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The corrosion and protection of metals in the building and construction industries *B. G. Callaghan*

Measurement of conductivity, capacity, electrical resistance and permeability of paint films in an aqueous solution  
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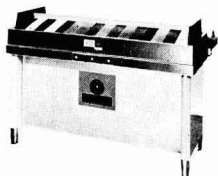
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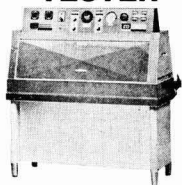


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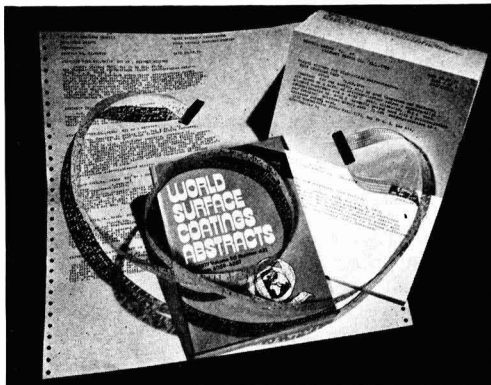
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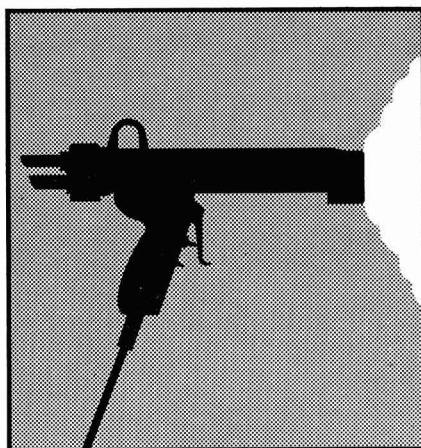
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# The theory and practice of pigment dispersion\*

By W. Carr

31 Linfold Drive, Wilmslow, Cheshire SK9 6DT†

## Summary

Pigment powders consist of aggregates of large numbers of basic particles of pigments, and the object of the dispersion process in the manufacture of paint and ink is to break these aggregations down to a level that is acceptable. This is because the optical properties of pigmented systems are a function of the size of the particles and aggregates. However, the final criteria are the optical properties of the dry paint or ink films and these are dependent on the pigment particle sizes in the films, which may or may not be the same as

those in the wet paints or inks.

In this paper, the whole process of manufacture and use of paints and inks, including storage, application and drying stages, are surveyed to see if the level of pigment dispersion is likely to be altered at any of the stages; to see in what directions the changes are likely to go; and to see if the effects which are observed in both laboratory and factory have any theoretical basis.

## Keywords

### *Types and classes of coatings and allied products*

industrial coating  
printing ink  
architectural coating

### *Types and classes of structures or surfaces to be coated*

substrate

### *Raw materials*

#### *prime pigments and dyes*

organic pigment

### *Processes and methods primarily associated with analysis, measurement or testing*

disc centrifuge

#### *manufacturing or synthesis*

flocculation  
thinning  
dispersion

### *Properties, characteristics and conditions primarily associated with materials in general*

colour  
particle size

### *bulk coatings and allied products*

stability  
shelf stability

### *dried or cured films*

gloss  
brightness

### *Equipment primarily associated with manufacturing or synthesis*

ball mill  
sand mill

## La théorie et la pratique de la dispersion de pigments

### Résumé

Les pigments sont des poudres composées d'aggrégats comprenant un nombre important de particules pigmentaires de base, et le but du procédé de dispersion lors de la fabrication de peintures et d'encres d'imprimerie est de réduire la grandeur de ces aggrégats à une échelle supportable. C'est parce que les caractéristiques optiques des systèmes pigmentés sont une fonction de la grandeur des particules et des aggrégats. Pourtant, les critères ultimes sont les caractéristiques optiques des films secs de peinture ou d'encre qui se dépendent de la gamme des grandeurs particulières se trouvant dans les films. Ces grandeurs pourraient être, ou non, les mêmes que celles qui se trouvent en les peintures ou les encres liquides.

Dans cet exposé l'auteur considère la gamme entière des procédés de la fabrication et de l'utilisation de peintures et d'encres, afin de noter s'il existe la possibilité qu'une amélioration ou qu'une altération du degré de la dispersion pigmentaire puisse se produire au cours de l'une ou l'autre des étapes, y compris le stockage, l'application et le processus de séchage; de s'informer comment, les changements vont probablement se produire, et de déterminer si les effets que l'on note au laboratoire et à l'usine ont quelque base théorique.

## Die Theorie und Praxis der Pigmentdispersion

### Zusammenfassung

Pigmentpulver bestehen aus Aggregaten einer grossen Zahl von elementaren Pigmentpartikeln, und der Zweck des Dispergierungsprozesses bei der Fabrikation von Lack- und Druckfarben ist, diese Aggregate zu einer akzeptablen Grösse abzurechnen. Dies ist nötig, weil die optischen Eigenschaften pigmentierter Systeme eine Funktion der Grösse der Teilchen und der Aggregate sind. Die endgültigen Kriterien sind jedoch die optischen Eigenschaften des trockenen Lack- oder Druckfarbenfilms, und diese sind von der Pigmentpartikelgrösse in den Filmen abhängig, welche möglicherweise, aber nicht notwendigerweise die gleiche, wie die in

den nassen Anstrichmitteln oder Druckfarben sein kann.

In dieser Abhandlung wird das gesamte Verfahren der Herstellung und Anwendung von Lacken und Druckfarben, einschliesslich Lagerungs-, Anwendungs- und Trockenstadien betrachtet um festzustellen, ob es nötig ist, den Grad der Pigmentdispersion in einem der Stadien zu ändern; um zu sehen, nach welcher Richtung hin sich Änderungen auswirken würden; und um zu sehen, ob für diese im Laboratorium und Fabrik beobachteten Auswirkungen eine theoretische Basis besteht.

\*Lecture presented to the Irish Section of the Association on 15 September 1978 and to the Manchester Section on 13 October 1978

†Formerly of the Pigments Division, Ciba-Geigy (UK) Ltd, Wythenshawe, Manchester M23 9ND

## Introduction

*Ref. 1*

In order to develop a reasonable level of colour strength, brightness and gloss, pigment powders have to be dispersed in a suitable vehicle until their particle sizes are in the sub-micron region. The actual size of the basic particles in most pigment powders is usually well below  $1\mu$ , but this smallness of the basic particles is the factor that ensures that in the powder form, the pigment particles are inevitably highly aggregated.

When particles are very small, their centres of gravity can become very close together in a powder, so close that the powerful short range forces of attraction, known as van der Waals or London forces, come into play and, in the absence of any opposing force, the particles cling to one another and form aggregates.

In the normal pigment powder, these aggregates are at least 20 microns in size. If they were smaller, the material would not be a powder but would be a dust or smoke and could not be handled.

Assuming the particles to be spheres, a pigment with a surface area,  $S$ , of  $40\text{ m}^2/\text{g}$  and a density,  $\rho$ , of  $1.5\text{ gms/ml}$ , would have a basic particle diameter,  $d$ , of  $0.1\text{ microns}$ , from the equation  $S=6/\rho d$ .

Eight million of these particles would be required to make up a speck of powder of 20 microns in size. This figure will give some idea of the degree of aggregation of organic pigments in powder form.

In use, these aggregates have to be broken down, or dispersed, in a suitable vehicle until their mean diameter is in the sub-micron region.

The electron micrographs shown in Figs. 1-6 illustrate these points. Such micrographs require some dispersion of the pigment in a suitable vehicle during the preparation stage, and these particular photographs have been prepared using both light and heavy dispersions.



Fig. 1. Electron micrograph ( $\times 20,000$ ) Carbon black, poor dispersion

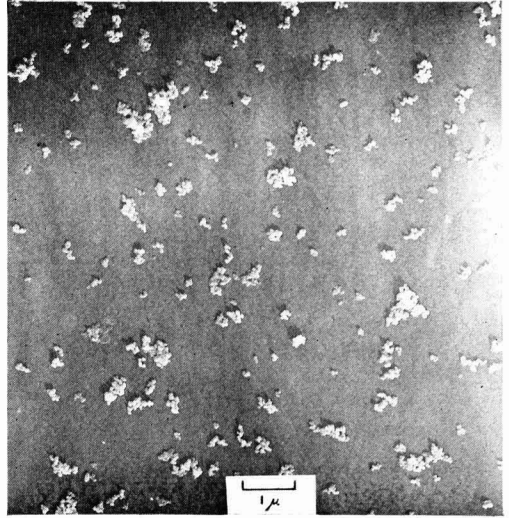


Fig. 2. Electron micrograph ( $\times 20,000$ ) Carbon black, good dispersion

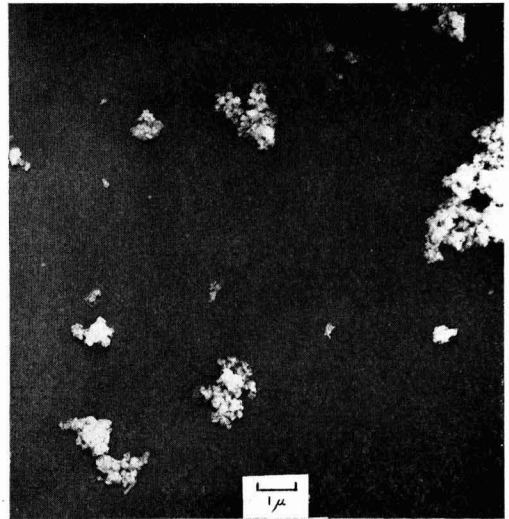


Fig. 3. Electron micrograph ( $\times 15,000$ ) Phthalocyanine blue, poor dispersion

The pictures of the well dispersed specimens show how the dispersion process breaks down the tremendous aggregates to much smaller ones, but not necessarily to the basic particles themselves. They also show that even after heavy dispersion, the particles are not uniform in size, but cover quite a range of sizes.

The van der Waals short range forces of attraction operate in dispersions of solids in liquids, as well as in the powder form. Consequently, after the dispersion process stops, the particles will re-aggregate unless there is a stabilising mechanism which can oppose the forces of attraction.

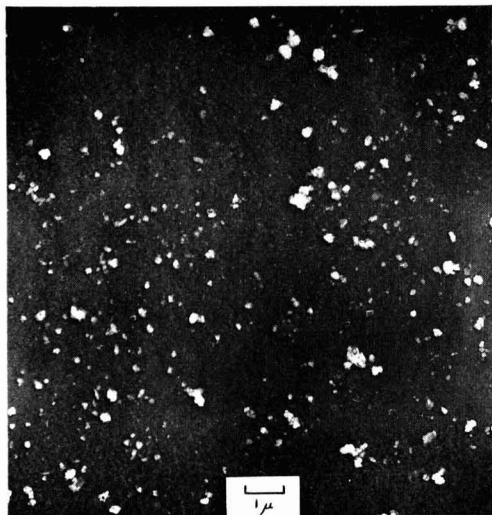


Fig. 4. Electron micrograph ( $\times 15,000$ ) Phthalocyanine blue, good dispersion

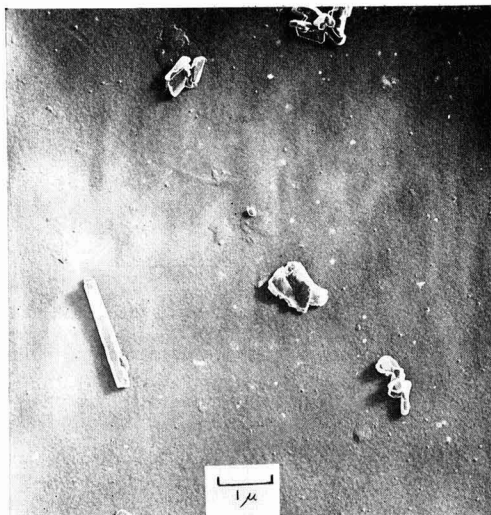


Fig. 6. Electron micrograph ( $\times 20,000$ ) Arylamide yellow G, good dispersion

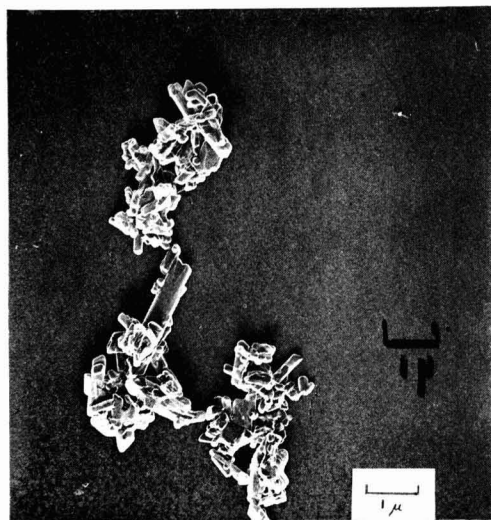


Fig. 5. Electron micrograph ( $\times 20,000$ ) Arylamide yellow G, poor dispersion

Two stabilising mechanisms are known which will prevent particles in a dispersion from re-aggregating. One depends on the adsorption of ions on to the particle surfaces to provide an electrostatic repulsive force between particles. The other depends on the adsorption of long chain molecules of a surfactant or resin from solution on to the surface of the particles to give an opposing force based on a steric hindrance mechanism.

These stabilising mechanisms have been discussed in detail by many authors, notably Parfitt<sup>1</sup>. Here it is sufficient to point out that whatever the stabilising mechanism, a dispersion of pigment particles in a liquid vehicle is an equilibrium system,

where the forces of attraction are opposed by forces of repulsion.

If this equilibrium is altered in any way during the manufacture, storage, or application of a pigmented system, such as a paint or ink, then the level of dispersion may alter. The dispersion level of a pigment in a paint or ink or similar system is, therefore, vulnerable to external forces until the system changes finally to a dry film of paint or ink.

It is now known that it is the dispersion level of the pigment in the final film that controls the optical properties of the film, such as colour strength, brightness, gloss and transparency. This dispersion level in the final paint or ink film may be the same as in the original wet paint or ink, but this is by no means certain.

It is proposed to survey the whole process of manufacture and use of paints and inks, from raw materials to final films, to see if the level of dispersion is likely to be altered at any of the stages, to see in what directions such alterations are likely and to see if the effects which are observed in both laboratory and factory have any theoretical basis.

The flow diagrams for paints and inks, shown in Figs. 7 and 8, illustrate the raw materials and the steps in the progress from pigment powder to final dry film. It is proposed to study the steps in these diagrams in detail to determine their effect on the level of pigment dispersion.

### Assessment of dispersion

Ref. 2

To do this in a quantitative manner, it is necessary to be able to assess dispersion levels in a quantitative manner. This means being able to measure mean particle sizes, or preferably, particle size distributions, in paints and inks.

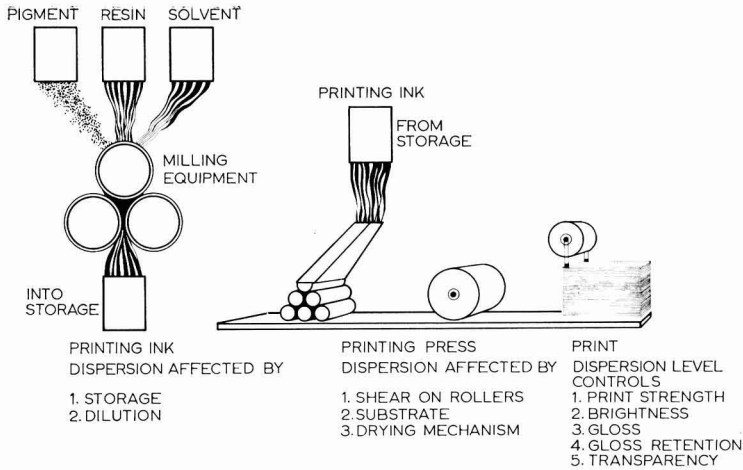


Fig. 7. Flow diagram – Pigment to print

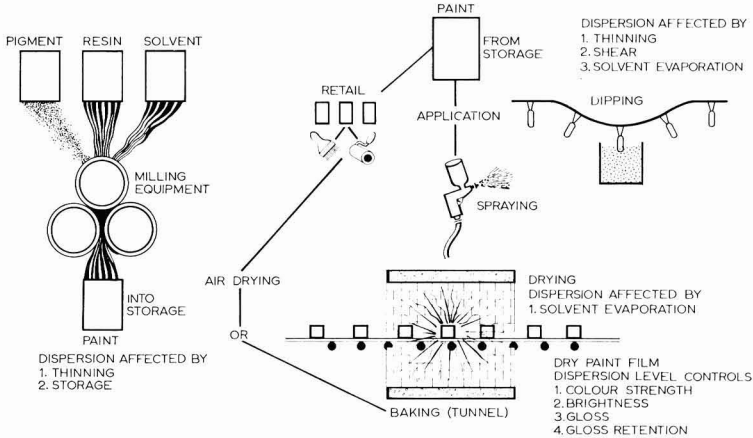


Fig. 8. Flow diagram – Pigment to paint film

This quantitative assessment is difficult experimentally. The particle sizes concerned are in the sub-micron range and well below the limit of optical microscopes. The particles themselves differ widely in chemistry from pigment to pigment, as do the vehicles in which they are dispersed. The concentration of particles is quite large and this too creates problems, as does the range of sizes in any one system.

The problems associated with the assessment of dispersion have been discussed in detail by the author elsewhere<sup>2</sup>. In the following work, three experimental approaches have been used, namely: centrifugal sedimentation, colour strength measurements, and optical density measurements to follow changes in the levels of dispersion of the pigments.

Centrifugal sedimentation has shown that the pigment particles in both paints and inks have a fairly wide size distribution, and this results experimentally in a particle size distribution curve. The 50 per cent diameter figure, which is often used for convenience, is that particle diameter above and below which there is 50 per cent by weight of the pigment particles.

Colour strength and optical density measurements give only mean diameters.

Armed with these techniques, it is possible to proceed step by step through the two flow diagrams to study the effect of each factor on the level of dispersion.

The examples and the results quoted in this review are from experiments carried out in the author's laboratories with a limited number of pigments, resins and solvents. This restriction was inevitable in order to keep the number of experiments within reason. A complete examination would have to include all types of pigments, vehicles, solvents, paints, inks, application and printing processes, all types of substrates and all types of drying mechanisms, and would have been a very ambitious project indeed. Nevertheless, even a limited examination of the flow diagrams from start to finish, from the point of view of pigment dispersion, may throw up important results, demonstrate the significance of various factors, or emphasise gaps in knowledge or understanding that would repay investigation.

Fortunately, for this review, the initial stages are the same in principle for both paints and inks, so that the influence of the raw materials, the method of manufacture and storage can be treated simultaneously for both products.

**Influence of the pigment**

As already pointed out, pigment powders consist of aggregates of huge numbers of basic particles. In the manufacture of paints and inks, the pigment powders have to be dispersed into the vehicles until these aggregates are broken down to a degree that is acceptable.

Whatever milling machinery is used, the initial breakdown of the aggregates is very rapid and then slows down appreciably, as a lower size limit is approached.

Typical curves for three pigments in a typical air drying aklyd resin are shown in Fig. 9. The pigments are a  $\beta$ -phthalocyanine blue, a carbon black and a pigment green B.

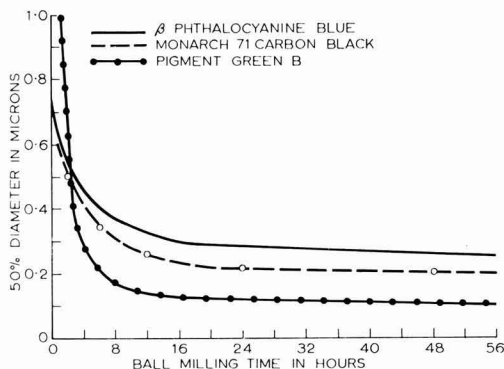


Fig. 9. Particle size versus ball milling times – paint stainers

In each case, it is seen that during the first four hours of milling, the rate of reduction in particle size is very rapid, although it does vary from pigment to pigment. After twelve hours milling, the rate of further reduction in mean diameter is very slow and the 50 per cent diameter becomes almost, but not quite, constant. The diameters at which the curves almost level off also vary from pigment to pigment.

The shape of these curves is what would be expected from theory. The mechanical energy breaks the aggregates down rapidly at the start and the particles begin to adsorb resin from the solution. This adsorption helps to stabilise the smaller aggregates and to prevent them from re-aggregating. The smaller aggregates are less easily broken down further by mechanical means. They also have a greater tendency to re-aggregate because, as they are reduced in size, they can approach each other more closely and the forces of attraction increase. To achieve stabilisation more resin must be adsorbed.

Fig. 10 emphasises how the effect of milling time on dispersion falls off as the particles become smaller. It shows that the percentage of particles under 2 microns rapidly reaches 100 per cent; the percentage of particles by weight under 1 micron reaches 100 per cent less rapidly; the percentage by weight of particles less than 0.5 microns increases less rapidly still with time and this tendency increases with still smaller particles.

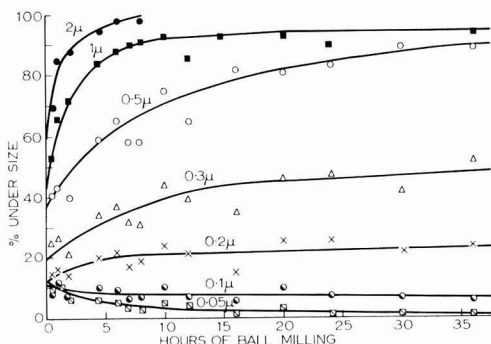


Fig. 10. Percentages of particles under specific sizes versus ball milling times – paint stainers

Although Fig. 9 shows that the 50 per cent diameters only decrease very slowly with further grinding after 12 hours, it must be realised that this further grinding may well have a significant effect on important application properties, such as strength, brightness and gloss.

In all pigmented systems, the particle sizes are far from uniform and the 50 per cent diameter figure does not give any indication of the size distribution. Consequently, further grinding, although it may not significantly reduce the mean diameter, will reduce the percentage of large particles, and therefore, lead to increases in colour strength, brightness and gloss.

**Pigment modifications**

As already mentioned, stability of pigment dispersions can be obtained by adsorption of resins on to the surface of the pigment particles. If the surface characteristics of the pigment particles are modified, then more or less resin may be adsorbed and this will alter the size level at which the system becomes stabilised.

*Easily dispersible* forms of some pigments are now available commercially in which the surface characteristics of the particles have been modified, so that they can adsorb more resin under similar conditions. Consequently, they will quickly give a good level of dispersion on milling compared with the ordinary form. Further grinding does not give any major improvements in dispersion.

Typical results for an improved dispersible form of  $\beta$ -phthalocyanine blue are shown in Table I.

Table I  
 *$\beta$ -Phthalocyanine blue in improved dispersible form (I.D.) in publication gravure inks*

Pigment form	I.D.		Standard powder	I.D.		Standard powder
	I.D.	I.D.	I.D.	I.D.	I.D.	I.D.
Medium	Phenolic			Ca-Zn Resinate		
Ball milling time (hours)	4	72	24	4	72	24
50% diameter (in microns)	0.18	0.20	0.32	0.26	0.26	0.36

*Pigment chips* represent products where the surface of the pigment has had abundant opportunity to adsorb resin molecules. Consequently, on milling into a medium, they will reach good levels of dispersion quickly by comparison with the normal powder, but again, prolonged milling does not improve the dispersion further. Typical results for a polyamide gravure ink, based on  $\beta$ -phthalocyanine blue, are shown in Table 2.

Table 2  
 *$\beta$ -Phthalocyanine blue in chip and powder form in Versamid 930*

Pigment	Ball milling time	50% diameter in microns
Chip form	2 hours	0.21
Chip form	16 hours	0.22
Standard powder	24 hours	0.32

The effect of the pigment itself in making a good dispersion may be summarised as follows: in non-aqueous systems, the stabilising mechanism preventing re-aggregation is usually the adsorption of the resin on to the surface of the pigment and this explains why breakdown of the aggregates is rapid at first and then tends to reach a limiting value. All pigments follow this general pattern, but differ in detail from one another because they differ in surface properties, and hence in both the speed and the extent of resin adsorption. If the surface characteristics of the pigment particles are altered, this will affect both the speed and the extent of the resin adsorption and consequently both the rate of dispersion and the final level of dispersion.

### Influence of the resin

By analogy with the above, it may be expected that different resins should have different affinities for the same pigment surface, and hence to have different stabilising actions. These expectations have been confirmed experimentally. For any given pigment, solvent and milling equipment, both the rate of dispersion and the final limiting level of dispersion may vary considerably with the type of resin used.

In publication gravure inks, for example, calcium-4B metal salts disperse much better in phenolic resin systems than in calcium-zinc resinate systems, when the solvent is rich in aromatic content.

Comparing ink and paint resins, a calcium-4B metal salt behaves quite differently in publication gravure resins than in alkyd resins. Fig. 11 shows how the 50 per cent diameters of the pigment in an alkyd based paint and a calcium-zinc resinate ink are reduced as ball milling proceeds. In the ink, the 50 per cent diameter is reduced to 0.17 microns after only 6-hours ball milling, but prolonged grinding does not reduce the 50 per cent diameter further.

With the same pigment in the paint stainer, the breakdown of the aggregates proceeds more slowly and a 50 per cent diameter of 0.17 microns is only reached after 30-hours grinding. On further grinding, however, this 50 per cent diameter keeps on decreasing, albeit slowly.

From the various size distribution curves corresponding to the various grinding times, the percentage by weight of particles under some specific size can be obtained and plotted against the times of grinding.

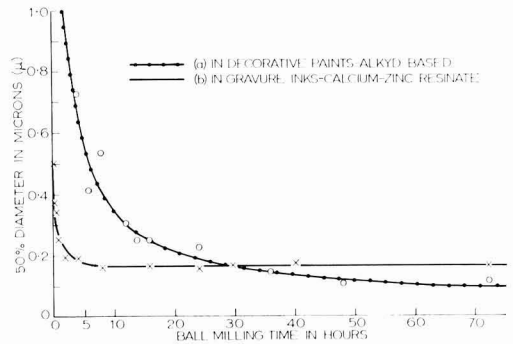


Fig. 11. Breakdown of calcium 4B metal salt in different resins

The resultant curves for the inks are shown in Fig. 12. The percentage of particles under 0.17 microns increases rapidly to approximately 52 per cent and then stays constant even on prolonged grinding. The percentage of particles under 0.15 microns increases at the start and then decreases slowly. The percentage of particles under 0.1 microns decreases with time of milling, rapidly at first, and then more slowly.

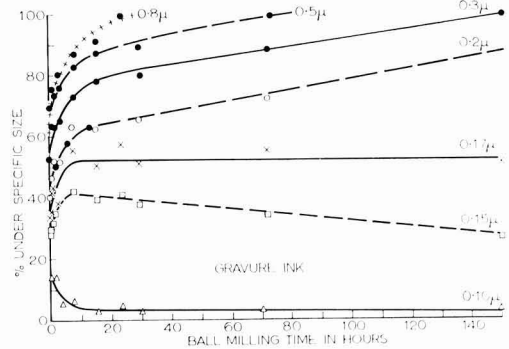


Fig. 12. Percentage of particles under specific sizes versus ball milling time - gravure ink

How can this and the difference in behaviour of the same pigment in the two resin systems be explained?

A tentative explanation is based on two assumptions. Firstly, that any particular resin molecule will exert its maximum stabilising action when adsorbed on to a particle of a certain size, and secondly, that the main difference between the ink and the paint resin lies in their homogeneity with respect to the chain lengths of their respective molecules.

Alkyd resins usually consist of a wide spectrum of molecular weight fractions and this will mean that their molecules have a wide range of chain lengths, so that they can stabilise a wide range of particle sizes.

The range of molecular weight fractions in a typical commercial calcium-zinc resinate resin is very narrow. This means that only a narrow range of chain lengths is present and they can stabilise efficiently only a narrow range of particle sizes.

This explanation would account for the phenomena illustrated in Figs. 11 and 12. The resinate molecules are capable only of fully stabilising particles of 0.17 microns. Particles



smaller than this are not completely stabilised and re-aggregate until their size increases to 0.17 microns.

The influence of the resin on pigment dispersion can, therefore, be summarised as follows:

The dispersing or stabilising action of a resin is dependent on the extent to which it is adsorbed on pigment surfaces. Different resins have different affinities for pigment surfaces and hence will have differing stabilising actions. The latter are also dependent on the homogeneity of the chain lengths of the resin molecules.

### Influence of the solvent

The primary function of the resin in paints and inks is to bind the pigment to the substrate after application by forming a continuous film around the pigment particles. To do this effectively, the resin is usually present in the wet paint or ink as a solution in a suitable solvent.

The secondary function of the resin is to stabilise the pigment particles in the wet paint or ink and to prevent them from aggregating. To do this the resin has to be adsorbed from the solution phase on to the surface of the pigment particles. There is, therefore, a competition for the resin molecules between the solvent phase and the pigment surface, and it would not be surprising if the level of adsorption of any particular resin on to a particular pigment was dependent on the solvent used and its solvent power for the resin.

Experimentally, it has been found that the composition of the solvent can have a marked effect on the level of dispersion achieved with the same pigment, the same resin and the same grinding time. The effect is particularly striking in liquid inks.

A typical set of results is given in Table 3.

Table 3  
Calcium-4B publication gravure inks  
Calcium-zinc resin in toluene/SBP5 blends,  
24-hour ball millings

Solvent (% toluene)	90	80	70	60	50	40	30	25
50% diameter (in microns)	0.37	0.35	0.30	0.10	0.07	0.08	0.09	0.09

This table shows the dispersion levels obtained when a calcium-4B metal salt is ball milled for 24 hours into a gravure ink medium consisting of a calcium-zinc resin in mixtures of toluene and the aliphatic petroleum distillate SBP5.

In all the inks, the pigmentation level, the pigment-binder ratio and the milling times were the same, the only differences being the composition of the solvent blend.

The results show that as the aromatic content is reduced, the level of dispersion increases, *i.e.* the system is stabilised at a lower size level.

In this system, the resin has good solubility in the aromatic component, but is virtually insoluble in the aliphatic portion. Consequently, in the blends rich in toluene, the solvent tends to reduce the extent to which the resin is adsorbed on the pigment. The stabilising effect is, therefore, reduced and the level of dispersion reached is coarser. As the toluene content is

reduced, the solubility of the resin is reduced. More resin is then adsorbed giving a better level of dispersion.

On the other hand, in a similar series of experiments using a modified phenolic resin, a different picture emerged. The results are shown in Table 4.

Table 4  
Calcium-4B metal salt gravure inks  
(phenolic resin - toluene/SBP5 blends)  
24-hour ball millings

Solvent (% toluene)	100	80	60	40
50% diameter (in microns)	0.07	0.07	0.08	0.09

With this resin, a very high degree of dispersion is obtained even with 100 per cent toluene as the solvent, and the dispersion level is independent of the solvent composition.

Separate experiments have shown that the adsorption of this phenolic resin on to the 4B metal salt from solvents is much greater than the adsorption of the calcium-zinc resin under the same conditions. It is, therefore, probable that the affinity of the phenolic resin for this pigment is so great that the restraining influence of the solvent on the level of adsorption is negligible.

Because it is adsorbed strongly on to particles of Ca-4B metal salts, even from solution in powerful solvents, this particular modified phenolic resin should be capable of functioning as an aid to dispersion for this pigment in different resin systems. This has been checked in melamine-formaldehyde stoving paints. It was found that the inclusion of a small amount of the phenolic resin did improve the level of dispersion of the Ca-4B metal salt under the same milling conditions.

### Influence of milling machinery

Printing inks and paints can now be made in a wide variety of dispersing machinery.

There is little published data on how the various types of mills compare with each other in their dispersing efficiency, but it would be naive to assume that they are all equal. Work carried out with paint stainers in laboratory ball mills and sand grinders show that these two types of mills differ markedly from each other, both in their rates of dispersion and final levels of dispersion, see Figs. 13 and 14.

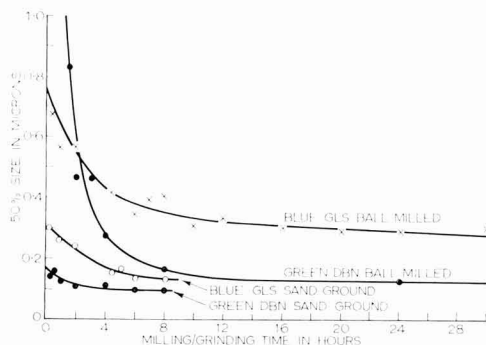


Fig. 13. Particle sizes versus milling times. Sand grinding and ball milling - blue and green pigments

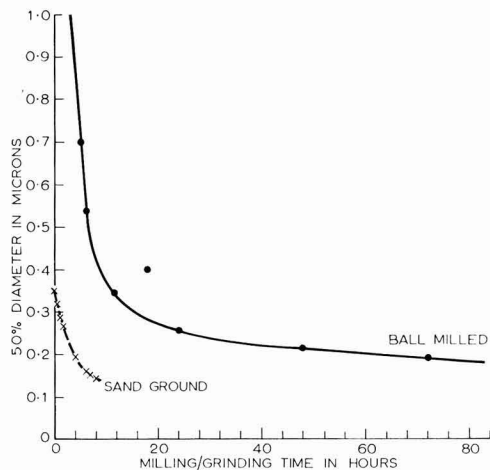


Fig. 14. Particle sizes versus milling times. Sand grinding and ball milling - violet pigment

Despite these differences in detail, the same general pattern is found with both milling techniques, namely a fairly rapid initial breakdown of the aggregates, followed by a slowing down and the approach to a limiting size. The initial part of the curves for sand grinding are not nearly as steep as those for ball milling. This is due to the fact that the initial pre-mixing process usually associated with sand grinding will of itself significantly break down the very large aggregates present in the original pigment powders.

This general type of dispersion curve - rapid initial dispersion, slowing down and approaching a limiting value - strengthens the belief that the dispersion process is a two-way process which eventually reaches an equilibrium. The mechanical energy supplied by the mill breaks down the very large aggregates present in the pigment powder; re-aggregation is prevented by the adsorption of resin from the vehicle. The

energy input varies from mill to mill both in quantity and rate. The adsorption of resin on to the pigment surface is dependent on the properties of the pigment surface, the affinity of the resin for the surface and the capacity of the solvents to restrain the adsorption. The efficiency of the resin as a stabilising agent once it is adsorbed, is a function of its molecular chain length relative to the size of the particles. As the pigment particles in any system are never uniform in size, a range of molecular chain lengths is believed to be an advantage in any particular resin. The finished paint or ink represents an equilibrium system in which the van der Waals forces of attraction are balanced by stabilising forces of repulsion.

It is believed that these are the principles that control or govern the levels of dispersion achieved in paints and inks. They explain why it is impossible to generalise about levels of dispersion which will be arrived at by different pigments, even when milled into the same resin vehicle under the same conditions. Other things being constant, this level will be determined by the affinity of the resin for the pigment and this, in turn, can vary with variations in the physical properties of the pigment.

**Significance of dispersion levels**

The importance of variations in dispersion levels varies with the actual pigment concerned and with the actual dispersion region in which the variations occur. These points are illustrated clearly in Figs. 15 and 16, which show the relationship between colour strength and particle size for a number of paint and printing ink pigments. These are experimental curves. Colour strengths were determined from the dry films, the dispersion levels from particle size measurements on the wet paints and inks, it being assumed that there was no alteration in particle sizes during application and drying. The curves show that the exact relationship between colour strength and particle size differs from pigment to pigment. However, all the curves have the same general shape and it can be seen that variations in particle size in regions greater than 1 micron, have little effect on colour strength. As the mean size falls below 1 micron, the colour strength becomes slightly more dependent on particle size. Once the mean size falls to 0.5 microns, further reductions in size give rise to very considerable increases in colour strength.

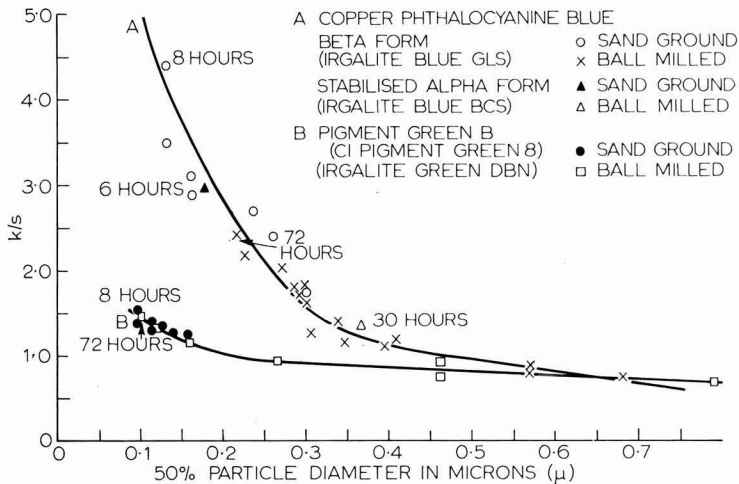


Fig. 15. Colour strength (k/s) versus particle size - blue and green pigments

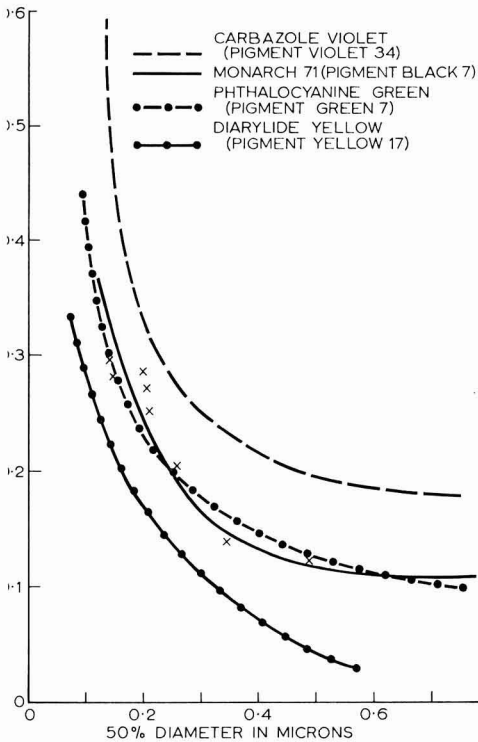


Fig. 16. Colour strength (k/s) versus particle size – violet, black, green and yellow pigments

Consequently, variations in dispersion level in this region, below 0.5 micron, can be very significant in terms of colour strength. For example, in the case of the carbon black, reducing the mean diameter from 0.5 to 0.3 microns will increase the colour strength by 50 per cent. Reducing the mean diameter from 0.5 to 0.2 microns will double the strength.

These massive changes in colour strength with dispersion in this size region help to explain the apparent strength differences in competitive brands of the same pigment. Such brands are chemically identical and have a similar level of purity, but differ in their physical properties, particularly in their adsorption capacities for the resin binder, then under standard milling conditions, one brand will disperse better and hence give better colour strength. The intrinsic colour strength of the pigments will be the same but their dispersibilities will be different.

It would be of interest to ascertain what levels of pigment dispersion are reached by commercial ink and paint manufacturers, as this would permit the determination of how efficiently they are using the pigments.

**Effect of storage**

For the inks and paints have been made and passed as being of a certain specification, even though the dispersion level of the pigment is unknown, there must inevitably be a time interval before they are used. What will happen to the level of dispersion during this interval? Can changes in dispersion be prevented?

The author's views on this question, based on his own measurements can be summarised as follows:

The determining factor is whether the pigment particles are in the true colloidal state or outside it. If they are in the true colloidal state, there will be a perfect balance between the forces of attraction and repulsion, and the particles will be so small that they will be prevented from settling by Brownian motion. If the particles are outside the true colloidal state, even by only a small degree, the balance between the forces of attraction and repulsion will not be perfect, and there will be a gradual coarsening of the particles, leading to a loss in colour strength and gradual sedimentation.

The literature is uncertain about the upper size limit for the true colloidal state, but it is believed that for organic pigments, this upper limit is approximately 0.3 microns. Pigment particles smaller than this will be inherently stable and will, therefore, not coarsen on standing. Particles greater than this will not be completely stable and will coarsen slowly on standing. This effect is illustrated in Figs. 17 and 18, which show particle size distribution curves for inks and paints, initially and after standing for some months. The curves representing before and after standing are identical to the left of 0.3 microns, but differ to the right of it, becoming coarser on standing.

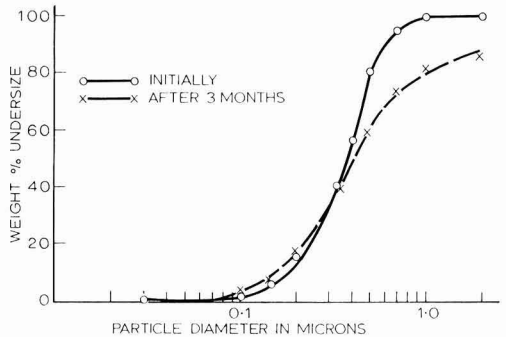


Fig. 17. Storage trials – calcium 4B gravure ink

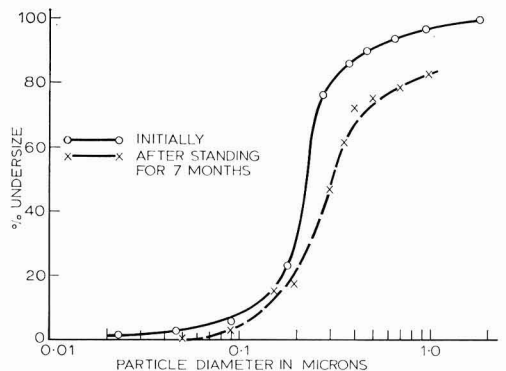


Fig. 18. Storage trials – Phthalocyanine blue paint stainer

If all the pigment particles in a paint or ink are below 0.3 microns, then they will all be in the true colloidal state and the whole system will be stable indefinitely on storage. This is illustrated in Fig. 19 for a gravure ink.

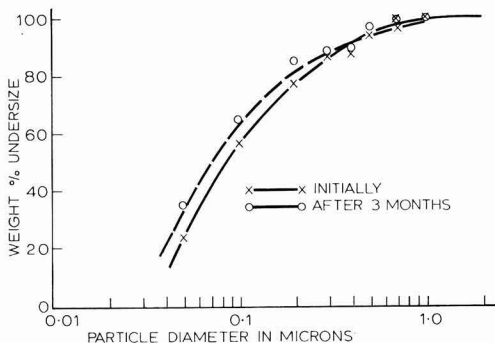


Fig. 19. Storage trials - calcium 4B gravure ink

According to these arguments, for a paint or ink to have satisfactory storage properties, *i.e.* to maintain its dispersion level and be free from sedimentation, all of the pigment particles should be less than 0.3 microns.

### Effect of thinning

Before any ink goes on to the press, or before any paint is applied, the operator may feel it incumbent to thin the ink or paint. Thinning or dilution of any nature involves the risk of coarsening the pigment dispersion by means of a phenomenon usually referred to as "dilution shock". As has been previously stressed, pigment dispersions in the sub-micron range represent equilibrium systems in which the forces of attraction that arise between very small particles in close proximity to each other are balanced by some repulsive or stabilising mechanism. In non-aqueous inks and paints, this stabilising mechanism is usually due to steric hindrance effects arising from resin or polymer adsorption on the surface of the pigments. This adsorbed layer is, in turn, in equilibrium between its affinity for the pigment surface and its solubility in the vehicle. The equilibrium can be disturbed by dilution with more liquid, and even if the disturbance is only temporary, by the time equilibrium is restored, some of the adsorbed layer may have been removed allowing some flocculation of the pigment to occur.

Practical ways of avoiding dilution shock are to carry out the dilution slowly, in stages if necessary, with agitation and to add some resin or surfactant to the diluting liquid. By this means, the risk of stripping some of the adsorbed layer from the pigment surface is minimised.

In the author's experience, the risk of dilution shock varies in extent from pigment to pigment in any particular system. The finer the original dispersion is, the better it is able to stand dilution and vice versa. This is not surprising as the better the dispersion, the greater the affinity of the resin for the pigment and the less likely it is to be stripped by dilution.

### Application of inks - Printing processes

During the application of paints and inks to substrates, they are submitted to a variety of operations and processes which could conceivably alter the equilibrium states present in the

wet inks or paints and, therefore, could conceivably alter the levels of dispersion.

These application techniques will be considered separately to see what are the likelihoods of dispersion changes taking place during them.

It is usually taken for granted that the dispersion level of inks as supplied will be unaffected on the press. Will this assumption stand up to a critical examination? Is the ink submitted to any shear on the press and, if so, is this shear likely to be greater than the shear to which it has already been subjected during manufacture? If the answer is yes, then the dispersion may be increased on the press.

On the other hand, is there any likelihood that the dispersion level of the pigment in the ink will be coarsened as it passes through the press? Would water picked up on a litho press, for example, cause some flocculation?

The possibility of extra shear on the press can be dismissed for liquid inks. If it can happen at all it would be most likely to occur on a litho press. Here, the number of ink distribution rollers is considerable, and the viscosity of the inks is high and the speed of the rollers is great. As the ink passes through the gap between each pair of rollers, there will be some smearing action and, as the ink emerges from each gap, there is considerable internal friction applied to it as the ink film is torn apart and splits.

These conditions are obviously capable of exerting a considerable dispersing force on the pigment in the ink, and this force will be the greater, the greater the overall viscosity of the inks.

In fact, the conditions on the press are in many ways similar to those occurring on the triple roll mills which are normally used to prepare litho inks.

From considerations of this nature, it is possible that on a litho press, a considerable amount of shear is applied to the ink, and this is confirmed by practical experience. Many inks which are comparatively stiff and stodgy in the duct, flow quite satisfactorily on the press. This is because they are non-Newtonian in character and their apparent viscosity decreases as the applied shear increases.

Whether this shear which the ink undergoes on the press is greater or less than the shear to which it was subjected during manufacture, is not known. If it is greater, the extra shear would improve the dispersion of the pigment.

In the other direction, that is, coarsening of the pigment dispersion, this again would be most likely to occur with litho inks. It is well known that during a printing run, such inks can pick up to 20 per cent of water. This addition to a pigmented non-aqueous system might easily upset the stabilising mechanism by which the pigment is kept in the dispersed state. If it does, the result can only be a coarsening of the level of dispersion.

Experimental evidence on this point is lacking.

The effect of the press on pigment dispersion is only likely to be significant with oil inks in general and with litho inks in particular.

### Application of paints

For the purpose of this section, which is to discuss the possible effect on dispersion level of the methods of paint application,

only application by hand, including the use of brush and roller, and application by spraying and dipping will be considered.

It is known that with some decorative paints, heavy brush-outs will give a deeper shade than light brush-outs. Blue shades used to be noted for this defect even when other shades, based on the same resin systems did not give the trouble. The defect used to be assumed to be caused by the flocculation of the blue pigment. Nowadays, it is believed that the heavy brushing increases the level of dispersion of the blue pigment and thereby produces greater strength. If the dispersion level of the blue in the original paint is increased, the heavy brushing is not able to improve the dispersion and the defect disappears.

Similarly, when industrial paints are applied by spraying and dipping, the sprayed film is often found to be stronger tinctorially than the dipped film. This extra strength may well be due to the extra shear experienced in the spray gun giving better dispersion. As in the case of brushing, if the original paint is very well dispersed, the extra shear in the spray gun will not give better dispersion. With stoving paints, however, the problem is complicated by the effects of rapid solvent evaporation, a factor which will be discussed later.

### Effect of substrate

It is possible that the nature of the substrate may affect the level of dispersion of the pigment in the final paint or ink film on the surface of the substrate. Such an effect, if it occurs, is likely to be more significant with inks than paints.

What does happen when an ink film is finally deposited on the substrate? If the latter is non-absorbent, the film split at the impression stage is likely to be similar to that between inking rollers and therefore a source of some shear. With absorbent substrates there must be some penetration of the surface by the ink as a whole, or by the vehicle with or without an appreciable portion of the pigment. It is known that in all pigmented systems, there is a fairly wide range of pigment particle sizes. In penetration of this sort, does the substrate act as a filter for all the particles or only the larger ones? If the latter, then the portion of the ink film which remains on the surface is likely to have a coarser size distribution than the portion of the ink which penetrates. This will in turn give weaker and duller films, but the phenomenon is complicated by the fact that undue penetration will give a thinner film on the surface and hence a weaker print strength even where there is no separation of the pigment particles.

An attempt was made to investigate this phenomenon with transmission electron microscopy of cross-sections of ink films, with little success. Scanning electron microscopy with ion etching may be a more suitable technique.

### Effect of drying mechanism

*Refs. 3-6*

Once the film of ink or paint has been laid down on the substrate, it starts to dry and the end result is a dispersion of pigment particles in a solid resin film. For any given pigment and film thickness and pigmentation level, the colour strength of the film is very dependent on the dispersion level of the pigment particles in the film (see the curves in Figs. 15 and 16). It is commonly assumed that this final dispersion level is the same as that in the original wet paint or ink, but it is pertinent to ask whether this assumption is justified, especially in rapid drying systems.

It is believed that with liquid inks and industrial stoving paints, there is now considerable evidence pointing to the fact that some flocculation of the pigment takes place on drying.

### Printing inks

With liquid inks, the evidence in support of this belief can be summarised briefly under two headings: (i) printing trials, and (ii) colour strengths of inks reduced with an opaque white ink.

(i) The printing trials were carried out at *Sun Printers Ltd.*, Watford. These trials, and the results obtained, have been described in more detail elsewhere<sup>3</sup> but the main findings can be readily outlined.

Pairs of publication gravure inks, made up from the same pigment and resin, but differing in solvent composition and having the same level of dispersion, were printed at 400 metres/minute on a GRI proofing machine, on coated and uncoated papers, using four different etching depths. Three different pigments were used, a blue, a black and a red, and three different resins. The solvents were blends of toluene and the aliphatic petroleum distillate SBP3.

The colour strengths of the prints were measured and compared. In each case, the same pattern of results was found: the ratios of the colour strengths of corresponding prints varied both with the substrate and the depth of etch.

The extent of the variations was considerable, and a typical set of results is illustrated in Table 5.

Table 5  
Print colour strengths - phenolic gravure inks,  
based on a Ca-4B metal salt  
Ink reference A: 80/20 Toluene/SBP3, - 0.15  $\mu$  50% diameter  
Ink reference B: 25/75 Toluene/SBP3, - 0.15  $\mu$  50% diameter  
Pigmented levels as printed Ink A=5.0%  
Ink B=4.8%

Ink/print step	Coated paper		Uncoated paper	
	k/s value	Relative strength	k/s value	Relative strength
A/1	5.43	100.0	1.76	100.0
B/1	5.28	97.2	2.81	159.0
A/2	1.04	100.0	0.65	100.0
B/2	0.87	83.6	0.75	112.0
A/3	0.071	100.0	0.074	100.0
B/3	0.054	76.0	0.067	90.0
A/4	0.045	100.0	0.048	100.0
B/4	0.035	77.7	0.044	91.0

A qualitative explanation for these and similar results is based on two assumptions. Firstly, the rapid drying of the inks after printing gives rise to marked flocculation of the pigment, and the extent of this flocculation varies with the composition of the solvent, being less with the toluene rich inks and greater with the toluene poor inks. Secondly, the toluene rich inks give greater strike through, particularly on uncoated papers.

These two assumptions can be shown to explain the observed phenomena.

(ii) If publication gravure inks, based say on a Ca-4B metal salt are reduced with a standard white gravure ink to give a

ratio of pigment to titanium oxide of 1:25, then films of these reduced inks can be drawn down and their colour strengths measured on a reflectance spectrophotometer.

The colour strengths can be plotted against the 50 per cent diameters of the original inks. The graph obtained is shown in Fig. 20, which also shows the corresponding curve for the same pigment in a decorative paint stainer.

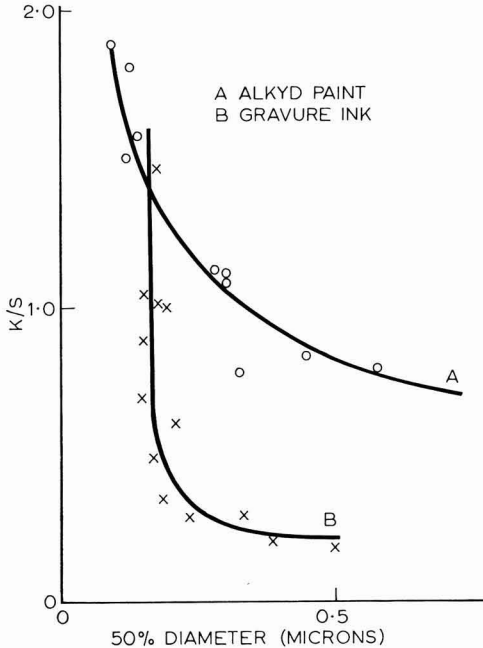


Fig. 20. Colour strength versus particle size. Calcium 4B in paints and inks

It will be seen that there is a marked difference in shape between the two curves. The curve for this pigment in air-drying paint agrees closely with the Mie theoretical curve for this pigment<sup>4</sup> and this in turn supports the view that in such paints the level of pigment dispersion in the dry film is the same as that in the wet paint. The marked difference in the shape of the two curves for the paint and ink films leads to a strong inference that the pigment dispersion in the ink has altered on drying in the direction of flocculation.

#### Industrial paints

With industrial stoving or baking paints, the suspicion that flocculation takes place on drying also arises from the differences between the curves of colour strength versus particle size obtained for a given pigment in different systems.

In Fig. 21, a curve of colour strength in the film versus particle size in the wet paint is shown for a dioxazine violet in an air drying, alkyd based, decorative paint. This curve is identical, within experimental error, with the theoretically predicted Mie curve for this pigment. The Mie curve is a plot of colour strength in the film versus particle size in the film. The agreement of the theoretical and experimental curves supports the view that particle sizes in the wet paint remain the same on drying. Fig. 22 also shows the experimental

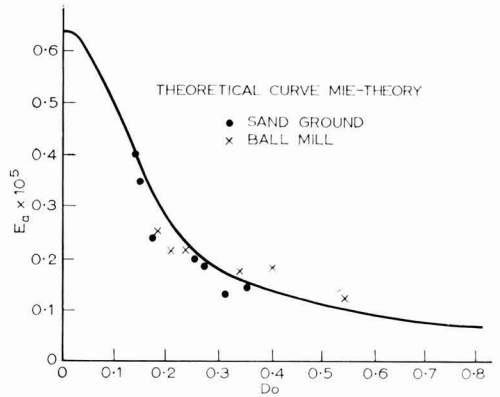


Fig. 21. Colour strength (absorption) versus particle size. Violet 6RLT - theoretical and experimental curves

curves of colour strength versus particle size obtained for the same violet pigment in a melamine-formaldehyde stoving enamel applied by both spraying and dipping. The curves for the spraying and dipping applications are different from each other and different from the corresponding curve for the same pigment in the air drying paint. These differences can be explained if it is assumed that with the stoving laquer, there is some flocculation of the pigment on drying<sup>5</sup>.

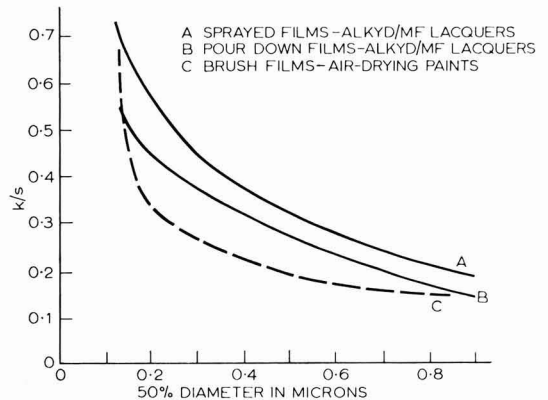


Fig. 22. Colour strength ( $k/s$ ) versus particle size for violet 6RLT in stoving paints and air drying paints

#### Optical densities

The suspicions aroused by the above trials need more direct experimental evidence before they can be confirmed. For this purpose, dispersion measurements have to be carried out on inks and paints and the dry films obtained from them by a method that is applicable to both wet and dry systems. One such method is the measurement of optical densities and the calculation of extinction coefficients and this technique has been applied on a limited scale to a number of gravure inks and stoving paints.

This work has been described in detail elsewhere<sup>6</sup>. In essence, it involves plotting curves of extinction coefficients versus particle sizes for the wet paints and inks and for the dry films derived from them. If there is no flocculation on drying, the two curves should be identical within experimental error.

The results for publication gravure inks based on a Ca-4B metal salt and a  $\beta$ -phthalocyanine blue, are given in Figs. 23 and 24 respectively.

The results for an industrial M/F stoving lacquer based on a dioxazine violet are shown in Fig. 25.

It will be seen that the curves for the wet inks and paint differ considerably from the curves for the corresponding dry

films in the level of values of the extinction coefficient, the curves for the dry films being the lower one in each case. It is believed that the lower values in the dry films demonstrate that the level of pigment dispersion in them is appreciably less than that of the wet systems.

To check this experimental approach, it was carried out also on the same pigments in air drying, alkyd based, decorative paint stainers. Films of these stainers dry slowly, mainly by oxidation. The results for the Ca-4B metal salt and the blue are shown in Figs. 26 and 27 and it will be seen that in each case, the curves for the wet paints and dry films are identical.

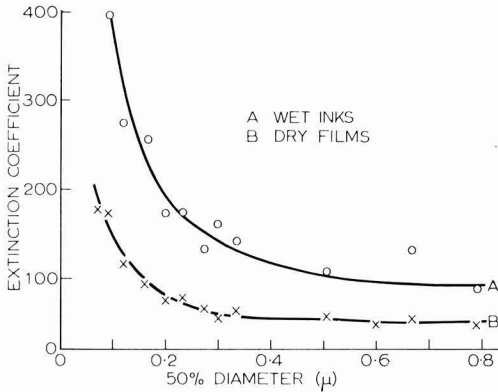


Fig. 23. Extinction coefficient versus particle size for calcium 4B in gravure systems - wet inks and dry films

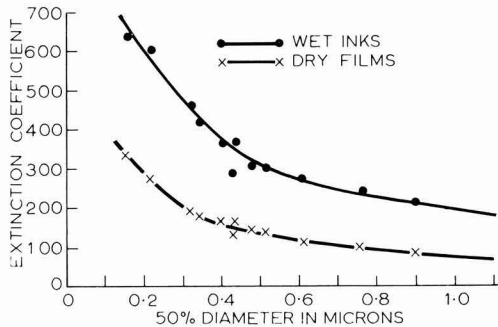


Fig. 24. Extinction coefficient versus particle size for phthalocyanine blue in gravure systems - wet inks and dry films

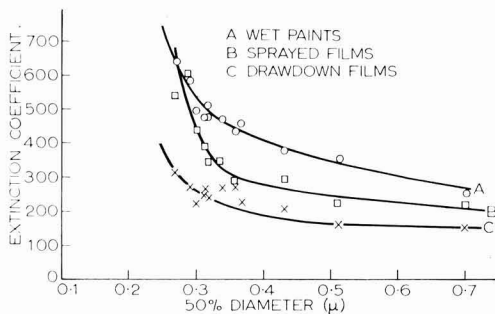


Fig. 25. Extinction coefficient versus particle size for violet 6RLT in stoving paints - wet paints and dry films

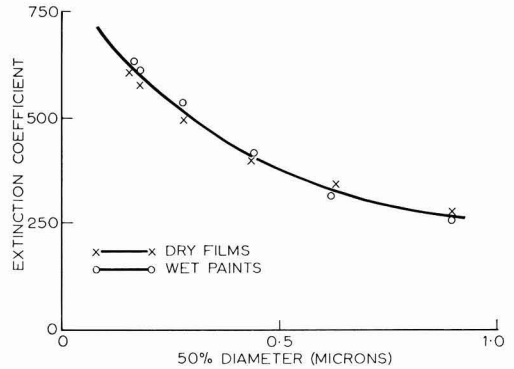


Fig. 26. Extinction coefficient versus particle size for calcium 4B in decorative paint stainers - wet paints and dry films

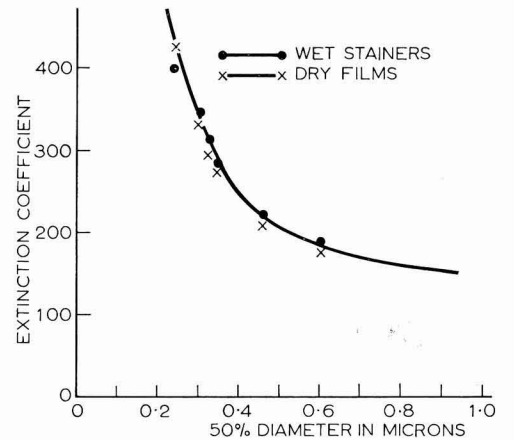


Fig. 27. Extinction coefficient versus particle size for phthalocyanine blue in decorative paint stainers - wet paints and dry films

These results on decorative paint stainers confirm the experimental approach and this in turn confirms the belief that there is some flocculation when drying takes place largely by solvent evaporation as with gravure inks and stoving lacquers.

Reflection on what takes place during rapid drying by solvent evaporation, would support the view that some flocculation of the pigment would be likely to occur. The equilibrium nature of dispersions in the wet state and the

vulnerability of this equilibrium to external influences has been repeatedly pointed out. Dilution shock is a familiar example. Very rapid drying by solvent evaporation must set up considerable physical forces in the wet films and these could well upset the dispersion equilibrium. Such rapid evaporation would be expected to give rise to some flocculation of the pigment by "evaporation shock", analagous to dilution shock.

In the cases quoted of the gravure inks, toluene is a good solvent for all the resins, whereas they are virtually insoluble in the aliphatic component SBP3. On evaporation of the solvent, the toluene rich ink may hold the resin in solution a fraction longer than the toluene poor ink and hence give rise to less flocculation. Therefore, the assumption that toluene rich inks will give somewhat less flocculation on drying is by no means unreasonable.

If water is considered as a solvent, then drying by solvent evaporation is a vital mechanism with many paints and inks. If such mechanism does give rise to pigment flocculation, then the extent and control of such flocculation would appear to be an important field of study, bearing in mind that it is the dispersion level of the pigment in the final dry film which controls the optical properties of the film.

## Conclusions

Reverting to the two flow diagrams, the survey of both has now been completed, starting from the raw materials and finishing up with the dry films. The objective has been to study the actual and potential effects of every raw material, every manufacturing step and every application step on the level of pigment dispersion, and to see if these effects can be explained qualitatively by any coherent theory.

It is evident that in the manufacture of paints and inks, the levels of dispersion achieved vary from pigment to pigment, and from resin to resin and can be affected by the solvents used.

These variations can be explained in terms of the equilibrium theory of pigment dispersion.

The stabilising force needed to oppose the van der Waals forces of attraction between very small particles, is considered to arise from a steric hindrance mechanism, particularly in non-aqueous systems, based on the adsorption of resin molecules from solution on to the surface of the pigment particles. The extent of this adsorption will depend on the nature of the pigment surface, the affinity of the resin molecules and the restraining action of the solvents, and these factors will account for the observed phenomena.

The above equilibrium theory will also explain the effects of storage times on dispersion levels.

If extra shear is applied to a system during application, the level of dispersion can be increased.

Where inks or paints dry by rapid solvent evaporation, there is strong evidence to indicate that some coarsening of the pigment or flocculation takes place. Here the rapid removal of the solvent is the external force that is disturbing the original equilibrium state.

Pigment dispersion can be seen, therefore, to vary with the formulation used, the method of manufacture, the storage period, the application methods, and the drying mechanism, and these variations arise from the fact that a dispersion of pigment particles in a liquid phase is a vulnerable equilibrium system.

The survey has shown too, how scanty is the knowledge of actual dispersion levels in any or all of these stages, but it will, it is hoped, serve as a stimulus to further work in this field.

[Received 12 June 1978]

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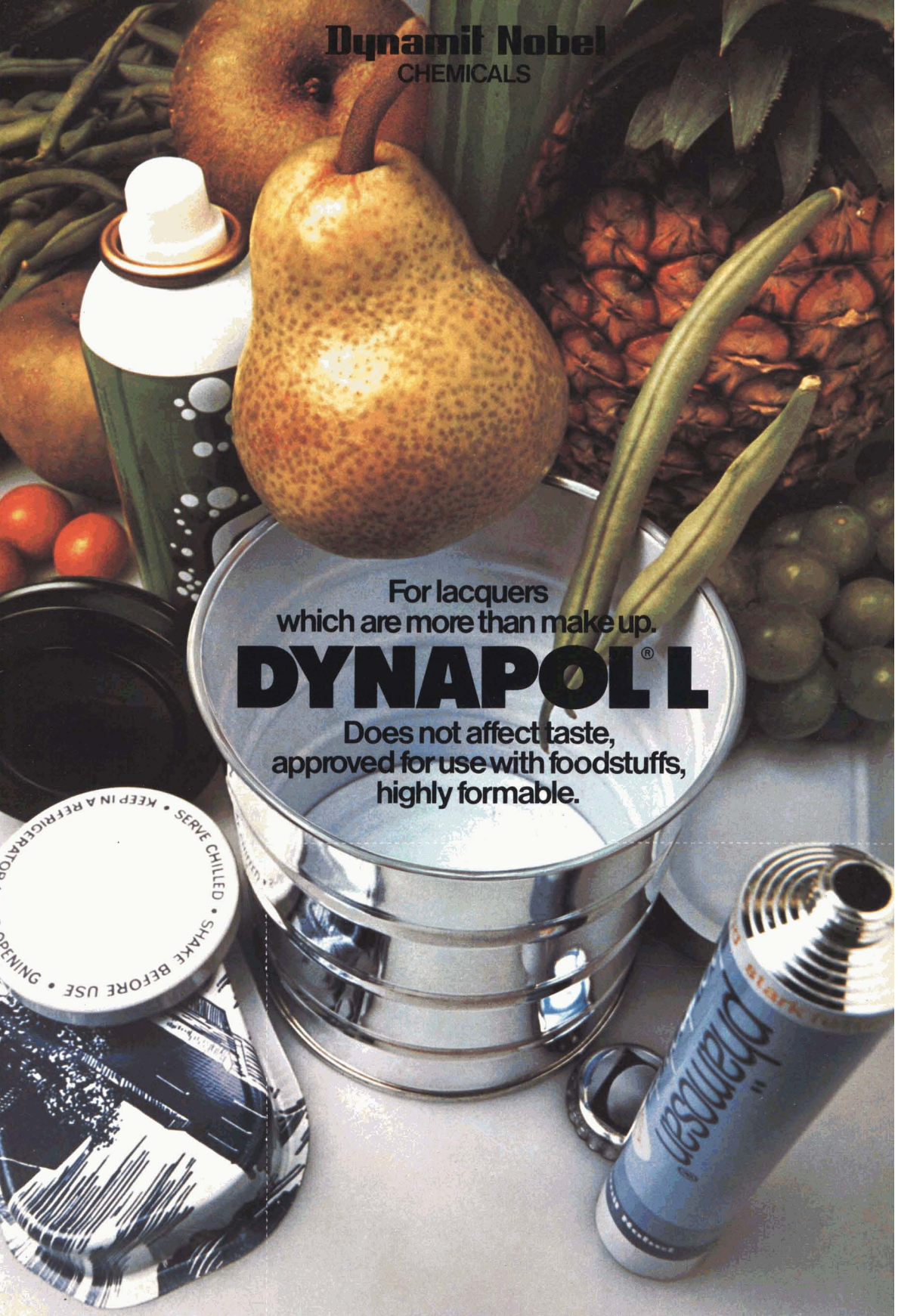
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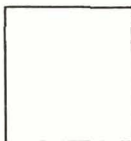
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# The corrosion and protection of metals in the building and construction industries\*

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## Summary

Various estimates have been made of the cost of corrosion to South Africa and these figures indicate that it could amount to R300 million per annum. A fair proportion of this is at the expense of the building and construction industry. In spite of the serious energy crisis the world is facing today, very little is written about the consumption of metals, although the situation is rapidly assuming serious proportions.

This paper is aimed at architects, engineers and building inspectors who are confronted daily with the problem of corrosion. It is intended to help them recognise the problem before it is too late, by highlighting various aspects of corrosion directly affecting the industry.

## Keywords

*Types and classes of coatings and allied products*

corrosion resistant coating

*Types and classes of structures or surfaces to be coated*

steel

metal

galvanised iron

*Raw materials for coatings  
chemically active pigments*

corrosion inhibiting pigment

*Processes and methods primarily associated with  
analysis, measurement or testing*

galvanising

service or utility

corrosion

electrolytic corrosion

## La corrosion et la protection de métaux dans le domaine des industries de construction

### Résumé

On a proposé de diverses évaluations du coût, en Afrique du sud, des effets nuisibles de corrosion, et les chiffres indiquent qu'il pourrait atteindre à R300 million par an. Une bonne proportion de cette somme est large des industries de construction. Malgré la crise sévère d'énergie à laquelle fait face le Monde aujourd'hui, on ne lit pas beaucoup au sujet de la consommation de métaux, bien que la situation atteinte rapidement à des proportions graves.

Cet exposé est visé sur les architectes, les ingénieurs et les experts-surveillants de bâtiments qui se trouvent chaque jour devant la problème de la corrosion. Son but est de les aider à identifier le problème, avant qu'il soit trop tard, en soulignant les divers aspects de la corrosion qui touchent directement les industries de construction.

## Korrosion und Metallschutz in den Bau- und Konstruktionsindustrien

### Zusammenfassung

Die für Südafrika durch Korrosion verursachten Kosten wurden verschieden hoch geschätzt; danach könnten sie R300 Millionen p.a. betragen. Ein erheblicher Teil davon geht auf Kosten der Bau- und Konstruktionsindustrie vor sich. Über den Verschleiss von Metallen wird sehr wenig geschrieben trotz der ersten, gegenwärtigen Energiekrise der Welt, und obwohl die Situation rapide

ernste Proportionen annimmt. Diese Abhandlung wendet sich an Architekten, Ingenieure und Bauinspektoren, die mit dem Korrosionsproblem von Tag zu Tag zu tun haben. Beabsichtigt wird, diesen Berufen darin zu helfen, dass sie das Problem erkennen können, ehe es zu spät ist, indem verschiedene die Industrie direkt betreffende Korrosionsprobleme beleuchtet werden.

## Introduction

*Refs. 1-5*

Several estimates have been made at various times of the cost of corrosion to various countries<sup>1,2</sup>. Using the guidelines provided by these countries, a figure based on 1.5 per cent of the Gross National Product would place the cost of corrosion to South Africa at R320 million per annum, based on 1974 figures<sup>3</sup>. To put this cost into perspective, this was roughly equivalent to the cost of all the dwelling houses completed in South Africa in 1973<sup>4</sup>.

A survey conducted at the end of 1969 by the Bureau of Statistics showed that the annual total maintenance costs for dwellings in the main centres of South Africa was in the

region of R37.5 million, with a considerable portion of this expended on maintenance painting and redecoration<sup>5</sup>. At this stage, some R40 million worth of paint was produced annually, of which it was estimated that 60 per cent of production was used in buildings, directly or indirectly.

## The need to conserve metals

*Ref. 6*

The immediate impact of the energy crisis needs no elaboration as everybody has experienced the frustration of fuel saving measures and the price rises of most commodities that have followed the higher oil prices in recent years. Day by day the press, radio and television emphasise the energy crisis and

\*Lecture presented at a meeting of the Transvaal Section on 23 February 1978

news of pollution with its effect on the environment, yet little has been written about the consumption of metals. The situation is rapidly assuming serious proportions.

The United States Bureau of Mines<sup>6</sup> has given the following estimates of the number of years it will take for some of the more important, proven non-renewable natural resources for metals to become exhausted if the world consumption continues to increase at the present rate:

Aluminium	31 years	Mercury	13 years
Chromium	95 years	Molybdenum	34 years
Cobalt	60 years	Nickel	53 years
Copper	21 years	Platinum Group metals	47 years
Gold	9 years	Silver	13 years
Iron	93 years	Tungsten	28 years
Lead	21 years	Zinc	18 years
Manganese	46 years		

Furthermore, it is believed that, even if an optimistic outlook were adopted and the assumption made that as yet undiscovered reserves would give a five-fold increase in resources, because of the present exponential consumption rate this would mean barely doubling the time available before the source of many metals becomes exhausted.

It is believed by many that declining metal resources will have a greater impact on civilisation than the energy shortage. There are several alternative sources of energy, but very few real alternatives to metals with their particular physical properties, which are often unique.

### Mechanism of corrosion

Most metals are derived from ores which undergo many metallurgical processes before the final product is produced. The basic cause of corrosion is the instability of the metal in its refined form. The process of corrosion is, essentially, a reversion of the metal to the ores from which it was derived. Many metals automatically form a thin oxide film on their surface, and in some instances this film is self healing and protective. This is one of the reasons why some metals corrode easily whilst others are corrosion resistant. For example, the oxide films present on steel surfaces tend not to be adherent or continuous. Corrosion begins rapidly at breaks in the millscale of hot rolled structural steel. On the other hand, the films formed on zinc and aluminium, normally considered to be very reactive metals, tend to be continuous, adherent and may even be self healing: thus these metals can provide a useful service life without additional protective measures.

Corrosion is the reaction of a metal to its environment. Obviously, therefore, both the nature of the metal and the environment are important factors in determining the rate of corrosion. The mechanism of the corrosion process is generally electrochemical. Electricity flows between certain active areas on a metal surface, known as "anodic sites", to other areas known as "cathodic sites". This results in the formation of an electrochemical cell, which in many ways is analogous to a simple torch battery with a zinc case as the anode, a carbon cathode core and an electrolyte as the environment.

In the case of steel, the anodic spots may be breaks in the millscale (for example on hot rolled steel), discontinuities or, possibly, the effect of pollutants on the oxide film of the metal. This electrochemical action causes destruction of the metal at the anodic site and is accompanied by another reaction at the cathodic site, so as to retain electrical neutrality. In atmos-

pheric corrosion, the cathodic reaction usually involves the consumption of oxygen from the air. The two reactions are typified below:



It is, therefore, not unusual to find that the controlling factors in atmospheric corrosion are the presence of a thin film of moisture on the metal surface (*e.g.* effect of high humidity), atmospheric pollutants (*e.g.* chlorides in marine environments, sulfur dioxide in industrial areas) and the availability of oxygen. Oxygen is abundantly available, but its access to the cathodic area may be limited by thin films (*e.g.* water, paints, oils), by crevice effects and by excess water (for example poor drainage of gutters, roofs, etc.).

### Bimetallic corrosion processes (galvanic)

The electrochemical nature of the corrosion process has already been indicated. Without going into all the fundamental aspects of the process, the following table of metal electrode potentials is provided as a guide to bimetallic corrosion cells. Each metal, when immersed in a specific solution of its own ions, will take up a potential relative to that solution. Arranged in a series, these potentials are known as the EMF (electromotive force) series.

#### Standard electrode potentials

Electrode		Potential (at 25°C, hydrogen scale)	
<i>Noble</i>	Gold	Au <sup>3+</sup> /Au	+ 1.50 Volts
	Platinum	Pt <sup>2+</sup> /Pt	+ 1.20 Volts
	Copper	Cu <sup>2+</sup> /Cu	+ 0.34 Volts
	Hydrogen	H <sup>+</sup> /H <sub>2</sub> (1 atm.)	0 Volts
	Iron	Fe <sup>2+</sup> /Fe	- 0.44 Volts
	Zinc	Zn <sup>2+</sup> /Zn	- 0.76 Volts
	Aluminium	Al <sup>3+</sup> /Al	- 1.66 Volts
<i>Active</i>	Magnesium	Mg <sup>2+</sup> /Mg	- 2.37 Volts

From this table it may be predicted that, if two metals are coupled together, for example zinc and copper, the potential difference (+ 0.34 to - 0.76 V, i.e. 1.10 volts) would be such that the nobler metal would be protected, whilst the more active metal would be corroded. This occurs in practice.

This concept is important because, although the above process can result in the deterioration of the structural metal, it can also be used to advantage as, by the correct selection of metals, it is possible to protect the structure itself. The following two examples illustrate the advantages and disadvantages of this concept:

**Bad practice.** If aluminium sheets are joined by means of copper fittings, a bimetallic cell is formed. In this cell the copper is the cathodic (protected) area and the aluminium is the anodic (corroded) area. This cell can cause serious corrosion of the aluminium.

**Good practice.** Galvanised steel presents an excellent example of how this principle can be used to advantage. The structural element (steel) is covered with a thin layer of metallic zinc. This has two advantages:

- the overall corrosion rate is lowered because zinc generally corrodes more slowly than steel;
- zinc is anodic to steel and, therefore, it is corroded preferentially. This implies that at any discontinuities or

gaps in the zinc film, the underlying steel will be protected at the expense of the zinc. This principle is used to great advantage in many metallic coatings, which are described below.

### The environment

#### *Atmospheric corrosion*

The corrosion rate of metals is profoundly affected by the climate and to a lesser degree by the mass, size, shape and angle at which the specimen is exposed. In atmospheric corrosion, the following factors play a major role in determining corrosion rates.

*Climate:* In the absence of rain, or gaseous or solid pollution of the atmosphere, serious corrosion does not occur where the relative humidity is below 70 per cent. Above this figure the corrosion rate depends on the pollutants present in the air. At 70 per cent relative humidity a thin invisible moisture film is present on the metal surface and this provides the electrolyte for the corrosion cell. Certain particles are hygroscopic, and if they settle on a metal surface, they may cause corrosion to occur at lower values of relative humidity. The ambient temperature may affect the corrosion rate, because diurnal temperature fluctuations determine the incidence and duration of condensation of the metal surface. Diurnal fluctuations in parts of South Africa may be as high as 30°C.

*Aggressive salts:* Corrosion is stimulated when the air contains sulfur dioxide and/or corrosive salts, such as chlorides and sulfates. The main sources of these types of atmospheric pollution are the combustion of coal and other fuels and sea water spray, which under certain wind conditions can penetrate many kilometres inland.

*Microclimates:* In general, the Durban environment may be described as an industrial marine environment, and the corrosion rate may vary considerably, according to where the metal is exposed. For instance, corrosion on the seaward side of the Bluff is much more severe than at Salisbury Island within Durban Bay. In terms of buildings, the environment may be further divided according to whether the exposure is indoors or outdoors. Indoor exposure is, generally, milder than outdoor but, even within a single building, the environment varies according to the room and the activities carried out in it. For example, the corrosion rate in a kitchen and bathroom is likely to be higher than that in a living room. On the other hand, where the building is used to house some industrial process, the internal atmosphere may be more corrosive than the overall external climate. These specific climates, which usually occur within relatively confined spaces, are termed "microclimates"; they should also be assessed when corrosion problems are being considered.

#### *Corrosion in soil*

The corrosion of metals in soil environments also proceeds by an electrochemical mechanism and the same criteria of corrosivity hold as for aqueous and atmospheric environments. In other words, the presence of salts in the soil (for example chlorides and sulfates) will make the surrounding water in the soil more conductive, and hence more corrosive. The presence of oxygen and possibly acidic conditions are other factors making this particular environment aggressive. There are, however, certain corrosive agents whose activity is uniquely experienced in soils and submerged environments and these are frequently responsible for the rapid failure of metal pipes

in underground environments. A few of these factors are considered here.

*Anaerobic soils:* Although oxygen is essential to the corrosion process, nevertheless anaerobic soils, such as waterlogged clays, are often highly corrosive because they contain anaerobic bacteria that can cause holes in galvanised steel pipework as little as 18 months. These sulfate reducing bacteria flourish in heavy clay soils, harbour mud and similar media.

*Acidic soils:* Certain natural soils are acidic because of the presence of organic acids (e.g. peaty soils), whilst others may be acidic as a result of the decomposition of waste pyritic deposits after mining, or by the pumping of acidic mine waters from mine shafts to the surface.

*Stray currents:* The South African Railways, apart from steam and diesel power, rely heavily on direct current traction systems. Stray currents (d.c.) in soils near railway lines may cause very severe corrosion of buried structures.

*Note:* Stray currents, as produced from direct current traction systems, from cathodically protected pipelines and from welding equipment, should not be confused with bimetallic corrosion problems, which produce galvanic corrosion currents.

#### *Corrosion and scaling problems in water*

*Refs. 7, 8*

For practical purposes in terms of buildings, comments in this section will refer to the corrosive environment encountered with potable waters, for example, within pipework and hot water storage (heater tanks). In general terms, the tendency for a metal to corrode and the type of corrosion that occurs in a particular water, will depend on two main characteristics of that water:

- the aggressive anions that may be present to promote corrosions, and
- the water's scale-forming characteristics.

*Factors governing internal corrosion of pipework by potable waters:* The corrosion of metals in water is an electrochemical process and, because of this, substances dissolved in the water may cause corrosion in two ways:

- (a) by lowering the electrical resistivity of the water. The most common substances of this type are chlorides and sulfates. Besides their influence on the electrical resistivity of water, they also play a role in the penetration and breakdown of protective films;
- (b) by stimulating the cathodic reaction in the corrosion cell. The two most common reactants of this type are oxygen and hydrogen ions. Chlorine (where excessive chlorination of the water is practised) may also be a cathodic stimulant.

*Factors governing scale formation by water:* Natural waters in the condition known as "hard" tend to cause scale deposition on surfaces. The degree of scaling on a metal surface is important. Where no scale is deposited, overall corrosion of the pipe may occur; the corrosion itself can lead to penetration or alternatively failure due to pipe blockage as a result of corrosion products. Partial scale cover, on the other hand, may lead to intensified local corrosion cells causing early failure due to pitting. If excessive scale is formed, this has undesirable effects such as the reduction in effective pipe

diameter and impairment of heat exchange properties (important to air conditioning and solar water heating equipment).

Hardness in waters is caused by the presence of dissolved salts. In most waters supplied by municipalities, temporary hardness, caused by the presence of calcium or magnesium carbonates and bicarbonates, is of greater importance to corrosion and scale formation, although permanent hardness, caused by the sulfates and chlorides of calcium and magnesium, may also be present in significant concentrations in some cases. The presence of calcium bicarbonate (which under certain conditions is deposited as highly insoluble calcium carbonate) is the most significant scale forming agent in waters for domestic and industrial use.

The scale forming tendency in such cases is governed by the total amounts of calcium and carbonate ions dissolved in the water, by the chemical equilibrium between these as influenced by the acidity and temperature of the water, and by the total quantity of dissolved solids present. Mathematical relationships between these quantities have been studied by various workers and, as a result empirical relationships have been derived which enable the scale forming tendency to be predicted. Two well known relationships of this type are the Langelier<sup>7</sup> and Ryznar<sup>8</sup> indices, which are calculated from a chemical analysis of the water.

A positive Langelier index indicates that the water is likely to deposit  $\text{CaCO}_3$  as a scale, whereas a negative value indicates that the water is undersaturated and is corrosive. This index, whilst useful in predicting whether or not the water will be scale forming or corrosive, does not give a quantitative relationship between water composition and scale forming or corrosive properties. The Ryznar index, on the other hand, does give a quantitative relationship between water composition and corrosive or scale forming properties. From a large number of known performance data this index correlates with water behaviour as follows:

waters of Ryznar index less than 6.0 are definitely scale forming;

indices between 6.0 and 7.0 seem most suitable for domestic waters;

corrosion is possible at values above 7.0 and is a certainty with indices above 7.5.

Table 1 gives the Langelier and Ryznar indices of some South African waters. Both of these indices have proved useful in predicting the behaviour of a water as regards corrosion and scale formation. It should be emphasised, however, that large amounts of chlorides and sulfates may bring about corrosion whatever the scale forming tendency of the water.

Table 1  
Langelier and Ryznar indices of  
some South African waters

Water	pH	pH <sub>s</sub>	Langelier index	Ryznar index
Durban	7.1	8.4	-1.3	9.7
Rand Water Board Zuikerbosch	7.95	7.5	+0.45	7.15
Cape Town Wemmershoek	8.05	8.12	-0.08	8.21
Pietermaritzburg Signal Hill	6.95	8.0	-1.05	9.05

### The corrosion rates for various metals and metal coatings in South Africa

Refs. 9-11

The corrosion rates of various metals, exposed for 5 years at different sites in South Africa<sup>9</sup>, are shown in Table 2.

These figures are presented as a guide to metal selection in the various areas. Obviously, steel would not be used uncoated in the severely corrosive marine areas.

Table 3 shows the performance of various metal coatings on steel at different sites in South Africa<sup>10</sup>. Although these results are based only on 4 years of exposure, they already indicate the inadvisability of using certain coatings in aggressive marine atmospheres. Whereas some coatings have failed badly, others have lasted extremely well, particularly the sprayed metal coatings. These tests reflect four years' exposure, but Ballard<sup>11</sup>, a world authority on sprayed coatings, has described an aluminium sprayed sample plate that has withstood the Durban atmosphere for twenty-two years.

Table 2  
Summary of atmospheric corrosion rates based on five years exposure

Metal or Alloy	Pretoria CSIR	Durban Salisbury Island	Durban Bluff	Cape Town Docks	Walvis Bay Military Camp	Pretoria Iscor Steelworks	Sasolburg Industrial	Simonstown* Marine
	µm/yr	µm/yr	µm/yr	µm/yr	µm/yr	µm/yr	µm/yr	µm/yr
Mild Steel	5.8	46.2	256.8	34.0	106.7	25.9	19.1	16.0
Corten	3.6	31.5	79.5	13.7	130.8	6.1	12.4	11.7
Zinc	0.330	2.464	12.141	3.251	82.575	3.175	1.702	3.226
Copper	0.813	1.270	2.464	0.864	4.343	4.013	2.438	1.854
Aluminium 3S	0.025	0.686	2.184	0.432	0.457	0.737		0.660
M57S	0.051	0.686	2.388	0.533	0.483			
50S	0.051	0.711	2.159	0.406	0.533			
B51S	0.025	0.737	3.810	0.432	0.610			
Stainless Steel 430	<0.0025	0.0610	0.2134	0.0762	0.1118			0.0991
304	<0.0025	0.0076	0.0356	0.0076	0.0127	<0.0025		
316	<0.0025	0.0051	0.0254	0.0076	0.0127			0.0152

\*Simonstown result based on 2 year exposure period (1974 to 1976)

Table 3  
Relative performance of various metal coatings on steel (4-year exposure period)

Coating Type	Coating Thickness $\mu\text{m}$	Number of years for up to 5% corrosion of surface area				
		Pretoria CSIR	Durban Salisbury Island	Durban Bluff	Cape Town Ysterplaat	Walvis Bay
Galvanised steel (commercial grade)	25	NC	1.5	1	NC	0.5
Zinc spray:						
Thin coating	50/75	NC	3	3	NC	1
Thick coating	100/125	NC	NC	NC	NC	2
Aluminium spray						
Thin coating	50/75	NC	NC	NC	NC	NC
Thick coating	100/125	NC	NC	NC	NC	NC
Zinc and aluminium spray (50 $\pm$ 50 $\mu\text{m}$ )	100	NC	NC	NC	NC	NC
Cadmium electroplated	10	NC	1	0.75	2	1
Tin electroplated	3/4	0.5	<0.5	<0.5	<0.5	<0.5
sprayed	50/75	<0.5	<0.5	<0.5	<0.5	<0.5

NC—Good, less than 5% rust staining on surface

The use of metal spray coatings has attained considerable importance in recent years. Its main advantage is that it is the only method of applying metal coatings that lends itself to field application and it is the only feasible method of applying heavy aluminium coatings to structural steel. For the sprayed metal to adhere well to the steel surface, it is necessary to provide a good mechanical key. The steel surface is, therefore, prepared by abrasive blasting to a "white metal" finish and the metal spraying is carried out as soon as possible after cleaning, but in any case on the same day.

Provided they are thick enough to withstand the service conditions for the desired life of the structure, these metallic coatings need not be painted; a minimum thickness of 100  $\mu\text{m}$  is normal. Heavier coatings usually require no painting (unless for aesthetic purposes) and lighter coatings (minimum 50  $\mu\text{m}$ ) usually need to be painted immediately and are not recommended alone for use in severely corrosive climates.

Exposure of duplex coatings (metal spray and organic coating) over steel have shown much promise, particularly over aluminium metal spray. The aluminium metal spray as an undercoat appears to extend the interval between maintenance coatings.

## Metals used in the building industry

Ref. 12

### Conventional steel

The metal most commonly used for structural purposes is ordinary carbon steel. Certain alloying elements (*e.g.* manganese) are used in the manufacture of such steels, but the total amount is usually less than one per cent. These small amounts of alloying elements have very little effect on the corrosion characteristics of the steel, the major exception being copper, which is discussed under low alloy steels.

In many situations, the natural corrosion rate of steel would be acceptable as regards safety, but is unacceptable as regards appearance. Most steel is used in the protected form.

### Protection of steel by masonry or concrete

A large tonnage of the steel used in the building industry is enclosed in masonry or concrete. As concrete has a pH of 12.6, steel is passivated on being embedded in the concrete. Provided that no other aggressive ions are included in the concrete mix (for example, an excess of calcium chloride) and that the concrete is reasonably impermeable to the penetration of chlorides from the atmosphere, the steel will be adequately protected by the concrete. Where problems arise, these can usually be attributed to poor mix design, inadequate compaction, or poor supervision. When steel corrodes in concrete the results are often spectacular as the steel corrosion products exert great pressures on the concrete, resulting in cracking and spalling. When reinforced concrete structures are designed for marine atmospheres, the following points should be carefully watched:

- (i) the minimum depth of cover over reinforcing should be 50 mm;
- (ii) the concrete should be well compacted and the mix should be such that not only will the strength requirements be met, but also the shrinkage kept to a minimum. A rich concrete would provide greater salt tolerance from the corrosion point of view, but if excessive shrinkage cracks occurred, they would more than offset the advantages of a rich mix;
- (iii) all material should be protected from contamination by sea salt (sodium chloride), before and during construction.

Many of the failures that have been investigated may be attributed to poor design, often coupled with poor workmanship.

Where masonry is used to encase the structural steel, the main problem is penetration of sodium chloride or sulfur pollutants to the underlying steel, particularly where joints in the brickwork are poor. Unless extra steel is provided to allow for the general corrosion during the life of a structure, the steel should be additionally protected by an appropriate protective system.

### Structural steel

Where the steel is exposed directly to the atmosphere or immersed in water, suitable steps must be taken to prevent corrosion. Under certain circumstances (for example immersed conditions) cathodic protection may be applied, but the most common form of protection is a protective coating. There are three broad classes of coatings: namely paints, metal coatings and plastic coatings.

The choice of coating material is basically one of economics. Most exposed steelwork is painted, and often additional protection is given by paint applied over a metal coating. Although it is not the aim of this paper to detail painting procedures, the following factors are considered important when planning ahead and estimating costs:

- (i) *Surface preparation.* This is most important, as the subsequent performance of a paint is closely related to the surface preparation before painting.
- (ii) *The paint system* should be suitable for the particular application and should provide a suitable basis for future maintenance overcoating.
- (iii) *The thickness of the paint* should be adequate.
- (iv) *Proper application* of the paint under controlled supervision and in suitable weather conditions is necessary.

Most of the paint failures investigated have been the result of poor surface preparation (for example, the presence of salts, millscale or grease). When considering maintenance painting, it should always be remembered that it is very important to repaint at an early stage. Once rusting has occurred, it is very difficult to obtain good paint performance over the rusted area and there is a tendency for accelerated breakdown to occur subsequently at these points. Wire brushes, scrapers, needle tools and flame cleaning will not remove all the rust. Certain rust types are only partially removed by these methods of cleaning and, unfortunately, the remaining rust is the virulent type containing the really aggressive salts that cause corrosion. These salts are concentrated at the rust/metal interface and with seasonal fluctuations in humidity and temperature they migrate through the rust to the outer surface<sup>12</sup>, undermining most paint coatings applied over rusty surfaces. Removal of the outer loose flakey rust is not adequate. At this stage only blast cleaning will remove this type of rust. It is, therefore, important to carry out regular inspections to ensure that maintenance is carried out before serious rusting has set in.

Metal coatings may often be used without additional coats of paint, although there are advantages, particularly with exterior steelwork, in using a duplex coat of metal coating plus paint. The metal coatings most commonly used in buildings are zinc and aluminium, applied either by hot dipping or spraying. Small components, such as fasteners, are often coated by diffusion (e.g. sherardised with zinc) or electroplated (e.g. zinc and cadmium). In general, there is a direct relationship between the life and the thickness of a coating, particularly with zinc coatings. These coatings corrode preferentially to steel, and in doing so provide sacrificial protection to the underlying steel.

Where structural steel is to be used in inaccessible places, (for example in industrialised buildings, bridges, etc.), it is good practice to make extensive use of sprayed metal coatings of adequate thickness. Where maintenance is difficult, if not impossible, these coatings will give a good service life and have the added advantage that, if necessary, the coating may

be applied *in situ* during construction. A further advantage is that metallic coatings are not susceptible to degradation by sunlight, which is a consideration of prime importance in a country such as South Africa.

### Low alloy steels

Low alloy steels are those to which relatively small percentages of alloying elements such as copper, nickel and chromium are added to give a total of about 1.5–2 per cent of alloying elements. *Corten* is a typical steel of this type (0.8 per cent Cr, 0.4 per cent Cu, 0.5 per cent Si and 0.15 per cent P). These low alloy steels corrode at approximately one third or less of the rate of ordinary mild steel. There is also some evidence that paints last longer when applied to these copper steels. However, these alloys must not be confused with the stainless steels as their properties are quite different. The low alloy steels are being used increasingly in the United States and United Kingdom for bridges and also for decorative purposes such as the cladding of buildings.

Initially these steels rust in the same way as unalloyed steels, but after 1–2 years the rust tends to become more protective, resulting in a drop in the corrosion rate. When used unpainted, there are obviously no maintenance problems. However, under certain conditions such improved corrosion resistance may not be attained, for example where severe condensation occurs, as happens under beams. In these areas it will be necessary to resort to paint. In certain climatic areas, e.g. Walvis Bay, it would not be advisable to use unprotected low alloy steels. From the decorative point of view it will be necessary for architects to educate people into accepting a rusty surface as a desirable feature in the decor of a building. It will also be necessary to educate architects into designing buildings suitable for the peculiarities of this material. It should always be remembered that the presence of water will aggravate the situation. During the early months of exposure, care must be taken to ensure that the rust coming from the building does not run on to light-coloured concrete, paintwork or other metals in the vicinity. Welds must be thoroughly cleaned to ensure that an evenly coloured rust film develops and fasteners should also be of the same material.

### Copper and copper alloys

Copper is often used as a roofing material in prestige buildings and also for components such as flashings, brackets and guttering. When exposed to the atmosphere, copper and its alloys gradually develop a dark colour, finally changing to a pale green. Once this familiar green protective patina has developed, very little is necessary in the way of maintenance. Development of the patina is a lengthy process, but artificial patinas have been developed which slowly transform to the natural patina.

Where copper and its alloys are used in the building industry, great care should be taken to avoid bimetallic contacts. Such contacts invariably lead to accelerated corrosion of the less noble metal, for example steel, aluminium and zinc. Furthermore, water running off copper roofs, guttering and flashings must not subsequently pass over bare steel or aluminium. The green stain may also discolour concrete.

The natural colour of copper metal and its alloys has not been used much for decoration purposes, because of the gradual change in colour. In recent years the situation has changed with the introduction of an inhibited clear acrylic ester lacquer called '*Ineralac*'. This has been found suitable



for outdoor purposes in some countries, and is also used extensively for indoor decoration purposes.

### Aluminium and its alloys

Aluminium, which rapidly forms a thin invisible protective film of aluminium oxide, has been used extensively for roofing, window frames and doors. As shown in Table 2, aluminium is an extremely corrosion resistant metal and from this point of view is pre-eminently suitable for the building industry, provided the right alloy is used for the particular purpose. In many instances the use of the correct alloy provides a highly corrosion resistant material which requires little or no maintenance. In general, it may be used unprotected unless it is in a position where dirt and moisture collect. Where external parts are exposed to rain, the surface usually remains reasonably clean and free from corrosion. Where dirt and corrosion products settle on a surface, it becomes more liable to corrode. The surface should, therefore, be periodically washed with mild detergent and, if necessary, lightly abraded with *stainless steel* wool. If this is done before pitting becomes deep, the surface may be protected by application of a thin film of oil or lanolin. Under no circumstances should ordinary wire wool be used as the abrasive. Where it is necessary to paint aluminium, it should be lightly brushed with a stainless steel wire brush to remove corrosion products, then painted with a wash primer followed by a corrosion inhibiting zinc chromate primer and finally with an aluminium pigmented top coat.

When aluminium and its alloys are used for decorative purposes, they are often anodised to preserve their original appearance. As already described, aluminium forms a thin protective film of aluminium oxide, the thickness of which may be artificially increased by the process called anodising. Such films absorb certain dyes, producing a variety of colours. Some of the dyes are more suitable than others for outdoor exposure.

Aluminium window frames may be anodised, but are frequently used unanodised and unpainted. This is usually satisfactory provided the environment is not too corrosive; direct exposure to sea spray, for instance, is not desirable. In moderately corrosive environments provision should be made for window frames to be washed at fairly frequent

intervals to prevent any accumulation of dirt and subsequent corrosion beneath the dirt. If possible, the frames should be washed when the window panes are cleaned.

Anodised aluminium has a high degree of corrosion resistance, but will not withstand the heavy accumulation of city dirt indefinitely. It should be washed down at least every twelve months (more frequently in heavily polluted atmospheres) with a mild detergent using nylon brushes. As stressed previously, preventive measures are often far less costly than remedial measures.

Aluminium can and does provide excellent service when used in buildings. However, there are certain precautions that should always be taken when this material is used in buildings. The need to choose the right alloy and to allow for regular cleaning as part of the maintenance has already been stressed. There are other practices that should be carefully followed. For example, aluminium is susceptible to alkaline corrosion; therefore, contact with concrete, mortar or masonry should be avoided unless the aluminium has been pre-coated with bitumen or a tar epoxy in the contact area. Contact with another aluminium surface or with wood can also lead to corrosion, and such areas should be protected. This is particularly important in the overlap areas of roofing sheets which should be protected in this manner. Bimetallic contacts should be avoided, particularly contact with copper and its alloys. Rusty water from corroded steel and water from copper roofing or gutters must not come into contact with aluminium. Aluminium should never be coated with paints based on lead or copper as these also lead to accelerated corrosion.

Fasteners should, preferably, be of aluminium or aluminium-sprayed steel. Should these be unavailable, stainless steel or heavily galvanised fasteners will usually prove satisfactory. If practicable, rubber or plastic insulation materials should be used to limit galvanic action.

Table 4 is a guide to the selection of the correct aluminium alloy for a specific purpose.

### Stainless steels

In general, steels containing more than 12 per cent chromium are classified as stainless steels. Thus, there is a complete

Table 4  
Aluminium alloys used in the building industry

Material	Recommended alloy	Generally recommended temper or condition	Nominal composition	Relevant BSS
1. (a) Roofing sheets, corrugated and longspan (b) Fully supported roofing	3S 2S	H ½H	1½% Mn Commercially pure Aluminium 99% Al	BSS 1470-NS3 BSS 1470-SIC
(c) Flashings where ductility is required	2S	O	Commercially pure Aluminium 99% Al	BSS1470-SIC
2. Roof truss members and beams	B51S D65S	TF TF	Si 1% Mg ½% Mn 2% Mg ½% Si ½% Cu ½%	BSS 1476-HE30 BSS 1474-HE20
3. (a) Gutters and down pipes manufactured from sheet (b) Gutters and down pipes extruded (e.g. tubing)	3SH M57S 50S	½H TF	1½% Mn 2% Mg Mg ½% Si ½%	BSS 1470-NS3 BSS 1470-NS4 BSS 1476-HE9
4. Cast brackets for gutters	160	As Cast	10/13% Silicon	BSS 1490-LM4
5. Window sections	50S	TB	Mg ½% Si 2%	BSS 1476-HE9
6. Aluminium foil, for use in buildings, available in various forms	2S	As Rolled	Commercially pure Aluminium 99% Al	—

family of stainless steels, often tailor made for specific purposes. In the building industry two basic types (18/8 and 18/10/3) are used extensively. The 18/10/3 alloy (18 per cent Cr, 10 per cent Ni and 3 per cent Mo), commonly known as type 316, is to be preferred in marine and industrial atmospheres. The 18/8 stainless steel is suitable for all interior work and for rural to mildly industrial atmospheres.

A negligible amount of corrosion occurs with type 316 stainless steel, although in very aggressive atmospheres some degree of pitting may occur after several years of exposure. The actual weight loss of metal may be slight, but there may be some degree of rust staining that will mar the decorative appearance. The stain may often be removed by water containing a detergent, thus the only maintenance required for these steels is the occasional removal of dirt. Like aluminium, stainless steels also form a thin protective film on the metal surface. Settled dirt may disrupt this film allowing rust stains to form. Periodic cleaning is, therefore, an integral part of the maintenance programme for stainless steel components. Stainless steel has been used for curtain walls, cladding, window frames, doors, shop fittings, door furniture, fasteners and mullions.

#### Lead and zinc

Lead may be used for roofing, gutters and ducts, as it requires very little maintenance. It is fairly resistant to industrial atmosphere, but care should be taken not to place it in contact with wood or damp mortar. Such contact areas should always be coated with, for example, bitumen.

Zinc may be used on its own, but conventionally is used in the form of galvanised steel. In South Africa, the commercial grade of galvanised steel is that most commonly used for sheeting in the building industry. This grade provides a total zinc coating of 275 g/m<sup>2</sup> which is approximately 20 micrometres thick per side. The results presented in Table 3 indicate that a life of two years may be expected at Salisbury Island and approximately six months at the severe marine site at the Bluff. Obviously, the use of unpainted commercial grade galvanised steel in Durban is not an economic proposition. Heavier grades of galvanising will extend the life proportionately, but are still considered unsuitable unless adequately coated<sup>13</sup>. It is also important

to paint sheet overlap areas in roofing and to paint contact areas between the galvanised steel and wood, mortar and concrete.

#### Conclusions

Metals have been used successfully in buildings throughout the years, often with the minimum of maintenance. The choice of the correct metal or alloy at the design stage is of the utmost importance. It is equally important to specify details to ensure that the metal is used in the correct manner.

Economics will govern the selection of materials, but the increasing cost of maintenance, shortage of skilled labour and the ease with which maintenance may be carried out, are also important. Adequate provision should always be made to ensure that all surfaces requiring maintenance are accessible. This is particularly important in industrialised building systems. Decorative metals may have excellent corrosion resistance, but do require periodic cleaning to retain their appearance.

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# Measurement of conductivity, capacity, electrical resistance and permeability of paint films in an aqueous medium

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## Summary

The object of this paper is to characterise the physical and electrical properties of a paint film either isolated or applied to a metallic substrate.

It has been shown that the resistance of a film is inversely proportional to the ionic permeability, that the capacity increases for films of high polarity and that these two parameters vary linearly with the thickness of the film and the area exposed.

## Keywords

*Types and classes of coatings and allied products*  
anticorrosive coating

*Types and classes of structures or surfaces to be coated*  
steel

*Processes and methods primarily associated with analysis, measurement or testing*  
immersion testing

*Properties, characteristics and conditions primarily associated with materials in general*

electrical resistivity  
electrical capacity  
electrical conductivity

## La détermination de conductivité, capacité, résistance et perméabilité de films de peinture dans un milieu aqueux

### Résumé

Le but de cet exposé est la caractérisation des propriétés et chimiques et physiques des films de peinture, soit détachés, soit sur un support métallique.

On démontre que la résistance du film est inversement proportionnelle à la perméabilité ionique, que la capacité s'augmente dans le cas de films de haute polarité, et que ces deux paramètres se varient, dans une manière linéaire, avec l'épaisseur du film et l'aire exposée.

On peut utiliser les mesures de la résistance pour déterminer la présence des défauts en films de peinture qui sont dus à l'altération mécanique et à l'emploi des liants et des pigments en vue d'améliorer l'efficacité du film en tant que barrière protectrice.

On peut utiliser les mesures de la capacité pour établir la polarité du film et pour déceler les changements de la composition chimique et de la polarité à cause des processus d'oxydation ou polymérisation pendant le vieillissement.

## Messung von Leitfähigkeit, Kapazität, elektrischem Widerstand und Durchlässigkeit von Lackfilmen in einer wasserhaltigen Umgebung

### Zusammenfassung

Zweck dieser Arbeit ist die physikalischen und elektrischen Eigenschaften von entweder einem isolierten oder auf metallischem Substrat befindlichen Lackfilm zu charakterisieren.

Es wurde gezeigt, dass der Widerstand eines Filmes umgekehrt proportional zu der ionischen Durchlässigkeit ist, dass die Kapazität für Filme hoher Polarität ansteigt, und dass diese zwei Parameter sich je nach Filmdicke und Exponierungsstelle linear verändern.

Die Messung des Widerstandes kann für das Entdecken von Fehlern im Lackfilm als Folge mechanischer Verschlechterung und der Wahl ungeeigneter Bindemittel und Pigmente benutzt werden, um einen besseren Sperrreffekt zu erzeugen. Die Messungen der Kapazität können dazu dienen, um die Polarität des Filmes festzustellen und um Veränderungen als Folge von Oxidation oder Polymerisationsprozessen beim Altern in der chemischen Zusammensetzung und Polarität zu entdecken.

## Introduction

### Ref. 1

The main purpose of a film of an anticorrosive paint is to protect the metallic substrate from the aggressiveness of the surrounding medium.

The behaviour of a protective system will depend on:

(a) the physical, electrical and electrochemical properties of the film;

(b) the surface characteristics of the metal and,  
(c) the environmental conditions.

The protective action is determined by a complex mechanism which includes the action of different factors. For this reason, this study has been carried out in stages in order to evaluate separately each of the individual aspects of the problem<sup>1</sup>.

The aim of this work was to characterise the physical and electric qualities of a paint film either when isolated or

applied to a metallic substrate and acting as a semipermeable membrane. In this way, the barrier effect of the film may be evaluated with reference to its electric conductivity and ionic transference. A knowledge of these properties is necessary for the determination of their behaviour prior to the passage of electric current and to establish the nature and concentration of the substances that pass through the film. Therefore, it is possible to determine qualitatively and quantitatively the ions which enter into reaction with the metal or with the inhibitive pigments and to establish the extent of the by-products in the reaction.

A knowledge of the physicochemical characteristics of the organic coatings will enable the determination of their possible behaviour in an aqueous medium (especially in saline solutions) and in this way establish the most adequate paint system suitable for an aggressive environment.

## Measurements of conductivity and permeability

### Preparation of the films

The film was applied to a brass plate  $15 \times 35$  cm and 2.5 cm thick which had been rectified and amalgamated. The coats of paint were applied using applicators of different thicknesses (between 75 and  $300 \mu$ ). After a drying time of 48 hours, the film was removed from the plate, washed with nitric acid (1:3 solution) to eliminate any residual mercury and then with distilled water. Finally, the film was air dried under laboratory conditions, and was then ready for use.

### Support cell

A PVC tube, open at each end, in the form of a flattened cylinder at one of the ends was used (Fig. 1); length 10 cm and a diameter 5 cm. The film is fixed to the flattened end using the binder of the paint as adhesive.

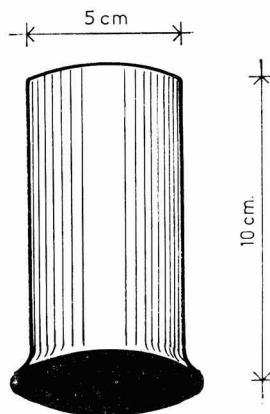


Fig. 1.

### Measurement of permeability

These are based on the measurement of the ionic transference through the film, as a function of the time in contact with the saline solutions. The tests were made with solutions of sodium chloride (36 g/l) and sodium hydroxide (40 g/l). Sodium chloride was chosen because it is the principal component of sea water and sodium hydroxide because of the alkalinity

which develops in systems that combine paint and cathodic protection.

The cells were immersed in a bath which contains the solution (Fig. 2). Twice distilled water is placed inside the cell and the system is hermetically sealed to avoid absorption of carbon dioxide.

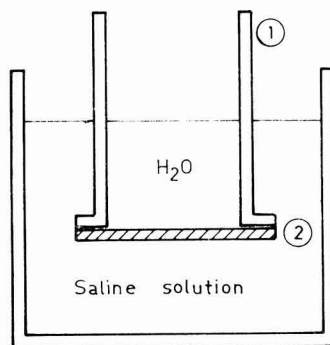


Fig. 2. Measurements of permeability. (1) PVC support; (2) paint film

To measure the velocity of passage of sodium chloride through the film, the solution in the cell is periodically checked to determine the sodium present by atomic absorption. The passage of sodium hydroxide through the film can be found from the determination of the sodium present and the pH changes during the process.

### Measurements of conductivity

These measurements are based on the determination of the changes which occur when different paint films are introduced between two stainless steel electrodes immersed in sodium chloride solution.

The system is similar to the previous one, except that the PVC support is filled with the same saline solution. The conductivity measurements were made using a conductivity bridge. The cells and electrodes are shown in Fig. 3.

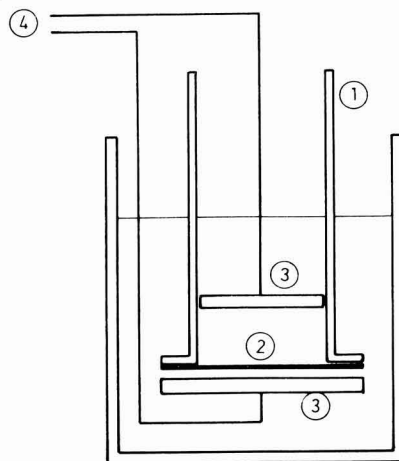


Fig. 3. Measurements of conductivity. (1) PVC support; (2) Paint film; (3) Electrodes; (4) Terminals

**Results**

The composition of the paints used is given in Table 1. Tables 2 and 3 show the results of the transfer measurements of sodium chloride and sodium hydroxide. Conductivity measurements are shown in Table 4. The variation of these parameters versus time is shown in Figures 4 and 5.

*Table 1*  
*Chemical characteristics of the paints tested*

Denomination	Composition
V	Vinyl resin VAGH
VF	Vinyl resin, 62%; ferric oxide, 38%
VC	Vinyl resin, 62%; zinc tetroxy-chromate, 38%
VFC	Vinyl resin, 62%; tetroxy-chromate, 31%; ferric oxide, 7%
FA10	Phenolic varnish, 90%; alkyd resin, 10%
FA20	Phenolic varnish, 80%; alkyd resin, 20%
FC37	Phenolic varnish, 63%; chlorinated rubber 20cP, 37%
FC20	Phenolic varnish, 80%; chlorinated rubber 20cP, 37%
FC11	Phenolic varnish, 89%; chlorinated rubber 20cP, 11%

*Table 2*  
*Sodium chloride transference*

Membrane	Thickness (μ)	Quantity of sodium transferred (mg NaCl/cm <sup>2</sup> )
V	20	0.06
V	40	0.04
V	60	0.01
FA10	30	0.48
FA10	60	0.23
FA20	30	0.80
FA20	60	0.39
FC11	30	0.15
FC11	60	0.07
FC20	30	0.09
FC20	60	0.04
FC37	30	0.07
FC37	60	0.03

Note: Stabilisation time, 60 days  
Exposed surface, 20cm<sup>2</sup>  
Average of 20 determinations  
Reproducibility: 10%

*Table 3*  
*Sodium hydroxide transference*

Membrane	Thickness (μ)	Final pH	Quantity of transferred sodium (mg NaOH/cm <sup>2</sup> )	
			Calculated by pH	Measured by atomic absorption
V	20	8.50	0.013	0.016
V	40	8.20	0.006	0.008
V	60	8.00	0.004	0.004

Note: Stabilisation time, 60 days  
Exposed surface, 20cm<sup>2</sup>  
Average of 20 determinations  
Reproducibility, 10%  
Initial pH ≈ 7.00  
Phenolic films do not resist to the sodium hydroxide.

*Table 4*  
*Measures of conductivity\**

Membrane	Thickness (μ)	Total resistance (Ω)	Resistance (Ω. cm <sup>2</sup> μ <sup>-1</sup> )
V	20	78 × 10 <sup>4</sup>	78 × 10 <sup>4</sup>
V	40	156 × 10 <sup>4</sup>	78 × 10 <sup>4</sup>
V	60	234 × 10 <sup>4</sup>	78 × 10 <sup>4</sup>
VF	30	78 × 10 <sup>4</sup>	52 × 10 <sup>4</sup>
VF	60	156 × 10 <sup>4</sup>	52 × 10 <sup>4</sup>
VC	30	17 × 10 <sup>4</sup>	11 × 10 <sup>4</sup>
VC	60	33 × 10 <sup>4</sup>	11 × 10 <sup>4</sup>
VFC	30	50 × 10 <sup>4</sup>	33 × 10 <sup>4</sup>
VFC	60	99 × 10 <sup>4</sup>	33 × 10 <sup>4</sup>
FA10	30	50 × 10 <sup>4</sup>	34 × 10 <sup>4</sup>
FA10	60	100 × 10 <sup>4</sup>	34 × 10 <sup>4</sup>
FA20	30	3 × 10 <sup>4</sup>	2 × 10 <sup>4</sup>
FA20	60	6 × 10 <sup>4</sup>	2 × 10 <sup>4</sup>
FC37	30	39 × 10 <sup>4</sup>	26 × 10 <sup>4</sup>
FC37	60	78 × 10 <sup>4</sup>	26 × 10 <sup>4</sup>
FC20	30	27 × 10 <sup>4</sup>	18 × 10 <sup>4</sup>
FC20	60	54 × 10 <sup>4</sup>	18 × 10 <sup>4</sup>
FC11	30	18 × 10 <sup>4</sup>	12 × 10 <sup>4</sup>
FC11	60	36 × 10 <sup>4</sup>	12 × 10 <sup>4</sup>
Uncoated iron	—	10	—

Note: Stabilisation time, 2 days  
Exposed surface, 20cm<sup>2</sup>  
Average of 20 determinations  
Reproducibility, 10%

\*The same values of resistance were obtained when measured with direct current and with 100Hz, except for the case of uncoated iron, which was measured at 1000Hz.

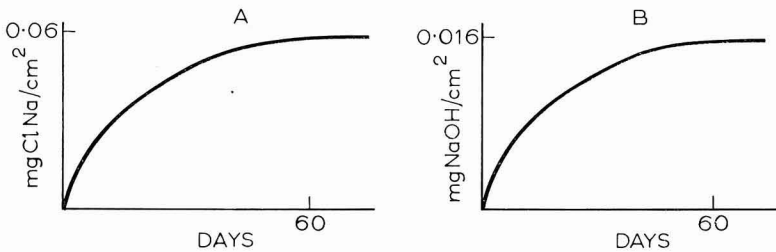


Fig. 4. Ionic transfer (example for vinyl film 20 μm)

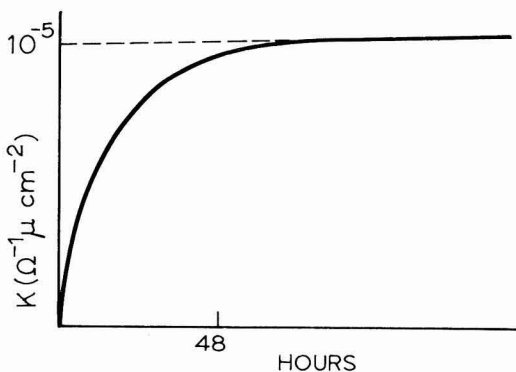


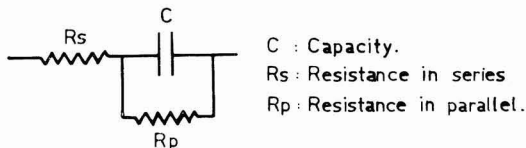
Fig. 5. Measurement of conductivity

**Measurements of capacity and ohmic resistance**

Ref. 2

**Theory**

Capacity and electrical phenomena which occur in a painted iron plate when a current passes may be compared to those shown by an equivalent circuit formed by a capacity (C), a resistance in series ( $R_s$ ) and a resistance in parallel ( $R_p$ ), shown diagrammatically in Fig. 6.



C : Capacity.  
 $R_s$  : Resistance in series  
 $R_p$  : Resistance in parallel.

Fig. 6. Equivalent circuit

When a potential difference is applied to a circuit of this type, a rapid increase in current is first observed (charging the capacitor); then the current decreases gradually to a constant value<sup>2</sup>. This value is the smaller, the greater the resistance in parallel and may be zero if the resistance is infinite.

Figure 7 shows the current variation versus time. The time that the current takes to reach to 0.368 of the peak current ( $I_p$ ) is called "time constant" ( $\tau$ ) of the system RC and is equal to the product of capacity and the resistance in series, that is:

$$\tau = R_s \cdot C \text{ (see appendix) } \dots \dots (1)$$

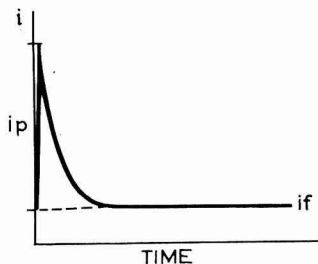


Fig. 7. RC circuit—Current-time diagram

The final current ( $I_f$ ) which passes after the capacitor has been charged, is given by the relation between the applied potential ( $V_{ab}$ ) and the sum of the  $R_s$  and  $R_p$  resistances, that is:

$$I_f = \frac{V_{ab}}{R_s + R_p}$$

The analysis of the RC circuit may be paralleled to the resistance and capacity changes which occur during the test.

**Resistance effects**

The final current may be due to leakage from the capacitor because of edge effects, or a current through electronic or ionic conduction.

From measurements in the air and in the saline solution it is possible to estimate the contribution of each of these effects.

When the experiment is performed in saline solution, the passage of current is changed by the variations of the "polarisation resistance", which includes the ohmic resistance and the charge and mass transference resistance. A blank test is performed with an uncoated iron sample to evaluate the contribution of the charge and mass transference overpotentials, in the total resistance.

**Capacity effects**

The capacity of the samples tested, cannot be so exactly determined as with a conventional capacitor, where the capacity is independent of the charge given. In the systems studied here, the passage of current modifies the composition of the double layer and, therefore, the capacity varies with the mode of operation.

The aim of this work is to evaluate the capacity effects of the various paint films tested, in order to obtain a semi-quantitative average value of their capacity and to establish the relationship between the different materials. The test was done with the same procedure for all the experiments.

**Measurements**

Ref. 3

Measurements of capacity and resistance were made in air having different degrees of humidity and in a 3.6 per cent sodium chloride solution.

When the measurements are taken in air, the cell used was an iron plate of the type SAE 1010 of  $15 \times 30 \times 2$  cm which had been rectified and deoxidised. The coating was applied to this plate and after a drying time of 48 hours, a cylindrical acrylic tube of 5 cm diameter and 10 cm height was fixed on the paint using a mixture of vaseline and paraffin. This device was placed in a sealed container whose humidity was kept constant by means of aqueous solutions of sulfuric acid<sup>3</sup>. The results are given in Table 5. Figure 9 shows a diagram of the system. The measurements were taken after two days' immersion.

Table 5  
 Relative humidity in sulfuric acid solutions

$H_2SO_4$ (g/cm <sup>3</sup> )	Relative humidity (%)	Vapour pressure (mm Hg)
1.20	80.5	14.0
1.50	18.8	3.3
1.70	3.2	0.6

Note: Temperature, 20°C.

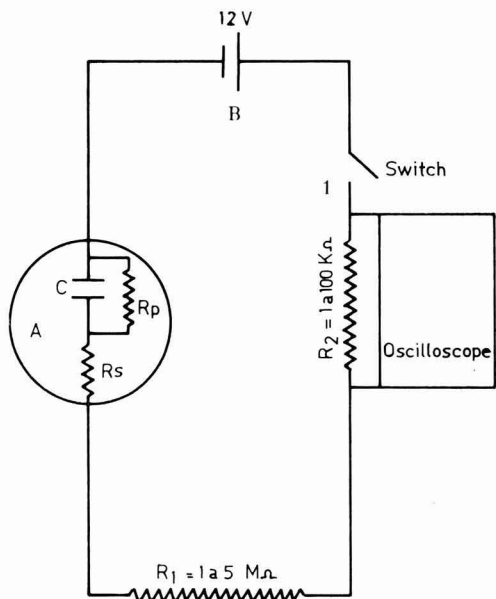


Fig. 8. Circuit for measuring resistance and capacity

A—cell; C—capacity;  $R_s$ —resistance in series;  $R_p$ —resistance in parallel

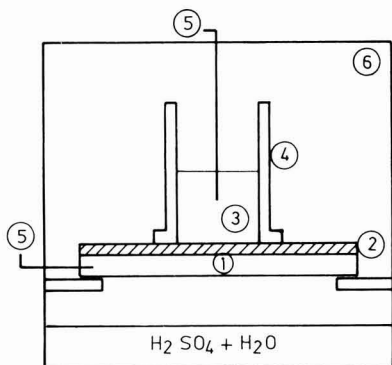


Fig. 9. Measurements of capacity and resistance in air. (1) Iron plate; (2) Paint film; (3) Mercury; (4) PVCII support; (5) Terminals; (6) Hermetically sealed container

The measurements in the aqueous medium were made on an iron plate similar to that used for the measurements in air. The coat of paint was applied, left to dry for 48 hours and then fixed to the acrylic tube. The tube was filled with a sodium chloride solution (3.6 per cent). The iron plate forms one of the electrodes and the other a stainless steel disc which is placed in the tube. This system is shown in Figure 10.

**Circuit**

Figure 8 shows the circuit used for the determination of the measurements of capacity and resistance in the transitory state.

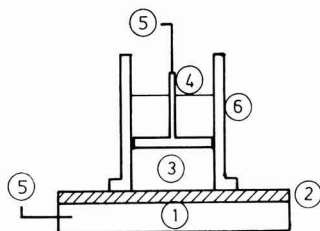


Fig. 10. Measurements of resistance and capacity in water. (1) Iron plate; (2) Paint film; (3) Saline solution; (4) Stainless steel electrode; (5) Terminals; (6) PVCII support

The circuit has a battery (B) that can supply potentials of 12 volts. The cell (A) is connected in series to a high resistance,  $R_1$  (approximately 1 MΩ) and to another smaller resistance,  $R_2$ . This smaller resistance is connected to the oscilloscope to measure the drop in potential caused by the passage of current.

Switch 1 synchronises, by means of an electronic system, the connection of the battery with the triggering of the time base of the oscilloscope. The oscilloscope employed was a Tektronix with memory.

**Calculations**

Equations (1) and (2) are applied respectively for the calculation of capacity and resistance. The total resistance (R<sub>ts</sub>) in series with the capacitor is equal to:

$$R_{ts} = R_1 + R_2 + R_s \dots \dots \dots (3)$$

The resistance in parallel is expressed by  $R_p$  and the total resistance of the circuit ( $R_t$ ) is:

$$R_t = R_1 + R_2 + R_s + R_p \dots \dots \dots (4)$$

If the time constant for two different values of  $R_1$  (1 M and 2 M) is measured, the combination of the equations (1) and (3) gives:

$$R_s = \frac{\tau_2(R_1 + R_2) - \tau_1(R'_1 + R_2)}{\tau_1 - \tau_2} \dots \dots \dots (5)$$

where  $\tau_1$  is the time constant for the system when  $R_{ts} = R_1 + R_2 + R_s$  and  $\tau_2$  is the constant when  $R_{ts} = R'_1 + R_2 + R_s$

Once  $R_s$  is established by means of the equation (5), the capacity, C, may be calculated by the following equation:

$$C = \frac{\tau}{R_1 + R_2 + R_s} \dots \dots \dots (6)$$

By means of the equation:

$$R_t = R_1 + R_2 + R_s + R_p = \frac{V_{ab}}{I_f} \dots \dots \dots (7)$$

and taking into account the equation (5), it is possible to calculate the resistance in parallel with the condenser ( $R_p$ ).

In this way, the values of capacity (C) and of the resistance  $R_t$  and  $R_p$  can be obtained.

The circuit response and its accuracy were verified by replacing the cell with a standard system of capacitor and resistors in series and in parallel. There were deviations in the measurements of about 5 per cent with respect to the absolute values and a reproducibility of 1 per cent.

**Results**

Table 1 shows the composition of the films tested. Tables 6 and 7 indicate the results of the measurements of capacity and resistance in the air and the corresponding measurements in the saline solution may be seen in Tables 8 and 9.

*Table 6  
Measurements of capacity in air*

Membrane	Thickness (μ)	Capacity*		
		ψ = 3.2%	ψ = 18.8%	ψ = 80.5%
V	15 and 30	2.2 × 10 <sup>-3</sup>	3.3 × 10 <sup>-3</sup>	5.0 × 10 <sup>-3</sup>
VF	15 and 30	2.7 × 10 <sup>-3</sup>	4.1 × 10 <sup>-3</sup>	6.0 × 10 <sup>-3</sup>
VC	15 and 30	8.0 × 10 <sup>-3</sup>	12.0 × 10 <sup>-3</sup>	18.0 × 10 <sup>-3</sup>
VFC	15 and 30	6.2 × 10 <sup>-3</sup>	9.3 × 10 <sup>-3</sup>	14.0 × 10 <sup>-3</sup>
FA10	15 and 30	13 × 10 <sup>-3</sup>	20.0 × 10 <sup>-3</sup>	29.0 × 10 <sup>-3</sup>
FA20	15 and 30	11 × 10 <sup>-3</sup>	17.0 × 10 <sup>-3</sup>	29.0 × 10 <sup>-3</sup>
FC37	15 and 30	7.1 × 10 <sup>-3</sup>	11.0 × 10 <sup>-3</sup>	17.0 × 10 <sup>-3</sup>
FC20	15 and 30	11 × 10 <sup>-3</sup>	17.0 × 10 <sup>-3</sup>	24.0 × 10 <sup>-3</sup>
FC11	15 and 30	13 × 10 <sup>-3</sup>	20.0 × 10 <sup>-3</sup>	29.0 × 10 <sup>-3</sup>

Note: Resistance in series, 10<sup>6</sup>Ω  
Surface, 20cm<sup>2</sup>  
Average of 10 determinations  
Reproducibility, 10%

\*The data for capacity are given in microfarads per cm<sup>2</sup> of surface and by microns of thickness.

*Table 7  
Measurements of resistance in air*

Membrane	Thickness (μ)	Resistance in parallel (Ω cm <sup>2</sup> μ <sup>-1</sup> )		
		ψ = 3.2%	ψ = 18.8%	ψ = 80.5%
V	20-40-60	2 × 10 <sup>8</sup>	1 × 10 <sup>8</sup>	0.9 × 10 <sup>8</sup>
VF	30-60	1.6 × 10 <sup>8</sup>	7 × 10 <sup>7</sup>	6.3 × 10 <sup>7</sup>
VC	30-60	3.5 × 10 <sup>7</sup>	1.5 × 10 <sup>7</sup>	1.3 × 10 <sup>7</sup>
VFC	30-60	8.0 × 10 <sup>7</sup>	4.0 × 10 <sup>7</sup>	3.5 × 10 <sup>7</sup>
FA10	30-60	9.0 × 10 <sup>6</sup>	4.0 × 10 <sup>6</sup>	3.0 × 10 <sup>6</sup>
FA20	30-60	6.0 × 10 <sup>6</sup>	2.5 × 10 <sup>6</sup>	1.8 × 10 <sup>6</sup>
FC37	30-60	6.1 × 10 <sup>7</sup>	3.3 × 10 <sup>7</sup>	3.0 × 10 <sup>7</sup>
FC20	30-60	4.2 × 10 <sup>7</sup>	2.3 × 10 <sup>7</sup>	2.2 × 10 <sup>7</sup>
FC11	30-60	2.9 × 10 <sup>7</sup>	1.5 × 10 <sup>7</sup>	1.4 × 10 <sup>7</sup>

Note: Resistance in series, 10<sup>6</sup>Ω  
Surface, 20cm<sup>2</sup>  
Average of 10 determinations  
Reproducibility, 10%  
Resistance for the oscilloscope, 200,000Ω  
Applied voltage, 24 volts

The resistance in series (R<sub>s</sub>), calculated using equation (5) is not taken into account since it is only about 1% of the resistance in parallel (R<sub>p</sub>).

*Table 8  
Measurements of capacity  
(samples immersed in sodium chloride solution, 3.6 per cent)*

Membrane	Thickness (μ)	Capacity (Microfarads/cm <sup>2</sup> )
Uncoated iron	—	5.0
V	30	6.6
VF	30	7.0
VC	30	11.0
VFC	30	9.7
FA10	30	15.0
FA20	30	13.0
FC37	30	10.3
FC20	30	13.0
FC11	30	16.0

Note: Resistance in series, 10<sup>5</sup>Ω  
Surface, 20cm<sup>2</sup>  
Average of 10 determinations  
Reproducibility, 10%  
Resistance for the oscilloscope, 1 000Ω  
Applied voltage, 24 volts

*Table 9  
Measurements of resistance  
(Samples immersed in sodium chloride solution, 3.6 per cent)*

Membrane	Thickness (μ)	Resistance (Ω. cm <sup>2</sup> μ <sup>-1</sup> )
Uncoated iron	—	10
V	20-40-60	2.3 - 10 <sup>6</sup>
VF	30-60	1.4 - 10 <sup>6</sup>
VC	30-60	1.7 - 10 <sup>5</sup>
VFC	30-60	5.7 - 10 <sup>5</sup>
FA10	30-60	4.5 - 10 <sup>4</sup>
FA20	30-60	2.8 - 10 <sup>4</sup>
FC37	30-60	4.0 - 10 <sup>5</sup>
FC20	30-60	2.6 - 10 <sup>5</sup>

Note: Resistance in series, 10<sup>5</sup>Ω  
Surface, 20cm<sup>2</sup>  
Average of 10 determinations  
Reproducibility, 10%  
Resistance for the oscilloscope, 1 000Ω  
Applied voltage, 24 volts

**Discussion of Results**

**Isolated film**

*Conductivity*

The resistance increases linearly with the thickness of the film (Table 4). In addition, the resistance diminishes when the polarity of the film increases. Figure 5 shows the variation of the resistance as a function of the immersion time.

*Permeability*

All the films tested resist the action of the sodium chloride solution, but only the vinyl film was not destroyed by the action of the NaOH.

The permeability decreases linearly with the thickness (Tables 2 and 3) and the transfer of chlorides increases with the film polarity.

In Figure 4, diagrams A and B show how the ionic transfer varies with the contact time. The comparison of the values of Tables 2 and 3 with the values of Table 4 shows a direct relationship between the conductivity and permeability of ions.

**Painted samples**

*Ref. 4*

*Resistance in air*

A circuit formed by a capacity, a resistance in series and another in parallel was considered equivalent to the system of a paint film on a metallic sample. However, the application of equation (5) has shown that the component in series is unnecessary.

The high resistance of the vinyl film, together with the linear increase of resistance with increasing film thickness, shows that the leakage effect of the current by the edges is minimal.

In all cases, the resistance increases linearly with the thickness. An increase in humidity decreases the resistance and this effect is the more marked the more polar the film.



*Resistance in water*

When a direct current is applied to the system, what is really measured is the polarisation resistance<sup>4</sup> of which the ohmic decrease is only a part. In all cases the resistance increases linearly with the thickness and diminishes with the polarity.

If a comparison is made between the measurements in air and in water, it can be clearly seen that there is a marked decrease of the resistance in water.

On the other hand, if the value of resistance between the painted samples immersed in water is compared to the same films isolated from the substrate, it will be observed that the resistance is smaller in the latter case.

*Measurements of capacity in air and in water*

When the measurements are taken in air, it has been observed that the capacity diminishes linearly with the thickness and increases with the polarity of the film and with an increase in the humidity. The capacity in water is greater than in the air.

In all cases, a greater capacity has been found than that of the uncoated iron and the difference is more noticeable for films of high polarity.

**Conclusions**

It has been established that a film subjected to the passage of a direct current behaves similarly to an electric model formed by a capacity and a resistance in parallel.

It has been shown that:

- (a) The resistance is inversely proportional to the ionic permeability.
- (b) The capacity increases for the films of high polarity.
- (c) The capacity (C) and the resistance (R) vary linearly with the thickness of the film (e) and the area (S) exposed, according to equations of the type:

$$C = K \frac{S}{e} \quad R = K' \frac{e}{S}$$

According to the above expressions, it can be inferred that the resistance measurements may be used to determine:

- (a) Compatibility between current density and paint systems in the case of cathodic protection.
- (b) Adjustment of the formulations of anticorrosive paints with an adequate choice of the binders and pigments in order to obtain a greater barrier effect as well as a better inhibiting power.
- (c) A study of failures of the paint film due to mechanical deterioration.

The measurements of capacity may be employed to establish the polarity of the film and to study the changes in its chemical composition and polarity due to oxidation of polymerisation processes during ageing.

[Received 27 April 1978]

**Appendix**

*Deduction of the equation for a circuit RC*

When, in the circuit of Fig. 11, the switch 1 is shut, the charge increases gradually to reach its final value. The differences of

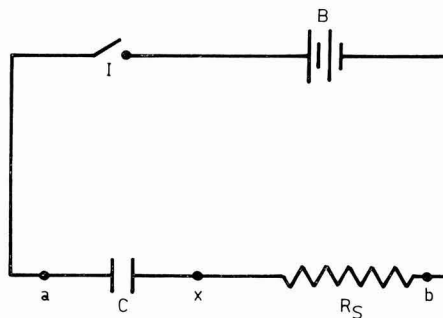


Fig. 11.

potential,  $V_{ax}$  and  $V_{xb}$ , are given at any moment by the equations:

$$V_{ax} = q/C \dots\dots\dots (1)$$

$$V_{xb} = IR = R dq/dt \dots\dots\dots (2)$$

where  $q$  is the charge of the capacitor and  $I$  is the current in the circuit in the moment considered.

But as:  $E = V_{ax} + V_{xb}$

then  $E = q/C + R.dq/dt \dots\dots\dots (3a)$

or  $CE = q + RC dq/dt \dots\dots\dots (3b)$

and, separating the variables

$$\frac{dq}{CE - q} = \frac{dt}{RC} \dots\dots\dots (4)$$

and integrating,

$$\int_0^q \frac{dq}{CE - q} = \int_0^t \frac{dt}{RC} \dots\dots\dots (5)$$

$$\left[ \ln(CE - q) \right]_0^q = \left[ \frac{t}{RC} \right]_0^t \dots\dots\dots (6)$$

Since  $q = 0$  for  $t = 0$ , it follows:

$$-\ln \frac{(CE - q)}{CE} = \frac{t}{RC} \dots\dots\dots (7)$$

$$q = CE [1 - e^{-t/RC}] \dots\dots\dots (8)$$

When sufficient time has passed, the term  $e^{-t/RC}$  becomes negligible and the charge  $q$  is near to its final value  $Q = CE$ , it may be written:

$$q = Q (1 - e^{-t/RC}) \dots\dots\dots (9)$$

Figure 12 is the graphical representation of equation (9). If the capacitor initially charged is discharged through the resistance  $R$ ,

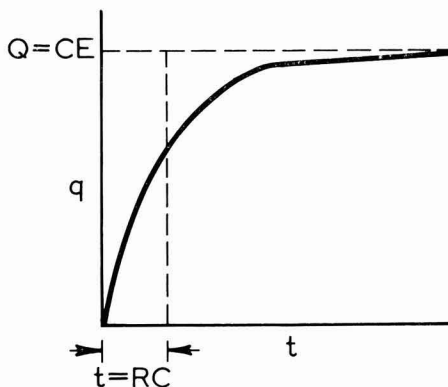


Fig. 12.

the charge diminishes with time in accordance to the equation:

$$q = Q e^{-t/RC} \dots \dots \dots (10)$$

This may be seen in Figure 13.

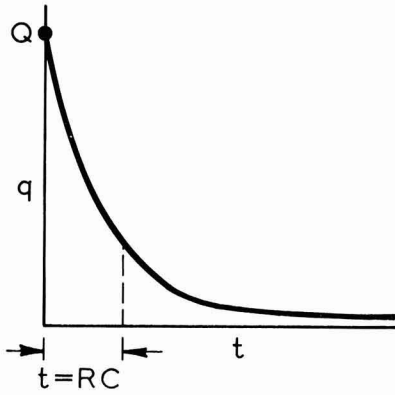


Fig. 13.

Equation (10) may be also expressed in terms of current giving:

$$I = I_0 e^{-t/RC} \dots \dots \dots (11)$$

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# Electrical resistance of electrodeposited rubber per unit coulomb

By S. Guruswamy

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## Summary

A method of evaluating the electrical resistance of electrodeposited rubber per coulomb passed is described, illustrated and used to

assess the current efficiency of the electrodeposition of rubber and to calculate the weight of rubber deposited in a particular situation.

## Keywords

*Types and classes of coatings and allied products*  
electrocoating

*Raw materials used in the manufacture or synthesis of ingredients for coatings*  
rubber

*Processes and methods primarily associated with analysis, measurement or testing*  
electrocoating

*Properties, characteristics and conditions primarily associated with materials in general*  
electrical resistivity

*dried or cured films*  
film thickness

*Miscellaneous terms*  
equivalent weight

## La résistance électrique du caoutchouc électrodéposé par coulomb

### Résumé

Une méthode pour évaluer la résistance électrique du caoutchouc électrodéposé par coulomb est décrite, et utilisée pour déterminer l'efficacité, au point de vue du courant consommé, du processus de

l'électrodéposition de caoutchouc et pour calculer la quantité de caoutchouc déposé dans une situation particulière.

## Der elektrische Widerstand pro Coulomb von elektrolytisch niedergeschlagenem Gummi

### Zusammenfassung

Beschreibung einer Methode zur Bestimmung des elektrischen Widerstandes von elektrolytisch niedergeschlagenem Gummi pro durchflossenes Coulomb, illustriert und angewandt zur

Bestimmung der gegenwärtigen Wirtschaftlichkeit der Elektrolyseverfahren für Gummi, sowie zur Berechnung des Gewichtes des in besonderen Situationen niedergeschlagenen Gummis.

## Introduction

Ref. 1-3

Ions can be identified by their electrochemical equivalent weights; the basis of which is the particular value of charge/weight ratio of the ion concerned. However, such calculations are not suitable for the classification of electrodeposition resins, although the "specific charge" (charge/cm<sup>2</sup>) can be profitably studied<sup>1</sup> as a parameter to monitor the electrodeposition at ordinary voltages from aqueous resin bath systems in industrial applications.

The resins being deposited can be differentiated, if it is possible to calculate from basic laboratory data the electrical resistance,  $\rho$ , of the electrodeposited film when the electrical charges of the individual particles<sup>3</sup> in the aqueous phase are neutralised by one coulomb of electricity. Variations in the values of this parameter,  $\rho$ , may indicate the extent of dehydration of the electrodeposited colloidal particles during compaction into the film deposit.

$\rho$  can be used to evaluate the compactness of the deposit<sup>2</sup>, when film thickness is combined with current-time data. In addition,  $\rho$  is also useful as a concept to aid further development in the area of electropainting/coating for industrial applications.

## Proposed method for the calculation of 'p'

The current,  $C_t$ , after any time of deposition,  $t$ , is given by:

$$C_t = \frac{\text{Voltage applied, } V}{\text{Bath resistance, } R_b + \text{Film resistance, } R_f}$$

This may be rewritten as:

$$\frac{1}{C_t} = \frac{R_b}{V} + \frac{R_f}{V} \dots \dots \dots (1)$$

Initially at time,  $t = 0$ , when no film has been formed  $R_f$  will be zero and therefore:

$$\frac{1}{C_0} = \frac{R_b}{V} \text{ where } C_0 \text{ is the current at } t = 0, \text{ that is, the initial current.}$$

It is assumed that the deposition will cause no significant change in the concentration of the bath, so that  $R_b$  will not change during a short period of deposition.

If  $C_t$  at some time,  $t$ , is defined as being equal to  $x C_0$  and by the definition of 'p', the film resistance at the time,  $t$ , will be  $p q$ , where  $q$  is the number of coulombs passed during the time =  $t$ .

Therefore,  $R_f = pq$ , and if  $q$  is equal to the average current passing during the deposition period multiplied by the time of deposition, then  $q$  may be written as:

$$q = \left[ \frac{C_t + C_o}{2} \right] t$$

Substituting the values  $R_b = V/C_o$  and  $R_f = pq$  into the original equation gives:

$$C_t = \left[ \frac{V}{C_o + pq} \right] \text{ or } pq = \left[ \frac{V}{C_t} - \frac{V}{C_o} \right]$$

then writing  $C_t$  as  $x C_o$  it is found that:

$$pq = \frac{V}{C_o} \left[ \frac{1-x}{x} \right] \text{ and therefore:}$$

$$p = \frac{V}{q} \left[ \frac{1-x}{x} \right] \frac{1}{C_o} \dots \dots \dots (2)$$

Now  $q$  may be taken as  $\left[ \frac{C_t + C_o}{2} \right] t = \frac{C_o}{2} (1+x)t$

which gives  $\frac{1}{C_o} = \frac{(1+x)t}{2q} \dots \dots \dots (3)$

Rewriting equation (2) and putting  $\frac{1}{C_o}$  as  $\frac{(1+x)t}{2q}$

gives:

$$p = \frac{V}{q} \left[ \frac{1-x}{x} \right] \left[ \frac{1-x}{2q} \right] t$$

$$= \frac{Vt}{2q^2} \left[ \frac{1-x}{x} - x \right] \dots \dots \dots (4)$$

If experimental data are available for the values of  $C_o$  and for  $q$  and  $C_t$  at various values of the time,  $t$ , when the value of  $x$  can be calculated from  $q = \left[ \frac{C_t + C_o}{2} \right] t$  by substituting  $x C_o$  for  $C_t$  giving

$$x = \left[ \frac{2q}{C_o \cdot t} \right] - 1 \dots \dots \dots (5)$$

then, knowing the value of  $x$  from (5) the value of the parameter,  $p$ , may be calculated from equation (2).

**Experimental results**

*Ref. 6*

Table 1 gives the calculated values of  $p$  and  $R_f$  for electro-deposited rubber films at 50 volts DC from an ammonia stabilised, commercially available natural rubber latex, for two selected times of 60 and 180 seconds. The numerical calculation is illustrated in the last column of the table for one particular case.

The results in Table 1 are analysed<sup>6</sup> by calculating the "d" values to compare x-y relation existing between  $c$ ,  $p$  and  $R$  values. For this purpose  $x$  represents the latex concentration values. The "d" values are shown in Table 2.

**Discussion and numerical values of parameters**

*Refs. 4, 7, 8*

The analysis shown in Table 2 indicates that values of  $d$  are comparable for the two timings (60 and 180 seconds) and hence the average of  $p$  and  $R$  values are reliable estimates of the two parameters. The estimates corrected for electrode area are shown in the last column of Table 2.

The charge vs concentration (given in Table 1 of reference 4) are analysed in Table 3. The analysis indicates that a reliable estimate of charge can be obtained by averaging all the data. The mean value of charge is shown in the bottom column of Table 3 ( $= 3.17 \times 10^{-13}$  coulombs).

Using the values of  $p = 26.3$  ohm/coulomb, and  $R = 856$  ohm/gm; the electricity needed to neutralise the charge of one gram of rubber  $= \left( \frac{856}{26.3} \right) = 32.6$  coulombs. Number of particles present in one gm of latex (size<sup>7</sup> 2580Å and density<sup>8</sup> 0.92)  $= \left[ \frac{1}{0.92} \times \frac{6}{\pi (2580 \times 10^{-8})^3} \right] = 1.21 \times 10^{14}$ .

Charge on individual particle of latex  $= \left[ \frac{32.6}{1.21 \times 10^{14}} \right] = 2.69 \times 10^{-13}$  coulombs.

Table 1  
Calculation of  $p$  and  $R$  from experimental results<sup>4</sup>

Concentration (%) of latex	Table 1 of reference 4 Data source						Definition of terms	Numerical calculations illustrated for 20% latex concentration
	1	2	3	4	5	6		
	(p) <sub>60</sub>	(p) <sub>180</sub>	(w) <sub>60</sub>	(w) <sub>180</sub>	(R) <sub>60</sub>	(R) <sub>180</sub>		
20	198	112	15.2	9.6	13.0	11.7	(1) and (2) ohms/coulomb of 60 and 180 seconds deposit	$C_o = 1869$ mA (from data in Figs 2 and 3 of reference 5) $p_{60} = \left( \frac{50}{33.3} \right) \left( \frac{1-0.039}{0.039} \right) \left( \frac{1000}{1869} \right) = 198$ $p_{180} = \left( \frac{50}{7.030} \right) \left( \frac{1-0.033}{0.033} \right) \left( \frac{1000}{1869} \right) = 112$ $R_{60} = \left( \frac{198}{15.2} \right) = 13.0$ $R_{180} = \left( \frac{112}{9.6} \right) = 11.7$
12	274	260	32.7	30.7	8.4	8.5		
6	280	252	47.8	43.7	5.9	5.8		
3	288	669	49.5	42.6	6.8	15.8		
1.5	16.6	17.8	30.8	33.2	0.51	0.54		

Basic experimental data substituted in equation (2)

Table 2  
Comparison of *d* values representing concentration as *x*

Ref. No.	<i>x</i> ( $x_n - x_{n-1}$ )	<i>y</i> corresponding to						Numerical illustration for $P_{60}$ case					
		<i>p</i> values (taken from Table 1)			<i>R</i> values (taken from Table 1)								
		60 sec.	180 sec.	<i>A</i>	60 sec.	180 sec.	<i>A</i>						
0	-8	198	112	472	372	-1888	-1488	13.0	11.7	21.4	20.2	-85.6	-80.8
1	-6	274	260	554	512	-1662	-1536	8.4	8.5	14.3	14.3	-42.9	-42.9
2	-3	280	252	568	921	-852	-1362	5.9	5.8	12.7	21.6	-19.0	-32.4
3	-1.5	288	669	305	323	-230	-253	6.8	15.8	7.3	16.3	-11.0	-12.2
4	1.5	17	18	—	—	—	—	0.51	0.53	—	—	—	—
		<i>A</i>		-4632	-4659	<i>A</i>		-159	168				
		<i>A<sub>0</sub></i>		199	199	<i>A<sub>0</sub></i>		199	199				
		<i>d</i>		-184.6	-185.7	<i>d</i>		-0.061	-0.064				
		Relative <i>d</i> value		1.00	1.00	Relative value of <i>d</i>		1.06	1.06				
		Mean value of <i>p</i>		237	237	Mean value of <i>R</i>		7.7	7.7				
		<i>d<sub>0</sub></i> corrected for area = 9cm <sup>2</sup>		26.3	26.3	<i>d<sub>0</sub></i> corrected for electrode area (= 9cm <sup>2</sup> )		856	856				
						<i>d</i>							
						<i>A</i>							
						<i>A<sub>0</sub></i>							
						<i>d</i>							
						Relative value of <i>d</i>							
						Mean value of <i>R</i>							
						<i>d<sub>0</sub></i> corrected for electrode area (= 9cm <sup>2</sup> )							

Table 3  
Evaluation of charge on rubber latex particle

Concentration of latex ( <i>x</i> )	Charge calculated from experimental data ( <i>y</i> )	Ref. No. ( <i>t</i> )	<i>y<sub>n</sub> + y<sub>n-1</sub></i>						Numerical illustration for $j_{60}$ case
			$(x_n - x_{n-1})$			$(x_n - x_{n-1}) \cdot (y_n + y_{n-1})$			
			60 seconds deposition	180 seconds deposition	60 seconds data	180 seconds data	60 seconds data	180 seconds data	
20	$0.544 \times 10^{-12}$	0	-8	$0.796 \times 10^{-12}$	$1.131 \times 10^{-12}$	$-3.184 \times 10^{-12}$	$-4.524 \times 10^{-12}$	$(x_n - x_{n-1}) = (12-20), (6-12), (3-6), (1.5-3)$	
12	$0.252 \times 10^{-12}$	1	-6	$0.425 \times 10^{-12}$	$0.459 \times 10^{-12}$	$-1.275 \times 10^{-12}$	$-1.377 \times 10^{-12}$	$(y_n + y_{n-1}) = (0.544 + 0.252), (0.252 + 0.173), (0.173 + 0.167), (0.167 + 0.268)$	
6	$0.173 \times 10^{-12}$	2	-3	$0.340 \times 10^{-12}$	$0.383 \times 10^{-12}$	$0.510 \times 10^{-12}$	$-0.575 \times 10^{-12}$	$A = \frac{1}{2} [0.796 \times (-8)], \frac{1}{2} [0.425 \times (-6)], \frac{1}{2} [0.340 \times (-3)], \frac{1}{2} [0.435 \times (-1.5)]$	
3	$0.167 \times 10^{-12}$	3	-1.5	$0.435 \times 10^{-12}$	$0.443 \times 10^{-12}$	$-0.327 \times 10^{-12}$	$-0.333 \times 10^{-12}$	$A_0 = \frac{1}{2} [(x_n)^2 - (x_0)^2] = \frac{(20 + 1.5)(20 - 1.5)}{2} = 199$	
1.5	$0.268 \times 10^{-12}$	4	—	—	—	—	—	$d = \frac{-5.296 \times 10^{-12} - 199}{\sqrt{2} \times (20 - 1.5)} = -7.60$	
		<i>A</i>		$-5.296 \times 10^{-12}$	$-6.809 \times 10^{-12}$				
		<i>A<sub>0</sub></i>		199	199				
		<i>d</i>		-7.60	-7.60				
		Relative value of <i>d</i>		1.00	1.00				
		Mean value of charge		$(3.167) \times 10^{-12}$	$3.17 \times 10^{-13}$				

The two values of charge agree and hence the following conclusions may be drawn:

- (1) One coulomb of electricity yields a deposit of electrical resistance of 26.3 ohms.
- (2) One gram of electrodeposited rubber has a resistance of 856 ohms.
- (3) The individual rubber latex particles carry a charge of  $2.93 \times 10^{-13}$  coulombs (average of 2.69 and 3.17).

### Applications

Ref. 9

The usefulness of the value of  $p$  and  $R$  can be illustrated by the following two applications:

- (1) calculation of current efficiency of rubber deposition;
- (2) estimation of weight of rubber deposited. Assume it is required to calculate the current efficiency of rubber deposition from a 5 per cent latex bath at 50 volts DC when experimental data are available on the initial current and current at the end of 60 seconds (Fig. 2 of reference 9) at various concentrations of latex.

The initial current = 130 mA/cm<sup>2</sup> and current at the end of 60 seconds = 38 mA/cm<sup>2</sup>. Hence  $x = \left(\frac{38}{130}\right) = 0.2923$ .

From equation (4)  $q = \sqrt{\left(\frac{50 \times 60}{2 \times 26.3}\right) \left(\frac{1}{0.2923} - 0.2923\right)} = 13.37$ .

From equation (5),  $\left(\frac{2 \times 13.37}{60 Co} - 1\right) = 0.2923$ .

Hence  $Co = 345$  mA/cm<sup>2</sup>.

This represents the theoretical current density needed. Since the observed current density is less than the theoretical, it is inferred that the deposition is taking place at maximum possible efficiency.

If the desired higher current density is achieved by reducing the anode area in relation to the cathode by a factor  $\frac{130}{345} = 0.3768$ , a higher current efficiency can be expected to be attained for the same values of  $x$ ,  $q$ ,  $t$ ,  $v$ . The new current efficiency can be evaluated as follows.

$$\text{Bath resistance } R_b = \left(\frac{V}{Co}\right) = \left(\frac{50}{0.345}\right) = 145 \Omega$$

$$\text{Film resistance } R_f = (pq) = (26.3 \times 13.37) = 3518 \Omega$$

$$\text{Calculated current at the end of 60 sec} = \left(\frac{50}{3518 + 145}\right) \times 1000 = 13.65 \text{ mA}$$

$$\text{The observed current at the end of 60 seconds} = 345 \times 0.2923 = 100.8 \text{ mA}$$

$$\text{Current to non-process items such as bath heating} = (100.8 - 13.7) = 87.1 \text{ mA}$$

$$\text{Energy that goes to non-process items} = \frac{50 \times 87.1}{1000} = 43.56 \text{ watts}$$

$$\text{If energy dissipation is at 5 watts per litre, volume to be provided} = \frac{43.56}{5} \approx 8.7 \text{ litre}$$

$$\text{Total energy input} = \frac{50 \times 100.8}{1000} = 50.4 \text{ watts}$$

$$\text{Current efficiency of deposition} = \left(\frac{50.4 - 43.56}{50.4}\right) \times 100 \approx 14 \text{ per cent}$$

Weight deposited at the end of 60 sec. can be estimated as follows:

$$\text{Film resistance of the bath at the end of 60 sec.} = 3518 \text{ ohms}$$

$$\text{Maximum weight of rubber that be deposited assuming 100 per cent efficiency} = \left(\frac{3518}{856}\right) = 4.11 \text{ g.}$$

$$\text{At a current efficiency of 14 per cent, weight of rubber deposited will be} = 4.11 \times 0.14 = 0.58 \text{ g.}$$

### Conclusion

Resistance per coulomb of electrodeposited material is a useful parameter which can be evaluated by independent measurements of current, size of depositing particles, and can be applied to calculate current efficiency of deposition and also the weight of rubber deposited under particular conditions.

### Acknowledgment

The author thanks Dr H. V. K. Udupa, Director for support and encouragement.

[Received 22 May 1978]

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## Next month's issue

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

**Anticorrosive properties of Mimosa (Wattle) tannin** by A. J. Seavall

**Subjective comparisons of gloss—What does influence you?** by W. E. Craker and S. P. Smart

**New water-soluble compositions** by A. M. Naser, A. Z. Gomma and M. Moustafa



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## West Riding

### Defoamers—Their theory and application with regard to the paint industry.

A meeting of the West Riding Section was held on Tuesday 5 September 1978 at the Mansion Hotel, Leeds. A paper dealing with defoamers was presented by Mr R. W. Harrison of Diamond Shamrock.

Foaming is one of the major impediments both in manufacture and application of emulsion paints. In manufacture it can cause increased dispersion times and can-filling problems. During the application of emulsion paints, foam will cause defects, such as cratering in the applied paint film. The use of chemical defoamers is a way of combatting foam formation.

Foam is basically a colloidal system consisting of a gas dispersing in a liquid. It is caused when the dispersed air bubbles do not coalesce with the continuous gas phase, i.e. burst. Pure liquids do not usually support foam formation because the uniformity between surface and interior of the liquid prevents the creation of a stable elastic film capable of producing and holding a stable form. Introduction of a third component, such as a surface active agent, alters the properties of the gas/water interface.

When a surfactant is added to water, the surface tension is reduced. Any excess of surfactant above that required to form a monomolecular layer on the water surface is dispersed through the water phase. It is then available for the formation of further monomolecular films when the surface area has been increased by the addition of air into the system. These films at the entrapped air/water interface assume a spherical shape and, hence, a bubble of air is created. The film around the bubble is relatively tough and elastic. It loses water only slowly and can support its own weight.

There are many theories on the action of defoamers, but the author considers the following to be the most probable:

For a chemical defoamer to be effective it must have the following requirements:

- (1) It must be able to be spread throughout the system without being soluble in the system. It must, therefore, have a lower surface tension than the foaming system.
- (2) It must be compatible with the system and have the correct balance of emulsifiers present. If too little, the defoamers will separate out as an oily layer at the surface. If too much, than the defoamer will become too dispersed and ineffective.

When a floating bubble meets water containing defoamer, the defoamer spreads within the water film surrounding the bubble. Because of the defoamers lower surface tension, this film will begin to thin due to loss of water. This will cause either rupture of the film or make it possible for smaller bubbles to coalesce into larger bubbles which are inherently less stable. Another factor in destabilising the surfactant-water film is that the hydrophobes within the defoamer will compete for those in the surfactant.

The problem is to choose the correct defoamer from the many types available and Mr Harrison outlined two laboratory producers for screening defoamers.

The lecture was well attended and gave rise to a lively discussion.

R.A.C.C.

## Auckland

### Factory visit

The Auckland Section organised a visit to the factory of New Zealand Starch Products Ltd for their meeting of 20 September, when 20 Members were conducted around the starch and glucose plant.

Maize starch is prepared by steeping the locally grown maize grain in sulphurous acid in water to soften the kernel which is then coarsely ground to separate the germ from the endosperm (flour). The germ is then dried, the oil expelled and the germ cake left. Starch and gluten are separated from the fibre and then from each other. The gluten is mixed with fibre to make a maize animal feed. The starch is concentrated in a series of hydroclones and converted to glucose. 99 per cent recovery of solids is obtained.

The wheat starch process begins with South Island or Australian flour which is made into a dough in which the protein (gluten) is hydrated. Washing removes the starch which is purified to remove bran, etc. (which are used for animal feed). The wheat gluten is used as a bread improver whilst the starch is concentrated for conversion to glucose.

Starch is acidified with hydrochloric acid to convert to sugar and dextrin. Neutralisation with soda ash removes colloidal material and the liquor is filtered through activated carbon. Calcium ions are removed in an ion exchange column and the glucose solution is concentrated for eventual use in the confectionery and food industry.

The Section Chairman, Mr R. Ness, proposed a vote of thanks to the guides for an interesting tour.

A.M.

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## Register of Members

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

### Ordinary Members

ASUBONTENG, SAMUEL KOFI, PO Box 2574, Accra, Ghana.  
(*General Overseas*)

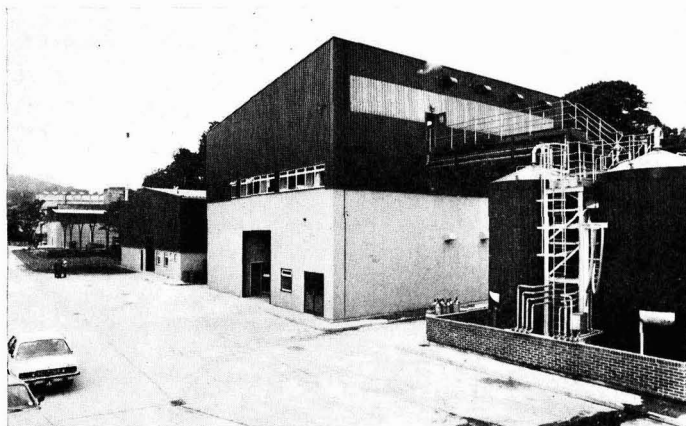
CHANDHOK, ANIL RATACHAND, BTech, 1 Om Sadan, 36th Road, Bandra, Bombay 40050, India.  
(*General Overseas*)

CHATFIELD, CHRISTOPHER JOHN, BSc, PhD, Chatfield Applied Research Laboratories Ltd, 13 Stafford Road, Croydon, Surrey CRO 4NG.  
(*London*)

FERCH, HORST, Degussa Wolfgang, Postfach 602, D-6450 Hanau 1, Germany.  
(*General Overseas*)

SOO, KONG SING, BSc, K S Paints Sdn Bhd, 8A Jalan 20/16A, Petaling Jaya, Selangor, Malaysia.  
(*General Overseas*)

# Information Received



The new Surfactants plant and Pigments Dispersion plant at the Stainland Works of Hoechst UK Ltd

## New factory opened

Hoechst UK Ltd opened a new factory at Holywell Green, near Halifax on 19 September. The new Stainland works were opened by the Minister of State at the Department of Industry, the Rt. Hon. Alan Williams MP. At present the surfactants and pigments plants are in operation, near the site of the textile processing plant which was closed in 1977.

The pigment dispersion plant will produce mainly aqueous dispersions of pigments supplied by the parent company in Germany, intended mainly for use in the paint, printing ink, textile, leather, wallpaper and other industries. The plant is modern and requires a minimum of manual handling. The processes are monitored in an adjacent quality control laboratory, with emphasis on the accuracy of colour, colour strength and degree of dispersion.

The surfactants plant is equally modern, but more complex, as reactions such as sulphonation and amination are performed under closely controlled conditions. The products are predominantly for use by the textile industries, including for example, bleaching and dyeing auxiliaries, sizing and desizing agents, scouring and softening agents and optical brighteners. Emulsifiers and demulsifiers are also manufactured.

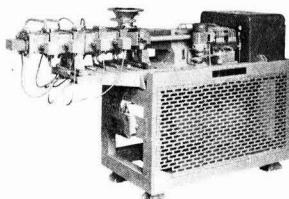
The buildings are relatively spacious and should allow the installation of additional plant when required. It is intended to transfer the present Manchester Offices and Laboratories to the Stainland site in due course.

## Paint factory on stream

The new paint factory of Greycloud Ltd, supplied as a turnkey operation and completed in 8.5 months, commenced production on 17 August. The main contractor responsible for the design, supply and installation of the plant and services was Mastermix Engineering Co. Ltd, and the design includes automatic dispersion equipment and efficient materials handling systems. The new factory has a capacity of 6 million litre p.a.

## Powder coatings plant

The Valentine Varnish & Lacquer Co. Ltd have opened a new powder coatings production plant in West Drayton which uses Werner & Pfleiderer's twin-screw mixing extruders type ZDS-K53 which are designed to produce up to 200 kg of powder material per hour. The powder coating production plant also incorporates premixing, storing and feeding equipment upstream of the extruder and also powder cooling grinding, classifying and weighing equipment downstream.



Werner & Pfleiderer's ZDS-K53 twin-screw extruder for powder coatings

## European supply of pigments

E. I. du Pont de Nemours & Co. Inc. of America have announced that a range of pigments and aromatic products formerly manufactured and supplied from the U.S. will now be marketed in Europe and sold by its subsidiaries in European countries. The range includes Ti-Pure titanium dioxide for use in paints, lacquers, paper, ink etc, Cinquesia quinacridones and Krolor pigment colours for the paint and plastics industries.

## Paint company take over

Warren Plantation Holdings Ltd, owners of tea, coffee and rubber plantations have received £1m loan from the Finance Corporation for Industry to purchase Joseph Mason & Co. Ltd, who specialise in the manufacture of industrial paints.

## New distillation capacity

Carless Chemicals are spending over £35,000 in refurbishing an existing column shell to provide a distillation capacity of 40,000 tonnes per year and a separation efficiency of over 35 theoretical stages. Situated on Teesside, the plant has been designed to handle the separation and recovery of a wide range of organic mixtures such as glycol, glycol ethers, hydrocarbons, alcohols, esters, ketones etc.

## Cathodic electrocoating licence

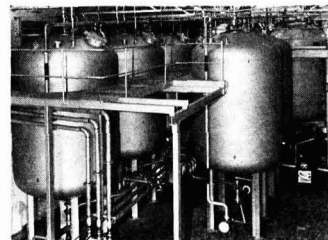
ICI Ltd have acquired a licence from PPG Industries Inc. of Pittsburg, U.S.A. for their cathodic electrocoat paint technology. The new agreement will enable ICI to offer a complete paint system for pretreatment and electropaint which is the most advanced in the world. PPG products will be available from ICI and its associates in the UK and Europe and will compliment ICI's expertise in both anodic and cathodic electrocoating and wide experience in metal pretreatment on which the overall performance of the complete paint system depends.

## U.K. agency

Samuel Banner & Co. Ltd have been appointed UK distributors for IMC Chemie GmbH, a subsidiary of International Minerals and Chemicals Corp. of Chicago, U.S.A. for the distribution of their range of nitro paraffins. Samuel Banner will be distributing a range of solvents and chemicals including the basic nitro paraffins, amino hydroxy compounds, antimicrobial agents, nitro hydroxy compounds and surface active agents for the paint, coatings, ink and chemical synthesis industries.

## Increased emulsion polymer activity

A substantial increase in capacity has just come on-stream at Scott Bader's emulsion polymer plant. Bulk storage capacity has been more than doubled and new drum filling and tanker loading points have been installed adjacent to the bulk storage area. The capacity of the plant has also been increased by the addition of a further reactor which has recently been brought on-stream.



The new installation at Scott Bader's Wollaston plant

## Consulting service

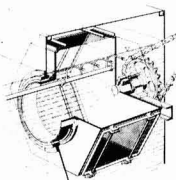
The new technical and marketing consulting service to assist foreign exporters of raw materials and licensors of technology to the coatings, synthetic resins and allied

industries in the USA has been set up, called Vista Associates. The consulting service has contacts in industry, government, trade press etc. in the American market.

## New products

### Rotating filters

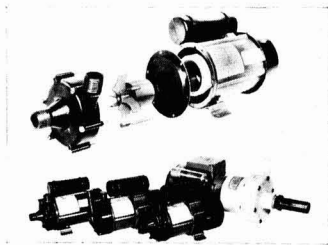
Otto Dürr has available a new rotating filter consisting of a hexagonal drum around which are mounted filter screens of between 200 and 400  $\mu\text{m}$ . Dirty fluid flows from the outside through the screens into the inside of the drum from where the filtered fluid flows into the clean tank. The filter is rotating all the time and has the effect of causing the trapped dirt to be dislodged and fall into the dirty tank, settling on the bottom as sediment. The new equipment is particularly useful in industrial washing machines where pollution of the washing solution can cause serious problems.



The rotating filter which is situated between the dirty and clean tanks

### Encapsulated magnetic pump

Totton Electrical Sales Ltd has available a new encapsulated magnetic pump (EMP) designed to handle corrosive fluids. The new high energy magnetic material Hera, which gives twice the power of conventional ceramic magnets, has been incorporated into the latest design enabling improvement in the gap tolerance between the two magnets which operate each pump.



The new EMP's from Totton Electrical Sales Ltd

### New pigment dispersions

The Bee Chemical Co. (UK) Ltd has available a new range of universal pigment dispersions (UCD) which are claimed to be compatible with all nonaqueous industrial finish vehicles. The use of UCD is claimed to cause a dramatic cutback in inventory, faster order and sample response, and gives products flash points above 32°, with no detractor from paint film properties.

### New spray respirator

3M have available a new valveless light-weight disposable respirator which offers protection against all paint formulations excluding those containing hardeners. The respirator weighs only 2 oz and the entire respirator is contained in the filter, thus removing the necessity of cleaning.



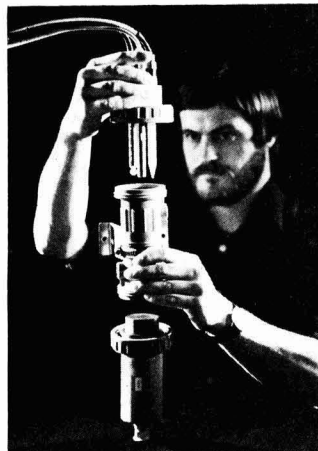
The disposable 8711 spray paint respirator from 3M

### UV-Visible spectroradiometer

Glen Creston Ltd have available the Model 741 portable spectroradiometer specifically designed for measuring ultraviolet spectral irradiance of sunlight, solar simulators and other UV sources. The design and selection of components are optimised for accurate spectral measurements over the 250 to 400 nm wavelength region.

### Ultrasonically cleaned pH meter

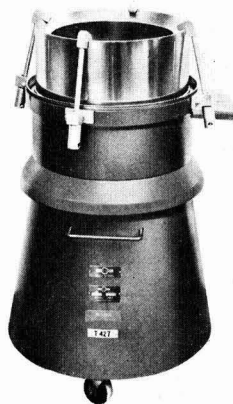
Siemens AG have introduced a new maintenance-free flow-type pH meter with ultrasonically cleaned electrodes which is particularly suitable for use with supersaturated solutions as crystalline precipitation or deposits of emulsifiable organic substances cannot foul the electrodes.



Siemens' new continuous pH meter with ultrasonically cleaned electrodes, which prevent fouling due to crystallisation or organic deposits

### New high speed strainer

Fussell Finex Ltd has introduced a heavy duty version of the well established high speed Finex 22 unit to meet the increased demand from the vinyl coating and paint industries for high capacity, ultra robust vibratory strainers. Driven by a standard or flameproof 2800 rpm motor via flexible coupling, the independent vibrator is fully adjustable for pitch and amplitude, an important feature when handling thick emulsions and thixotropic paints.



The Russell Finex 22 heavy duty high speed strainer

### New bodying agent

Cole Chemicals Ltd has available from the Troy Chemical Corporation, USA, a new additive called Trokyd 42BA which is particularly effective in correcting low viscosity in ready-made batches of oil-based paints, as it works by bonding directly with the vehicle, thus reducing the risk of causing flocculation. It builds a non-thixotropic viscosity rapidly, and can be used in gloss paints as well as undercoats without affecting the appearance.

## Conferences, courses etc

### Fouling—Science or art?

The Institute of Corrosion Science and Technology and the London and South-Eastern branch of the Institution of Chemical Engineers are organising a conference to be held at the University of Surrey on 27-28 March 1979 with the title "Fouling—Science or art?" which will cover fouling in industrial plant.

### New publications

The Ceramic Colours Division of Degussa, has published two new information bulletins on crinkle enamels used in the decoration of glass, and on dusting golds which are used in the decoration of porcelain, glass and enamel. Both bulletins are available in German and English.

### Toixide publications

Toixide International have published a booklet listing the publications available from them describing their ranges of products.



The OCCA Exhibition, which is known as the international focal point for technical and commercial display and discussion in the surface coatings industries, is the most important annual event of its kind in the industries, and it offers an unparalleled opportunity for personnel in the manufacturing industries to meet and discuss their requirements with their counterparts in the supplying industries.

Many young technologists and scientists who visited earlier Exhibitions have now risen to high positions within their organisations, and the advantage to exhibitors of keeping in constant contact with them needs hardly be stressed.

The thirty-first annual Exhibition organised by the Association, OCCA-31, will be held at Alexandra Palace, London on the following dates:

Tuesday 3 April .. 09.30 to 17.30 hrs.  
Wednesday 4 April 09.30 to 17.30 hrs.  
Thursday 5 April .. 09.30 to 17.30 hrs.  
Friday 6 April .. 09.30 to 16.00 hrs.

Already, support for the Exhibition has been received from many organisations both from the UK and overseas countries, comprising applications for space from organisations new to the exhibition as well as established exhibitors. The closing date for applications to exhibit is given as 31 October 1978, and during November the first allocation of space will take place to applications registered before that date.



Visitors to the OCCA-30 Exhibition came from over 50 countries and admissions by season ticket of over 10,000 were recorded. Right: A view of the Association's Information Centre at the OCCA-30 Exhibition

# OCCA-31 Exhibition

Alexandra Palace, London, 3-6 April 1979

The international focal point  
for the  
surface coatings industries

Good support for OCCA-31 from  
many countries

Applications for space received after the closing date will be considered, and allocated any space available after the initial allocation has taken place, but organisations wishing to take space at the Exhibition are urged to ensure that their applications are registered as soon as possible so that any preferences they may have as to stand size, shape and position may be carefully considered.

colour will be used from north to south and the yellow colour from east to west.

Any organisation wishing to receive further details of OCCA-31 should write to the Director & Secretary of the Association at the address on the Contents page to receive a copy of the Invitation to Exhibit and Application form.



## Theme of the Exhibition

The aim of the Exhibition is the presentation of technical and commercial information relating to advances in the surface coatings industries. The Committee stipulates that a technically trained person who has knowledge of the products displayed be available on the stand throughout the Exhibition.

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

## Motif for the Exhibition

The motif, designed by Robert Hamblin, emphasises the unique aspect of the OCCA Exhibitions, which annually provide an international focal point for the surface coatings industries. In 1978, exhibitors were drawn from 16 countries and visitors from over 50 countries. The two main colours of the motif, green and yellow, will be incorporated on the facias of the stands and it is intended to organise complementary floral displays in the Exhibition Hall. The use of these colours will create a pleasing contrast as visitors move from corridor to corridor at the Exhibition, as the green

The interest shown in the OCCA-31 Exhibition as a direct result of the highly successful OCCA-30 Exhibition held in April this year has been considerable, and already companies have asked for larger stands than they have had in previous years. Additionally, several companies who have not previously shown at OCCA Exhibitions as well as some who were not able to be present at OCCA-30 have contacted the Association requesting that sites be reserved for them.

The Exhibition Committee was particularly pleased to see the large number of exhibits at OCCA-30 from companies new to the Exhibition, both from the UK and many overseas countries, and this emphasises the continuing importance of this annual Exhibition to the world surface coatings industry and demonstrates its international character. The number of stands at OCCA-30 was larger than at the Exhibition for several years, and the number of companies was also greater. It will be appreciated that an exhibitor may request a stand of the size to suit his requirements, and thus the Committee points out that it is possible for organisations to demonstrate their products in a cost effective manner; however, there is no restriction on the maximum size of stand an exhibitor may request, and exhibitors are now permitted to serve alcoholic refreshments to their visitors on the stands.

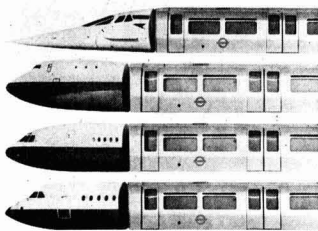
## Admissions at OCCA-30

Visitors to the OCCA-30 Exhibition are known to have come from over 50 overseas countries, and admissions by season ticket of over 10,000 were recorded at the entrance during the four days.

All Members of the Association receive a free season admission ticket with their copy of the Official Guide, and organisations exhibiting receive complimentary admission tickets to distribute to their customers. In addition, many trade associations are also sent tickets for distribution to their members. Thus, many visitors to the Exhibition have season admission tickets provided in advance.

However, an analysis\* of the tickets purchased at the entrance to the hall, sold mainly to visitors who have come as a result of the Association's widespread publicity rather than having been invited by exhibitors, shows that 34 per cent of these visitors came from overseas, with a significant proportion coming to the Exhibition from outside Europe. Particularly impressive amongst these visitors from overseas was the high proportion of top personnel: 61 per cent of them were managers, directors or owners of companies, with a 55/45 split between technical and commercial people.

# Fly the Tube



Take the Piccadilly Line to Heathrow Airport.  
It's the only way to fly.

With visitors from the United Kingdom, the split between technical and commercial personnel was 64/36; again there was a large proportion of senior management, although there was also a strong representation of section heads/group leaders and chemists.

These figures indicate the great value to organisations of exhibiting their products and developments at OCCA Exhibitions, which continue to attract each year large numbers of interested visitors from all over the world. The Exhibition provides a forum where exhibitors can discuss their products with the senior executives and technical personnel of many organisations whom they would not otherwise be able to contact, or to whom it would be prohibitively expensive to send representatives.

\*Sample of 1600 completed tickets taken from those purchased at the entrance to the Exhibition.



The west side of Alexandra Palace

## Facilities at Alexandra Palace

The Association has full use of the facilities at Alexandra Palace during the period of the Exhibition which include a restaurant, bars, a cafeteria and a private exhibitors' bar. Another facility which is of considerable benefit to those travelling to the Exhibition by car is the ample free car parking space within the Palace grounds.

For visitors travelling to the Exhibition on the underground system, the Association will once again be running a free bus shuttle service to and from the Exhibition, this year from Wood Green Station on the Piccadilly Line. The extension of the Piccadilly Underground Line to the Heathrow Central terminal was opened in late 1977, and this now provides a direct link for travellers arriving at the airport to both central London and to Wood Green Station and the bus shuttle service to the Exhibition.

## Improvements at Alexandra Palace

In July 1978 work was started on a comprehensive refurbishment of the facilities at Alexandra Palace, and much of this has now been completed. The floor of the Great Hall, in which the Exhibition is held, has been resurfaced and the walls and pillars have been redecorated. The West Corridor and the restaurants and bars have also been completely refurbished, and the work to the exterior of the building is scheduled to be completed by the time of the Exhibition next year. These improvements will add to the pleasantness of the venue, set in extensive parklands, and will provide an excellent setting for this international focal point for the surface coatings industries.

## Information in foreign languages

As in previous years, the Association will be circulating information leaflets in six languages which will contain application forms for those wishing to purchase copies of the Official Guide and season admission tickets before the Exhibition. Interpreters will once again be in attendance at the Information Centre at the Exhibition to assist foreign exhibitors and visitors with their queries.

## Official Guide

This unique publication contains descriptions of all companies and their exhibits at the Exhibition and is issued to each member of the Association at home and abroad as well as to all visitors to the Exhibition with their admission tickets. It is published several weeks in advance of the dates of the Exhibition to allow visitors the maximum opportunity to plan the itinerary of their visits. In 1978, for the first time, the Official Guide contained a chart classifying the products on show into the various types, and it is intended to produce a similar chart for the Official Guide to OCCA-31. This chart is invaluable to visitors, especially those who have only a limited amount of time available, as it provides a quick, easy reference of all the companies present who are displaying the products in which they are interested.



## Advertising facilities

Advertising space is available in the Official Guide, both to companies who will be exhibiting at the Exhibition, and also to other organisations. This important publication is constantly referred to both before the Exhibition and afterwards as a convenient record of the latest developments in the industry. Consequently, organisations wishing to take advertising space in the Guide should book their requirements as soon as possible in order to ensure a prominent position. Details of the advertising rates and media data are available from Mr D. M. Sanders at the Association's address.

## OCCA Biennial Conference 1979

*Stratford  
-on-  
Avon*

20-23 JUNE 1979 STRATFORD HILTON HOTEL

The next biennial Conference of the Association will be held at the Stratford-upon-Avon Hilton Hotel, Stratford-upon-Avon, from Wednesday 20 to Saturday 23 June 1979, and the theme for the Conference will be:

### The challenge to coatings in a changing world

It is envisaged that the papers to be presented will be concerned not only with the challenge of new materials and the substitution of traditional ones, new methods of

and Development Officer by writing in the first instance to the Director & Secretary at the Association's address on the Contents page.

Stratford-upon-Avon is a new venue for the OCCA Conference, and it is expected that it will prove popular and interesting to delegates. It is well connected by major roads and motorways, and there is a good service from London by coach. For the ladies attending the Conference, the social programme is hoped to include coach parties to nearby Warwick Castle, Leaming-



A view of Anne Hathaway's Cottage, situated close to Stratford-upon-Avon, which contains a museum of Shakespearian articles

construction and the problems of application, but also with the effects of new legislation (both national and international) and the sociological, climatic and leisure aspects of life in the last quarter of the twentieth century.

As on previous occasions, full preprints of the papers will be published for despatch to delegates in advance of the Conference, since it is the custom at OCCA Conferences for the author to outline briefly his paper, highlighting the points of interest, thus allowing much more time for general discussion with the delegates who will already have been able to familiarise themselves with the work by reading the preprints. It is important, therefore, that any person, whether or not a Member of the Association, who feels that a report of his work could form the basis of a suitable paper, should contact immediately the Honorary Research

and Coventry Cathedral. There will also be a visit to Oxford and Blenheim Palace. The Royal Shakespeare Theatre is close to the Stratford Hilton Hotel, and delegates will be able to attend performances in the evenings. It is also hoped to arrange a boat-trip along the River Avon. The Association's Annual General Meeting will be held on the Friday afternoon after the last Technical Session, and in the evening the Association will organise a Dinner Dance.

Forms for registration will be despatched to all Members of the Association attached to Sections in the UK, Ireland, and the General Overseas Section early in 1979, and any non-member wishing to receive a registration form should write to the Director & Secretary of the Association who will send details as they become available.

## Obituary

E. P. Gotham

Mr E. P. Gotham, an Ordinary Member attached to London Section, died on 17 September, aged 47 years, after a long illness.

Peter joined Ripolin Ltd in 1951 on being demobbed from National Service with the RAF, and was appointed Chief Chemist in 1955. He later became Works Director and gained the position of Technical Director in 1968. After leaving Ripolin in 1976, he joined Kenitex Ltd, but his health was already beginning to fail, and he left them after only a few months.

Peter enjoyed sailing and skiing, but his great pleasures were his work and reading. He had an intense interest in paint technology, and always insisted that commercial considerations were part of the technology. He was also a very kind man, and was keen to help others in their work. His encouragement to young chemists to look beyond a career at the laboratory bench was unfailing, and his dedication was an inspiration to them.

He will be missed by his many friends in the paint industry all over the world, and in particular by his ex-colleagues from Ripolin.

D. Timpson

## News of Members

Mr T. A. Fillingham, a founder member of the Hull Section, retired recently after a lifetime in the surface coatings industry; his last 15 years being with Marfleet Refinery Company Ltd. He served on the Hull Section Committee and was Chairman from 1949/50. He also served as a Vice-President of the Association from 1953/54 and is remembered for his dedicated contribution to the Scarborough Conference and the social events of the Hull Section. All his friends in the Section wish him a long and happy retirement.

Mr M. Hess, an Ordinary Member attached to the London Section and a Fellow in the Professional Grade, who is an internationally well known author in the field of paint technology and a consultant chemist, has been made an Honorary Life Member of the Association of Consulting Scientists, the British Section of the Union Internationale des Laboratoires Independants.

Mr K. R. W. Chitty, a former Chairman of the Thames Valley Section, has assumed responsibility for the Solvents Marketing Division as well as Resins, Elastomers and Urethanes at Shell Chemicals UK Ltd. This is the result of the restructuring of the company's activities, forming three divisions instead of four: Chemicals; Plastics; Solvents and Resins. The last, headed by Mr Chitty, embraces all activities of the former Solvents Division except glycol ethers marketing which has been transferred to the Chemicals Division.



## Bristol Section

### Annual Dinner Dance

Shown right at the Bristol Section Annual Dinner Dance held on Friday 31 March, a report of which appeared in the September issue of *JOCCA*, page 367, are (left to right): Mr G. H. Tennant (President, Birmingham Paint Varnish and Lacquer Club), Mrs Tennant, Mr Harper, Mrs E. N. Harper (Chairman, Bristol Section), A. McLean (President), Mrs McLean.

At the Dinner Dance, a Commendation award was presented to Mr D. N. Fidler on behalf of the Association.



## London Section

### Colour instrumentation symposium

The London Section in association with the London Region of the S.D.C. are organising a one-day symposium on Colour Instrumentation to be held at the Thames Polytechnic, Wellington Street, Woolwich, on Friday 17 November commencing at 10.00 a.m.

The charge for the symposium is £8.00 for Members and £12.00 for non-members, and applications should be made by 10 November to Dr R. C. Denney, Thames Polytechnic, Wellington Street, London SE18 6PF.

## Professional grade

At a meeting of the Professional Grade Committee held on 11 October 1978, the following Ordinary Members of the Association were admitted to the categories shown. The Section to which each Member is attached is shown in brackets.

### Fellows

Derek Arthur Bayliss (*London*)

Sigmund Leonard Davidson (*General Overseas—USA*)

Robert Philip Hanson (*Newcastle*)

Raymond Simon (*Irish*)

Ralph Peter Johannsen (*Cape*)

### Transfer from Associate to Fellow

Sunil Kumar Ghosh (*General Overseas—India*)

### Associates

Reginald Herbert Dennis (*London*)

Albert Henry Beckly (*London*)

George Derek Leathley (*Auckland*)

Rex Henry Hitchmough (*London*)

Bernd Scheinost (*Natal*)

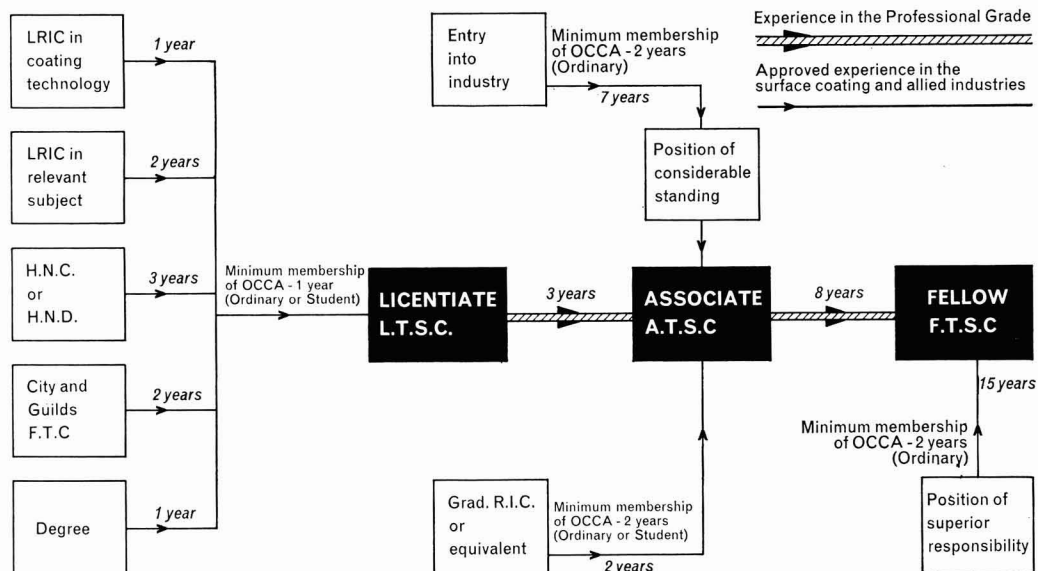
Albert Arend Spaargaren (*Natal*)

John Charles Bax (*London*)

### Courses for LicentiateShip

Following the publication in the August issue of *JOCCA* of a list of colleges offering courses in Paint Technology, able to offer help to Ordinary Members wishing to prepare dissertations for the LicentiateShip (LTSC), we have been informed that Slough College of Higher Education has facilities for preparing students for this. Those interested should contact Mr H. Bray, Slough College of Higher Education, Wellington Street, Slough SL1 1YG.

## Routes to the Professional Grades



Note: At present there is no restriction on Students up to 21; between 21 and 25 a certificate from the employer or college confirming the course being taken is required.

## Jordan Award

This award was instituted by the late Mrs M. R. Jordan in memory of her husband Dr L. A. Jordan, who was President of the Association 1947-49 and an Honorary Member, and who died in December 1964. The Committee invites applications for the fifth award of £100.

The rules of the Award are:

1. The Award will be made for the best contribution to the science or technology of surface coating by a Member of any nationality working in either the academic or industrial field who is under the age

of 35 at the date of application.

2. The final date for submission of applications will on this occasion be 31 December 1978 and it is hoped to present the award at the Stratford-upon-Avon conference in the following June.

3. The selection of the recipient of the Award will be made by a Committee under the chairmanship of the Association's Hon. Research and Development Officer.

4. There will be two methods of application. First, by the submission of a paper describing original work by the candidate which is offered for publication in the

*Journal* or has been so published during application. The alternative method will be by recommendation by a superior for work which for reasons of commercial secrecy cannot be published; in this case the candidate will be expected to submit a dissertation on a topic relating to his work and demonstrating his superior knowledge of the principles thereof. The Award is for individual merit and clear evidence of the candidate's own contribution will be required if a paper is offered under joint authorship.

5. Applications should be addressed to the Director & Secretary at the Association's offices.

## Forthcoming Events

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

### November

*Auckland Section:* "Talk and inspection of the Water Treatment Plant, Auckland Regional Authority at Titirangi, by Mr D. Payne. *Details to be announced.*

#### Thursday 2 November

*Newcastle Section:* "Recent advances in pigment dispersion and dispersion equipment" by Mr R. W. English and Mr J. Perkins, Mastermix Engineering Co. Ltd, at St. Mary's College, Elvet Hill Road, Durham, at 6.30 p.m.

#### Monday 6 November

*Hull Section:* "The safe use of solvents and the trend towards development of low aromatic grades" by G. Hicks of Esso Chemicals Ltd, at the George Hotel, Land of Green Ginger, Hull, at 6.30 p.m.

*Manchester Section:* "Quality control" by Mr Murray of Crown Decorative Products Ltd, at the Woodcourt Hotel, Sale, at 6.30 p.m.

#### Tuesday 7 November

*West Riding Section:* "The testing of hazardous chemicals with particular reference to the requirements of the Health and Safety at Work Act" by Mr D. H. Pullinger, Assistant Scientific Director, Bazelton Laboratory Europe Ltd, at the Mansion Hotel, Roundhay Park, Leeds 8, at 7.30 p.m.

#### Thursday 9 November

*Midlands Section—Trent Valley Branch:* "Effect of coatings on the quality of drinking water" by Dr N. P. Burman, at the Crest Hotel, Pastures Hill, Littleover, Derby, at 7.00 p.m.

*Scottish Section:*—"The academic-industrial interface". Joint meeting with ASDC, at Albany Hotel, Glasgow, at 7.30 p.m.

*Thames Valley Section:* "N.A.D.s. A progress report" by Mr M. Waghorn of ICI Paints Ltd, at the Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks, at 6.30 p.m. for 7.00 p.m.

### Wednesday 15 November

*Manchester Section: Student Lecture* "Additives improve emulsion paints" by Mr J. B. Clarke of Allied Colloids Ltd, at Manchester Literary & Philosophical Society, George Street, Manchester, at 4.30 p.m.

*Ontario Section:* "A review of current drier technology" by Mr L. Campay, at the Constellation Hotel, Toronto, at 6.00 p.m.

#### Thursday 16 November

*Midlands Section—Student Lecture:* "Mineral pigments through the ages" by Mr E. Hare, at the Calthorpe Suite, County Ground, Birmingham, at 6.30 p.m.

#### Friday 17 November

*London Section:* "Colour instrumentation". Day meeting in association with the Society of Dyers and Colourists, London Region, at Thames Polytechnic, Woolwich, at 10.00 a.m.

### Wednesday 22 November

*Scottish Section—Eastern Branch:* "Hydrocarbon resins" by A. Malatesta of Esso Chemicals Ltd, at the Murrayfield Hotel, 18 Corstorphine Road, Edinburgh at 7.30 p.m.

#### Friday 24 November

*Bristol Section: Ladies' Evening* "The colouring and decoration of pottery" by Mr A. J. Simkin of Blythe Colours Ltd, at the Royal Hotel, College Green, Bristol, at 7.15 p.m.

*Irish Section:* Annual Dinner Dance, at the Clarence Hotel, Dublin, at 8.00 p.m.

*West Riding Section:* Dinner Dance, at the Crown Hotel, Harrogate, *details to be announced.*

## December

#### Monday 4 December

*Hull Section:* "The manufacture of self adhesive labels" by R. Couch of Harlands of Hull Ltd. *Details to be announced.*

#### Tuesday 5 December

*West Riding Section:* "Pencil manu-

facture" by D. W. Tee of The Cumberland Pencil Company Ltd, to be held at the Mansion Hotel, Roundhay Park, Leeds, 8, commencing at 7.30 p.m.

#### Thursday 7 December

*Thames Valley Section:* "Accelerated weathering tests—objectives and choice of methods" by Dr M. L. Ellinger of Ault & Wiborg Paints Ltd, to be held at the Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks, commencing at 6.30 p.m. for 7.00 p.m.

*Scottish Section:* "Biodeterioration in surface coatings" by Dr D. Allsop of University of Aston to be held at the Albany Hotel, Glasgow, commencing at 6.00 p.m.

*Newcastle Section:* "Paint Research Association and the surface coatings industry" by J. H. Arendt of the Paint Research Association to be held at St. Mary's College, Elvet Hill Road, Durham, commencing at 6.30 p.m.

#### Friday 8 December

*Manchester Section:* "Long-life paint systems—sensible methods of test at last" by F. Timmins of British Rail Ltd, at Manchester Literary & Philosophical Society, George Street, Manchester, commencing at 6.30 p.m.

*Irish Section:* "Dispersion techniques" by R. Ward of Torrance & Sons Ltd, to be held at the Clarence Hotel, Dublin, commencing at 8.00 p.m.

#### Wednesday 13 December

*Ontario Section:* Ladies' Night, *details to be announced.*

#### Thursday 14 December

*Scottish Section—Eastern Branch:* "Scientific aspects of carton printing" by D. Lawson, from Wm. Thyne Ltd, at the Murrayfield Hotel, 18 Corstorphine Road, Edinburgh at 7.30 p.m.

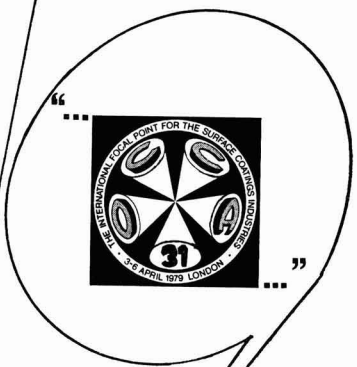
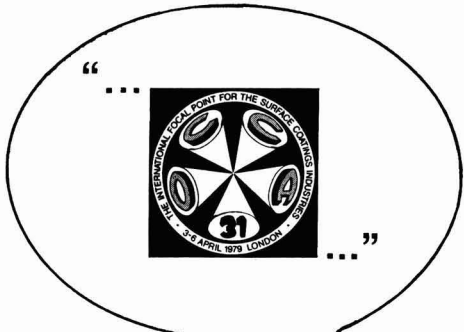
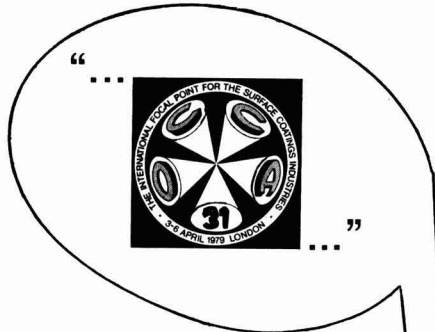
## 1979

### January

#### Wednesday 17 January

*Ontario Section:* Tour of MacLean Hunter by S. P. Wyszowski.

# THEY'RE ALL TALKING ABOUT MEETING AT THE OCCA EXHIBITION . . .



See page 434 for details



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**Shell Chemicals**

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### Urethane Chemicals

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### Base Chemicals

Ethylene, propylene, butadiene, dicyclopentadiene, benzene, toluene, solvent xylenes, ortho xylene, para xylene, cumene, styrene monomer, sulphur, Versatic 10, Dutrex and Shellflex grades, naphthenic acids, premium needle coke.

### Industrial Chemicals

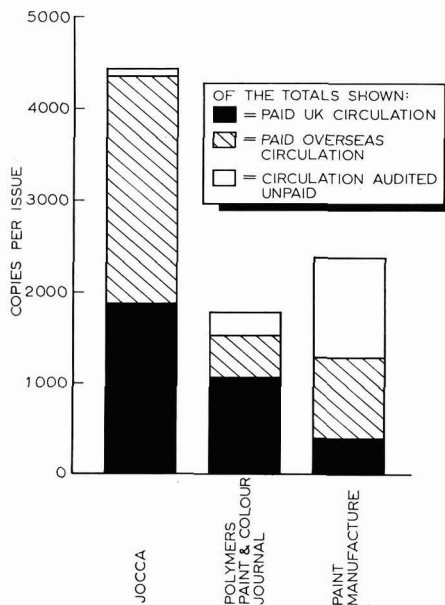
Chemical solvents, phenol, hydrocarbon solvents, detergent alkylates and alcohols, ethylene oxide, glycols and derivatives, plasticisers and plasticiser alcohols, epichlorhydrin, glycerine.

### Speciality Chemicals

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\*available in certain areas.

## Comparison of circulations of U.K. publications to the paint, printing ink and allied industries



(Reference Audit Bureau of Circulations Reviews, Jan-Dec 1977)

For full details of advertising in this, and other Association publications, contact D. M. Sanders, Assistant Editor

## Journal of the Oil and Colour Chemists' Association (JOCCA)

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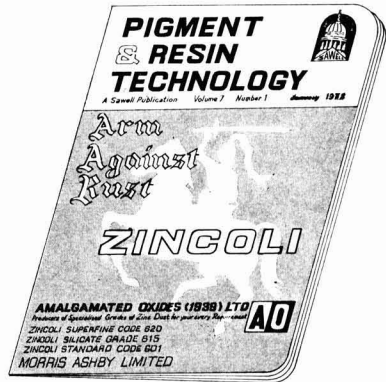
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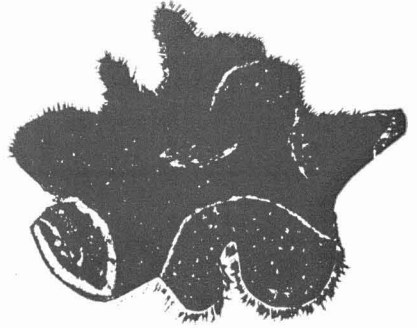
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## APPOINTMENTS VACANT

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## New R & D Centre Challenge West Midlands

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Please telephone for an application form, or write with full details to:  
Robert Kane,  
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Birmingham B4 7EU.  
Telephone: 021-359 6100.



## MISCELLANEOUS

### West Riding Section

#### 1978 Dinner Dance

The twentieth annual Dinner Dance of the West Riding Section of the Association will be held on Friday 24 November 1978 at the Crown Hotel, Harrogate. The charge for tickets will be £8.50 (inc. VAT).

Special accommodation rates have been arranged with the hotel, of £9.50 for a single room, and £16.00 for a double room. Applications for these rooms should be made direct to the Hotel Manager, mentioning that it is for the OCCA function.

Application for tickets for the Dinner Dance should be made by 4 November to Mr N. Cochrane, The Coach House, Red Holt, Hainworth Wood Road, Keighley, W. Yorks BD21 5BJ.

## SITUATIONS WANTED

#### Paint Executive,

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## JOURNALS FOR DISPOSAL

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Media data information and sample copies available from D. M. Sanders at the address on the Contents page.



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Swale Chemicals, a member of the Brent Chemicals International Group, develops, manufactures and markets inks and coatings for the paper, film and foil converting industry. Two additional chemists, each with at least 5 years' experience in the development of liquid inks and/or paper and board overlacquers, are needed to join the team at the Croydon Research Laboratory which deals with product development and provides technical service for the UK and overseas.

Applicants should be used to formulating successfully on their own initiative and be fully conversant with flexo and gravure ink technology relevant to flexible packaging, or with coatings for paper and board. These vacancies present opportunities to join a rapidly expanding company which provides the satisfaction of working on new developments from their inception to final customer approval.

Please write with details of qualifications and experience to:—

**Brian J. Green, Swale Chemicals Limited,**  
Swale House, 164 Thornton Road, Thornton Heath, Surrey, CR4 6BB.

## LEGAL NOTICE

### 'RFW' Grey Micaceous Iron Oxide

In the brochure entitled as above and made available to visitors to the Oil and Colour Chemists' Association exhibition held at Alexandra Palace, London from April 18th to April 21st 1978 and published by our company, C. E. Ramsden and Co. Ltd, in conjunction with Fergusson Wild and Co. Ltd, and distributed by H. Haeffner and Co. Ltd, a statement was made that 'RFW' Grey Micaceous Iron Oxide "represents an economic alternative to the traditional sources of supply for this type of material with the additional advantages of continuous product development and strict quality control".

It has been drawn to our attention and that of Fergusson Wild and Co. Ltd and H. Haeffner and Co. Ltd, that this statement could be taken to refer to Karntner Montanindustrie GmbH.

The three companies, C. E. Ramsden and Co. Ltd, Fergusson Wild and Co. Ltd, and H. Haeffner and Co. Ltd wish to make it clear that this statement was not intended to imply that Karntner Montanindustrie GmbH do not have continuous product development nor strict quality control.

They unreservedly withdraw the statement and apologise if any such interpretation has been put on the statement.

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Further details and application forms can be obtained from **Mr. M. Nixon, Chairman, Eastern Branch, 3E Lairds Hill, Cumbernauld, Glasgow G67 1HH.** Tel: 02367-25905 (Home) 02366-61221 (Business)

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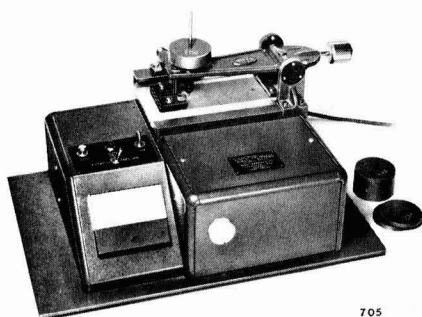
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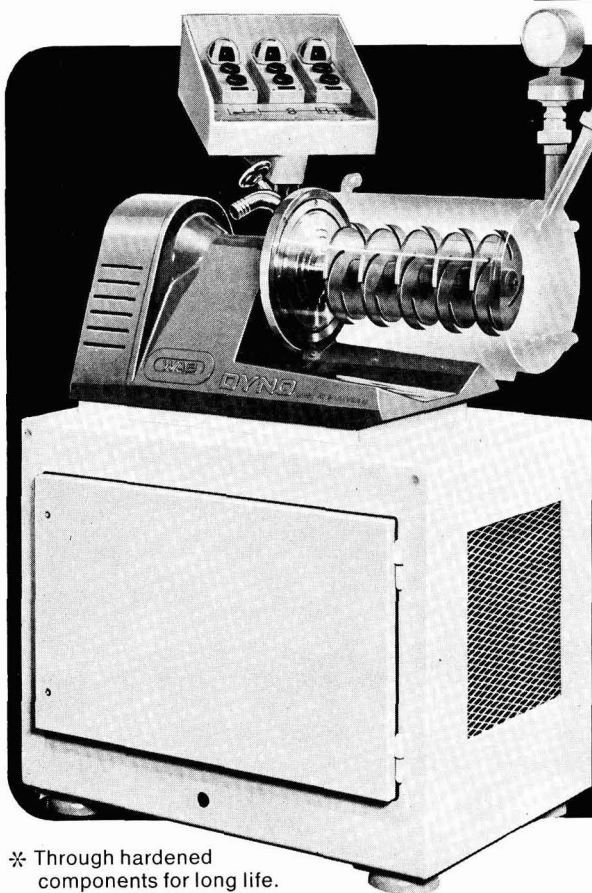
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