were obtained. With about 100 per cent humidity a very weak maximum was observed; some condensation could have taken place. It was very difficult to get 100 per cent humidity and avoid any condensation at the surface of the film.

DR. H. W. TALEN referred to what had been said about the adhesion between the interfaces of pigment and medium. A similar problem occurred in stretched rubber. On stretching a piece of rubber containing inert fillers, holes around the pigment particles (vacuoles) appeared, and the specific gravity of the stretched rubber was less than that of the unstretched.

On the other hand, vacuoles did not appear in rubber filled with active filler, such as carbon black, and the specific gravity did not change on stretching. Had similar phenomena been observed in paint films?

DR. FUNKE said that Dr. Zorll and he were trying to determine whether the stress/strain behaviour of the films was influenced by the presence of water, and had constructed a device for measuring the stress/strain relationships of wet films and comparing these with those for dry films. If the pigment was reinforcing in the presence of water, not much difference would be expected, but if reinforcement was affected by the penetration of water different strain/stress relationships might be expected.

MR. R. R. DAVIDSON said that at Welwyn Hall Research Association the Schippel effect which Dr. Talen had described had been investigated in relation to water uptake. Plasticised polyvinyl chloride was filled with representative mineral fillers. Above about 30 per cent volume loading the load/extension curves for dumb-bell specimens showed stress maxima. The stress was suddenly relieved by breakdown of the particle-matrix adhesion with formation of vacuoles (the Schippel effect). Vacuole formation was indicated by whitening of the specimen and was proved by demonstrating a density decrease. The maximum stress (yield stress) thus gave a measure of particle-matrix adhesion. Decreases of adhesion on addition of some surfactants and large increases with others had been demonstrated.

There was a catastrophic decrease however on water-immersion; because of specimen thickness, long immersion times were used. No surfactant (bonding agent) which resisted this destruction of filler-matrix adhesion by water had been found. This was in full agreement with Dr. Funke's work. He also had been unable to find an inorganic filler-matrix combination which resisted adhesion breakdown by water.

DR. D. PATTERSON suggested that another method of determining whether a second order transition was involved would be to make measurements of the dielectric losses.

This would give rather different information from the dynamic testing previously suggested. Had Dr. Funke considered this?

In the literature on polymers, it could be seen that the actual glass transition temperatures had often been determined by dielectric loss methods, and it was a

fairly easy and convenient method of carrying out a survey of quite a large range of water concentrations and temperatures.

DR. FUNKE said this method had not been attempted.

He felt it would also be interesting to apply this method for determination of the glass transition range of paint films, in order to see which method could generally be applied.

MR. A. W. LANDMANN asked whether this technique could be used on emulsion polymer films. It seemed that all the work had been done on solutions, and with the higher concentrations of colloids, all of which were water sensitive; would this technique be applicable?

DR. FUNKE answered that, in earlier work, water absorption of unpigmented paint films, including emulsion paint films, was measured. It was a very difficult task, because unpigmented emulsion paint films had a very soft consistency, and it was very hard to manipulate them. Several commercial types of vinyl emulsion paint films were compared, and it had been found that the water uptake was relatively high. As long as the emulsion particles had not coalesced during the film formation, a high water uptake was obtained, but most of the water was probably located at the interfaces of the resin particles. But if the films were treated at a higher temperature, the water uptake decreased very significantly.

No experiments had been carried out on emulsion paints which were pigmented.

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## Next month's issue

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

**"Reflectance at paint-substrate boundaries,"** by *D. F. Tunstall*.

**"Some effects of media on the lightfastness of colouring matters,"** by *A. P. Gates and D. Patterson*.

**"Flocculation, flotation and flooding in phthalocyanine/titanium dioxide pigmented paints,"** by *V. T. Crowl*.

# Reviews

## THE PETROLEUM CHEMICALS INDUSTRY

By R. F. GOLDSTEIN AND A. L. WADDAMS. Pp. viii + 523 : London : E. & F. Spon Ltd. Price £6.

This is the third edition of a successful treatise on a subject of importance to users of organic chemicals in a wide sector of industry, including that of particular interest to readers of this Journal. More and more of the established raw materials used in resins and paints are now being produced from petroleum or natural gas and the development of new derivatives on a commercial scale has led to fresh technical progress in the consumer industries. The book tells a fascinating story of these developments and points the way to even greater diversification in the future. Although primarily concerned with the chemistry of the processes described, economic considerations have been kept well to the fore and commendable courage has been shown when revising the previous edition in eliminating those that have become obsolete, thus avoiding an unnecessary increase in size.

It is stated that the object of the book is to set down the major routes to the important petroleum chemicals and to explain their end uses. This raises the question of what can be described as a petroleum chemical, and no clear answer has been given by the authors, who have admitted that the decision is a difficult one. It seems fairly clear from the text that compounds such as glycerol and phthalic anhydride are included, but no explanation is given of their end uses—they are mentioned only very briefly. If, on the other hand, propylene is the petroleum chemical and glycerol the end product, then there is more justification for the claims made. The difficulty has arisen from the use of a loose term that has not been adequately defined. It is surely erroneous to describe compounds not present in petroleum, but derived from it by a long series of chemical reactions, as "petroleum chemicals."

The objective stated in the introduction—to survey those fields of industrial organic chemistry in which oil is the most economic raw material—gives a much better indication of the scope of the book. Nevertheless, areas of competition with other sources of organic chemicals, such as coal or vegetable products, are also covered, as well as those where the oil route has not yet been established as the most economical one, but where there seems to be a chance that it might succeed in the future. The result is a well-balanced account covering the technical and patent literature up to the early part of 1966. There are also chapters on the history of industrial petroleum chemistry, the sources of petroleum hydrocarbons and on economics and statistics.

It is indeed seldom that a book is encountered in which so much care has been devoted to the provision of material outside the actual text to assist and inform the reader. In addition to the usual indices, there are lists of abbreviations and of the patent specifications mentioned in the text, four appendices giving the boiling points of hydrocarbons, charts showing the routes to various chemicals starting from petroleum, the olefins and coal, and conversion and statistical tables. It is, therefore, surprising that insufficient attention has been given in the subject index to the needs of certain specialist readers. If you are interested in detergents or synthetic rubber, then you may find what you want,



but not if you are a paint or resin technologist. References to certain raw materials such as phthalic anhydride and pentaerythritol occur, and epoxy resins have been deemed worthy of attention, but a large proportion of the other items of interest is to be found only in an indirect manner by looking up the appropriate raw material or by browsing through the text. This is a failing that would not be very difficult to remedy in future editions.

The main value of the book from our point of view is the lucid manner in which it provides up-to-date information concerning the manufacture from petroleum of many of our raw materials, and for this it can be thoroughly recommended.

M. R. MILLS.

### PRINCIPLES OF COLOUR TECHNOLOGY

By F. W. BILLMEYER, JR., AND M. SALTZMAN. Interscience Publishers, 1966. Pp. x + 181. Price £4 16s.

Whilst the unconventional style of this book might at first sight create an unfavourable impression, a more detailed study reveals that it is likely to prove a very suitable text-book for the student, being designed specifically for those interested in becoming colour technologists in the paint and allied industries. No prior knowledge of the subject is assumed. The essential physical basis of colour science is first explained in simple language, followed by the more important colour-order systems (CIE, Munsell, etc.), and then by a detailed treatment of colorimetry. The authors finally turn to coloured materials, explaining such matters as the difference between dyes and pigments and going on to explain the laws of colour mixture, with particular reference to the type occurring in pigmented compositions such as paints (for which they propose the term "complex-subtractive mixture"). The application of these laws to the production of matches by computer is described in some detail. Metamerism is explained and here again new terminology is introduced, the term "conditional" match being used for "metameric" match, and "invariant" match for "non-metameric" or "spectral" match.

A useful feature is the provision on each page of a wide margin which is used for a number of purposes—summarising the salient points in the adjacent text, making relevant quotations from other authors, setting out equations expressing in quantitative form the relationships dealt with in the text, and for explanatory diagrams.

There is a useful annotated bibliography of the more important books and papers and a further list of others without abstracts. Only publications in English are included. There are a few errors in the text, but a list of errata may be obtained from the senior author at Rensselaer Polytechnic Institute, Troy, NY.

The book is written throughout from the point of view of the paint technologist and, although some space is devoted to dyeing, other branches of colour technology (such as colour printing, photography and television) receive only very brief mention.

D. R. DUNCAN.

## DICTIONARY OF ORGANIC COMPOUNDS—THIRD SUPPLEMENT

By R. STEVENS (Editor). London : Eyre & Spottiswoode (Publishers) Ltd., 1967. Pp. 279. Price £10.

This third supplement to the fourth edition of what is still affectionately known as "Heilbron," calls for all the superlatives so freely used by reviewers of its forerunners. It represents a monumental effort on the part of both its compiler and its publisher, who together have managed to present, early in 1967, a distillation of much important material from the literature of 1966. Additionally, the opportunity has been taken to make good a number of "notable omissions" from the main work and first two supplements.

Whilst this reviewer is lost in admiration of the system, not to mention the erudition, which makes such a compilation possible, he is reminded that his readers are not, in the main, seekers after knowledge for its own sake, and feels under some obligation to indicate the value of the book to those of his own kidney.

First, one cannot but be struck by the great preponderance of references to "Tetrahedron" and other journals of British or American origin; so much so that one must call into question the breadth of coverage. Secondly, whilst the parent work adequately covered most of the ordinary organic chemicals under their systematic names, successive supplements have been increasingly notable for their content of weirdies, and particularly of biologically important compounds entered under trivial names. This volume lists innumerable metabolites, carotenoids, antibiotics and the like, together with glycosides and alkaloids isolated from the most unlikely sources. There is no real shortage of recognisable organic compounds but few of those now detailed are likely to interest workers in the coatings field. This may be a sign of what is happening to organic chemistry, but the only entries which the coatings technologist might reasonably be expected to recognise were 9,10-epoxy stearic acid, the lower nitrates of pentaerythritol, the tetramethylnaphthalenes, hexavinylbenzene, tetraphenylphthalic acid, *t*-butyl phenyl ether, the geometric isomers of 1,2,4,5-cyclohexanetetrol, and copalic acid.

This volume is a magnificent piece of work, beautifully made and printed. If you possess the earlier parts you may want to have it for the sake of completeness, but, if your interests are anything like the reviewer's, you are unlikely to use it fruitfully more than once a year.

A. R. H. TAWN.

# Information Received

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

A new microhardness tester has been announced by **Carl Zeiss**. This can be attached to the Zeiss Standard Universal Microscope, the Photomicroscope and the Ultraphot II, and is interchangeable so that a wide range of diamond indenters and microhardness methods may be applied. A detailed survey of the technique as applied to the new tester is contained in the Zeiss information leaflet No. 62.

**Storry Smithson** have recently developed a new heavy duty protective coating for metal and concrete, available in a wide range of colours.

The new product, *Regnavin*, is a single-pack vinyl-based thixotropic paint, claimed to be capable of giving single films of thickness of four or five times that of conventional paints, and to have high resistance to acids, alkalis, water and many salts.

**May and Baker Ltd.** announce that the stability of the ordinary grade of their Karl Fischer reagent has been improved by a revised formulation. The reagent is said to be more viscous in use than the previous formulation.

*Bexrez 200* series is the name of the new series of terpene copolymer resins announced by **B.X.L.** Developed by the Chemicals Division of Bakelite Xylonite Ltd., the resin, it is claimed, will substantially reduce raw material costs in the chemical industry. Behaving basically the same as a conventional terpene resin, the new resin has potentially the same applications, particularly in paints and varnishes.

**L. Stechler and Co. Ltd.** announce that, as a result of the installation of a new increased capacity granulating plant, they are now able to reduce charges substantially, and to extend their services and offer a number of new technical advantages.

Stechler can now supply all standard grades of natural rubber, most synthetics, and a large number of compounds and reclaim.

The recent overall increase in the prices of resins for paint manufacture may well be offset in the case of general purpose stoving finishes by a new, low cost base material, claim **Cray Valley Products Limited**.

The material, *Synolac 67X*, is an alkyd stoving resin evolved from a new blend of fatty acids. Stoved paint films based on *Synolac 67X* are said to show good colour retention, adhesion and hardness.

**Farbwerke Hoechst AG** Technical Information Leaflet No. 41, issued recently, deals with the weather fastness of organic pigments in air-drying synthetic resin finishes. Colour reproductions of several Hoechst pigments, weathered for 16 months, are shown.

The **John Harris** division of **Coates Brothers (Industrial Finishes) Limited** have recently added *G601 Dual Purpose Laminating Adhesive* to their range of print finishing varnishes and laminating adhesives. A one-component product, *G601* is claimed to be suitable for the lamination of both cellulose acetate and oriented polypropylene films.

A new titanium dioxide pigment, *Tioxide R-XL*, for use in matt latex paints, has been announced by **British Titan Products Company Limited**. With a smaller  $\text{TiO}_2$  content (85 per cent) than any other grade of *Tioxide*, and an oil absorption of 30, *R-XL* is claimed to be a new concept in rutile pigment design, to have very high chalk resistance, and to give exceptional opacity in latex paints.

Further changes have been announced by **Blundell-Permoglaze Ltd.** in their rationalisation programme. The name *Permura* has now been changed to *Permoglaze Latex Wall Finish*, and a similar product, *Pammex*, has been discontinued. Changes in the colour range have also been made.

The **Du Pont Company (United Kingdom) Limited** have announced that a new Du Pont methacrylate monomer, which, it is claimed, is expected to lead to improved polymers for adhesives, coatings and binders, is now available in Europe.

The monomer, 2-ethylhexyl methacrylate, may be copolymerised with methyl methacrylate and other vinyl or acrylic monomers, and is said to provide effective internal plasticising action as well as the good outdoor durability common to methacrylate resins. The new ester can also be used to produce tacky homopolymers for pressure-sensitive adhesives or as components of coatings and inks to provide improved flexibility and adhesion.

A new laboratory analysis system, *Mecolab*, is announced by **Joyce Loebel and Co. Ltd.** Claimed to be adaptable to almost any methods, *Mecolab* provides an automatic analysis service, giving results directly on punched or printed tape.

The instrument is normally supplied for four channel operations (successively) and is claimed to require as little as 15 microlitres per test. Each stage operates at a rate of 240 samples per hour, giving a claimed practical output for analyses such as blood sugar analysis of 150 samples per hour.

**Revertex Ltd.** have recently issued Technical Bulletins on three of their *Revacryl* acrylic copolymer emulsions. These are *Revacryl 144* and *244*, styrene/acrylic ester copolymers, and *Revacryl 231*, a partially colloid stable acrylic copolymer emulsion of medium particle size.



**We'll willingly prove how Microcal ET can cut the costs of your emulsion paint... yet still give you hiding power like this.**

### **Interested?**

Microcal ET is a remarkable synthetic fine silicate—particle size controlled—that will enable you to cut the cost of your emulsion paint, with no loss of quality or performance.

Alternatively, Microcal ET can improve the quality of your emulsion paint if required—without any increase in production cost.

Or even improve opacity—at the same cost.

Microcal ET was developed by Crosfield and the complete documented story is now available. If you'd like a copy, or any further information, please drop us a line.

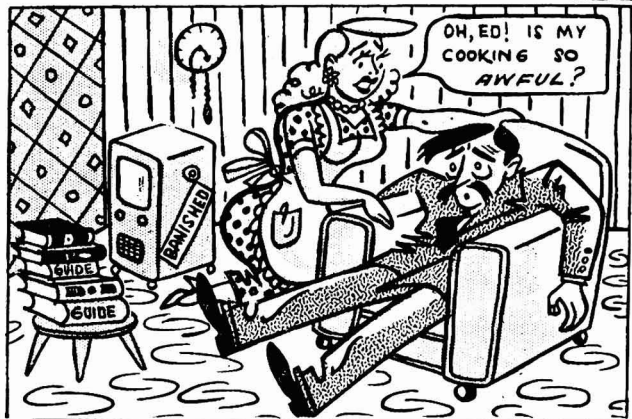
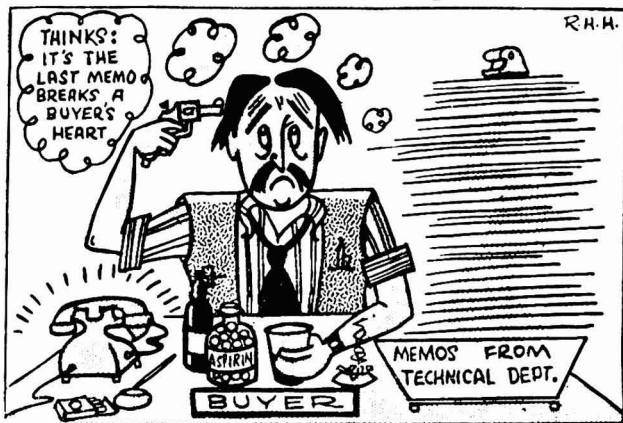


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Tel: Warrington 31211

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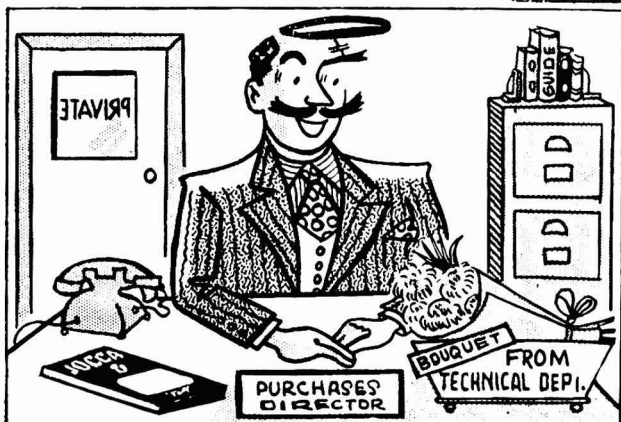
ONCE, THE BUYER  
WAS A HARASSED MAN

... with stacks of memos from the technical department daily mounting higher on his desk—all of them about raw materials, plant and equipment for the paint, printing inks, linoleum and allied trades ...



It was even affecting his home life. The television set was banished and the sports page forgotten. In desperation he consulted Dr. X, the Chief Chemist, who at once advised him to take JOCCA\*

"After all," said the Chief Chemist, "you have only to recall that JOCCA\* has an unrivalled world-wide circulation among the technical types, who create the demand, to realise why so many companies use its pages to advertise raw materials or plant or equipment ..."



Nowadays, of course, the newly promoted Purchases Director is calm, poised, confident, etc. and the current number of this *Journal* is always on his desk.

For details of advertising and subscriptions write to:—

JOURNAL OF THE OIL & COLOUR

CHEMISTS' ASSOCIATION \*

Wax Chandlers Hall Gresham Street  
London E.C.2



# 20th OCCA Technical Exhibition

**25-29 March 1968**

The Exhibition Committee is pleased to report that the space allocated to exhibitors at 20-OCCA (the Association's Twentieth Technical Exhibition) at Alexandra Palace, London, N.22, exceeds that at any previous Exhibition. There will be 104 stands, including exhibitors from ten overseas countries—Belgium, Denmark, Finland, France, Germany, Holland, Italy, Sweden, Switzerland and the United States of America. Of the companies showing, 11 have never shown at previous OCCA Technical Exhibitions, whilst 22 others did not show at the 1967 Exhibition.

In order to assist those planning to visit the Exhibition, a map showing the various ways in which Alexandra Palace can be reached from Central London will be reproduced in each copy of the *Official Guide*, which will be sent without charge to all members of the Association early in the New Year. Copies of the *Official Guide* will also be sent individually to chemists and technologists on the Continent of Europe, to technical colleges and, through the courtesy of trade associations, to companies in the paint, printing ink and pigments industries in the United Kingdom.

The map is also being reproduced separately in a folder which gives

directions in six languages (French, German, Italian, Russian, Spanish and English) and copies of these will be sent with the *Official Guides* despatched to the Continent. Copies are also available to intending visitors and they will be despatched without charge upon application to the General Secretary of the Association. The six language cards will also be sent to many paint and printing ink manufacturing companies on the Continent of Europe.

A free bus shuttle service will be operated by the Association from Wood Green Underground Station (Piccadilly Line), and there are free car parking facilities at Alexandra Palace.

Amongst the facilities available at Alexandra Palace are two restaurants, together with buffets and several bars.

As in previous years, the Exhibition Luncheon will be held at the Savoy Hotel, London, W.C.2, on the opening day, 25 March. Principal officers of other scientific bodies, industrial research associations and organisations representing both suppliers and consumers will be invited to attend.

The Exhibition will be open on five days, and it is felt that this arrangement will benefit companies, particularly those in the provinces and overseas, wishing to arrange a rota for their technical staff

to visit the Exhibition. The hours of opening will be as follows:

Monday 25 March	.. 15.00—18.30
Tuesday 26 March	.. 10.00—18.00
Wednesday 27 March	.. 10.00—18.00
Thursday 28 March	.. 10.00—18.00
Friday 29 March	.. 10.00—16.00

Following the practice at previous Exhibitions, a stand will be devoted to Technical Education and parties of sixth form science and technical college students will be invited to attend in the mornings, when they will be given short introductory talks before touring the Exhibition. The Technical Education stand will show not only the courses available in the technology of the paint, printing ink and allied industries and the technical careers open to new entrants, but will also display an historical survey of the development of printing inks.

Representatives from 30 overseas countries attended the 1967 Exhibition, and in order to assist the increasing number of both overseas visitors and exhibiting companies, interpreters will again be in attendance (French/German/Spanish). There will be no charge for admission to the Exhibition, or for copies of the *Official Guide*, which will be available from the Association's Information Centre at the Exhibition or from the Association's offices prior to the Exhibition. Over 11,500 people visited the 1967 Exhibition.

Any company or individual who wishes to receive a copy of the *Official Guide*, when available early in 1968, should write to the General Secretary, R. H. Hamblin, Oil & Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London, E.C.2.

## Alphabetical List of Exhibitors—20 OCCA

- |   |  |
|---|--|
| †Albright & Wilson (Mfg) Ltd.<br>Allied Chemical Corporation  | Cray Valley Products Ltd.<br>Crosfield, Joseph, & Sons Ltd.  |
| †Amalgamated Oxides (1939) Ltd.<br>AMF International<br>Amoco International S/A<br>Anchor Chemical Co. Ltd.   | Degussa<br>DH Industries Ltd.  |
| *Baker Castor Oil Company, The<br>BASF United Kingdom Ltd.  | *Diap A/S  |
| †Beck, Koller & Co. (England) Ltd.<br>Berk Ltd.<br>BIP Chemicals Ltd.<br>Boehm, Fredk., Ltd.<br>Boulton, William, Ltd.  | †Dow Chemical (UK) Ltd.<br>Draiswerke GmbH<br>Durham Raw Materials Ltd.<br>Elcometer Instruments Ltd.  |
| †BP Chemicals (UK) Ltd.<br>British Celanese Ltd.<br>British Titan Products Co. Ltd.<br>Bush, Beach & Segner Bayley Ltd.<br>Campbell, Rex, & Co. Ltd.<br>Carless, Capel & Leonard Ltd. | †Esso Chemical Ltd.<br>Farbenfabriken Bayer AG<br>Ferranti Ltd.<br>Geigy (UK) Ltd.<br>Grampian Press Ltd.  |
| †Chemische Werke Huels AG<br>Chemieanlagen  | †Hardman & Holden Ltd.<br>Harlow Chemical Co. Ltd.<br>Hoechst Chemicals Ltd.   |
| †Churchill Instrument Co. Ltd.<br>Ciba (ARL) Ltd.<br>Ciba Clayton Ltd.  | †Hygrotherm Engineering Ltd.<br>Imperial Chemical Industries Ltd.  |
| *Columbian International (GB) Ltd.  | *International Colloids Ltd.   |
| †Cornbrook Resin Co. Ltd.   | *Jenag Equipment Ltd.  |
| †Cox's Machinery Ltd.   | †Joyce, Loebel & Co. Ltd.<br>Kingsley & Keith (Chemicals) Ltd.<br>Kronos Titanium Pigments Ltd.<br>Kunsttharsfabriek Synthese NV<br>Laporte Industries Ltd.<br>Lennig Chemicals Ltd. |



**Alphabetical List of Exhibitors—20 OCCA—continued**

- Little, J. H., & Co. Ltd.  
 Livingston Electronics Ltd.  
 Marchant Bros. Ltd.  
 Mastermix Engineering Co. Ltd., The  
 Meazzi, Dott. Edoardo  
 Meijer's, Rudolph, Inc.  
 Microscal Ltd.  
 †Modo Products (Chemicals) Ltd.  
 Molteni Off. Mecc. of Milan  
 Novadel Ltd.  
*Paint, Oil & Colour Journal*  
 Paint Research Station  
 Pfizer Ltd.  
 †PIRA  
 Polyvinyl Chemie Holland NV  
 \*Pound, A. V., & Co. Ltd.  
 \*Pretema AG  
 †Pure Chemicals Ltd.  
 Research Equipment (London) Ltd.  
 †Resinous Chemicals  
 Rhone-Poulenc  
 \*Sachtleben AG  
 Sawell Publications Ltd.  
 Scado Archer Daniels NV  
 †Seaton, John L., & Co. Ltd.  
 †Shawinigan Limited  
 Sheen Instruments (Sales) Ltd.  
 Shell International Chemical Co. Ltd.
- \*Silver, Peter, & Sons (Engineers) Ltd.  
 Silverson Machines Ltd.  
 \*Smith, Herbert, & Co. (Grinding) Ltd.  
 Spelthorne Metals Ltd.  
 †Sterling Colour Co. Ltd.  
 Surface Coating Synthetics Ltd.  
 Svenska Oljeslageri Aktiebolaget  
 †Tintometer Ltd.  
 Titaandioxydefabriek Tiofine, NV  
 Titanium Intermediates Ltd.  
 Torrance & Sons Ltd.  
 †Torsion Balance Co. Ltd.  
 \*Union Carbide Belgium NV  
 Unitechna  
 Vinyl Products Ltd.  
 Vuorikemia Oy  
 Wacker Chemie  
 Winkworth Machinery Ltd.  
 OCCA Information Centre  
 Technical Education Stand  
 British Red Cross Society  
 National Provincial Bank Ltd.  
 Interpreters  
 GPO Self-Service unit

\*Denotes companies who have not exhibited at previous OCCA Exhibitions.

†Denotes companies who did not exhibit at 1967 OCCA Exhibition.

## Jordan Award

As announced at the Annual General Meeting, Council has been very pleased to receive from Mrs. L. A. Jordan a bequest for the institution of an Award in memory of her late husband, Dr. L. A. Jordan, who was President of the Association 1947-49, became an Honorary Member in 1955 and presented the first Commemorative Lecture in 1963.

Louis Arnold Jordan, C.B.E., was the Founder Director of the Research Association of British Paint, Colour and Varnish Manufacturers from its inception in 1926 until his retirement in 1959. He died on 1 December 1964 at the age of 72. He had a distinguished academic career at the Royal College of Science and in the 1914-18 war was concerned with explosives. After the war he held appointments in the chemical industry and for a time was the scientific

adviser to the State of Bhopal. As well as his Directorship of the Paint Research Station and Presidency of the Oil and Colour Chemists' Association, he took an active interest in many other bodies connected with the industries and education; he was a member of the Senate of London University and Professor of Chemistry at the Royal Academy of Arts 1958-62. After his retirement he visited India and the Far East on official visits.

It is intended that the first Award of £100, which will be in cash and entirely at the disposal of the recipient, shall be made at the time of the Association's Jubilee Celebrations in May 1968 and thereafter it is hoped to make the Award biennially.

The Award is open to all members of the Association up to the age of 35 on

the final date for the submission of applications which, on this occasion, will be 31 December 1967. There will be two methods of application. First, by direct application in which a paper is submitted of original work which has either been published in the *Journal* or is so submitted for publication. The alternative method would be by recommendation by a superior for work which for reasons of commercial secrecy cannot be published; in this case some form of dissertation would be required from the candidate. It is stressed that all members of the Association wherever resident may

apply for the Award and the submission will be judged on scientific and technological content and its merit as a contribution to industry or the Association.

The selection of the recipient for the Award will be made by a Committee under the Chairmanship of the Association's Hon. Research and Development Officer, Mr. A. T. S. Rudram. Applications are now invited for the first Award and these should be addressed in the first instance to the General Secretary from whom further particulars can be obtained.

## Manchester Section

The 4th Annual Conference of the Non-Destructive Testing Society of Great Britain is to be held at The University of Keele between 12 and 15 September, 1967. Concurrently with the Conference a Manufacturers' Exhibition of Equipment, which will include some of the latest advances in X-ray and ultrasonic inspection, will be open.

Any OCCA Members wishing to take advantage of the opportunity this Conference offers are assured of a warm welcome. Details are available from the Hon. Sec., Manchester Section.

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### Courses in surface coating technology in Manchester

The following courses will be held during 1967/68 at John Dalton College of

Technology, Chester Street, Manchester.

The City and Guilds "Paint Technicians," course, (subject 357) which now replaces subject 9B; Paint Technology.

The City and Guilds Full Technological Certificate in the subject, "Application of Surface Coatings."

Higher National Certificate Endorsement in Chemical Technology with special reference to Polymers and Surface Coatings, qualifying for the award of L.R.I.C.

Day release will be required for all the above courses and enrolment will be held on 11, 12, 13 September, 1967 during the hours 10.30 a.m.-12 noon. 2.00 p.m.-4.00 p.m., 6.00 p.m.-7.30 p.m.

The College lecture term commences 18 September 1967.

## Scottish Section

### Newton Cup

A golf match was played at Harburn Golf Club on 23 June between the Scottish Section and the Eastern Branch. Mr. H. Newton, a founder member of

Scottish Section, kindly presented the Newton Cup to be played for annually between the Section and the Branch. This first match, comprising five two-ball foursomes, was won by the Scottish Section by four matches to one.

## South African Section

### First National Convention

The South African Section held its first National Convention at the Drakensberg Gardens Hotel, Underberg, Natal, from 4 to 6 August.

On the morning of Saturday 5 August three papers were read :

The development of urethane and urethane-ureas as surface coating compositions, by Dr. A. Lowe (ICI Dyestuffs Division).

Hot melts for paper packaging applications, by Mr. H. Esser (Hercules Inc., USA).

Analysis of paint and polyesters by gas chromatography, by Prof. G. M. Hamilton (South African Paint Research Institute).

All three lectures provoked lively discussion from the floor.

The results of the sports events arranged for Saturday afternoon were as follows :

*Golf.*—Individual Stableford : 1st, J. S. Sinton ; 2nd, D. Dewberry. Individual net : P. A. Draper. Inter-section event winner : Natal.

*Tennis.*—1st, Mrs. P. Robinson/H. Esser ; 2nd, T. Tompson/O. G. J. Crosby.

There was also a special award to Miss A. Mackenzie—"Best legs on the court."

Squash was played by several of those present, as was bowls.

This first convention was felt by all to have been a remarkable success. This was, in no small measure, due to the energy and efforts of the Transvaal Branch and in particular their Chairman, Mr. Sinton. In his opening address, Mr. McDonald, the SA Section Chairman, brought the efforts of Mr. Sinton to the notice of the delegates and paid tribute to his hard work in organising this convention.

C. E. S.

### News of Members

Mr. R. J. Pierce, an Ordinary Member attached to the London Section, has been appointed consultant editor of the *British Ink Maker*, the official journal of the Society of British Printing Ink Manufacturers.

Mr. Pierce is a member of the Management Committee of the Fishburn Printing Ink Co.

Mr. E. W. Holdsworth, an Associate Member attached to the Manchester Section, has been appointed Sales Manager for British Resin Products' Epok surface coating resins. Mr. Holdsworth was previously Assistant Sales Manager.

Dr. W. Carr, an Ordinary Member attached to the Manchester Section, has

been appointed an honorary lecturer in pigment physics to the Colour Chemistry Department of the University of Leeds. Dr. Carr will commence his duties in the autumn of this year, but will of course continue his work as Technical Manager of the Pigments Physical Laboratories of Geigy (U.K.) Ltd.

Mr. R. R. Coupe, an Ordinary Member attached to the London Section, has been appointed Head of the Science Department at the London College of Printing.

Mr. W. Hannah, an Ordinary Member attached to the Scottish Section, is resigning from his position as Managing Director of Thos. Hinshelwood & Co. Ltd., after 55 years with the firm.

Mr. Hannah will retain the position of Chairman of the company.

**OCCA Publications**

Members may be interested to learn that the Introduction to Paint Technology, and Volumes I and II of the Paint Technology Manuals, the present editions of which are out of print, are being revised. A new chapter is to be added to each to incorporate the latest developments in the particular field covered by the publication.

A copy of the first issue of a new journal "Advances in Colloid and Interface

Science," has been received in this office. It is hoped to be able to publish a review in the near future.

**Programme change**

The lecture by Mr. A. G. North, to be given to the London Section at East Ham Technical College, will now be on Thursday 14 December, and not on Thursday 7 December, as stated in the August *Journal*. This change was caused by difficulties with the availability of the College facilities.

# Register of Members

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

**Ordinary Members**

- BEAGLE, ROBERT JAMES PHILIP, B.SC., M.SC., Science Dept., Brixton School of Building, Ferndale Road, London, S.W.4. (*London*)
- BENKO, TULLIO SERVIO, c/o Multiglo Inks Pty., Ltd., 61-69 Baxter Road, Mascot, New South Wales, Australia. (*New South Wales*)
- BULL, JOHN H., A.R.A.C.I., A.S.T.C., 105 Hunter Street, Bankstown, New South Wales, Australia. (*New South Wales*)
- FERGUSON, DONALD A., Australian Packaging Industries, Fenndell Street, Chester Hill, New South Wales, Australia. (*New South Wales*)
- LEACH, KENNETH ALFRED, A.I.R.I., 66 Linden Road, Dunstable, Beds. (*London*)
- PRICE, PETER JOHN, A.S.T.C., B.SC., British Paints Pty., Ltd., Gow Street, Bankstown, New South Wales, Australia. (*New South Wales*)
- RUSHTON, JOHN BERNARD, B.SC., AVON Cosmetics Ltd., Nunn Mills Road, Northampton. (*Midlands*)
- SCIPIO, FREDERICK J., Unilever-Emery NV, PO Box 2, Gouda, Holland. (*Overseas*)
- SWIFT, MAURICE ALFRED, D.S.T.C., R.A.C.I., Nopec Beith Pty., Ltd., Union House, 247 George Street, Sydney, New South Wales, Australia. (*New South Wales*)

**Associate Members**

- GRAINGER, GORDON ARTHUR, c/o Australian Hoechst, 520 Gardeners Road, Mascot, New South Wales, Australia. (*New South Wales*)
- JONES, SYDNEY ERIC, c/o Multiglo Inks Pty., Ltd., 61-69 Baxter Road, Mascot, New South Wales, Australia. (*New South Wales*)
- MOORE, MISS LUCY CLARE, 11 Palace Road, Baulkham Hills, New South Wales, Australia. (*New South Wales*)

**Junior Member**

- AWRAMENKO, SLAVEK, 5 Greenhill Place, Midsomer Norton, Bath, Somerset. (*Bristol*)

# Forthcoming Events

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

## Monday 2 October

*Hull Section.* A talk by Mr. P. J. Gay, title to be announced later, to be held at the Hull College of Technology, at 7.00 p.m.

## Thursday 5 October

*Newcastle Section.* "Coil Coating," by Mr. D. S. Newton, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

## Monday 9 October

*London Section—Southern Branch.* Film Evening presented by Hoechst (U.K.) Ltd., to be held at the Keppels Head Hotel, The Hard, Portsmouth, at 7.30 p.m.

## Tuesday 10 October

*West Riding Section.* "The Work and Activities of the Paint Research Station," by Dr. S. H. Bell, to be held at the Griffin Hotel, Boar Lane, Leeds, 1, at 7.30 p.m.

## Thursday 12 October

*Scottish Section.* "Painting the Q.4," by Mr. A. Pisacane (John S. Craig & Co. Ltd.), to be held at the Lorne Hotel, Sauchiehall Street, Glasgow, at 6.00 p.m.

## Friday 13 October

*Manchester Section.* "Towards Automation," by Mr. H. R. Touchin at the Manchester Literary & Philosophical Society, 36 George Street, Manchester, 1, at 6.30 p.m.

*Hull Section.* 24th Annual Dinner and Dance at the Hotel Eden, Willerby.

## Saturday 14 October

*Scottish Section—Student Group.* "Explosives and the North Sea Search," by Mr. J. E. Dolan (I.C.I. Ltd.), to be held at the Lorne Hotel, Sauchiehall Street, Glasgow, at 10.00 a.m.

## Wednesday 18 October

*London Section.* "Irradiation Curing of Paint Films," by Dr. F. L. Dalton at New Engineering Block, University College, London, W.C.1, at 6.30 p.m.

## Friday 20 October

*Midland Section.* "Law of Contracts of Employment," by Mr. D. Mather, to be held at Chamber of Commerce House, Birmingham, 15, at 6.30 p.m.

*Manchester Section.* Annual Dinner and Dance at the Piccadilly Plaza Hotel.

## Wednesday 25 October

*Scottish Section—Eastern Branch.* "Carbon Blacks," by Mr. Mynett (Columbia International) to be held at the Wee Windaes Restaurant, High Street, Edinburgh, at 7.30 p.m.

## Friday 27 October

*Irish Section.* "The Measurement of Colour by Instrumentation," by Mr. P. V. Foote—Introduction by Dr. S. H. Bell, to be held in the Imperial Hotel, Cork, at 8.00 p.m.

*Bristol Section.* "Methods of Paint Application," by Mr. A. A. B. Harvey (Institute of Metal Finishing), to be held at the Royal Hotel, Bristol, at 7.15 p.m.

## Tuesday 31 October

*Thames Valley Section.* "Practical Contributions to the Analysis of Paints," by Mr. E. L. Deeley, to be held at the Royal White Hart Hotel, Beaconsfield, Bucks., at 7.00 p.m.

## Wednesday 1 November

*South Australian Section.* "Gloss Assessment," by Mr. M. D. Stewart.

## Thursday 2 November

*Newcastle Section.* "Sand Grinding," by Mr. I. Berg, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

*Bristol Section.* "New Oils and Fatty Acids for Resin and Varnish Manufacture," by Mr. K. B. Gilkes, British Resin Productions Ltd. Joint Meeting with Birmingham Paint Varnish and Lacquer Club, to be held at the Imperial Hotel, Birmingham, at 7.15 p.m.

#### Monday 6 November

*Hull Section.* "Electron Beam Curing of Coatings," by Mr. A. R. H. Tawn, Cray Valley Products Ltd., to be held at the Hull College of Technology, at 7.00 p.m.

#### Wednesday 8 November

*London Section.* Student Invitation Lecture "The Why and Wherefore of Dispersion," by Dr. G. D. Parfitt. To be held at London School of Hygiene & Tropical Medicine, Keppel Street, London, W.C.1, at 6.30 p.m.

#### Thursday 9 November

*Midland Section—Trent Valley Branch.* "Industrial Finishing in the Cycle Industry," by Mr. J. L. Barrow (Raleigh Industries Ltd.), to be held at British Rail School of Transport, London Road, Derby, at 7.30 p.m.

#### Friday 10 November

*Manchester Section.* Joint Meeting with Engineers to discuss the Value of Paint Protection—Mr. F. Dunkley at the Manchester Literary & Philosophical Society, at 6.30 p.m.

*South Australian Section.* Annual Dinner—Buckingham Arms Hotel.

#### Saturday 11 November

*Scottish Section—Student Group—*"Driers and Paint Formulae," by Dr. D. Atherton (John S. Craig Ltd.) and "Chemistry of Driers," by Mr. C. Finlay (Nuodex Ltd.), to be held at the Lorne Hotel, Sauchiehall Street, Glasgow, at 10.00 a.m.

#### Monday 13 November

*London Section—Southern Branch.* "Accelerated Weathering," by Mr. H. A. Hipwood, to be held at the Keppels Head Hotel, The Hard, Portsmouth, at 7.30 p.m.

#### Tuesday 14 November

*West Riding Section.* "Ceramic Paints," by Mr. C. Butler and "Marine Finishes," by Mr. A. Hearson and Dr. A. Christie, to be held at the Griffin Hotel, Boar Lane, Leeds, 1, at 7.30 p.m.

#### Thursday 16 November

*Scottish Section.* "Solvents: Some Current Topics," by Mr. C. J. Nunn and Mr. L. A. Tysall (Shell Research Ltd.), to be held at the Lorne Hotel, Sauchiehall Street, Glasgow, at 6.00 p.m.

#### Friday 17 November

*Midland Section.* "Improved Efficiency in Smaller Paint Factories," by Mr. R. W. English, to be held at Chamber of Commerce House, Birmingham, 15, at 6.30 p.m.

*London Section.* Ladies Night at the Criterion-in-Piccadilly, London, W.1, at 7.30 p.m.

#### Wednesday 22 November

*Scottish Section—Eastern Branch.* "Dispersible Organic Pigments," by Mr. Gray and Mr. Birrell (Geigy (U.K.) Ltd.), to be held at the Wee Windaes Restaurant, High Street, Edinburgh, at 7.30 p.m.

#### Friday 24 November

*Irish Section.* "Paint Testing for a Purpose," by Mr. R. B. Simon, to be held at The Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

*Bristol Section.* "Crime Detection," by Chief Inspector F. Clash, Bristol Police, to be held at the Royal Hotel, Bristol, at 7.15 p.m.

*West Riding Section.* Annual Dinner and Dance to be held at the Granby Hotel, Harrogate.

#### Wednesday 29 November

*Thames Valley Section.* "The Examination of Pigments used by Artists in Paints," by Miss Plesters, to be held at the Royal White Hart Hotel, Beaconsfield, Bucks., at 7.00 p.m.



HAT.33

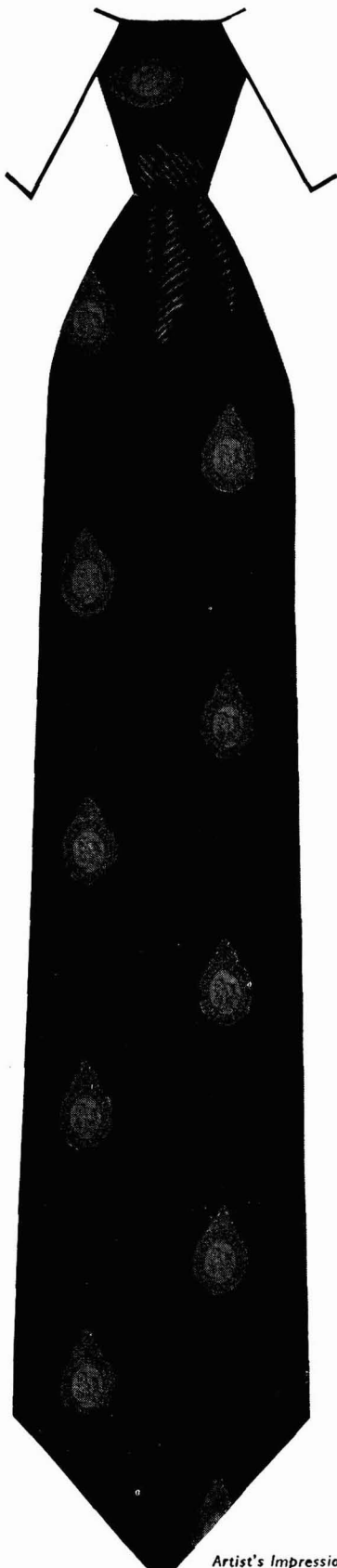
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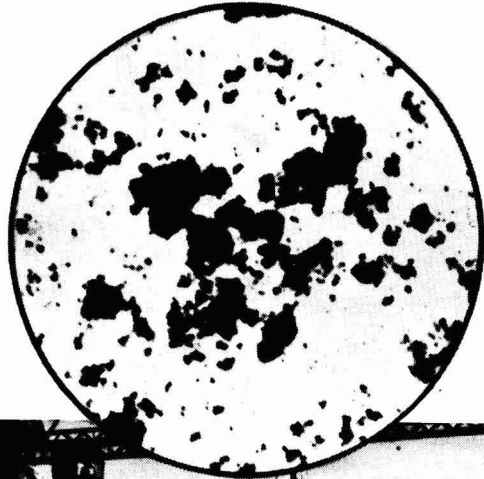
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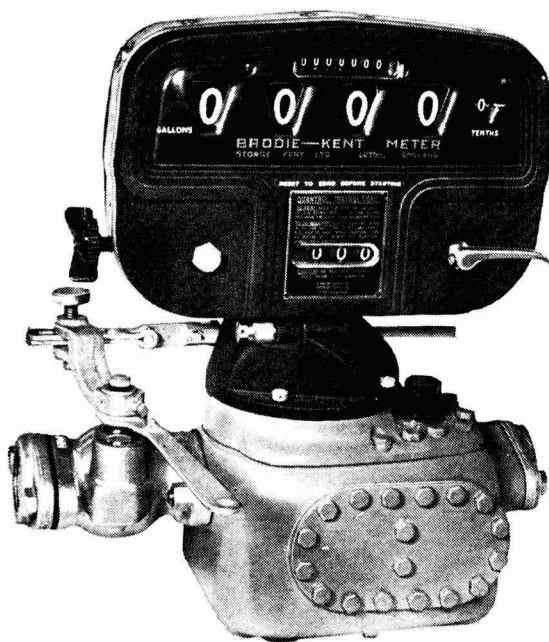
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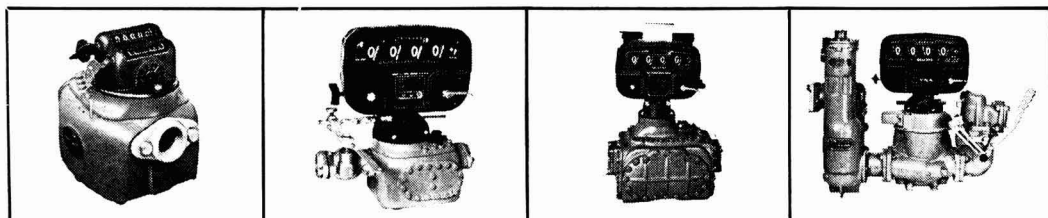


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