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**OWING TO THE EFFECTS OF THE EMERGENCY  
CONDITIONS ISSUES OF THE JOURNAL ARE BEING  
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**JOURNAL OF THE  
IL &  
COLOUR  
CHEMISTS'  
ASSOCIATION**

Some aspects of film formation in emulsion paints. Parts I and II  
*P. D. Aronson*

The determination of copper, mercury and arsenic in antifouling  
paints by means of X-ray fluorescence

*C. L. Miniussi and R. H. Perez*

# OIL & COLOUR



# CHEMISTS'

## ASSOCIATION



# TECHNICAL EXHIBITION

# OLYMPIA LONDON APRIL 1974

The motif for the twenty-sixth Technical Exhibition of the Oil and Colour Chemists' Association, designed by Robert Hamblin, shows the flags of the enlarged European Economic Community, linked by the initials OCCA. By converging on the flag of the United Kingdom, the motif symbolises the welcome extended by OCCA for many years to exhibitors and visitors, both from these countries and further afield, to its Exhibitions in London, one of the capital cities of the EEC.

**PLEASE COMPLETE AND RETURN THIS COUPON FOR A COPY OF THE OFFICIAL GUIDE TO THE EXHIBITION WHEN PUBLISHED IN FEBRUARY/MARCH 1974**

To: Director & Secretary, Oil & Colour Chemists' Association, Priory House, 937 Harrow Road, Wembley, Middlesex England, HA0 2SF  
We are interested in visiting the OCCA-26 Exhibition (23-28 April 1974 at Empire Hall, Olympia, London). Please send us a copy of the Official Guide when available. NOTE Each member of the Association will be sent a copy automatically.

**BLOCK LETTERS PLEASE**

**Pigments**

**NEW YORK, July 26** — No relief in sight for titanium dioxide supplies. Even with one major producing some profits in excess of 30%

**Pigments**

**NEW YORK, Sept. 27**—The titanium dioxide shortage was unchanged and frustrating, frustrating, nerve-wracking and serious to paint and paper makers to build up their inventories. Orders on final production is very tight and pressuring producers.

**Titanium dioxide**

The overall situation looks grim with a new 50,000 tonnes sulphate plant being closed by the Italian government because of the pollution problem. Before this occurred the situation was already bad due to the closure of sulphate plants in the US.

# M100 is the answer!

For months past, supplies of TiO<sub>2</sub> to the world's paint manufacturers have become increasingly more critical. And the global shortage of TiO<sub>2</sub> is likely to continue. Which is a very good reason why you should be considering

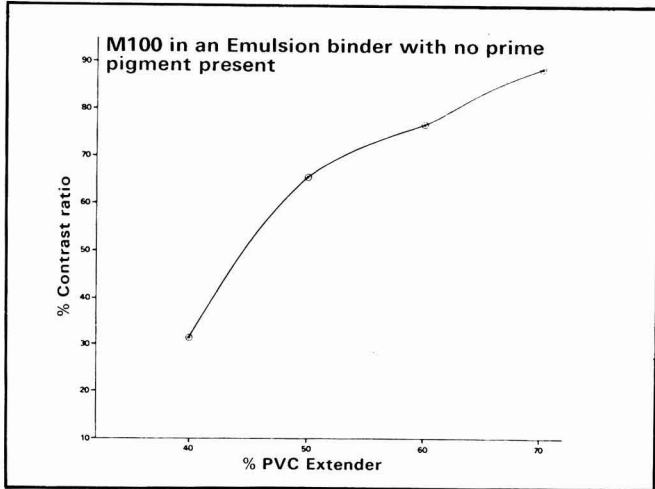
using ECC's M100 high-performance pigmenting extender to replace scarce and costly TiO<sub>2</sub>.

M100 is a high-brightness calcined clay which, compared to most other extenders, gives improved brightness, improved

opacity and better scrub and wash resistance – all at much lower cost than TiO<sub>2</sub>.

Two more big benefits: M100 will soon be supplied in convenient shrink-wrapped palletised form. And, from now on, you are guaranteed ample supplies of M100, thanks to a considerable recent increase in production capacity!

The graph shows the virtues of M100 in an emulsion binder containing no TiO<sub>2</sub>.



**NATURE**

A calcined china clay of high brightness.

**CHEMICAL PROPERTIES**

|  |                |
|--|----------------|
| Chemical Analysis                            | %              |
| SiO <sub>2</sub>                             | 52-53          |
| Al <sub>2</sub> O <sub>3</sub>               | 43-44          |
| Water soluble salt content (to BS 1795:1965) | 0-32%          |
| pH of water slurry at 10% solids             | 5.0±0.5        |
| Moisture content                             | 0.5% (maximum) |

**PARTICLE SIZE DISTRIBUTION**

|                      |                |
|----------------------|----------------|
| 300 mesh residue     | 0-10 (maximum) |
| Above 10 microns     | 10-0 (maximum) |
| Finer than 2 microns | 50-0 (minimum) |

**PHYSICAL PROPERTIES**

|  |                       |
|--|-----------------------|
| Brightness                                       |                       |
| Dry, reflectance at 4570 Å                       | 91.5 ± 1.0%           |
| Particle shape                                   | X-ray amorphous       |
| Refractive index                                 | 1.60                  |
| Oil absorption (spatula rub-out to BS 1795:1965) | 49.0                  |
| Water absorption (spatula rub-out)               | 55.0                  |
| Specific surface area                            | 8.5 m <sup>2</sup> /g |
| Hardness (Mohs' scale)                           | 4.0                   |
| Specific gravity                                 | 2.5                   |



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## Transactions and Communications

# Some aspects of film formation in emulsion paints. Part I.\*

By P. D. Aronson

Tioxide International Limited, Central Laboratories, Portrack Lane, Stockton-on-Tees, Teesside, TS18 2NQ

### Summary

The work described in this two-part paper has been undertaken to gain a better understanding of the processes involved during drying of latex paint films.

Difficulties of poor film formation may occur if the total environment in which the paint dries is unsuitable.

Such difficulties arise most frequently when a formula is changed or "improved", and the first part of this paper reviews some of the ways in which a given formula can be altered to increase its opacity.

It is suggested that there are at least six aspects to consider before a change is made, and the influence of each on opacity is discussed, supported by experimental results.

### Keywords

*Types and classes of coatings and allied products*  
emulsion paint

*Processes and methods primarily associated with drying*  
or curing of coatings  
film formation

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

*Bulk coatings and allied products*  
pigment volume concentration

## Quelques aspects de la formation des feuillets de peintures-emulsion. Première Partie.

### Résumé

L'étude décrite dans cet exposé à deux parties a été entreprise afin de gagner une meilleure compréhension des processus qui se passent pendant le séchage des feuillets de peintures émulsion.

Les difficultés à cause d'une formation de feuillet défective peuvent se produire dans le cas où l'environnement global reste inconvenable au cours du séchage du feuillet.

Telles difficultés se mettent en évidence le plus fréquemment

lorsque l'on modifie ou améliore la formule. Dans la première partie de cet exposé on passe en revue certains des moyens par lesquels une formule donnée peut être modifiée afin d'augmenter son opacité.

On suggère qu'il y a au moins six aspects à être considérés avant que l'on fasse aucune modification, et on discute, à l'aide des résultats expérimentaux, l'influence qu'exerce chacun d'eux sur l'opacité.

## Einige Gesichtspunkte Betreffend die Filmbildung bei Dispersionsfarben—Teil I

### Zusammenfassung

Die in dieser, in zwei Teile zerfallenden Abhandlung, beschriebenen Arbeiten wurden unternommen, um ein besseres Verständnis für die mit dem Trocknen von Filmen aus Latexfarben zusammenhängenden Vorgänge zu gewinnen.

Sich durch schlechte Filmbildung äussernde Schwierigkeiten können dann eintreten, wenn die Umgebung, in welcher der Farbfilm trocknet, dafür gänzlich ungeeignet ist.

Solche Schwierigkeiten entstehen am häufigsten, wenn ein Rezept

geändert oder "verbessert" wird. Der erste Teil der hier beschriebenen Abhandlung betrachtet einige der Schritte, mit deren Hilfe eine gegebene Rezeptur zum Zwecke einer Opacitätsverbesserung geändert werden kann.

Es wird vorgeschlagen, dass zumindest sechs Gesichtspunkte in Betracht gezogen werden müssen, ehe eine Änderung vorgenommen wird; die Einwirkung einer jeden auf die Opazität wird besprochen und mit experimentellen Resultaten belegt.

## Некоторые аспекты образования пленок в эмульсионных красках. Часть I.

### Резюме

Работа описанная в настоящей статье, в двух частях, производилась с целью получить более хорошее понятие о процессах происходящих во время сушки латексоподобных красочных пленок.

Трудности связанные с плохой формацией пленок могут иметь место если общая окружающая обстановка, в которой краска высыхает, является неподходящей.

Такие трудности всего чаще возникают когда меняется или «усовершенствуется» формула, и первая часть настоящей статьи анализирует некоторые методы при помощи которых заданная формула может быть изменена с целью повышения непрозрачности.

Отмечается что следует принимать во внимание по крайней мере шесть аспектов, до осуществления перемены и обсуждается влияние каждого из них на непрозрачность, с подтверждением экспериментальных результатов.

\*First presented to the West Riding Section's Seminar on "Future trends in surface coatings", 3-4 September 1970.

## Introduction

Ref. 1-12

There are two properties demanded of a latex paint when it dries. First, it must form an integrated film; secondly, it must be opaque. Obvious as these points may be, it is important that both are borne in mind—particularly, when devising new formulations for future products. In what ways are the paint formulae for the next decade likely to differ from those currently in use?

Past progress and present trends<sup>1-3</sup> in technology seem to indicate that one way in which emulsion paints of the future will differ is in having greater opacity, approaching the ultimate of complete and uniform opacity in one coat, for both interior and exterior types of paint.

Paint manufacturers and suppliers of raw materials alike have a major part to play in the development of such high-opacity formulations, which in addition need improved application properties and longer life at the same (or even lower) cost.

The flow diagram shown in Fig. 1 indicates broadly how the opacity of an emulsion paint may be improved. The diagram has been divided into two areas marked *A* and *B*. In area *A*, the left-hand part contains a box representing a standard paint formula ("Present emulsion paint") which may be altered to gain higher opacity in at least six different ways. When manufactured, the modified formulation ("New wet paint") will yield, by the process of film formation, a dry paint film having better optical performance.

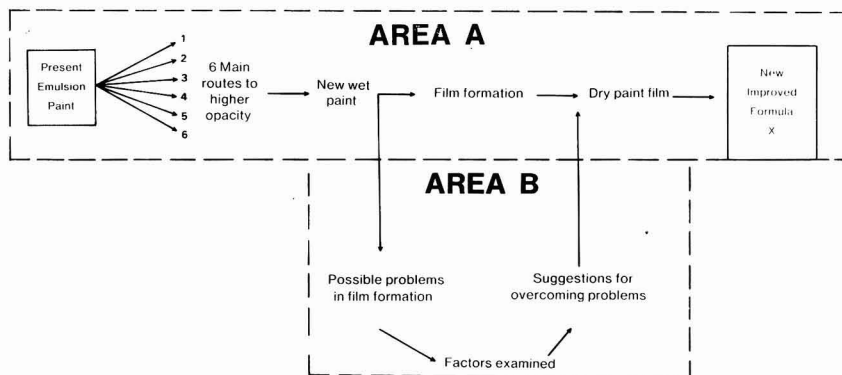


Fig. 1. Flow diagram: improving opacity in an emulsion paint

It is just possible that in addition to higher opacity, other aspects of the new paint—cost, application, flow, levelling, storage stability, scrub resistance—may be satisfactory. Unfortunately, it is also possible that in developing higher opacity, difficulty in forming an adequate film may arise (area *B*). The author has examined the main factors that influence film formation, and the principles of paint formulation that may help resolve difficulties of film formation in latex paints are reviewed in this paper.

Although much work on the subject of film formation, particularly with unpigmented latices, has already been published,<sup>4-12</sup> there remain many gaps to be filled in the understanding of what happens when paint films dry. Some

of the features of film formation in latex paints have been studied, and in particular those that relate to the drying process and the nascent film, and some of the changes that take place at this time in different formulae have been observed using relatively new interference-microscope techniques.

The influence of composition on opacity is considered here (area *A* of the flow diagram); the second part of the paper (page 66) includes a discussion of how changes in the formulation may affect the process of film formation (area *B* of the flow diagram).

## Influence of formula on opacity

There are many ways in which the opacity of a latex paint may be increased. As suggested in Fig. 1 (on the left of area *A*), there are at least six main ways of doing this:

1. Greater percentage of titanium pigment at same total pigment volume concentration (PVC).
2. Higher opacity grade of titanium pigment.
3. Different extender grade or type.
4. Increase in total PVC.
5. Coarser particle size emulsion.
6. Thicker paint film.

Each of these routes will be considered.

### Greater percentage of titanium pigment at the same total PVC

The opacity of a latex paint increases with increasing titanium dioxide ( $\text{TiO}_2$ ) volume concentration, up to maximum opacity (100 per cent contrast ratio). As with other types of coating, this relationship is not linear<sup>13, 14</sup> but, for the grade of  $\text{TiO}_2$  selected here (Type IV), it follows the shape of the curve shown in Fig. 2, where contrast ratio at a fixed spreading rate of  $15\text{m}^2\text{ l}^{-1}$  (approx.  $80\text{yd}^2\text{ gal}^{-1}$ ) is plotted against volume concentration of titanium pigment. These results were derived from paints which contained  $\text{TiO}_2$  only, without extender, and could be useful in developing formulae for glossy latex paints. There is a rapid improvement in opacity



up to 85-90 per cent contrast ratio, but beyond that region the pigment functions less efficiently due to overcrowding of the particles.

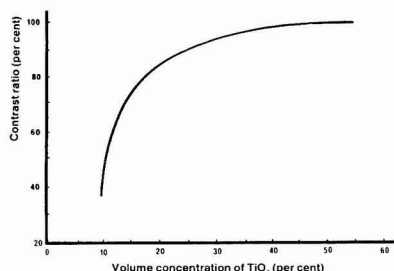


Fig. 2. Contrast ratio versus PVC in unextended emulsion paints

The relationship between titanium pigment level and opacity in those systems which contain extender is of more practical value to the emulsion paint chemist. Fig. 3 shows this relation in simple paints, extended with whiting to total PVCs of 40, 50, 60 and 70 per cent, with increasing levels of titanium pigment. (Emulsion *A* was used—see Table 1). Full details of the formulae used may be obtained from the author, but they were carefully derived by computer and space does not permit their inclusion in full here. As an

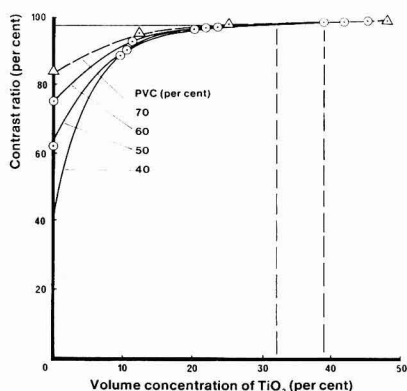


Fig. 3. Contrast ratio versus titanium dioxide volume concentration

example of the way in which the paints were formulated and modified to accommodate increases in PVC, formulations with PVCs ranging from 40 to 70 per cent at 20 per cent  $\text{TiO}_2$  (by weight) are detailed in Appendix A.

These formulae, and others similar but at different  $\text{TiO}_2$  levels, were used to prepare latex paints in the laboratory. Contrast ratios, again at a fixed spreading rate of  $15\text{m}^2\text{ l}^{-1}$ , were measured by a standard procedure and together with PVC and  $\text{TiO}_2$  volume concentration values (see Appendix A), were used to plot the graph shown in Fig. 3. The lowest volume of  $\text{TiO}_2$  required for a given contrast ratio in this type of formula can be read off from the curves in Fig. 3. For example, a contrast ratio of 98 per cent (which in practical terms represents complete opacity\*) requires 39 per cent  $\text{TiO}_2$  by volume at a total PVC of 40 per cent, in this system. This decreases to about 32 per cent  $\text{TiO}_2$  when the PVC is increased to 70 per cent.

Considered in other terms, on a weight/weight basis, a 98 per cent contrast ratio corresponds in these formulae to about 35 per cent  $\text{TiO}_2$  at 40 per cent PVC and 25 per cent  $\text{TiO}_2$  at 70 per cent PVC. That is approximately  $490\text{g l}^{-1}$  ( $5\text{lb TiO}_2\text{ gall}^{-1}$ ) in the first case and  $360\text{g TiO}_2\text{ l}^{-1}$  ( $3.5\text{lb gall}^{-1}$ ) in the second.

At 0 per cent  $\text{TiO}_2$ , the contrast ratio of the paint at 50 per cent PVC is considerably greater than that at 40 per cent PVC. This is a consequence of the phenomenon of dry hiding, and indicates that the critical PVC has been exceeded at 50 per cent in this system. The increase in dry hiding becomes proportionately less as the PVC is made higher: this suggests that there are less voids present in the dry film and that the extender and latex pack more uniformly at higher PVCs.

The most common reason for increasing the total PVC is to reduce the raw materials' cost (RMC), whilst still maintaining the opacity level; however, it must be asked what happens to the RMC when PVC is raised, if the opacity level is also increased? One interesting answer is indicated in Fig. 4, which is a plot of RMC versus increasing  $\text{TiO}_2$  level (and hence against increasing opacity). This shows that paints pigmented at a total PVC of 70 per cent are still lower in cost, over the range of  $\text{TiO}_2$  concentrations examined, and have higher opacity than corresponding paints at 40 per cent PVC, made with the same extender and emulsion although they contain the same volume of titanium pigment

Table 1  
Characteristics of emulsions used in PVC ladder

| Emulsion | Type                 | Non-volatile (per cent) | Minimum film forming temperature ( $^{\circ}\text{C}$ ) | Particle size ( $\mu\text{m}$ ) | Stabilising system               |
|----------|----------------------|-------------------------|---|---------------------------------|----------------------------------|
| A        | Va/ethylene          | 54                      | 6   | < 0.3                           | Mainly surfactant                |
| B        | 100 per cent acrylic | 50                      | 8   | 0.3                             | Part colloid/<br>part surfactant |
| C        | Styrene/acrylic      | 50                      | 10  | < 0.2                           | Mainly surfactant                |
| D        | Styrene/acrylic      | 50                      | 22  | 0.1                             | Mainly surfactant                |

\* A contrast ratio of 100 per cent theoretically denotes complete opacity, but a tolerance of 2 per cent is normally allowed for the human eye, implying that 98 per cent would be adequate.

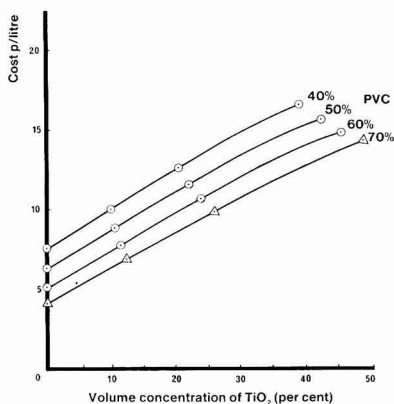


Fig. 4. Raw material cost versus titanium dioxide volume concentration

In this comparison, raw material costs at 70 per cent PVC are some 25 to 50 per cent lower than at 40 per cent PVC, the actual amount depending upon TiO<sub>2</sub> volume concentration.

#### Higher opacity grade of titanium pigment

Several grades of titanium dioxide which impart higher opacity in emulsion paints have been especially developed in recent years by pigment manufacturers. Normally, this higher opacity is achieved by applying a greater volume of silica and alumina to the TiO<sub>2</sub> core than is found with more conventional grades of titanium pigment.

The more voluminous coating of a typical special grade (*Tioxide R-XL*) compared to that of a general-purpose grade (*Tioxide R-CR2*) is clearly evident in the electron micrographs of Fig. 5. It is thought that the special pigments develop their superior optical properties by preventing flocculation of TiO<sub>2</sub> during film formation, thus leaving discrete scattering centres within the film. The prime particles of pigment (crystallites) which constitute the scattering centres, have a larger size (about 0.25 $\mu$ m) than those of a conventional grade, this size being better suited to the development of high opacity in emulsion paints. Having a lower specific gravity than usual (about 6 per cent lower), such special grades provide a slightly greater volume yield of paint for a given weight of pigment, as demonstrated by the two formulations detailed in Appendix B. This type may be used to replace conventional grades either by volume or

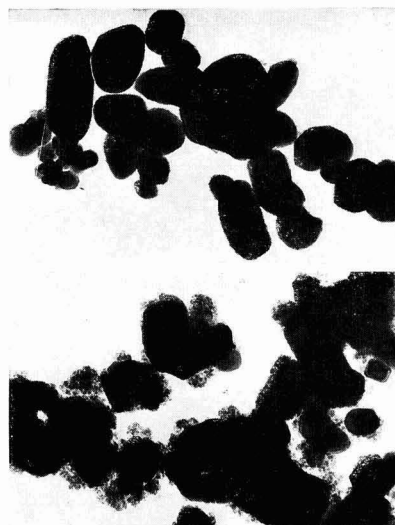


Fig. 5. Electron micrographs for a general purpose grade of titanium dioxide (top figure) and for a high opacity latex grade titanium dioxide (lower figure). 1.54 inches  $\equiv$  1 $\mu$ m

by weight and still give opacity improvement<sup>13</sup> at similar cost.

The main features of the two formulations detailed in Appendix B are summarised in Table 2. It shows that, when changing from a conventional grade to a high opacity latex grade of titanium pigment, the opacity (contrast ratio), volume yield and PVC each increases, but that the raw material cost per litre decreases slightly.

In the author's experience, scrub resistance is often improved but, on the other hand, use of heavily coated grades of TiO<sub>2</sub> in some formulations may result in more porous films and slightly poorer stain removal properties<sup>14</sup> as a consequence of their higher water demand. These deficiencies, however, can be compensated for by minor formulation changes and important advantages can still be demonstrated for this type of pigment.

#### Different grades of extender

The selection of a better grade of the same extender type—such as whiting or talc—with superior colour, higher brightness and smaller mean particle size, will give better appearance and generally produce higher opacity in the final paint film.

Table 2  
Main features of formulae in appendix B

| Property       |        | High opacity grade TiO <sub>2</sub> | Conventional grade TiO <sub>2</sub> | Change | Change (per cent) |
|----------------|--------|-------------------------------------|-------------------------------------|--------|-------------------|
| Contrast ratio | %      | 97.1                                | 95.4                                | +1.7   | +1.8              |
| Volume yield   | litres | 70.98                               | 70.49                               | +0.49  | +0.7              |
| PVC            | %      | 46.42                               | 45.34                               | +1.08  | +2.4              |
| Raw material   | p/l    | 12.63                               | 12.72                               | -0.09  | -0.7              |

### Different types of extenders

Extenders often differ in specific gravity, refractive index, water demand\* (this may also apply to the different grades of the same extender and particle shape).

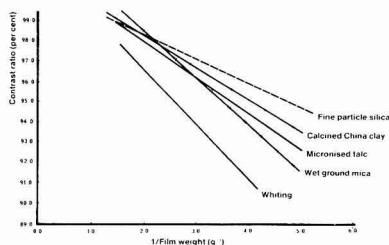


Fig. 6. Contrast ratio versus the inverse of film weight for different extenders at 48 per cent PVC

As with the special grades of  $\text{TiO}_2$ , a lower specific gravity leads towards a greater volume contribution in the dry paint, whilst a higher refractive index gives greater opacity. Increased water demand tends to reduce the critical PVC and this leads to even higher opacity as a result of dry hiding.

Lamellar extenders, such as talc, mica or china clay, tend to give greater opacity than nodular types,<sup>17</sup> (except for the fine particle extenders which are even better in this respect than lamellar types) and at the same time are better able to distribute the stresses which arise due to film contraction in the drying process. A comparison of the opacity given with different extenders (when replaced on an equal volume basis) at different film weights per unit area is shown in Fig. 6, where contrast ratio is plotted against the reciprocal of film weight. Over the range of contrast ratio considered here, this plot is essentially linear.

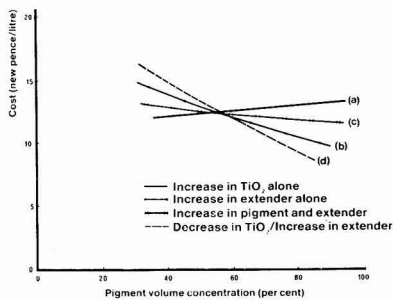


Fig. 7. Paint cost versus total PVC

It has been shown<sup>18, 20</sup> that fine particle extenders can improve opacity and brightness in emulsion paints. Normally, they are used to replace some of the titanium pigment with a view to reducing raw material costs at the same level of opacity. The economies of such a replacement are, however, closely linked to the type of emulsion and grade of pigment used in the formulation.

As with  $\text{TiO}_2$ , it is important to consider that paint properties other than opacity may be influenced by the use of fine particle extenders. There is evidence that porosity and film

integrity could be impaired. Ease of application, flow and levelling may also suffer at high levels (15-20 per cent replacement of  $\text{TiO}_2$ ) of fine particle extender, but exterior durability (chalk resistance) does not appear to be affected.

### Increase of total PVC

An increase of the total PVC in order to improve the opacity of extended latex paints does not always bring about a reduction in raw materials cost, and some ways of changing PVC are more economical than others.

There are at least four main ways of effecting this change:

- Increase in titanium pigment level alone,
- Increase in extender level alone,
- Increase in pigment and extender level simultaneously, and
- Decrease in pigment with increase in extender level.

The relation between total PVC and RMC of paints formulated by each of these routes is shown in Fig. 7.

(a) Increasing PVC by raising the  $\text{TiO}_2$  level will produce a rapid increase in opacity up to 85-90 per cent contrast ratio and a significant, but less rapid improvement up to a contrast ratio of about 98 per cent. Beyond this level the pigment functions even less efficiently because over-crowding of the  $\text{TiO}_2$  results in less light being scattered per unit weight of pigment, and the rate of change of opacity is very much reduced. This was shown earlier in Fig. 3.

If the  $\text{TiO}_2$  level is already at the optimum, increasing it by a relatively large amount to raise the opacity only slightly, therefore, becomes prohibitively expensive. (Curve (a) of Fig. 7).

(b) Keeping the  $\text{TiO}_2$  level constant and increasing the extender level does result in an increase of opacity and a decrease in RMC as would normally be expected. (Curve (b) of Fig. 7).

Even if the quantity of  $\text{TiO}_2$  in the original formulation was at the optimum level required for a contrast ratio of 98 per cent, according to Fig. 3, it is evident that the same percentage of  $\text{TiO}_2$  at a higher overall PVC will then become too high. This implies inefficient use of titanium pigment at elevated PVCs, resulting again in an unnecessarily high RMC.

(c) It is sometimes thought that in formulating an emulsion paint a specific blend of pigment and extender exists for best optical efficiency which holds for all PVC levels and which only alters when the pigment or extender grade are changed. The cost/PVC relation when  $\text{TiO}_2$  and extender are kept in constant proportion is shown as curve (c) of Fig. 7.

This approach, however, ignores the part played by the emulsion in the packing of the dried film, which does vary and depends upon (among other considerations) the emulsion particle size and overall PVC.

Again, referring to Fig. 3, less  $\text{TiO}_2$  is required at higher PVCs for 98 per cent contrast ratio and hence the pigment/extender ratio should alter with changing PVC.

\*Water demand is defined as the volume of water required by a pigment or extender to give a fluid paste, and is expressed in ml water per 100g of pigment.

Much of the laboratory work by paint chemists studying the influence of total PVC on various parameters (for example raw material cost or opacity) consists of preparing a large master batch of milbase which is let down with decreasing amounts of latex to give a "PVC ladder." This approach is certainly convenient, but in the light of this discussion on the efficient use of pigment, it is perhaps not entirely valid: it fails to take into account the real need for changing the ratio of pigment to extender when total PVC is changed.

(d) One way to determine the optimum  $\text{TiO}_2$  level for any given PVC is to plot contrast ratio (CR) versus  $\text{TiO}_2$  volume concentration (VC) at different levels of PVC, as in Fig. 3. The relationship between  $\text{TiO}_2$  VC and PVC is very nearly linear, and the percentage of  $\text{TiO}_2$  required to produce any desired contrast ratio may be read from the graph.

It was shown earlier that the levels of  $\text{TiO}_2$  required to give 98 per cent CR at 40 per cent and 70 per cent PVC were 39 per cent and 32 per cent by volume, respectively.

Using these values, the levels of  $\text{TiO}_2$  to give a CR of 98 per cent at intermediate PVC's have been derived by simple interpolation and the appropriate formulae computed and costed. RMC is plotted against total PVC as curve (d) on Fig. 7.

In this curve, the level of  $\text{TiO}_2$  decreases, at the rate derived by interpolation, as the PVC and extender levels increase. Of the four, this is the most economic way to increase total PVC, and because the opacity level is maintained (in this case at 98 per cent contrast ratio) this is also the most efficient route.

The overall effect of extender on RMC at different  $\text{TiO}_2$  VCs was found to be additive or subtractive depending on the particular extender(s) and latex used in the formulae.

Nonetheless, the relative positions of each of these curves will normally remain the same for different extenders and media, and the conclusion holds that the most efficient manner to increase total PVC is by route (d).

Although interior emulsion paints are frequently formulated with only small amounts of (and sometimes with virtually no)  $\text{TiO}_2$  at high PVCs, the call for greater opacity, the opportunities that are offered by the newer emulsions having much enhanced pigment binding capacity, and the eternal cry for stable costs all require a greater efficiency of  $\text{TiO}_2$  usage.

## Appendix A

Some of the paint formulae as used for Fig. 3; 20 per cent  $\text{TiO}_2$

|  | 1       | 2               | 3      | 4      |
|--|---------|-----------------|--------|--------|
|  |         | parts by weight |        |        |
| Tioxide R-XL                                       | 20.00   | 20.00           | 20.00  | 20.00  |
| Snowcal 6ML whitening                              | 14.07   | 18.48           | 22.26  | 25.54  |
| Five per cent Calgon PT solution                   | 2.72    | 3.07            | 3.38   | 3.64   |
| Three per cent Natrosol 250 MR solution            | 25.00   | 25.00           | 25.00  | 25.00  |
| Water  | 4.74    | 8.18            | 11.13  | 13.68  |
| Nuodex 321 Extra                                   | 0.12    | 0.12            | 0.12   | 0.12   |
| Copolymer emulsion "A"                             | 33.35   | 25.15           | 18.11  | 12.02  |
| Totals   | 100.00  | 100.00          | 100.00 | 100.00 |
| Pigment volume concentration, vol. per cent        | = 40.00 | 50.00           | 60.00  | 70.00  |
| $\text{TiO}_2$ volume concentration, vol. per cent | = 20.36 | 22.05           | 23.75  | 25.45  |
| Pigment/binder quotient, mass/mass                 | = 1.80  | 2.65            | 3.93   | 6.11   |
| $\text{TiO}_2$ /binder quotient, mass/mass         | = 1.05  | 1.37            | 1.86   | 2.68   |
| Relative density of paint                          | = 1.36  | 1.39            | 1.43   | 1.46   |
| Cost per kilo, new pence                           | = 9.20  | 8.20            | 7.33   | 6.59   |
| Cost per litre, new pence                          | = 12.52 | 11.47           | 10.52  | 9.66   |
| Non-volatile content of paint, mass per cent       | = 53.00 | 53.00           | 53.00  | 53.00  |
| Non-volatile content of paint, vol. per cent       | = 36.10 | 34.28           | 32.62  | 31.12  |

## Coarser particle size emulsions

These do increase opacity<sup>21</sup> but have the disadvantage of decreasing the critical PVC<sup>22</sup>. In addition, this route to higher opacity is unfavourable in terms of RMC compared with that using the finer particle-size acrylic, styrene/acrylic or olefin copolymers of today. For heavily-pigmented systems, it is important that emulsions with good hiding power be used if other film properties are to be maintained. Because the newer types of emulsion have superior pigment binding capacity, higher PVCs at lower cost may be attained without impairing other paint properties and sometimes without exceeding the critical PVC.

## Thicker paint film

The opacity of an emulsion paint improves as its spreading rate decreases and the film becomes thicker, because more of the incident light is scattered by the film. There are three main ways of changing a formulation so that more paint per unit area is applied in a single coat:

1. Increase total solids of the paint, adjusting the thickener type and level to maintain flow, levelling and application properties.
2. Reduce the ease of brushing with alternative colloids and extenders.
3. Use thixotropes (thixotropy inducing agents) such as organic titanates, organic zirconates, natural or synthetic swelling clays.

## Conclusions

Altering a given latex paint formula, by any of the six routes discussed, will result in a new wet paint that on drying should give a dry film with higher opacity. This modified product could conceivably be acceptable immediately with all its properties—such as opacity, application, flow, levelling, storage stability, scrub resistance, durability—at the desired level.

Difficulties may sometimes be experienced in obtaining satisfactory film formation of the new paint, however, on some substrates and in some environmental conditions. This aspect will be discussed in the second part of the paper.

[Received 19 July 1973]

## References

See Part Two of this paper on page 81.

**Appendix B****Conventional type of TiO<sub>2</sub>**

|  | Kilos (wet) | Litres (wet) | Kilos (dry) | Litres (dry) |
|--|-------------|--------------|-------------|--------------|
| Tioxide R-CR2                            | 21.00       | 5.185        | 21.00       | 5.185        |
| Microtalc AT1                            | 17.10       | 5.897        | 17.10       | 5.897        |
| Five per cent Calgon PT solution         | 4.60        | 4.600        | 0.23        | 0.230        |
| Five per cent Tergitol NPX               | 4.10        | 4.100        | 0.20        | 0.205        |
| Three per cent Cellosize QP4400 solution | 9.70        | 9.700        | 0.29        | 0.291        |
| Water                                    | 14.90       | 14.900       | 0.00        | 0.000        |
| Butyl carbitol acetate                   | 0.40        | 0.408        | 0.00        | 0.000        |
| Nuodex 321 Extra                         | 0.10        | 0.100        | 0.02        | 0.025        |
| Ten per cent ammonium hydroxide          | 0.60        | 0.600        | 0.00        | 0.000        |
| Vinyl acetate/acrylate copolymer         | 27.50       | 25.000       | 15.12       | 12.604       |
| Totals                                   | 100.00      | 70.490       | 53.97       | 24.437       |

|  |   |       |
|--|---|-------|
| Pigment volume concentration, vol. per cent          | = | 45.34 |
| TiO <sub>2</sub> volume concentration, vol. per cent | = | 21.21 |
| Pigment/binder quotient, mass/mass                   | = | 2.39  |
| TiO <sub>2</sub> /binder quotient, mass/mass         | = | 1.32  |
| Relative density of paint                            | = | 1.41  |
| Cost per kilo, new pence                             | = | 8.96  |
| Cost per litre, new pence                            | = | 12.72 |
| Non-volatile content of paint, mass per cent         | = | 53.97 |
| Non-volatile content of paint, vol. per cent         | = | 34.66 |

**High opacity latex grade of TiO<sub>2</sub>**

|  | Kilos (wet) | Litres (wet) | Kilos (dry) | Litres (dry) |
|--|-------------|--------------|-------------|--------------|
| Tioxide R-XL                             | 21.00       | 5.676        | 21.00       | 5.676        |
| Microtalc AT1                            | 17.10       | 5.897        | 17.10       | 5.897        |
| Five per cent Calgon PT solution         | 4.60        | 4.600        | 0.23        | 0.230        |
| Five per cent Tergitol NPX               | 4.10        | 4.100        | 0.20        | 0.205        |
| Three per cent Cellosize QP4400 solution | 9.70        | 9.700        | 0.29        | 0.291        |
| Water                                    | 14.90       | 14.900       | 0.00        | 0.000        |
| Butyl carbitol acetate                   | 0.40        | 0.408        | 0.00        | 0.000        |
| Nuodex 321 Extra                         | 0.10        | 0.100        | 0.02        | 0.025        |
| Ten per cent ammonium hydroxide          | 0.60        | 0.600        | 0.00        | 0.000        |
| Vinyl acetate/acrylate copolymer         | 27.50       | 25.000       | 15.12       | 12.604       |
| Totals                                   | 100.00      | 70.980       | 53.97       | 24.927       |

|  |   |       |
|--|---|-------|
| Pigment volume concentration, vol. per cent          | = | 46.42 |
| TiO <sub>2</sub> volume concentration, vol. per cent | = | 22.76 |
| Pigment/binder quotient, mass/mass                   | = | 2.39  |
| TiO <sub>2</sub> /binder quotient, mass/mass         | = | 1.32  |
| Relative density of paint                            | = | 1.40  |
| Cost per kilo, new pence                             | = | 8.96  |
| Cost per litre, new pence                            | = | 12.63 |
| Non-volatile content of paint, mass per cent         | = | 53.97 |
| Non-volatile content of paint, vol. per cent         | = | 35.11 |

# Some aspects of film formation in emulsion paints. Part II.\*

By P. D. Aronson

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## Summary

The second part of this two-part paper indicates how the mechanism of film formation may be influenced by changes of formula or environment. This mechanism has been studied by colour time-lapse cine photography. Use of novel interference microscope techniques has shown how stresses that develop during the drying process may be relieved by cracking; this also shows that cracks originate at paint film defects, which are commonly present both internally and on the surface of latex paints. In systems that do not

crack on drying, the stresses developed are evidently relaxed or redistributed. By simple experiment, a measure has been obtained of the residual stress in different dry paint films.

Some of the many factors influencing cracking are examined and from the information gathered and presented here, possible remedies to improve film formability can be suggested.

## Keywords

*Types and classes of coatings and allied products*  
emulsion paint

*Raw materials: prime pigments and dyes*  
titanium dioxide

*Processes and methods primarily associated with drying or curing of coatings*  
film formation

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

## Quelques aspects de la formation des feuillets de peintures-émulsion. Deuxième Partie.

### Résumé

Dans la deuxième partie de cet exposé on donne une indication de la manière par laquelle le mécanisme de la formation de feuillet peut être influencé par des changements de formule ou d'environnement. Ce mécanisme a été étudié au moyen de la cinéphotographie en couleurs où il s'agit des intervalles prédéterminés entre chaque pose. L'emploi des techniques nouvelles dans le domaine de la microscopie interférentielle a montré la manière par laquelle les forces qui se développent lors du processus de séchage peuvent être dissipées par la formation de craquelures; cette technique révèle que ces craquelures ont leur origine aux défauts du feuillet de peinture, qui sont présents très souvent soit à l'intérieure, soit

sur la surface des feuillets de peintures-émulsion. En systèmes qui n'ont pas de tendance à la formation de craquelures lors du séchage, les forces qui se développent sont évidemment relâchées ou réparties. Par une simple expérience on a obtenue une mesure de la force résiduelle dans de divers feuillets de peinture secs.

On considère certains des plusieurs facteurs qui exercent une influence sur la formation de craquelures et à partir des données que l'on a ramassées et ci-présentées, on peut proposer les remèdes éventuels pour améliorer la formation de feuillet des peintures-émulsion.

## Einige Gesichtspunkte Betreffend die Filmbildung bei Dispersionsfarben—Teil II

### Zusammenfassung

Der zweite Teil dieser (zweiteiligen) Abhandlung gibt an, wie der Filmbildungsmechanismus durch Änderungen in der Rezeptur oder in der Umwelt beeinflusst werden kann. Der Mechanismus wurde mit Hilfe farbiger Zyklus-Kinophotographie untersucht. Die Anwendung neuartiger Interferenzmikroskopiertechniken zeigte wie Spannungen, welche beim Trocknungsvorgang entstehen, durch Reißen entlastet werden können; dies zeigt ebenfalls, dass Risse an Anstrichfilm—Fehlstellen entstehen, welche allgemein sowohl im Innern von als auch an der Oberfläche von Latex-

farben vorhanden sind. In Systemen, die beim Trocknen nicht reißen, sind die entstandenen Spannungen offenbar gelockert oder weiter verteilt. Durch ein einfaches Experiment wurde ein Wert für die restliche Spannung in verschiedenen getrockneten Anstrichfilmen erhalten.

Einige der zahlreichen Faktoren, welche Reißen beeinflussen, werden geprüft und auf Grund der gesammelten und hier vorgelegten Information können mögliche Massnahmen zur Verbesserung der Filmbildung vorgeschlagen werden.

## Некоторые аспекты образования пленок в эмульсионных красках. Часть II.

### Резюме

Вторая часть настоящей статьи описывает каким образом механизм образования пленок может подвергаться влиянию изменения формулы или окружающей среды. Этот механизм изучался цветной промежуточной киносъемкой. Применение новой технологии интерференционного микроскопа показало каким образом напряжения, возникающие в течение процесса сушки, могут быть понижены растрескиванием; это также показывает что трещины образуются у дефектов красочной пленки, которые обычно находятся как внутри так и на поверхности латексоподобных красок. В системах которые не

растрескиваются при сушке, возникающие напряжения являются явно релаксационными или перераспределенными. Путем простого опыта получена мера для остаточных напряжений для различных сухих красочных пленок.

Рассматриваются некоторые из многих факторов влияющих на растрескивание и из полученной информации, здесь описанной, рекомендуются возможные средства для улучшения образования пленок.

## Introduction

As suggested in Part I of this paper, higher opacity in latex paints is currently being sought by the paint manufacturer. However, whilst higher opacity can be achieved by any of the

approaches discussed earlier, this property has no durable value unless a coherent and integral paint film is formed on drying.

Many factors influence the quality of the final film. The

\*First presented to the West Riding Section's Seminar on "Future trends in surface coatings", 3-4 September 1970.

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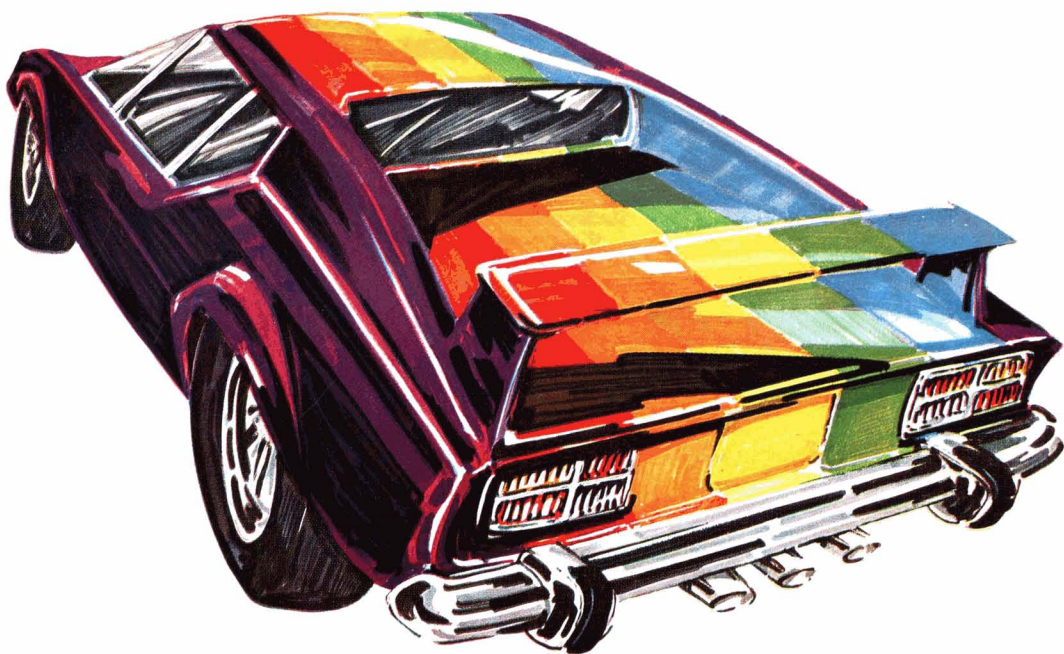
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most important of those controlling film formation in its early stages (the first 1 to 2 hours after application) are listed in Table 3, but not necessarily in the order of their importance.

Table 3

*Film formation—main factors*

1. Total pigment volume concentration
2. Latex
3. Titanium pigment
4. Extender
5. Internal stress
6. Drying rate
7. Film thickness
8. Temperature
9. Substrate porosity
10. Relative humidity

The first five of these parameters can be controlled by the chemist who formulates the paint: by modifying the total PVC, the type, the grade and the amount of latex, titanium

pigment, or extender, the paint formulator can also control to some extent the degree of internal stress residual in the paint film when it dries. These factors will now be discussed in turn and illustrated by appropriate experimental results.

**Factors under the control of the formulator**

*Ref. 11*

**Total pigment volume concentration**

Failure to form a coherent film on drying can lead to cracking. To demonstrate how the degree of cracking depends on PVC, drawdowns were prepared (wet film thickness 0.015in or 380 $\mu$ m) of simple latex paints at increasing total PVCs on glass plates (150mm  $\times$  100mm  $\times$  2mm) and allowed to dry in a constant temperature/humidity laboratory (21°C, 65 per cent RH). After drying, some of the paint films cracked, as shown in Fig. 8.

A useful way of rating such panels is one based on standards\* devised by the Netherlands Paint Research

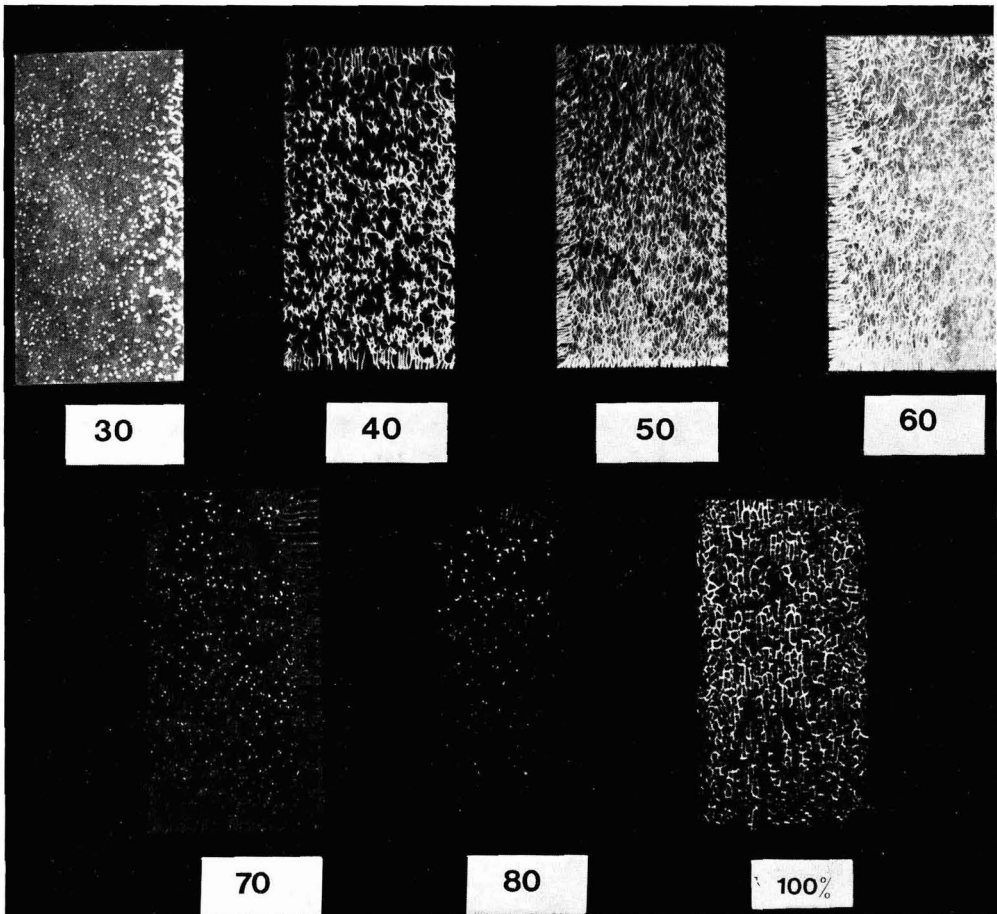
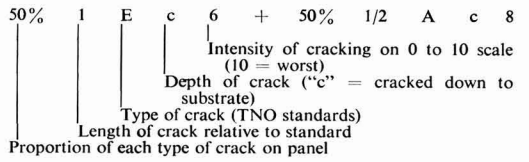


Fig. 8. Influence of PVC on cracking (Numbers in the white squares are percentage PVC)

\*Available in the UK from Elcometer Ltd, Droydsden, Manchester.

Association (TNO). With these standards, differences in crack length, type and intensity may be assessed. The three main types of fracture encountered in these simple latex (or "emulsion") paints are shown in Fig. 9. In the author's work, different types of crack were evident on the same panel: this is indicated in the crack rating values of Table 4, together with an estimate of the proportion of each type of crack on each panel. The results used for Table 4 are presented diagrammatically in Figs. 10A, B, C and D for greater clarity. Four emulsions, labelled A, B, C, D and detailed in Table 1, Part 1 of this paper, were used at each PVC (except at 100 per cent PVC, which represents the millbase and so contains no emulsion). As an example, a typical crack rating

(Table 4 "B" with 70 per cent PVC) is shown below, together with an explanation of each of the terms in the first half.



With reference to the differing results found with the four different emulsions, coalescing solvents were intentionally



Fig. 9. From left to right: Type A, Type E and Type J fractures, based on reference standards produced by Verfinstituut TNO, Holland

Table 4  
 Crack rating: PVC ladder with four emulsions

| PVC | Emulsion*             |                       |                          |                         |
|-----|-----------------------|-----------------------|--------------------------|-------------------------|
|     | A                     | B                     | C                        | D                       |
| 40  | 0                     | 0                     | 0                        | 1/10Ec1                 |
| 50  | 0                     | 1/20Ec1               | 0                        | (50%)1Ec10+(50%)1Jc10   |
| 60  | 1/10Ec2               | 1Ec8                  | (50%)1/2Ec9+(50%)1/8Ac9  | (50%)Jc10               |
| 70  | 1/5Ec4                | (50%)1Ec6+(50%)1/2Ac8 | (50%)1/3Ec8+(50%)1/8Ac1  | 1Jc10                   |
| 80  | 1/2Ec6                | (50%)1Ec5+(50%)1/2Ac6 | (50%)2/3Ec8+(50%)1/10Ac1 | (50%)1/2Ec8+(50%)1/2Ac9 |
| 90  | (50%)1Ec9+(50%)1/4Ac9 | (50%)1Ec4+(50%)1/2Ac8 | (50%)1Ec8+(50%)1/10Ac1   | (50%)1/2Ec9+(50%)1/2Ac9 |
| 100 | 2Jc10                 | 2Jc10                 | 2Jc10                    | 2Jc10                   |

\*See Table 1 (Part 1) for key to emulsion type.

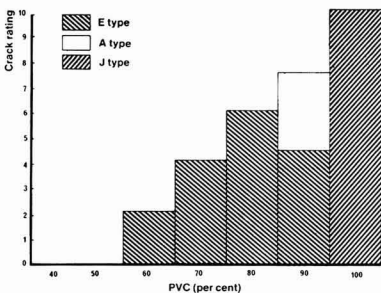


Fig. 10a. Crack rating versus percentage PVC for emulsion A

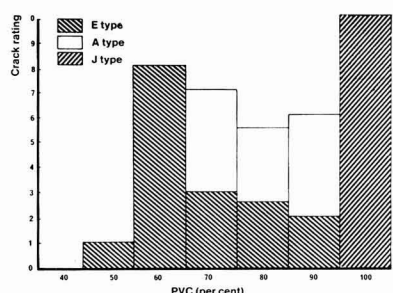


Fig. 10b. Crack rating versus percentage PVC for emulsion B

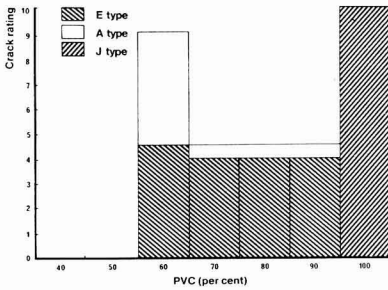


Fig. 10c. Crack rating versus percentage PVC for emulsion C

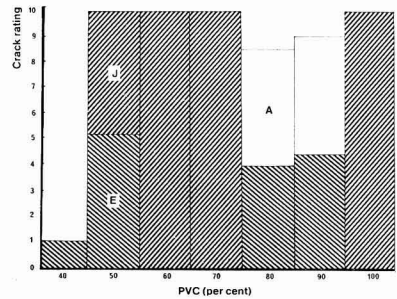


Fig. 10d. Crack rating versus percentage PVC for emulsion D

omitted from the paints so that a high intensity of cracking could be obtained at that temperature (20°C).

When developing full formulae for practical use, the recommendations made by the polymer manufacturers on type and level of coalescent should be followed, of course, in any given case. In this way the full potential of a polymer can be achieved safely.

Why does the intensity of cracking depend on PVC level? It is normally expected that at PVC values below the critical and at temperatures above the minimum film forming temperature (MFFT), most emulsion paints will dry to yield a coherent film. As suggested by many workers, such films are not entirely homogeneous. The author's work with a microscope has shown that in addition to surface defects (such as air bubbles and water globules), these films are likely to contain internal defects. These consist of holes, formed as a consequence of poor packing of pigment and extender.

A phenomenon termed "bridging" is evident around large extender particles; the bridges are believed to be composed of TiO<sub>2</sub> and binder. Such defects (vacuoles<sup>11</sup>) are evidently formed by the action of convection currents, which may be of the type responsible for the Bénard cell formation, commonly seen in the flotation phenomena of solvent-based paints. From a close examination of many hundreds of feet of cine film taken of emulsion paints drying under a microscope, it is envisaged that the following processes occur during paint film formation:

Water migrates to the paint surface prior to evaporation and carries with it the small TiO<sub>2</sub> and emulsion particles. Most of the TiO<sub>2</sub> particles appear to be in close proximity to the emulsion, and adhere to the advancing dry edge of paint, possibly by a charge-induced effect or by pigment-emulsion-pigment adhesion. Some of the particles are displaced, from the mass streaming through the extender matrix, to the sides of the "stream". Once this has begun, more and more particles are entrapped at the sides, and "bridge building" begins.

It may perhaps be likened to the way that twigs and leaves floating down a stream become stuck between rocks, and then act as sluices which catch other particles so that before long the whole stream becomes dammed.

Bridging is a curiously rapid hydrodynamic process and may be caused by localised concentration of surfactant (due to evaporation of water) resulting in pigment flocculation.

This isolates sections of the paint in such a way that they contain volumes having only small amounts of TiO<sub>2</sub> and hence develop into a film that on a microscopic scale is quite heterogeneous.

Evidence of this transportation of smaller particles is shown by observations of dilute emulsion paints in transmitted light, confirmed by electron micrographs of the edges of freeze-cracked paint films, which show an "icing layer" on the surface, and this layer appears to consist of a higher concentration of TiO<sub>2</sub> than normal. There is no sign in the micrographs of extender in the surface layer, indicating greater sedimentation of extender and greater mobility of TiO<sub>2</sub> during drying. Both of these aspects are illustrated in Figs. 11 (drying edge) and 12 (micrographs), taken from a cine study of paint film formation.

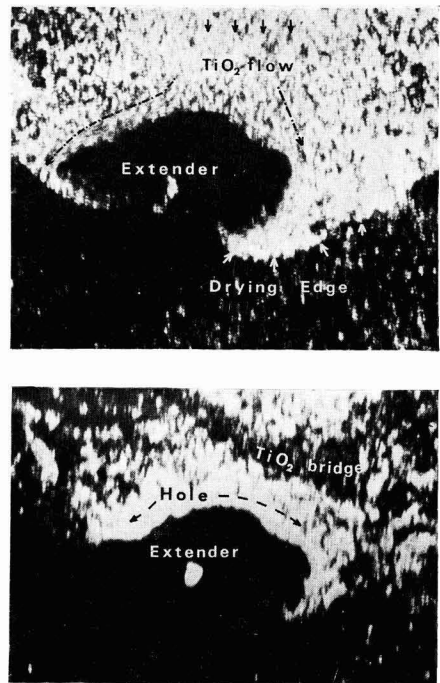


Fig. 11. Film formation in an emulsion paint (a) during drying (top figure) and (b) when dried (lower figure)

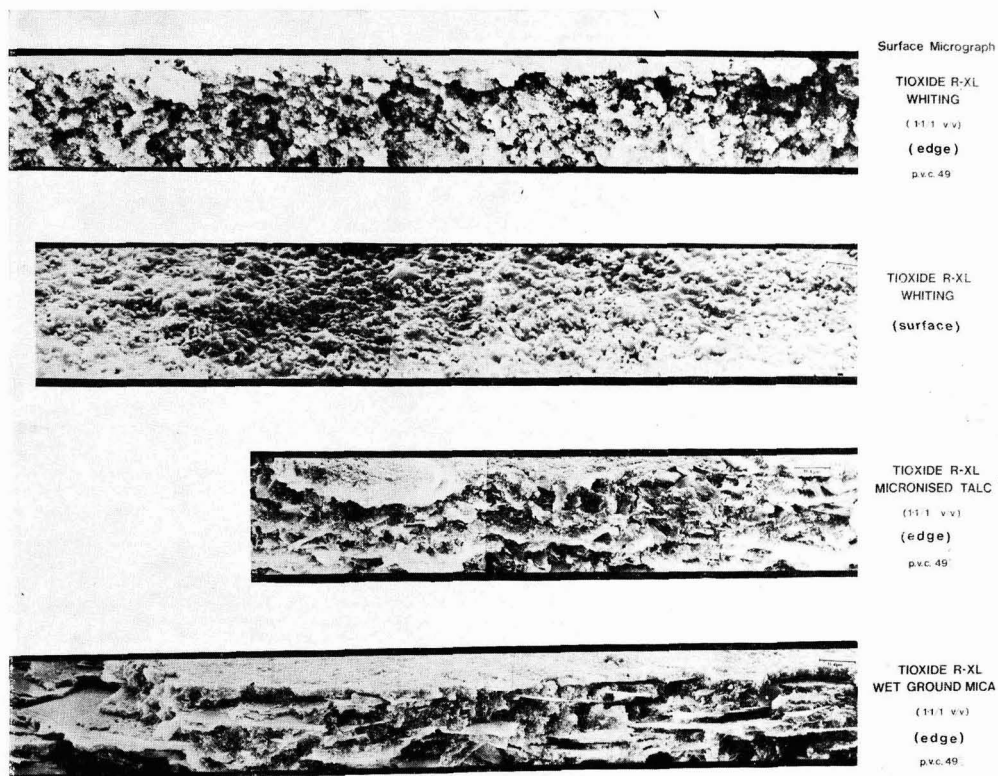


Fig. 12. "Stereoscan" electron micrographs of emulsion paints. 1.1/1 v/v

As the volume of pigment and extender increases, the number of internal film defects, resulting from the bridging phenomenon just described, increases in proportion. These defects act as stress raisers and may become the source of fractures in the paint unless the stress induced by the large volume change can be relieved or distributed by the pigment/polymer matrix. Consequently (in answer to the original question), an increase of PVC increases the number of stress raisers and with it, the intensity (frequency) of cracking. However, since raising the PVC increases the amount of pigment or extender particles, there are more particles available to dissipate the energy of fracture. These two factors function in opposition—on the one hand increasing crack intensity by raising the stress, and on the other hand decreasing crack intensity by dissipating fracture energy. The two evidently work at different rates and, as a consequence, the intensity of cracking reaches a balance; for many emulsion paints this is in the range 60 to 70 per cent PVC, and thereafter the crack intensity decreases (Fig. 8).

As shown in Fig. 8, the intensity of cracking for the millbase (PVC approximately 100 per cent) is markedly higher than for paints containing emulsion. This is possibly caused by a significantly faster rate of drying of the millbase, which results in a high rate of stress build-up. Consequently, there is much less time in which the stress may be relaxed before immobilisation occurs.

### Latex

As mentioned in Part 1, it is important to select latices with good binding power for heavily-pigmented high-opacity systems. One hundred per cent acrylics, styrene/acrylics, and olefin copolymers all offer important advantages over the older pva copolymers in this respect.

With increasing hardness, a paint becomes more likely to crack, particularly under adverse conditions of application. Having already selected an emulsion on the basis of its binding power performance, it is essential that care be then taken to select the correct type and right level of coalescing solvent. With acrylic copolymers, for example, it is well known that ester derivatives of glycol ethers (such as diethylene glycol monobutyl ether acetate) should be avoided, as they may hydrolyse on storage yielding acetic acid; this may cause gelation of the paint, rendering it unusable. The non-esterified glycol ethers are preferred for use with these copolymers.

In addition, with the styrene/acrylic emulsions, a blend of white spirit and diethylene glycol mono butyl ether (1/1 by weight) is cheaper and, at the correct level, can be as effective as a normal coalescing solvent.

The minimum level of coalescing solvent for any given paint system can be determined in the laboratory by drawing

down thick films (0.015 to 0.030 in or 375 to 750 $\mu$ m) containing a suitable coalescing solvent, increasing in amount from, say, 0 to 2 per cent by weight on the paint. A porous substrate (for example, unsealed card) is suitable and the drawdowns are allowed to dry at the lowest temperature and humidity likely to be encountered during practical application. The minimum level of coalescent at which cracking is not observed should be that selected for the paint formula. A level greater than this may result in a further decrease in opacity due to improved polymer coalescence, and again if too great a proportion is used, problems of poor freeze/thaw stability and low tensile strength may occur. Using a coalescent level lower than that determined by this test may, of course, give rise to mud cracking after practical paint application under similar conditions of temperature and humidity.

### Titanium pigment

As the volume concentration of TiO<sub>2</sub> increases at fixed PVC, so the degree of cracking (beyond threshold values of TiO<sub>2</sub> VC and PVC) increases. As shown in Fig. 13, the crack rating at 70 per cent PVC generally increases with TiO<sub>2</sub> volume concentration, above a threshold TiO<sub>2</sub> VC of 15 per cent.

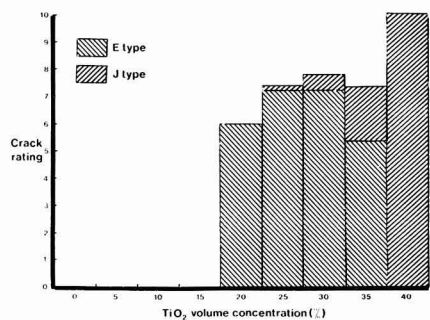


Fig. 13. Crack rating versus titanium dioxide volume concentration at 70 per cent PVC

Change in the grade of TiO<sub>2</sub> need not result in any alteration of dry film integrity. Thus, changing to a high opacity emulsion paint grade from a conventional pigment in a system which already shows mud cracking, will result in a paint which cracks to about the same extent. In a paint containing the conventional grade pigment and which does not crack, replacement by a high opacity type to yield a paint having either equal opacity or equal cost, can result in a new formula with equal or better resistance to cracking. Replacement at equal weight will usually result, however, in a greater tendency for cracking to occur, because the higher water demand of this grade results in shorter drying time (i.e. time to pigment immobility) and higher residual internal stress.

Four formulations are detailed in Appendix C, together with data on opacity and cracking, to demonstrate the effect of replacing a conventional type of pigment with a high opacity grade at equal opacity, at equal cost and at equal weight, in turn.

### Extenders

Extenders may be grouped conveniently into 3 classes when considering their influence on film formation:

1. Those which retard cracking.
2. Those which contribute to cracking.
3. Those which have little effect on cracking.

It is tempting to relate this classification directly to particle shape, with 1, 2 and 3 corresponding to lamellar, ultrafine and nodular shape. The true situation is not as simple as this, as water demand also plays an important part in cracking—high water demand going hand in hand with tendency to crack, although talc (which has a high water demand and lamellar shape) retards cracking and belongs to class 1.

Table 5 indicates some of the extenders examined in this work, together with relevant information on properties such as water demand and particle shape, which influence selection of an extender for use in any latex paint system.

Table 5  
Extenders

| Extender                     | Chemical nature                       | Particle shape     | Mean particle size ( $\mu$ m) | Relative density | Refractive Index | Water demand (ml/100g) | Surface area ( $m^2g^{-1}$ ) |
|------------------------------|---------------------------------------|--------------------|-------------------------------|------------------|------------------|------------------------|------------------------------|
| Barytes .. .. .              | BaSO <sub>4</sub>                     | Nodular            | 10                            | 4.45             | 1.64             | 20                     | 1.60                         |
| China clay .. .. .           | Natural aluminium silicate            | Lamellar           | 10                            | 2.60             | 1.58             | 62                     | 11.60                        |
| Calcined China clay ..       | Amorphous aluminium silicate          | Lamellar           | 20                            | 2.00             | 1.61             | 116                    | 10.4                         |
| Natural whiting .. .. .      | CaCO <sub>3</sub>                     | Nodular            | 20                            | 2.70             | 1.60             | 35                     | 2.2                          |
| Crystalline calcite .. .. .  | CaCO <sub>3</sub>                     | Nodular            | 5                             | 2.65             | 1.65             | 34                     | 3.2                          |
| Crystalline calcite .. .. .  | CaCO <sub>3</sub>                     | Nodular            | 20                            | 2.70             | 1.60             | 32                     | 2.6                          |
| Crystalline calcite .. .. .  | CaCO <sub>3</sub>                     | Nodular            | 20                            | 2.70             | 1.65             | 28                     | 1.1                          |
| Precipitated calcite .. .. . | CaCO <sub>3</sub>                     | Nodular            | 5                             | 2.70             | 1.66             | 124                    | 6.7                          |
| Dolomite .. .. .             | Ca, Mg(CO <sub>3</sub> ) <sub>2</sub> | Nodular            | 20                            | 2.80             | 1.62             | 28                     | 2.0                          |
| Asbestine .. .. .            | Magnesium silicate                    | Fibrous (acicular) | 15                            | 2.80             | 1.58-1.62        | 118                    | 17.9                         |
| Waterground mica .. .. .     | Aluminium-potassium silicate          | Lamellar           | 100                           | 2.80             | 1.57-1.59        | 118                    | 3.2                          |
| Waterground mica .. .. .     | Aluminium-potassium silicate          | Lamellar           | 40                            | 2.80             | 1.57-1.59        | 144                    | 6.6                          |
| Talc .. .. .                 | Magnesium silicate                    | Lamellar           | 5                             | 2.90             | 1.57             | 144                    | 8.2                          |
| Talc .. .. .                 | Magnesium silicate                    | Lamellar           | 20                            | 2.90             | 1.57             | 130                    | 4.8                          |
| Talc .. .. .                 | Magnesium silicate                    | Lamellar           | 20                            | 2.77             | 1.57             | 210                    | 5.1                          |
| Silicate .. .. .             | Hydrated CaSiO <sub>3</sub>           | Ultrafine          | 0.3                           | 2.10             | 1.47             | 210                    | 26.5                         |
| Silicate .. .. .             | Hydrated Al silicate                  | Ultrafine          | 0.3                           | 2.10             | 1.47             | 212                    | 54.3                         |
| Silicate .. .. .             | Diatomaceous silica                   | Nodular            | 40                            | 2.30             | 1.40-1.49        | 218                    | 2.5                          |
| Silicate .. .. .             | Al silicate                           | Ultrafine          | 0.03                          | 1.95             | 1.45             | 185                    | 67.9                         |

A tendency to contribute to cracking does not, of course, preclude an extender from being selected for a given formulation; many other properties must be considered.

Refractive index, specific gravity, chalk resistance, sheen (low angle gloss) level, storage stability, application properties, durability, cost and the possibility (always open) of altering other components, must all be taken into account before a final choice is made. Of course, in an attempt to gain the best of several worlds, blends of different extenders from the different groups are often selected: talc for crack resistance, barytes for easier application and chalk resistance, and an ultra-fine particle extender for high opacity.

#### Antifoaming agents

Air bubbles were mentioned earlier in connection with the origin of cracking on the surface. Suitable antifoaming agents may be employed to avoid these, but although the degree of cracking is thereby reduced, it is by no means eliminated. This is believed to be a consequence of the part played by other surface defects (water bubbles) and internal defects (vacuoles) as originators and propagators of cracks.

There is a danger that in using too much antifoaming agent, problems such as cissing or pinholing may arise because of poor dispersion of the agent in the paint or poor wetting on the substrate. This should be checked by suitable testing.

#### Miscellaneous components

*Ref. 23*

A wide range of thickening agents, dispersants and surfactants have been examined in connection with mud cracking<sup>23</sup>. No evidence was obtained to show that these exert much influence in either direction—nor would any be expected in view of the relatively small proportions of each normally found in conventional emulsion paints. It is feasible to suppose, however, that relatively large amounts of these materials may be included in paints at high PVC (80 to 90 per cent): in such cases their influence might be significant. For example, surfactant level is often calculated as a percentage by weight on the weight of TiO<sub>2</sub> plus extender. Hence, at high PVC, the effect of surfactant on mud cracking may become important, but there was no evidence of this in paints pigmented at up to 75 per cent PVC.

Likewise, there is no evidence that use of wetting agents to improve tint acceptance has any influence on mud cracking, despite some decrease in surface tension and even though their use is sometimes suggested as a possible cure for fracture in paint films.

#### Internal stress

*Ref. 5-7, 24*

##### *The cause of fracture*

All of the factors discussed in the preceding sections—PVC, latex, pigment and extender type, antifoam agents—influence the degree of fracture that may be observed; the processes by which fracture occurs in an emulsion paint will now be discussed.

Fracture in an emulsion paint comes about as a result of stresses which arise in the film as it contracts in volume during drying. This volume contraction results in strains which may

be resolved in directions parallel and normal to the surface, and it is the strain parallel to the surface which causes a crack to open up to visible dimensions. The strain normal to the surface can have a curious effect, which will be discussed later. As seen under the microscope, fracture happens only when the paint has lost its free water and it is not concurrent with drying up to this stage. During the liquid, mobile stage, the film stresses are absorbed probably by work done in re-orientation of the pigment, extender and emulsion particles: as more water evaporates these become immobilised and re-orientation is then no longer possible.

Further stresses which subsequently develop as a consequence of capillary and wet sintering forces,<sup>5-7</sup> must now be relieved by work performed in other ways, such as by coalescence and flow of the polymer, stress distribution by the extender/pigment matrix, internal shearing and even by curling or warping of the substrate if the paint-substrate adhesion is great enough.

Should sufficient relief not occur in these ways (for example, if the binder is relatively hard or the extender cannot distribute the stress over a large volume, or the substrate is rigid and not deformed), then stress relief can only come about by cracking of the paint film.

There are two rate-controlled phenomena, therefore, which are relevant to cracking in paint systems:

1. Rate of stress increase through drying of the paint  
 $dS_{INC}/dt$

This controls the rate at which stress is built up.

2. Rate of stress relief  
 $dS_{REL}/dt$

which is dependent upon

(a) the rate at which the pigment/extender/polymer matrix can deform

and (b) the rate of bending (curling or warping) of the substrate.

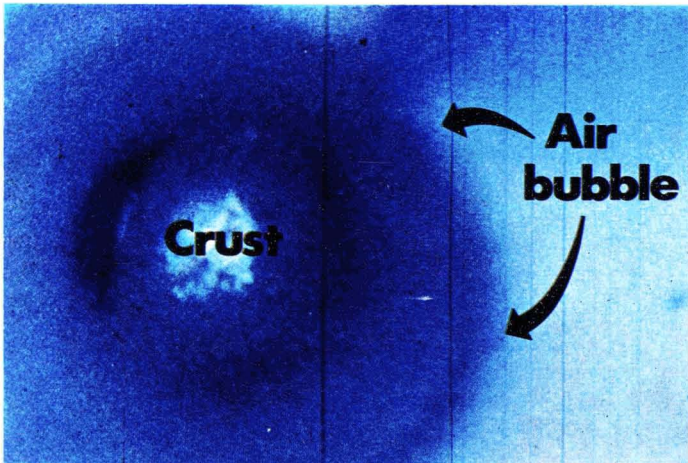
From these two concepts, the total stress at any given time  $t$  is  $S$  where

$$S = \int_0^t (dS_{INC}/dt). dt - \int_0^t (dS_{REL}/dt). dt$$

If at time  $t$ , the value of stress  $S_{REL} < \text{stress } S_{INC}$  then fracture of the paint film will occur when the total stress  $S$  reaches a threshold value that is controlled by the tensile strength  $T$  of the film. That is, fracture occurs if  $S > T$ .

Internal stress is likely to be highest in the coating in areas where defects occur: these defects are evident both on the surface and internally. Surface defects consist of air bubbles or water globules; internal defects appear to be vacuoles formed by bridging during drying.

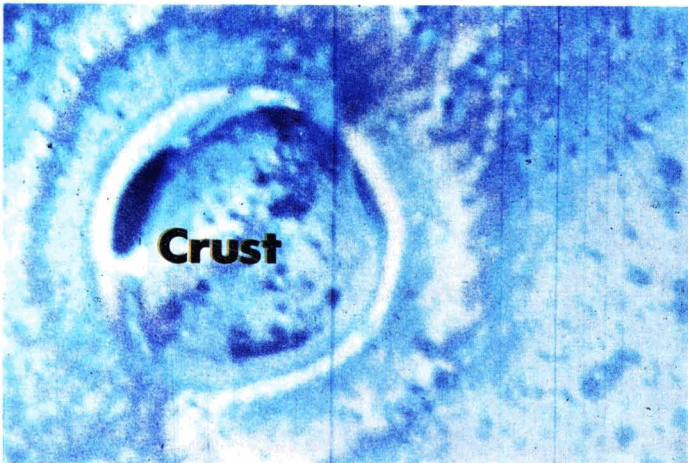
Because internal stress is highest at such points, the cohesive strength of the paint film is most likely to be exceeded here. Then, as a result of the drive to relieve stress, catastrophic cracking originates at some of these defects and is propagated via other defects in the crack line. As a simple analogy, crack propagation may be likened to the way in which a cream cracker biscuit fractures when buttered. If you press too hard with the knife to spread the butter, cracking is



initiated at the point of greatest pressure (usually directly under the knife) and the cracks are then propagated via the holes in the biscuit. The effect can be shattering if the stress is high, as when hard butter is used!

That forces exist in a paint film which act in a direction normal to the surface is well demonstrated in some of the sequences taken from a film, five frames of which are shown in Figs. 14 A, B, C, D and E. Fig. 14A shows the surface crust over an air bubble in a wet emulsion paint. As the paint dries, its contours change and with it the coloured interference patterns (Fig.14B).

Fig. 14A. Air bubble in wet paint film



The crust is then pulled vertically downwards by the strain acting in the direction normal to the surface. The crust subsequently moves across to the top right-hand portion of the periphery, where coalescence between the crust and the body of the paint film takes place (Figs. 14C and 14D). The crust then reinforces this area of the film and incipient cracks do not develop. Cracking takes place only at the top and bottom of this reinforcement (Fig. 14E).

Fig. 14B. Changes in contour during drying

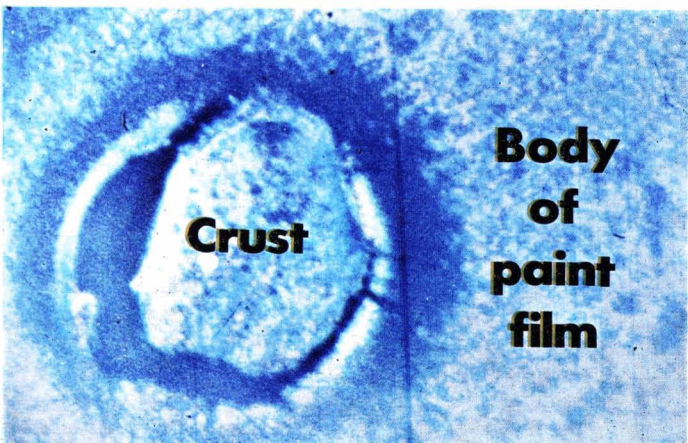


Fig. 14C. Onset of coalescence between crust and film

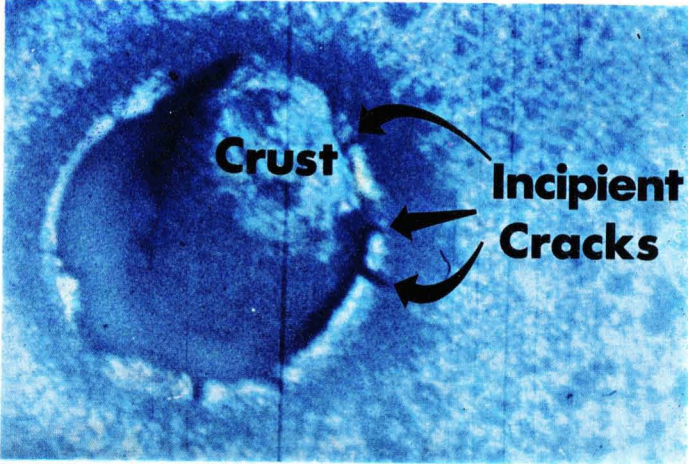


Fig. 14D. Crust reinforces part of film

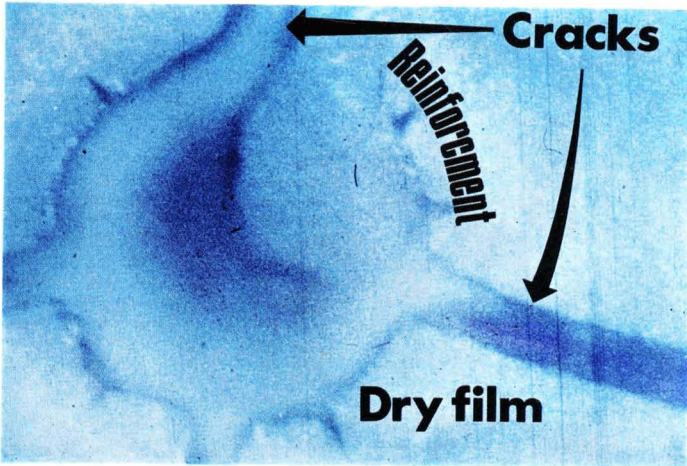


Fig. 14E. Cracks extend from weak points in the dry film

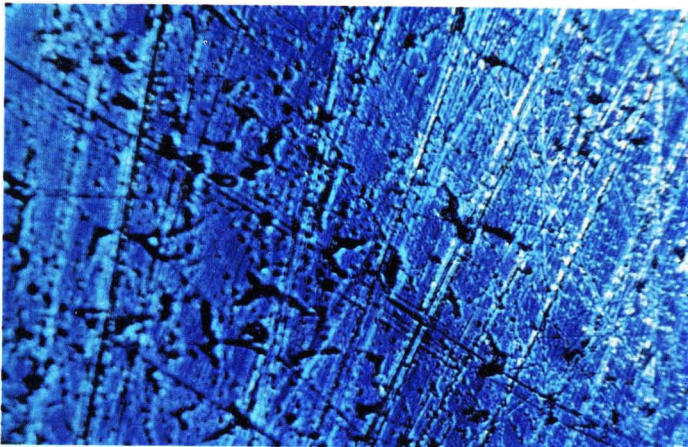


Fig. 20. Surface of steel plate seen through an interference microscope



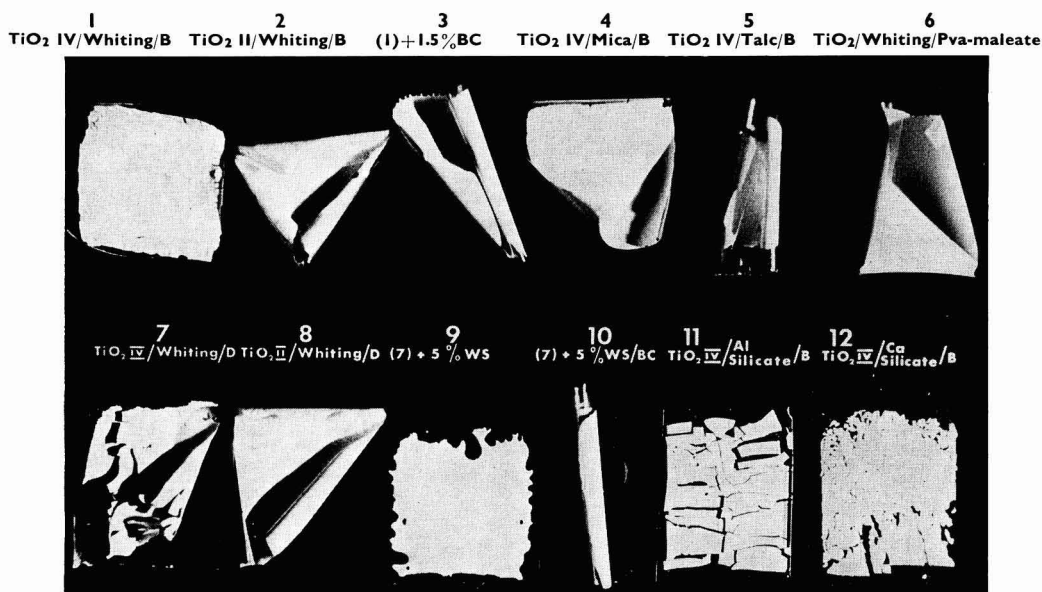


Fig. 15. Deformation of a flexible substrate by the drying of different formulations

Further qualitative studies showed what happens to paints which were allowed to dry on flexible substrates that may curl and thereby relieve part of the internal stress. Some of our results are depicted in Fig. 15.

The twelve paint systems shown are each briefly described below, and details of the formulations used are presented in Appendix D.

1. Type IV  $\text{TiO}_2$ /whiting/emulsion B/(PVC 49 per cent). Under the drying conditions used for this test ( $21^\circ\text{C}$ , 65 per cent RH) at this film thickness (0.015in when wet), this paint has cracked and relieved sufficient stress so that no curling of the polythene substrate was necessary.
2. Type II  $\text{TiO}_2$ /whiting/emulsion B/(PVC 49 per cent). Changing the grade of  $\text{TiO}_2$  has reduced (but not eliminated) the intensity of cracking. Some residual stress remained which was relieved by curling; this has occurred symmetrically to give an approximately isosceles triangle.
3. Addition of 1.5 per cent diethylene glycol mono butyl ether ("Butyl Carbitol") to paint 1 has cured the cracking problem, but there has been sufficient residual stress to curl the substrate as shown.
4. Replacing the whiting in paint 1 with an equal volume of  $40\mu\text{m}$  water-ground mica has alleviated cracking and there is little residual stress.
5. Replacing the whiting in paint 1 with an equal volume of micronised talc also alleviates cracking, but residual stress is still present.
6. Using a softer emulsion with coarser particle size (pva/maleate copolymer) in place of emulsion B produces a result similar to paint 4.

7. In contrast to paint 6, a harder emulsion aggravates the cracking, as expected.
8. Changing the grade of  $\text{TiO}_2$  in the paint with whiting and the hard copolymer D has had a similar result to the change from 1 to 2; that is, the crack intensity has been reduced.
9. Addition of 5 per cent white spirit to paint 7 cures the cracking and there appears to be no internal stress after drying.
10. Using a 1/1 blend of white spirit and butyl Carbitol at 5 per cent by weight on the paint gives high residual stress: combined with good adhesion to the polythene a "cigar" shape then forms. This is perhaps the oddest result of all.
11.  $\text{TiO}_2$  type IV/aluminium silicate/emulsion B gives complete failure by cracking, implying that the stress developed during drying exceeds the cohesive strength of the dry film.
12.  $\text{TiO}_2$  type IV/calcium silicate/emulsion B. Similar to paint 11 but the cracks are much finer.

#### Measurement of internal stress

To gain a quantitative assessment of internal stress development, an attempt was made to measure the stress remaining in several paint systems after drying by means of a simple bending beam experiment.

The substrates were steel shims  $25\mu\text{m}$  (0.001in) thick and 10cm long to which wet paint films were applied  $225\mu\text{m}$  (0.009in) thick, by means of doctor blade and extra shims.

After drying for 48 hours under controlled temperature conditions, the shims were supported on knife edges in such a way that gravity effects were balanced out (Fig. 16).

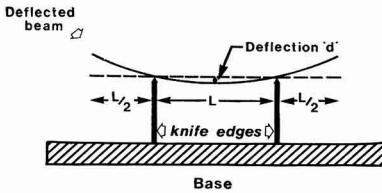


Fig. 16. Simple bending beam experiment to measure stress development ( $d$  = deflection of beam from unstressed position,  $S \propto d$ )

The stress developed by contraction of the paint film during drying caused the beam to curl slightly; the deflection from the unstressed position was measured with a travelling microscope and from this deflection, the stress was calculated, using the following equation\* developed by Corcoran,<sup>24</sup> for the measurement of stress in organic coatings:

$$S = (d E t^3)/(3 c L^2 (t+c) (1-\nu)) \dots \dots \dots (1)$$

- where  $d$  = deflection
- $L$  = length of plate
- $E$  = elastic modulus of plate
- $t$  = thickness of plate
- $c$  = thickness of coating
- $\nu$  = Poisson's ratio for plate

Each beam was previously calibrated by loading its centre with known (milligram) weights and measuring the corresponding deflection with the travelling microscope.

The elastic modulus  $E$  was then calculated from the results of this calibration by the equation:

$$E = (mgL^3)/(4 st^3b) \dots \dots \dots (2)$$

- where  $s$  = deflection
- $m$  = mass added midway between supports

- $L$  = separation of supports
- $b$  = width of the plate

Substituting equation (2) in (1)

$$S = (d m g L)/(12 sbc (t+c) (1-\nu)) \dots \dots \dots (3)$$

If  $m'$  is the mass that, from the calibration curve will produce the deflection  $d$ , equation (3) simplifies to

$$S = (m' g L)/(12 bc (t+c) (1-\nu)) \dots \dots \dots (4)$$

Using this equation, the residual stress of six different emulsion paints has been calculated. Details are given in Table 6.

From these results, the following conclusions can be drawn:

- (i) The residual stresses in tests 1, 2, 3 and 5 are all of the same order, approximately one per cent of the ultimate tensile strength of the paint film (usually  $5 \times 10^7$  dyne  $\text{cm}^{-2}$  at an extension rate of 10 per cent of the original length per minute).
- (ii) The residual stress in test 5 with a pigment of type II is nearly an order of magnitude greater than when a pigment of type IV is used in the same system (test 4). Neither of these paints had cracked, apparently, and hence it would seem reasonable to predict that paint 4 would be less likely to crack during the life of the film than paint 5, because it is less stressed (assuming, of course, that the relative internal stress values of these two paints does not change with age).
- (iii) Paint 6 has relieved its internal stress so effectively, by cracking on the shim, that no stress remained in the film when dry.

This concludes the discussion of the factors affecting mud cracking that are under the direct control of the paint formulator.

Table 6  
Calculation of stress developed during drying of different formulations

| Shim No. | Paint details         |                  |             |             | Stress developed (dynes $\text{cm}^{-2}$ ) |
|----------|-----------------------|------------------|-------------|-------------|--|
|          | TiO <sub>2</sub> type | Extender         | Emulsion    | Plasticiser |  |
| 1        | IV                    | Whiting          | B           | —           | $3.6 \times 10^5$                          |
| 2        | IV                    | Whiting          | B           | 1.5% Bc     | $6.7 \times 10^5$                          |
| 3        | IV                    | Whiting          | pva/maleate | —           | $2.8 \times 10^5$                          |
| 4        | IV                    | Whiting          | D           | —           | $8.9 \times 10^4$                          |
| 5        | II                    | Whiting          | D           | —           | $6.4 \times 10^5$                          |
| 6        | IV                    | Calcium silicate | B           | —           | zero                                       |

(a) Use of this equation is perhaps not strictly justified, since  $t$  should be greater than  $c$  for the equation to be completely valid. Otherwise  $\nu$ , Poisson's ratio for the coating, is required but is not known.  
 (b) The coating is assumed to be isotropic but microscopic examination shows it is not. However, although the results will not be absolutely correct they will be relative and it should still be reasonable to compare them in assessing the influence of formulation changes on internal stress development.



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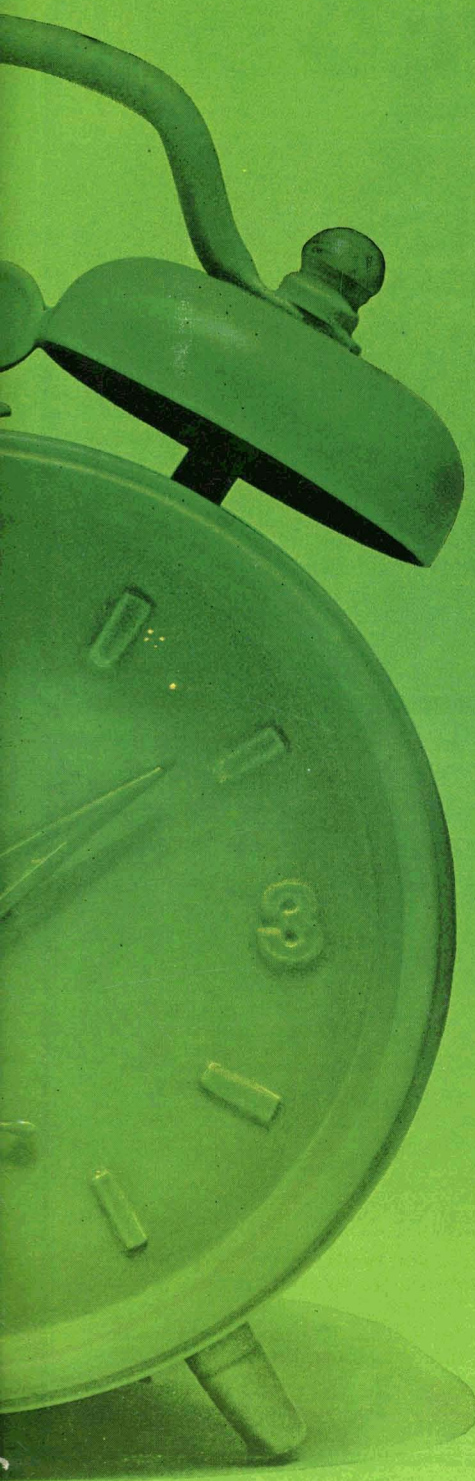
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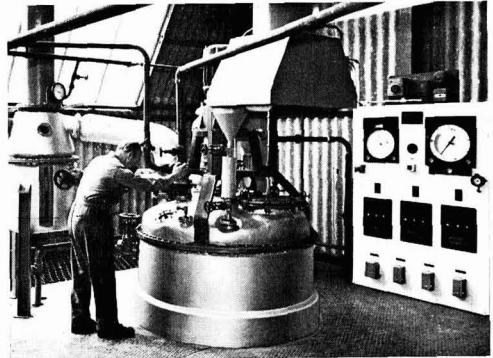
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**Environmental factors**

The remaining five factors listed earlier in Table 3 (drying rate, film thickness, temperature, substrate porosity, and relative humidity) are less under the control of the paint chemist. Being environmental factors, their influence depends largely on the conditions prevailing at the time of application, and probably the best the formulator can do, is to modify his formulation so that it can survive the harshest conditions under which the paint is expected to form a film.

Some of the evidence for the importance of each of these aspects, taken from the author's laboratory work, is described below.

**Drying rate**

The influence of drying rate on cracking in latex paints is closely bound to other factors, particularly temperature, humidity, substrate porosity, wind and some of the ingredients in the paint. Of the paint ingredients, humectants, oils and volatile solvents (for example glycerol, pine oil and coalescing solvents) are probably the most important in this respect.

Unfortunately, the function of such ingredients in a drying paint film is manifold and it is often difficult to devise an experiment which adequately separates one function from another. As an example of this, addition of coalescing solvent (transient plasticiser) does reduce the tendency to crack, but it does so in two main ways: firstly, the minimum film forming temperature of the polymer (and hence of the paint) is lowered, thereby improving the deformability of the system. Secondly, addition of plasticiser reduces the speed of drying, and so allows longer time for relaxation of stress to take place.

The graph of the ratio (weight wet paint/weight dry paint) versus time during drying (Fig. 17) demonstrates how the drying rate decreases on addition of coalescing solvent.

The paints used here were based on emulsion D (see Table 1 in Part 1) and to one of them was made a direct addition of 5 per cent White Spirit (WS): this accounts for the slight difference in weight ratio at zero time (1.89 as opposed to 1.79). The divergence of the curves demonstrates how the addition of WS slows down the drying of this paint system.

The times taken for the two paints to become "half dried" (that is, for the weight ratios to become 1.445 for the paint containing white spirit and 1.395 for the paint without it) are 76 and 56 minutes, respectively.

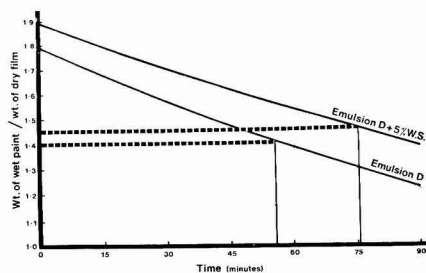


Fig. 17. Drying rate

When completely dry, the paint containing white spirit was crack free: the paint without it showed gross cracking.

**Thickness and temperature**

Ref. 25, 12

The influence that film thickness and ambient temperature can have on cracking intensity are indicated in Table 7. From this table it is evident that as the temperature increases, the maximum allowable thickness of the dry paint to give a fully integrated film, also increases progressively.<sup>25</sup> Thus with the paint used in this example, the maximum thickness allowable increases from 50µm at 5°C to 250µm at 40°C!

Because the thickness of the dry paint film has an important effect on cracking, it should be possible to eliminate mud cracking in borderline cases by slightly reducing the total solids content of the wet paint.

Addition of water or a thickener solution to reduce the solids by between 3 and 6 per cent by weight has been found to be sufficient in many cases. This, of course, will reduce the raw material cost but also decrease the opacity, which will be especially noticeable in one-coat finishes.

In cases where two or more coats are needed for complete obliteration of a substrate, the same number of coats may still be adequate with the thinned paint, particularly for some tints such as blues and greys which normally give very high opacity even in a single coat.

It has already been established<sup>12</sup> that for an emulsion which is predominantly surfactant stabilised (colloid free), the rate of film integration decreases with thickness. From this, it can be predicted that cracking intensity will increase with film thickness for such an emulsion. Conversely, the rate of

Table 7  
Crack rating versus film thickness at different temperatures

| Wet film thickness |       | TNO crack rating                        |                           |                              |
|--------------------|-------|---|---------------------------|------------------------------|
| Inches             | µm    | 5°C                                     | 21°C                      | 40°C                         |
| 0.001              | 25.4  | 0                                       | 0                         | 0                            |
| 0.002              | 50.8  | 0                                       | 0                         | 0                            |
| 0.005              | 127.0 | 1/6 Ec1                                 | 0                         | 0                            |
| 0.01               | 254.0 | 1/3 Ec 10                               | 1/10 Ec 1                 | 0                            |
| 0.015              | 381.0 | (40%)1/3 Ec10/(40%)1 Ec10+(20%)1/2 Jc10 | 1/3 Ec 5                  | (66%)1/10 Ec1/2+(34%)1/2 Ac2 |
| 0.030              | 762.0 | 1/2 Jc 10                               | (50%)3/2 Ec9+(50%)2/3 Jc9 | (75%)1 Ec7+(25%)1 Ac7        |

film integration of a colloid stabilised emulsion is not a direct function of the film thickness and cracking intensity should not be so dependent, therefore, on film thickness.

However, although many types of commercially available emulsions have been used, it has not yet been possible to differentiate systems that are predominantly colloid or surfactant stabilised purely on a basis of cracking tendency.

**Influence of substrate**

Increased porosity of the substrate on which the paint is applied increases the tendency for cracking to develop in the dry film. There are at least two reasons for this. Firstly, increased porosity increases the drying rate and there is, therefore, a shorter time for stress relaxation. Secondly, increased porosity allows greater loss of the emulsion into the substrate, thereby resulting in a slight increase in pigment volume concentration that may aggravate the defect: for example, at 60 per cent PVC a loss of 2 per cent in the emulsion by "wicking" into the substrate results in an increase in PVC of about 3 per cent.

The extent to which various substrates influence cracking tendency is exemplified by the experimental results shown in Table 8. In this experiment one paint was applied at the same wet film thickness (60µm) to substrates of different porosity and allowed to dry in air under controlled temperature conditions. Crack intensity was assessed after drying using the TNO standards described earlier (Fig. 9), and a measure of substrate porosity obtained from the 20° gloss level of a standard air drying alkyd paint (Tioxide R-CR2 in Beckosol P470 at P/B of 0.8/1) applied to each substrate.

A porosity index PI was calculated for each substrate from the equation

$$PI = \frac{20^\circ \text{ gloss level over glass}}{20^\circ \text{ gloss level over other substrate}}$$

Thus the PI for glass is 1.00.

These results show that increase in porosity gives an increase in the width of the cracks, but little change occurs in the type of cracks observed, suggesting perhaps that (for a given paint) drying rate does not influence the manner in which a paint film cracks.

**Relative humidity**

Increasing the relative humidity decreases the rate of drying and decreases the propensity for cracking to occur to practically negligible proportions. This is shown in Fig. 18, where percentage RH from 0-90 per cent is plotted against crack rating for a simple paint system at 45 per cent PVC based on emulsion D, a hard unplasticised copolymer.

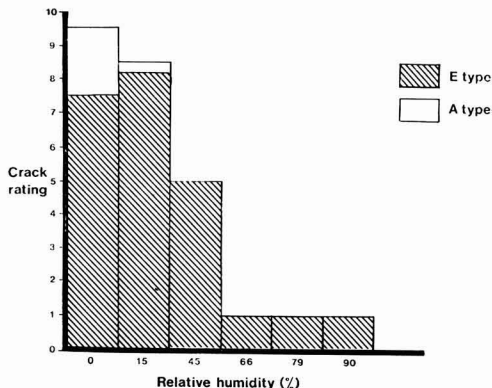


Fig. 18. Crack rating versus relative humidity for emulsion D

The influence of humidity may be likened to that of a transient plasticiser, for it is known that water can exert a plasticising influence, which is particularly strong in the case of vinyl acetate homopolymer emulsions. This is borne out by the observation that under the influence of humidity and temperature, the opacity of a given paint decreases, presumably as a result of better coalescence of the binder. There is consequently a reduction in the number of interior voids, and less dry hiding occurs.

Having illustrated the importance of considering each of these ten parameters when formulating latex paints, it is now pertinent to consider possible methods of observing their influence, at first hand.

One method used employs a novel optical microscope arrangement, which is particularly useful for observing the appearance of film defects—especially cracks.

**Production of defects**

**Optical microscope**

Ref. 12, 26, 27

Under a low-power optical microscope (operating at magnifications of the order of × 50), a surprising number of defects become visible on the surface of a wet latex paint. Most of these defects consist of air bubbles or water globules and they produce imperfections in the surface of what otherwise appears to be a uniform paint film when it dries.

Table 8  
Cracking tendency for various substrates

| Type of substrate                               | Porosity index | TNO crack rating                  |
|---|----------------|-----------------------------------|
| Glass .. .. .                                   | 1.00           | (75%) 3/4 Jc 10 + (25%) 3/4 Ec 10 |
| Sealed side of Moresst HP chart (07P) .. .. .   | 1.07           | 3/4 Jc 9                          |
| Coated card .. .. .                             | 1.64           | 1/2 Jc 9                          |
| Uncoated card .. .. .                           | 1.82           | 1 Ec 9                            |
| Unsealed side of Moresst HP chart (07P) .. .. . | 2.10           | 1 Jc 8                            |
| Whatman No. 4 filter paper .. .. .              | 26.40          | 7/8 Jc 10                         |
| Compressed fibre packing .. .. .                | 52.00          | 3/2 Jc 10                         |



Such imperfections are undoubtedly a nuisance when experimenting with such properties as opacity, permeability or tensile strength, and this necessitates their careful removal by straining, centrifuging,<sup>12</sup> or the addition of suitable antifoam agents.

Nuisance as they are, water and air bubbles appear to be a common component of emulsion paint films. They may have been mixed into the paint during manufacture, stirred in during thinning with water, or else entrained during application; in practice, they give rise to defects in the drying paint, acting as stress raisers which initiate cracking (and to some extent promote it). In cases where cracking does not occur, the bubbles may collapse at a late stage in the drying—when the polymer cannot deform easily—thus contributing to pin-hole formation.

In addition to the laboratory work described in the preceding sections, the effects of various paint components, particularly pigment, extender, emulsion and transient plasticiser, on film formation have been observed using a Nacet 300 Interference Microscope incorporating a Nomarski interference device<sup>26, 27</sup>. With this equipment, small defects in a surface viewed by reflected light appear in three dimensions as a result of optical interference, producing what look like contour lines, each characterised by a different colour of the spectrum.

By calibrating the microscope, the height as well as the linear dimensions of a small object may be measured. The optical arrangement used is shown in Fig. 19.

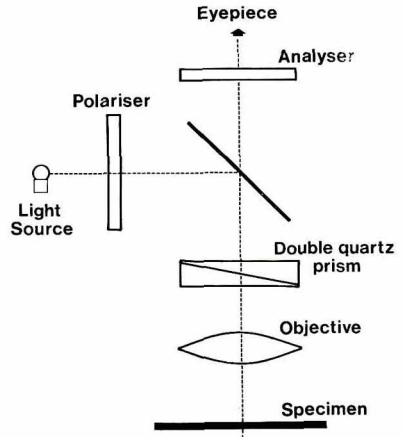


Fig. 19. The Nomarski interference microscope

Alteration of the double prism setting by means of a lever alters the path difference and results in changes in the coloured pattern: the setting is altered to give the best viewing conditions, and can be used to distinguish positive and negative relief effects.

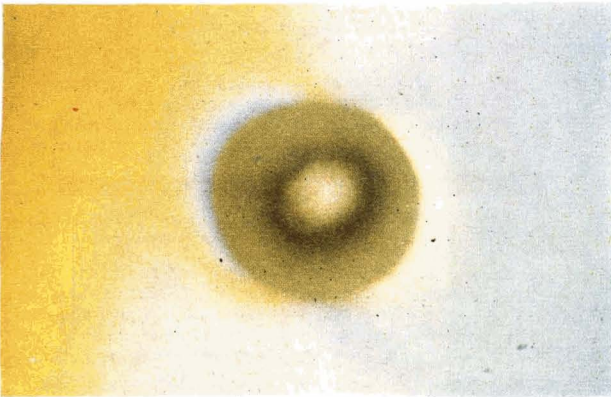


Fig. 21. Interference pattern for the wet paint film

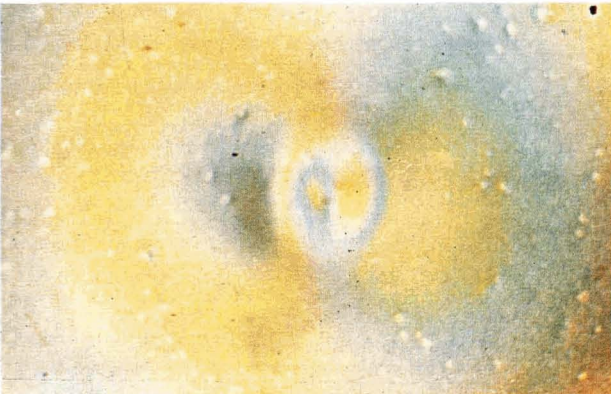


Fig. 22. After drying for 20 minutes

The interference microscope was designed for metallurgical uses and with it, the minute scratches in the surface of a steel plate can be seen as in Fig. 20. The author thought it might be interesting to examine emulsion paints under this instrument with the aim of seeing what happens to surface defects during drying.

A bubble on the surface of a white emulsion paint may give an image as shown in Fig. 21, taken immediately on application of the paint to a microscope slide. The diameter of these individual bubbles is of the order of 70 to 80 $\mu$ m, which is too large in comparison with the wavelength of light used to produce first order interference patterns of the type shown; a bubble, therefore, usually appears as a dark area.

As the paint film dries, it contracts in volume, the surface shrinks towards the substrate and pigment and extender particles are thrust out from the surface. The particles evident as lumps in Fig. 22 (taken 20 minutes after application) are about 15 $\mu$ m in diameter; each of these corresponds to a flocculate of about 60 individual TiO<sub>2</sub> crystallites or roughly one extender particle.

With continuing drying, water gradually evaporates

completely from the film: the surface layer of water disappears, pigment and extender scatter more of the incident light and the interference pattern fades away, as in Fig. 23. Some time later if the paint is drying in an unsuitable environment, the film may develop cracks, as shown in Fig. 24, and here another colour effect becomes visible—this time from the glass microscope slide used as substrate.

A glass slide viewed through this microscope appears to have the interference pattern shown in Fig. 25: the coloured bands are produced as a result of interference between light reflected at the upper and lower surfaces of the slide, which are not exactly parallel and give rise to interference, therefore, at slightly different wavelengths, similar to those produced by a small angle glass wedge in optical interference work (but not entirely similar, due to the contribution of the Nomarski device). These fringes are localised at the glass surface and are independent, therefore, of the paint film thickness. They were very useful, nonetheless, for showing clearly with this microscope when cracking has occurred right through the film.

The process of fracture in emulsion paints is clearly demonstrated in a 16mm film made during this work\*.

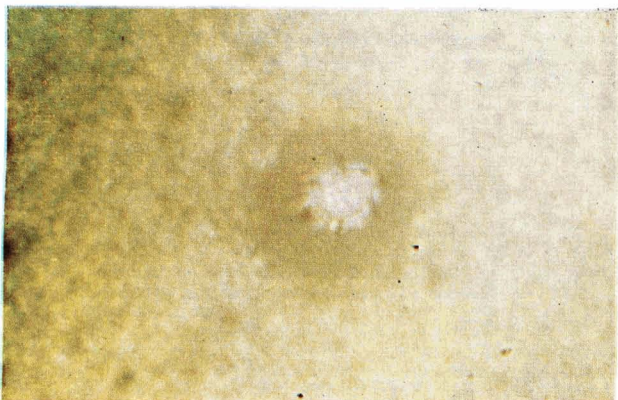


Fig. 23. After drying for 40 minutes

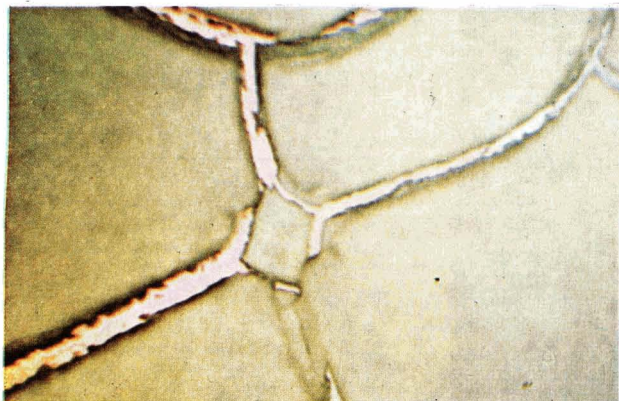


Fig. 24. After drying for 60 minutes

\*Screening of the film can be arranged at any time by contacting the author at the address given at the beginning of this paper.

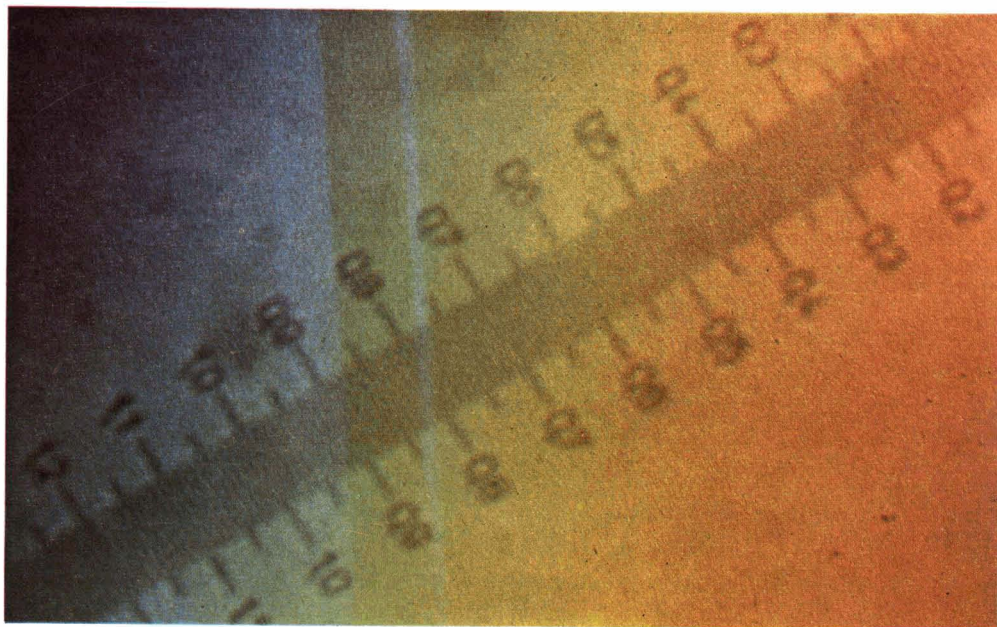


Fig. 25. Glass slide interference pattern. One scale division (for example 0.7 to 0.8) is equivalent to  $100\mu\text{m}$

## Conclusions

Film defects, whether arising (a) internally by bridging or by vacuole formation or (b) on the surface as a result of air bubbles or water globules, are commonly present in dried emulsion paints.

These defects may promote cracking if the stress developed during film formation is not otherwise relieved. Relief may occur by re-distribution of stress, semi-elastic flow, internal shearing or even warping of the substrate.

The opacity of an emulsion paint can be improved by taking advantage of the newer pigments, extenders and emulsions that are available. Poor film integrity need not result if components are so selected to allow the paint to relieve stresses during drying.

Where cracking of a paint becomes a serious problem it may possibly be overcome in the following ways without major re-formulation:

(a) Reduction in total solids of the paint by 3 to 6 per cent. As shown in this paper, dry film thickness has an important effect on mud cracking: it is possible, therefore, that by reducing the dry film thickness in individual coats, cracking may be eliminated under the prevalent drying conditions and, where two or more coats are needed for complete obliteration, the same number of coats may still prove adequate.

(b) Addition of more coalescing solvent of a suitable type will lower the minimum film-forming temperature of the paint and, at a sufficiently high level, will eliminate cracking.

(c) Addition of a suitable antifoaming agent, if not already present, may reduce cracking slightly.

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## Appendix C

Effect of replacing standard TiO<sub>2</sub> by high opacity grade

| Formula | Pigment | Cost/litre | Opacity  | TNO crack rating*          | Comments   |
|---------|---------|------------|----------|----------------------------|--|
| 1       | R-CR2   | 11.65p     | Standard | (1/4) Lc1<br>(very slight) | Standard TiO <sub>2</sub> grade  |
| 2       | R-XL    | 11.60p     | 12.5% up | (1/2) Lc8                  | Equal weight R-XL gives higher opacity but more cracking                               |
| 3       | R-XL    | 11.65p     | 15% up   | (1/2) Lc4                  | Equal cost with R-XL gives even higher opacity, less cracks than (2)                   |
| 4       | R-XL    | 10.95p     | Equal    | (1/2) Lc1<br>(very slight) | Equal opacity gives lower cost; cracking similar to (1) with standard TiO <sub>2</sub> |

\*375μm wet films applied to porous card and dried at 4°C.

| Formulae .. .. .                              | 1      | 2               | 3      | 4      |
|---|--------|-----------------|--------|--------|
|   |        | Parts by weight |        |        |
| Tioxide R-CR2 .. .. .                         | 13.95  | —               | —      | —      |
| Tioxide R-XL .. .. .                          | —      | 13.95           | 14.00  | 12.21  |
| M100 China Clay .. .. .                       | 11.63  | 11.63           | 11.47  | 12.11  |
| Snowcal 6ML Whiting .. .. .                   | 23.26  | 23.26           | 22.95  | 24.21  |
| 3 per cent Natrosol 250HR .. .. .             | 13.95  | 13.95           | 14.00  | 14.00  |
| 5 per cent Calgon PT .. .. .                  | 2.33   | 2.33            | 2.42   | 2.43   |
| Water .. .. .                                 | 9.29   | 9.29            | 8.91   | 9.03   |
| Butyl Carbitol Acetate .. .. .                | 1.40   | 1.40            | 1.25   | 1.24   |
| Epok V8300 .. .. .                            | 24.19  | 24.19           | 25.00  | 24.78  |
| Totals .. .. .                                | 100.00 | 100.00          | 100.00 | 100.00 |
| Pigment volume concentration .. .. .          | 59.73  | 60.20           | 59.20  | 59.73  |
| TiO <sub>2</sub> volume concentration .. .. . | 12.44  | 13.46           | 13.41  | 11.64  |
| Pigment/binder quotient .. .. .               | 3.86   | 3.86            | 3.71   | 3.75   |
| TiO <sub>2</sub> /binder quotient .. .. .     | 1.10   | 1.10            | 1.07   | 0.94   |
| Relative density of paint .. .. .             | 1.51   | 1.50            | 1.50   | 1.49   |
| Cost per kilo .. .. .                         | 7.71   | 7.71            | 7.77   | 7.31   |
| Cost per litre .. .. .                        | 11.65  | 11.60           | 11.65  | 10.95  |
| Non-volatile (by weight) .. .. .              | 61.46  | 61.46           | 61.46  | 61.46  |
| Non-volatile (by volume) .. .. .              | 41.84  | 42.13           | 42.30  | 42.42  |

## Appendix D

## Influence of formula on internal stress

| Ingredient  | Formula (parts by weight) |        |        |        |        |        |        |        |        |        |       |       |
|---|---------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|-------|
|   | 1                         | 2      | 3      | 4      | 5      | 6      | 7      | 8      | 9      | 10     | 11    | 12    |
| Tioxide R-XL (Type IV TiO <sub>2</sub> ) .. .. .  | 24.17                     | —      | 24.17  | 24.17  | 24.17  | 24.17  | 24.17  | —      | 24.17  | 24.17  | 24.17 | 24.17 |
| Tioxide R-CR2 (Type II TiO <sub>2</sub> ) .. .. . | —                         | 24.17  | —      | —      | —      | —      | —      | 24.17  | —      | —      | —     | —     |
| Snowcal 6ML whiting .. .. .                       | 16.11                     | 16.11  | 16.11  | —      | —      | 16.11  | 16.11  | 16.11  | 16.11  | 16.11  | —     | —     |
| 40μm MICA .. .. .                                 | —                         | —      | —      | 16.76  | —      | —      | —      | —      | —      | —      | —     | —     |
| Microtalc ITI .. .. .                             | —                         | —      | —      | —      | 16.52  | —      | —      | —      | —      | —      | —     | —     |
| Aluminium silicate .. .. .                        | —                         | —      | —      | —      | —      | —      | —      | —      | —      | —      | 11.68 | —     |
| Calcium silicate .. .. .                          | —                         | —      | —      | —      | —      | —      | —      | —      | —      | —      | —     | 12.57 |
| 5% Calgon PT solution .. .. .                     | 4.83                      | 4.83   | 4.83   | 4.83   | 4.83   | 4.83   | 4.83   | 4.83   | 4.83   | 4.83   | 4.83  | 4.83  |
| 3% Natrosol 250MR solution .. .. .                | 10.07                     | 10.07  | 10.07  | 10.07  | 10.07  | 10.07  | 10.07  | 10.07  | 10.07  | 10.07  | 10.07 | 10.07 |
| Nuodex 321 Extra .. .. .                          | 0.09                      | 0.09   | 0.09   | 0.09   | 0.09   | 0.09   | 0.09   | 0.09   | 0.09   | 0.09   | 0.09  | 0.09  |
| Water .. .. .                                     | 15.33                     | 15.33  | 15.33  | 15.33  | 15.33  | 17.02  | 15.33  | 15.33  | 15.33  | 15.33  | 15.33 | 15.33 |
| Butyl Carbitol .. .. .                            | —                         | —      | 1.53   | —      | —      | —      | —      | —      | —      | —      | 2.50  | —     |
| White spirit .. .. .                              | —                         | —      | —      | —      | —      | —      | —      | —      | 5.00   | 2.50   | —     | —     |
| 100% acrylic latex ("B") (50%) .. .. .            | 29.40                     | 29.40  | 29.40  | 29.40  | 29.40  | —      | —      | —      | —      | —      | 29.40 | 29.40 |
| PVA-maleate copolymer (53%) .. .. .               | —                         | —      | —      | —      | —      | 27.71  | —      | —      | —      | —      | —     | —     |
| Hard copolymer ("D") (50%) .. .. .                | —                         | —      | —      | —      | —      | —      | 29.40  | 29.40  | 29.40  | 29.40  | —     | —     |
| Totals .. .. .                                    | 100.00                    | 100.00 | 101.53 | 100.65 | 100.41 | 100.00 | 100.00 | 100.00 | 105.00 | 105.00 | 95.57 | 96.46 |
| Pigment volume concentration .. .. .              | 49.4                      | 48.2   | 49.4   | 49.4   | 49.4   | 48.6   | 46.8   | 45.7   | 46.9   | 46.9   | 49.4  | 49.4  |
| TiO <sub>2</sub> volume concentration .. .. .     | 25.8                      | 24.1   | 25.8   | 25.8   | 25.8   | 25.4   | 24.5   | 22.8   | 24.5   | 24.5   | 25.8  | 25.8  |
| Pigment/binder quotient .. .. .                   | 2.6                       | 2.6    | 2.6    | 2.7    | 2.7    | 2.6    | 2.6    | 2.6    | 2.6    | 2.6    | 2.3   | 2.4   |
| TiO <sub>2</sub> /binder quotient .. .. .         | 1.6                       | 1.6    | 1.6    | 1.6    | 1.6    | 1.6    | 1.6    | 1.6    | 1.6    | 1.6    | 1.6   | 1.6   |
| Relative density .. .. .                          | 1.4                       | 1.4    | 1.4    | 1.4    | 1.4    | 1.4    | 1.4    | 1.4    | 1.4    | 1.4    | 1.4   | 1.4   |
| Non-volatile content (by weight) .. .. .          | 55.6                      | 55.6   | 55.6   | 55.8   | 55.7   | 55.5   | 55.6   | 55.6   | 52.9   | 52.9   | 53.5  | 53.9  |
| Non-volatile content (by volume) .. .. .          | 35.9                      | 35.4   | 35.8   | 35.9   | 35.9   | 36.9   | 37.5   | 37.0   | 34.4   | 34.7   | 35.9  | 35.9  |

# The determination of copper, mercury and arsenic in antifouling paints by means of X-ray fluorescence

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## Summary

X-ray spectrophotometry has been successfully applied to the qualitative and quantitative determination of copper, arsenic and mercury in antifouling paints. Qualitative determinations can be made on the sample without any previous treatment or separation.

For the determination of copper and arsenic, the sample is treated with a mixture of nitric and sulfuric acids and the spectrometric determination is performed on the solution. Copper interferes with the determination of arsenic; as copper concentration increases

the intensity of the arsenic line decreases. The use of potassium bromide as an internal standard avoids this interference.

In the determination of mercury, organic matter is destroyed by treatment with nitric acid, using a reflux condenser to avoid loss of mercury by volatilisation. The spectrometric analysis is performed on the solution. The interference caused by the presence of other metals such as iron, copper, zinc and lead is studied.

## Keywords

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

*Equipment primarily associated with  
analysis measurement or testing  
spectrophotometer*

*Process and methods primarily associated with  
analysis, measurement, or testing  
fluorescent spectroscopy*

## Le dosage, au moyens de la fluorescence de rayons-X, de cuivre, mercure et arsenic en peintures «anti fouling.»

### Résumé

On a employé avec succès la spectrophotométrie aux rayons-X pour doser quantitativement et qualitativement cuivre, mercure et arsenic en peintures «anti fouling.» Le dosage qualitatif peut s'effectuer sur un échantillon sans aucune séparation ou traitement préalable.

En ce qui concerne le dosage de cuivre et d'arsenic, on traite l'échantillon par un mélange des acides sulfurique et nitrique et l'on effectue le dosage spectrométrique sur la solution qui en résulte. Le cuivre donne des ennuis au cours du dosage de l'arsenic;

à mesure que la concentration de cuivre s'augmente, l'intensité de la ligne d'arsenic se diminue. L'emploi du bromure de potasse en tant qu'étalon interne évite cette interférence.

Dans le cas du dosage du mercure, on détruit aucune matière organique au moyens du traitement par l'acide nitrique en utilisant un condenseur à reflux afin d'éviter la perte de mercure par volatilisation. L'analyse spectrophotométrique s'effectue sur la solution qui reste. On étudie les ennuis provoqués par la présence d'autres métaux tels que fer, cuivre, zinc et plomb.

## Die Bestimmung von Kupfer, Quecksilber und Arsen in Antifoulingfarben durch Röntgenstrahlenfluoreszenz

### Zusammenfassung

Röntgenstrahlen—Spektrophotometrie wurde zur qualitativen und quantitativen Bestimmung von Kupfer, Arsen und Quecksilber in Antifoulingfarben mit Erfolg angewandt. Qualitative Bestimmungen können am Muster ohne irgendwelche Vorbehandlung oder Trennung vorgenommen werden.

Zur Bestimmung von Kupfer oder Arsen wird das Muster mit einer Mischung von Salpeter und Schwefelsäure behandelt und die spektrometrische Bestimmung wird an der Lösung ausgeführt; in dem Masse, in welchem sich die Kupferkonzentration erhöht, vermindert sich die Intensität der Arsenlinie. Die Verwendung

von Kaliumbromid als ein interner Standard vermeidet diese Störung.

Bei der Bestimmung von Quecksilber werden organische Stoffe durch Behandlung mit Salpetersäure zerstört, wobei, um Verlust an Quecksilber durch Verflüchtigung zu vermeiden, ein Rückflusskondensator benutzt wird.

Für die spektrometrische Analyse wird die Lösung verwandt. Die durch die Anwesenheit anderer Metalle, wie z.B. Eisen, Kupfer, Zink und Blei, verursachten Störungen werden untersucht.

## Определение меди, ртути и мышьяка в необрастающих красках при помощи рентгенофлуоресценции

### Резюме

Рентгенофлуоресценция успешно применялась для качественного и количественного определения меди, мышьяка и ртути в необрастающих красках. Качественное определение может быть проведено на образце без какой либо предварительной обработки или осаждения.

Для определения меди и мышьяка, образец обрабатывается смесью азотной и серной кислот и спектрометрическое определение проводится на растворе. Медь препятствует определению мышьяка; по мере того как концентрация меди

повышается, интенсивность уровня мышьяка понижается. Применение бромистого калия в качестве внутренней нормы устраняет эту помеху.

В определении ртути, органические вещества истребляются обработкой азотной кислотой, применяя противоточный конденсатор для избежания потери ртути испарением. Спектрометрический анализ проводится на растворе. Изучается помеха причиняемая присутствием других металлов, как например железо, медь, цинк и свинец.

## Introduction

X-ray fluorescence differs from most other modern instrumental analytical techniques, for example spectrography, flame spectrophotometry, in that it is essentially applicable to components which are present in the material to be analysed in relatively large amounts. This means that the main components can be determined with less error and that it is not necessary to work at extreme dilutions.

In the special case of antifouling paints, copper, arsenic and mercury may be determined by this means. X-ray fluorescence is due to the excitation of the atoms of the material to be analysed by means of a beam of polychromatic and very energetic X-ray radiation emitted by a suitable generator. The excited atoms then emit a secondary radiation, called fluorescence, at wavelengths in the X-ray region characteristic of the element concerned. The fluorescent radiation is passed through a crystal in which it is diffracted in accordance with Bragg's laws, and which thus acts as a collimator; the angle of diffraction and the intensity of the fluorescence are determined by means of a goniometer and recorder.

The method may be considered from two aspects:

- the qualitative determination of the components present in the sample to be analysed (this is restricted to those elements which give suitable fluorescence and limited by the power of the equipment in use);
- the quantitative determination of these components.

Qualitative analysis constitutes a most valuable auxiliary technique in any laboratory dealing with the analysis of paints of very varied composition, since it may be carried out without any previous treatment of the sample and within a few minutes. A scan of 20-25°, using a lithium fluoride crystal, covers a spectral zone in which the elements of main interest are to be found (As, Cu, Pb, Zn, Hg etc.), and can be completed within fifteen minutes. Not only is much time saved but a semi-quantitative estimate of the amounts may also be obtained from the diagrams.

It was hoped that the determination of copper, arsenic and mercury in antifouling paints could be carried out directly on the paint without any pretreatment. However, the complexity of the sample and the relatively high concentration of the elements to be determined caused a very marked matrix effect. This difficulty cannot be overcome by comparison with blank samples of similar composition, since they are not likely to be available and would be very difficult to prepare. The solution to the problem was found to lie in the use of aqueous solutions in which dilution greatly decreases the matrix effect and where the preparation of blanks is simpler because standard solutions may be used.

The sample is treated to destroy organic matter, to prevent losses due to volatilisation of the elements to be determined and to work in acid solutions. The advantage of this procedure is that simultaneous determination of copper and arsenic is possible.

## Experimental

### Determination of copper and arsenic

#### Preliminary tests

For the determination of copper (Cu) and arsenic (As), the influence of Cu on the fluorescent radiation intensity due to

As was tested. Working with pure solutions, it was shown that the intensity  $K_{\alpha}$  of the arsenic line decreases as the concentration of copper increases; this can be seen in Fig. 1. As this type of interference may be greater in the case of a more complex solution, the difficulty was avoided by the use of a technique of general application.

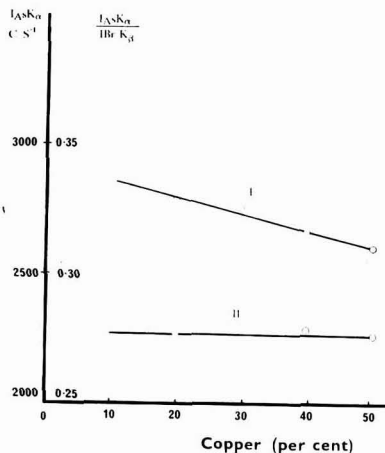


Fig. 1. Sample corresponding to 5 per cent  $As_2O_5$ , direct method (I); sample corresponding to 5 per cent  $As_2O_5$ , internal standard method (II)

The internal standard method is the most generalised way to avoid matrix effects where they are not very great. Bromide was used as the internal standard, and for this purpose its  $K_{\beta}$  line was chosen. For arsenic, the  $K_{\alpha}$  line was used. Fig. 1 shows the result of tests carried out with solutions in which the arsenic and bromide concentrations were kept constant and the copper concentration was varied. The ratio  $(I_{As}K_{\alpha}) / (I_{Br}K_{\beta})$  is plotted as a function of the percentage copper present.

The results justify the adoption of the internal standard method to eliminate the effect of copper interference. The influence of other elements in the paint was not studied, since the results show clearly that with this technique there was no interference by other elements which were also present.

#### Proposed technique

The method proposed is as follows. Treat a 0.5g sample of the paint to be analysed with 10ml of nitric acid in a beaker. Heat and reduce it to a small volume, add 10ml of sulfuric acid diluted 1 : 1 with water and heat until white fumes of  $SO_3$  are obtained. Repeat the treatment with nitric acid and evaporation with sulfuric acid until all organic matter is completely destroyed. Dilute and filter if necessary (for example, if  $PbSO_4$  is present) and place in a 50ml volumetric flask. Add 10ml of 10 per cent KBr solution and make up to volume. This solution is used in the X-ray spectrometer.

The calibration curve was obtained from standard arsenic and bromide solutions in which the arsenic concentration was varied and the concentration of bromide kept constant and equal to that added to the unknown sample. To these solutions, copper and sulfuric acid were also added in order that their composition should be similar to that of the sample.

In order to test the method for the determination of arsenic, paint samples of known and variable composition and free from arsenic were used. Measured amounts of arsenic were added to 0.5g portions of the samples prior to the treatment with nitric and sulfuric acids.

The conditions used for the X-ray spectrometer were:

Cr anode, 40Kv and 20mA

Coarse collimator

LiF crystal

Scintillation counter, 1,000v

On mylar, in air

Fixed time plus clock, 6 seconds, FS 64 without discrimination

As: peak  $K_{\alpha}$  33.9°, background 33.5°

Br: peak  $K$  26.8°, background 27.7°.

Tables 1 and 2 show the results obtained. The values in Table 1 correspond to recovery tests, whilst Table 2 shows  $As_2O_3$  values corresponding to chemically and X-ray analysed samples. A simple comparison of these values justifies the validity of the proposed method.

Table 1  
Results of "recovery" tests for copper and arsenic

| Sample | Weight of the sample g | Added $As_2O_3$ mg | Recovered $As_2O_3$ mg | Difference D | $D^2$ |
|--------|------------------------|--------------------|------------------------|--------------|-------|
| 1      | 0.5                    | 25.00              | 25.00                  | 0.00         | 0.00  |
| 2      | 0.5                    | 25.00              | 24.30                  | 0.70         | 0.49  |
| 3      | 0.5                    | 25.00              | 25.00                  | 0.00         | 0.00  |
| 4      | 0.5                    | 25.00              | 24.25                  | 0.75         | 0.56  |
| 5      | 0.5                    | 25.00              | 25.20                  | 0.20         | 0.04  |
| 6      | 0.5                    | 20.00              | 19.75                  | 0.25         | 0.06  |
| 7      | 0.5                    | 20.00              | 20.80                  | 0.80         | 0.64  |
| 8      | 0.5                    | 30.00              | 29.80                  | 0.20         | 0.04  |
| 9      | 0.5                    | 30.00              | 30.20                  | 0.20         | 0.20  |
| 10     | 0.5                    | 35.00              | 33.80                  | 1.20         | 1.44  |
| 11     | 0.5                    | 35.00              | 34.50                  | 0.50         | 0.25  |

Standard deviation = 0.595      Relative error (per cent) = 2.20

Table 2  
Arsenic determination on paint samples

| Sample | $As_2O_3$ per cent<br>Chemical approach | $As_2O_3$ per cent<br>X-ray | Difference |
|--------|---|-----------------------------|------------|
| 1      | 3.00                                    | 2.85                        | 0.15       |
| 2      | 4.70                                    | 4.65                        | 0.05       |
| 3      | 7.50                                    | 7.45                        | 0.05       |
| 4      | 5.60                                    | 5.50                        | 0.10       |

In the case of copper determination, although the X-ray technique does not offer any particular advantages over a chemical method for a single determination of this element only, it does have advantages in the presence of arsenic, since the analysis for both elements can be made on the same solution in one determination after the other. The same internal standard as for arsenic is used, which is equivalent to extending the operational time by 4 to 6 minutes, the time required to carry out readings corresponding to the  $K_{\alpha}$  copper line, peak and background.

The calibration curve is prepared from standard solutions, the bromide concentration being kept constant and that of

copper being varied. The ratio between the intensities of the  $K_{\alpha}$  copper line and the  $K_{\beta}$  bromide line being plotted as a function of copper concentration, as explained in the case of arsenic.

In the case of copper, the influence of the other elements in the solution have not been studied. Undoubtedly, this would be high for any direct reading method and for this reason the internal standard method has been adopted.

A check on the proposed method was carried out electrolytically. One gram of the sample was weighed out, treated as already described, and diluted to 50ml. The X-ray determination was carried out on a 25ml aliquot, and the remainder used for the electrolytic determination. Table 3 shows the results of both methods.

Table 3  
Comparative study of copper determination electrolytically and by X-ray fluorescence

| No | Copper, per cent electrolytically | Copper, per cent X-ray | Difference D | $D^2$ |
|----|-----------------------------------|------------------------|--------------|-------|
| 1  | 18.6                              | 18.4                   | 0.2          | 0.04  |
| 2  | 17.4                              | 17.4                   | 0.0          | 0.00  |
| 3  | 17.4                              | 18.1                   | 0.7          | 0.49  |
| 4  | 19.4                              | 19.6                   | 0.2          | 0.04  |
| 5  | 26.2                              | 26.4                   | 0.2          | 0.04  |
| 6  | 26.4                              | 26.5                   | 0.1          | 0.01  |
| 7  | 36.1                              | 35.6                   | 0.5          | 0.25  |

Standard deviation = 0.38: relative error, per cent = 1.6.

## Determination of mercury

### A study of the interferences

The effect of the interferences which might be caused by the presence of iron, copper, zinc and lead, which are usually present in antifouling formulations, in the solutions obtained after the destruction of organic matter and used for the determination of mercury, has been studied in solutions designed to have similar compositions.

Bismuth was used as an internal standard for mercury determination and was added at the same concentration to the solution of the unknown sample and the standard solutions used for constructing the calibration curves. The  $L_{\alpha 1}$  mercury and the  $L_{\alpha 1}$  bismuth lines were chosen for use. The ratio of the intensities ( $I_{Hg L_{\alpha 1}}/I_{Bi L_{\alpha 1}}$ ) is plotted against the mercury concentration.

The working conditions of the X-ray spectrophotometer were:

Cr anode, 40Kv and 20mA

Coarse collimator,

Scintillation counter, 1000v,

Sample on mylar and in air,

Fixed time, 64 seconds. Scale factor, 64,

Without discrimination,

Crystal, LiF,

Mercury,  $L_{\alpha 1}$  line: peak  $2\phi = 35.9^\circ$ , background  $2\phi = 35.2^\circ$ ,

Bismuth,  $L_{\alpha 1}$  line: peak  $2\phi = 32.9^\circ$ , background  $2\phi = 32.2^\circ$ .

Table 4 shows the values corresponding to the study of the interferences which might be caused by the presence of

lead and zinc. The tests were made using standard solutions of mercury, zinc and lead. The amounts of the interfering elements are expressed in the Table in mg per 50ml of solution, to which 5ml of one per cent bismuth nitrate solution and 5ml of nitric acid diluted 1:1 with water were also added. The standard solutions required to construct the calibration curves were prepared to contain the same concentrations of bismuth and nitric acid but with varying mercury content.

For the lead containing solutions, the background reading for the bismuth line was carried out at  $2\phi = 38^\circ$ , whilst for zinc it was performed at  $2\phi = 35.2^\circ$ .

A similar experiment was made to study the influence of the presence of iron and copper in the sample solution to be analysed. The results are shown in Table 5. It will be seen that the presence of copper enhances the fluorescent emission of mercury from the higher values obtained. The interference tests were repeated with the addition of the interfering elements concerned to the standard solutions used for the construction of the calibration curves. The results are given in Table 6.

The solutions used for the calibration values shown in Table 6 contained, in addition to the internal standards for mercury and bismuth, 150mg  $\text{Fe}_2\text{O}_3$ , 150mg  $\text{CuO}$ , 50mg  $\text{PbO}$  and 50 mg  $\text{ZnO}$  per 50 ml of solution. According to the amount of mercury present, it is necessary to prepare standard solutions containing amounts of the interfering

elements as equal as possible to the amounts present in the unknown sample to be analysed.

#### *Volatilisation of mercury*

Tests were made to check that mercury was not being lost by volatilisation during the treatment of the sample to remove organic matter. For this purpose, a paint containing additional mercury was heated in an Erlenmeyer flask with and without a reflux condenser. In the first case 100 per cent recovery of the mercury was obtained, but without the condenser this fell to 76 per cent.

#### *Proposed technique*

Place 2g of the sample to be analysed in an Erlenmeyer flask fitted with a ground glass neck carrying a reflux condenser. Add 30ml of concentrated nitric acid and reflux for one hour, cool and transfer to a 100ml volumetric flask and dilute to the mark with distilled water. Filter a portion and transfer 25ml of the filtrate to a 50ml volumetric flask, add 5ml of one per cent bismuth sub-nitrate solution and 5ml of 1:1 nitric acid (to prevent hydrolysis of the bismuth salt) and dilute to the mark.

The solution is placed in the X-ray spectrophotometer and the intensities of the  $\text{Hg L}_{\alpha 1}$  and the  $\text{Bi L}_{\alpha 1}$  lines measured. From the ratio of these intensities, the percentage of

Table 4  
*Interferences caused by the presence of zinc and lead*

| Sample | Zinc concentration<br>(in $\text{ZnO}$ )<br>mg per 50ml sample | Lead concentration<br>(in $\text{PbO}$ )<br>mg per 50ml sample | Mercury concentration<br>(in $\text{HgO}$ )<br>mg per 50ml sample |       |
|--------|--|--|---|-------|
|        |  |  | Added   | Found |
| 1      | 25   | —  | 25.0  | 25.2  |
| 2      | 50   | —  | 25.0  | 25.2  |
| 3      | 100  | —  | 25.0  | 25.4  |
| 4      | —  | 25   | 25.0  | 25.0  |
| 5      | —  | 50   | 25.0  | 25.0  |
| 6      | —  | 100  | 25.0  | 24.2  |

Table 5  
*Interferences caused by the presence of iron and copper*

| Sample | Iron concentration<br>(in $\text{Fe}_2\text{O}_3$ )<br>mg per 50ml sample | Copper concentration<br>(in $\text{CuO}$ )<br>mg per 50ml sample | Mercury concentration<br>(in $\text{HgO}$ )<br>mg per 50ml sample |       |
|--------|---|--|---|-------|
|        |   |  | Added   | Found |
| 1      | 100   | —  | 25.0  | 25.4  |
| 2      | 200   | —  | 25.0  | 24.7  |
| 3      | —   | 100  | 25.0  | 29.3  |
| 4      | —   | 200  | 25.0  | 29.6  |

Table 6  
*Results with mercury with interfering elements*

| Sample | Concentration of interfering elements<br>in mg per 50ml sample |              |              |              | Mercury concentration<br>in mg Hg per 50ml sample |       |
|--------|--|--------------|--------------|--------------|---|-------|
|        | $\text{Fe}_2\text{O}_3$  | $\text{CuO}$ | $\text{PbO}$ | $\text{ZnO}$ | Added   | Found |
| 1      | 50   | 200          | 25           | 25           | 15.0  | 14.8  |
| 2      | 150  | 100          | 25           | 25           | 15.0  | 14.9  |
| 3      | 100  | 150          | 25           | 25           | 30.0  | 29.5  |
| 4      | 200  | 50           | 25           | 25           | 30.0  | 30.0  |
| 5      | 100  | 100          | 50           | 50           | 30.0  | 30.2  |
| 6      | 200  | 200          | 25           | 25           | 30.0  | 29.3  |



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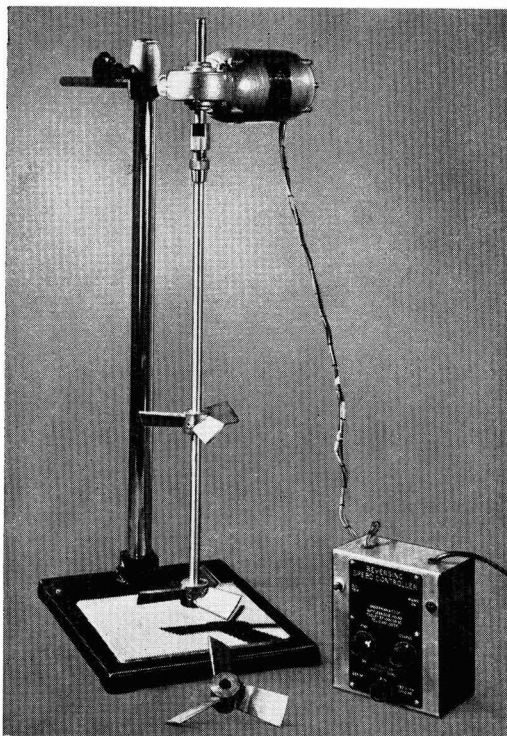
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mercury present may be obtained by reference to the calibration curves.

The standard solutions required for the construction of the calibration curves were prepared as follows:

2.5; 5.0; 7.5 and 10ml of a standard solution of mercury (5mg per ml) were added respectively to four 50ml volumetric flasks. 7.5ml of iron solution ( $20 \text{ g}^1 \text{ l}^1 \text{ Fe}_2\text{O}_3$ ), 2.5ml copper solution ( $20 \text{ g}^1 \text{ l}^1 \text{ CuO}$ ), 2.5ml zinc solution ( $20 \text{ g}^1 \text{ l}^1 \text{ ZnO}$ ), 215ml lead solution ( $20 \text{ g}^1 \text{ l}^1 \text{ PbO}$ ), 5ml of one per cent bismuth sub-nitrate solution and 5ml of 1:1 nitric acid was added to each flask and the solutions were diluted to the mark.

These solutions correspond to the concentrations which would be obtained from a paint sample which contained;  $\text{Fe}_2\text{O}_3$  30 per cent,  $\text{CuO}$  30 per cent,  $\text{ZnO}$  10 per cent,  $\text{PbO}$  10 per cent and 2.5; 5.0; 7.5 and 10 per cent mercury in turn.

### Results

The application of this method to antifouling paints was carried out on mercury-free samples, to which known amounts of this element were added. The determination of mercury by chemical means is difficult because of the complex mixture remaining after the organic matter has been destroyed. The paint was prepared in the laboratory and the absence of mercury confirmed by qualitative X-ray fluorescence tests on an untreated sample. The addition of mercury to the paint was made to the sample which had already been weighed and was ready for treatment. The addition was made in the form of a mercuric nitrate solution to give HgO contents varying from 1 to 8 per cent of the paint. The results obtained are given in Table 7.

Table 7  
X-ray fluorescence tests for mercury

| Sample | Hg added, in HgO per cent | Hg found, in HgO per cent |
|--------|---------------------------|---------------------------|
| 1      | 1.00                      | 1.00                      |
| 2      | 2.00                      | 2.10                      |
| 3      | 3.00                      | 3.00                      |
| 4      | 4.00                      | 4.00                      |
| 5      | 5.00                      | 4.94                      |
| 6      | 6.00                      | 5.92                      |
| 7      | 7.00                      | 7.08                      |
| 8      | 8.00                      | 8.12                      |

### Conclusions

A technique has been developed for the qualitative analysis of paints which is very rapid and reliable. It also allows subsequent quantitative analysis.

For copper and arsenic, quantitative analysis in paints can be carried out simultaneously without previous separation of other metals. An error of 2.1 per cent for copper and 1.6 per cent for arsenic may be regarded as satisfactory for this type of sample. The simultaneous determination of these elements is advantageous since the most time consuming operation is the destruction of organic matter in the sample.

The method for the quantitative determination of mercury also has the advantage of simplicity. Only a short time is required for the determination, and the error can be as low as 1.5 per cent. Each reading on the sample takes no more than 10 minutes.

[Received 24 April 1973]

## Next month's issue

The Honorary Editor has accepted the following papers for publication and these are expected to appear in the March issue:

The prevention of gelation during the maleinisation of dehydrated castor oil by *A. M. Naser, N. A. Ghanem and N. I. Sadik*

Painting concrete by *B. Lindberg*

Wood varnishes from wattle bark extract by *H. M. Saayman*

# Reviews

## INTUMESCENT PAINTS

### Bibliographies in Paint Technology No. 22.

By D. J. Jones

R. H. Chandler Ltd., Braintree, Essex, 1973, pp. 48. Price £5.00

This bibliography, largely based on the Paint Research Association's World Surface Coatings Abstracts (WSCA) (Formerly Review) for the period 1956-73 is reasonably comprehensive in content but, because of its unusual arrangement, not immediately accessible to the student seeking general information. The technology of intumescent paints is presented in the guise of an alphabetical encyclopaedia of related terms which, at first sight, is much less informative than the more usual state of the art review, for example, Vandersull's very good review in *J. Fire and Flammability*, 1971, 2, 97-140. However, it will provide the harassed chief chemist who is thrown a request for instant information by his directors with quick answers on specific acid-release agents or the functions of particular components in fire-retardant paints. The listing of 103 relevant patents with brief abstracts will also be valuable. Entries in the encyclopaedia are usually informative but could have been improved

by reference to wider sources, especially the most useful bibliographies and Research Notes emanating from the Fire Research Station, Boreham Wood.

T. R. BULLETT

## ACRYLIC POWDER COATINGS

### A preliminary bibliography

R. H. Chandler Ltd., Braintree, Essex, September, 1973, pp. 15. Price £2.00.

This is one more addition to the range of useful Chandler bibliographies. As in many fields covered by coating abstract journals, the proportion of patent specification to general literature articles continues to increase—in the present case reaching about four to one. There is a sameness about the acrylic powder coating patents described, which are in most cases fairly obvious developments from solution acrylic resins. Anyone engaged in this field will certainly find this bibliography of value.

L. A. O'NEILL

## Section Proceedings

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### Hull

#### Some aspects of personnel management

Seventeen members and nine visitors assembled at the Barrow Haven Inn, Lincolnshire on Tuesday 6 November to hear a lecture given by Mr K. Yates of Laporte Industries Limited. Mr Yates indicated that his lecture which was entitled "Some aspects of personnel management" would be an informal one, and he invited the audience to comment and ask questions at any stage. He asked the audience to consider the statement, "People are basically lazy and will avoid work if they can." This had been the underlying assumption by management in its use of such devices as time clocks and close supervision of the labour force. He then reviewed some recent findings by Frederick Herzberg, which suggested that other approaches might be of assistance to management in its handling of people. Herzberg had shown that factors affecting people's attitudes to their jobs fell into two categories according to whether they produced satisfaction or dissatisfaction. Salary, security, status, a satisfactory company policy and administration and the existence of appropriate working conditions were termed "hygiene" factors; these had to be maintained to prevent dissatisfaction but were not, in themselves, sufficient to bring out the best in people. Genuine job satisfaction was created only by motivating factors such as the interest of the work itself, responsibility, recognition, achievement and opportunities for growth and advancement.

Mr Yates commented that the routine associated with many jobs had increased over the past 35 years and that the skill content had decreased. This had bred dissatisfaction and it was now necessary for management to provide job enrichment in order to use people more effectively.

One study of the influence of motivation factors on the job performance of professionally qualified laboratory

workers was described in some detail. Hygiene factors were maintained constant and job enrichment was provided in three areas with the intention of producing better scientists: on the technical side, the members of the group were allowed to issue final research reports over their own name without checking, they became involved in project planning and were encouraged to follow up ideas of their own; on the financial side they were allowed to requisition analytical and maintenance services over their own signature; on the managerial side the senior members of the group devised and implemented a training scheme and became involved in selection interviewing and performance appraisal. To measure the effect of the changes, the members of the experimental and control groups were asked to prepare reports at monthly intervals. Better reports were produced by the experimental group and in several cases these were of outstanding merit.

Mr Yates lecture was well received, and a high level of audience participation was achieved. Mr K. B. Smith in his vote of thanks to the lecturer, congratulated him on the skill with which he had presented it.

J.A.H.

#### Under-25 Lecture: Organic pigments in paints and printing inks

A lecture arranged mainly for younger members of the Section, was given by Mr R. C. Platts of Victor Blagden & Company Limited at the Dorchester Hotel, Hull on Monday 29 October.

Mr Platts gave a general account of the properties of pigments and then discussed the more important pigments on an individual basis. An especially attractive feature of the evening was the circulation of paint and ink films which illustrated defects such as bleeding, silking, instability towards

heat and metamerism etc, to which the speaker had previously referred.

A discussion period followed, after which Mr A. R.

Vanspall thanked the lecturer for his contribution towards a successful evening. The meeting was attended by eight members and nine visitors.

J.A.H.

## Manchester

### Symposium on wall coverings

Over 200 delegates attended a one day Seminar on wall coverings at UMIST, Manchester, on 18 September 1973, showing the interest in this subject. Seven papers were presented, and consideration was being given to the publication in full of these papers in the *Journal* and, therefore, no reports are given at this stage.

### Communications and industrial relations

Some 35 members and visitors attended a meeting held at Literary and Philosophical Society on Friday 9 November

at 6.30 p.m. to hear Mr W. Davies, of the Manchester Business School, give a talk with the title "Communications and industrial relations".

After defining communication as "accurate transmission of ideas to achieve a desired objective," Mr Davies proceeded to give a masterly display of the art of communication in a most entertaining manner. This was followed by a lively discussion period and rounded off by a witty vote of thanks from Mr H. Cook, which was received with well deserved acclamation.

A.McW.

## Midlands

### Solvents and safety

Approximately 30 members and guests attended a lecture on "Solvents and safety" given by Mr Silcox, H. M. District Inspector of Factories, Derby, at the British Rail School of Transport on 8 November 1973. Mr K. W. Smith was to have given the talk but had recently been transferred and Mr Silcox had bravely stepped into the breach.

Mr J. A. Burns, Vice-Chairman, welcomed Mr Silcox to the area and the meeting. He expressed the hope that the cordial relationship which industry had with H. M. Inspector of Factories would continue.

In his talk, Mr Silcox dealt at length with specifications, regulations and codes of practice governing the storage, transportation and health hazards relating to flammable substances.

The lecture was followed by a lively and at times mirthful question time, and the vote of thanks for a very interesting evening was given by Mr S. N. Hawley.

C.V.W.

compounds, in an effort to widen the colour range. The quinacridone reds had been developed in this way, and the textile vat dyes yielded some pigments of very high light fastness. The complex manufacturing methods which had to be adopted were reflected in their high cost.

Examination of the older, established pigments and textile dyes led to a recognition of the importance of the imide group in conferring insolubility. The technique of "doubling-up" of molecules could often improve lightfastness and resistance to migration. The earlier trial and error methods had now been greatly simplified by the introduction of advanced instrumentation.

The lecturer concluded by showing several photomicrographs of phthalocyanine blue pigments taken through both the scanning and the transmission electron microscopes.

The lengthy discussion which followed was a good indication of the interest aroused by this lecture, and by the lecturer's lively presentation; Dr Inman was assisted during the discussion by his colleague, Mr A. Honiball. A vote of thanks was proposed by Mr H. J. Griffiths.

F.W.C.

### Recent progress in organic pigments

The lecture was presented by Dr E. R. Inman, of CIBA-Geigy Ltd., to a meeting on 16 November 1973.

The lecturer's aim was to give an impression of the developments in the technology of organic pigments as seen from within the pigment industry. The large number of patents published gave a good impression of the scale of these developments, and their end usage in inks, paints and plastics had been responsible for the bulk of the improvements.

The recognition of phthalocyanine blue in 1928 had produced a profound effect on pigment technology, and a series of slides illustrated the many modifications possible, and the effects of these on the resultant pigments. The phenomena of flotation and flooding were also illustrated, together with slides showing how these defects could be minimised by pigment modification.

The work carried out on the phthalocyanines had led to the introduction of a number of new techniques, including salt grinding and acid pasting. These techniques were widely applied both to existing pigments and to potential pigmentary

### Trent Valley Branch

#### Joint visit to the Royal Doulton Works, Burslem

Some 30 members and their wives drawn from the Section and the Trent Valley Branch spent a very interesting day at the Royal Doulton Works, Burslem on 1 November 1973.

The Section visitors toured the Works in the morning and then met the Trent Valley party at an excellent luncheon held at the George Hotel, a stone's throw from the works.

The Branch members spent a very interesting and instructive afternoon touring the extensive works and after a visit to the showrooms, were entertained to tea and biscuits in the canteen.

Arrangements for the visit were made by Mr D. D. Kimber, the Section Social Secretary.

C.V.W.

Owing to the difficulties experienced in the printing industry during the three-day working week, it has been necessary to delay publication of some Section Proceedings.

# Information Received

## Akzo Chemie UK Ltd.

From 1 January 1974, the component companies of the UK Chemical Division of the Dutch owned Akzo Group have been trading under the identity of Akzo Chemie UK Ltd. The British based companies of Novadel Ltd., Interstab Ltd., Greyer, Brecheisen & Co. Ltd., Ormerod Taylor & Sons Ltd, The Perox Chemicals Co. Ltd. and Cefarol Products Ltd. are now divisions of the one integrated company, so that for example Novadel Limited trade as Akzo Chemie UK Limited Novadel Division.

## Albright & Wilson Ltd. expand organo-tin chemicals production

Production capacity of Albright & Wilson Ltd's. Industrial Chemicals Division plant for the manufacture of organo-tin chemicals is to be increased by 50 per cent. Work on a £300,000 expansion of the Stratford, London, plant has already begun and should be completed early this year.

Concurrently with this expansion, manufacture of "TBTO" will be transferred to the Division's Oldbury works.

## BIP reorganisation

British Industrial Plastics has announced that all its subsidiary company activities in materials, processing machinery and moulding will be re-grouped into divisions of the former organisation:

Chemicals division covers production and sales of thermosetting moulding powders and resins at the Oldbury, Worcs., and the Liverpool sites previously operated by BIP Chemicals Limited. Engineering division has taken over the production of "Bipel" injection and compression moulding machinery from BIP Engineering Ltd.

Moulding division embraces both the trade moulding activities of the Streetley Manufacturing Co. Ltd. and production of the "Filon" grp sheet of BIP Reinforced Products Limited.

In addition to these three new Divisions, there is the Sheet and Film and Pvc Divisions set up on 1 October 1973.

## Degussa plant in USA

Degussa has founded a new subsidiary in America, the Degussa Alabama Inc, with a site near Mobile, Alabama. The company intends to build a 16 000 metric tonnes per year methionine plant and a 5 400 metric tonne per year Aerosil plant on this site. This is considered as a first development phase with both plants planned for operation by 1976.

## English China Clays appoint distributor for whittings

In order to give a better service to its customers for Queensgate whittings, English China Clays Sales Company Limited has appointed a new distributor who will deal only with those companies who deal with chalk whiting in under 8 tonne lots. All enquiries should be addressed to this distributor, Whitfield & Son Ltd., 23 Albert Street, Newcastle, Staffs.

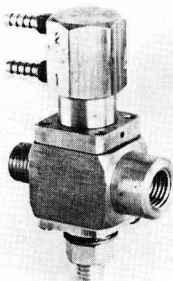
## Hüls licences for China

Chemische Werke Hüls AG will grant to China "know how" licences for the manufacture of ethylene oxide by the air oxidation process as well as for the manufacture of ethylene glycols. The projected plants will have a capacity of 35,000 and 45,000 tons per year, respectively. The process technology will be made available by Hüls; the engineering will be provided by Messrs. Still, Pecklinghausen. The licences will be granted within the scope of an agreement concluded between the French companies Technip and Speichim and the Chinese National Technical Import Corporation (CNTIC) concerning the erection of a petrochemical complex which is to be built 60km south of Shenyang (Mukden) in southern Manchuria. The contract will have a value of about FF 1.2 billion.

## New products

### Fluid Control Valve

Nordan UK Limited has announced a "Series 47" fluid control valve designed for use with most types of adhesives, paints and other industrial fluids eliminating the problems of adhesive drip and poor cut-off.



Nordan control valve

## New silane-coated atmospheres from Jacobson van den Berg.

Atmospheres, the light-weight filler for polymers recently introduced by Jacobson van den Berg & Co. (UK) Ltd., is now being silane-coated for increased bonding strength in GRP products.

## ... UK agent for Sedapol and corrosion inhibitors

A range of anti-settling agents for paints, inks and varnishes from Supercolori of Italy is now available in the UK from Jacobson van den Berg. It includes "Sedapol" 44 and 48, which are based on Wyoming Bentonite. Sedapol 44 is specially formulated for low to medium polarity systems and 48 for high polarity systems.

In addition, a new range of corrosion inhibitors is available. The inhibitors, designated "562" and "620," were developed by the French firm Produits Chimiques Lombard-Gerin for emulsion paints and are already widely used on the Continent.

## Miniforma available in UK

J. & William Burt Ltd., UK distributors for the German printing machine manufacturers Goebel of Darmstadt, has announced the availability of the competitively priced Miniforma continuous stationery forms press with a universal printing unit. Maximum working bed width is 400mm, with a maximum printing width of 380mm.

## Oil-water separation by Boulton

William Boulton Limited has introduced a new system for separating oil from washwater. This system has been designed to meet the increasing demand of manufacture for an economical method of treating industrial effluent comprising oil and water to conform with the stringent requirements of the River Authorities.

The sealed system made from corrosion resistant materials for continuous operation is claimed to be 40 per cent cheaper to install than other comparable systems.

## PTFE lubricant powder from ICI

A new addition to the "Fluon" range of PTFE lubricant powders has been announced by ICI Plastics Division. Coded "Fluon" L171, it is a lubricant powder with a median particle size of 3 to 4 microns, which disperses readily in liquids when using either high or low-shear mixers.

The new product has been developed as an additive to coating-resins and printing inks where it imparts a significant reduction in coefficient of friction and ensures retention of the gloss and hardness of the base resins. Dispersions of L171 have relatively low viscosity and low thixotropy compared with those produced from other PTFE lubricant powders.

## SRL chain stopped alkyd

The current shortage of some basic raw materials used in the production of styrene modified alkyds has prompted Synthetic Resins Ltd. to introduce "Beckosol 12-101", a chain stopped pure drying oil alkyd recommended for use in fast air drying industrial paints and fast curing low bake enamels. The company claims very good gloss retention on exterior exposure and fast drying, excellent resistance to oils and greases, water and general weather conditions, and reasonable resistance to acids and alkali.

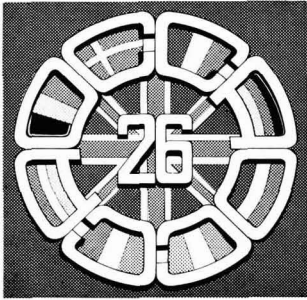
## "Tefzel" Handbook

A new 27-page handbook presenting data for material selection and product design using "Tefzel" ETFE fluoropolymer is now available in English, French and German from Du Pont Limited.

## Conference, courses, symposia

### Particle Workshop

Loughborough University of Technology and Warren Spring Laboratory have collaborated to organise a particle workshop consisting of 5 lectures and practical and tutorial sessions. The course will be held at Loughborough from 25 to 29 March 1974 and further details are available from Mr J. Wilcox, Centre for Extension Studies, University of Technology, Loughborough, Leics.



## Shortages of raw materials enhance the value of this unique forum for technical display and discussion

### OCCA 26 Exhibition

23-26 April 1974, Empire Hall, Olympia, London

APPLICATIONS ARE STILL BEING ACCEPTED

Never has the value of the Association's annual Technical Exhibition been so apparent as during the present shortage of raw materials for the surface coatings industries, since the Exhibition provides an unique forum for technical discussion between the personnel using these resources and the suppliers. Grasping this opportunity to explain to the technical personnel in the industries the optimum use of those resources available, many companies will be using this splendid platform to show how they are helping their clients during these critical times, and the Exhibition Committee is pleased to report that the countries represented at this year's Exhibition are widespread and include, for the first time, three more representatives from Eastern Europe. The full list of countries represented will be as follows: Australia, East Germany, Finland, France, Holland, Hungary, Italy, Poland, Rumania, Spain, Switzerland, USA and West Germany.

Applications for stand space can still be accepted, and if received soon might be included in the Official Guide, but in any case late applications will be featured not only in the April (Preview) issue of this *Journal* but also in an addendum to the Official Guide given to all visitors at the

entrance to the Exhibition. Any company wishing to exhibit should contact the Director & Secretary of the Association at the address shown on the front cover of this *Journal* (or telephone 01-908 1086—telex 922670.)

#### International character

The Exhibition, which has long been known as the forum for technical display and discussion for the surface coatings industries, in 1973 attracted visitors from more than 50 overseas countries, and there was direct contribution by exhibitors from 14 overseas countries. The motif chosen for this year's Exhibition shows the flags of the enlarged European Economic Community and, by converging on the flag of the UK, symbolises the welcome extended for many years to exhibitors and visitors not only from these countries but from farther afield to the OCCA Exhibitions in London, one of the capital cities of the European Economic Community. To further the aim of a truly international character, the Exhibition is widely advertised in technical journals both at home and in many technical journals overseas. Furthermore, it has been the practice for many years to issue information cards in six languages (English, French, German,

Italian, Spanish and Russian) and these are widely distributed to firms and individuals in many countries. Interpreters are available at the Exhibition without charge to help both exhibitors and visitors alike.

#### Official Guide

As far as present conditions permit, the *Official Guide* will be prepared well in advance of the dates of the Exhibition so that copies can be circulated widely, both to members and non-members, thus allowing visitors an opportunity to plan their itineraries. As well as maintaining the Exhibition's unique position as a purely technical display, manned by technical personnel, the Exhibition Committee has for many years followed the successful policy of encouraging visitors in this way, and by making no charge for admission so that the maximum flow of communication between exhibitors and visitors can take place.

#### Travel Agents

The Wayfarers Travel Agency Ltd. has been allocated Stand 26 at the Exhibition, and will be prepared to advise on and arrange hotel accommodation and travel facilities.

## PMATA merges with PA

The members of the Paint Manufacturers and Allied Trades Association (PMATA) agreed to merge with the Paintmakers Association (PA) from January 1974. The PA is forming a new Group for small manufacturers which will be open to appropriate PMATA and existing PA members. This new Group will elect two representatives to sit on the PA Council (the governing body).

The PMATA was formed during the Second World War by a number of smaller paint manufacturers to resist a Board of Trade scheme for concentration. It succeeded in defeating that scheme and continued

after the war to act as a "watchdog" for the interests of its members.

In recent years, a number of PMATA members have also been members of the PA, which was formed in 1963 from two former associations. The PA has sought to represent the interests of companies of all sizes and has honoured some of its smallest members with the Presidency or the Chairmanship of its local Sections.

It is expected that the formation of a unified trade association, which may be seen as a reaction to the Devlin report published in November 1972, will strengthen the paint industry's representation with the many authorities which now impinge on its activities. OCCA expresses its wishes for success for the new Association.

## Manchester Section

#### Dinner Dance

This was held at the Piccadilly Hotel, Manchester on Friday 25 October. Over 400 members and their guests were present. The Section was very pleased to be able to welcome as guest of honour one of its

own members, Mr T. E. Johnson, together with a number of other Section Chairmen and their ladies.

Once again a very successful combination of dance band and disco was adopted and all present had a marvellous evening.

## West Riding Section

#### Dinner and Dance

The Section held its fifteenth Annual Dinner and Dance at the Crown Hotel, Harrogate on Friday 23 November 1973.

The President, Mr L. H. Silver, in proposing the toast to the Section, expressed his pleasure that so many old friends were present on this happy occasion, particularly as he was speaking as a member of the Section as well as President.

The Section Chairman, Mr D. Morris, echoed these sentiments and gave a special welcome to the many past Chairmen of the Section who had made a special effort to attend this function, which celebrated the twenty-first year since the formation of the West Riding Section. He also welcomed the considerable number of guests including the Chairmen and their ladies from the Bristol, Hull, London, Manchester, Newcastle, Scottish and Thames Valley Sections as well as Mr R. H. Hamblin, Mr and Mrs A. R. H. Tawn and Mr and Mrs D.

Newton. As a mark of esteem from the members of the West Riding Section, the Chairman presented a silver candelabra to the President and his wife. He also presented both the West Riding Chairman's Trophy and the OCCA Golf Trophy to Mr R. Hardy. Finally, the Chairman presented a memento to Mr M. Cochrane and his wife in recognition of all the hard work they had put in over many years in organising the function and contributing in so small measure to its success.

Mr D. Grey, as a founder member and one of its earliest Chairmen, responded on behalf of the ladies, guests and Past Chairmen.

Following dinner, everyone adjourned to the ballroom where the floor remained crowded until 1.00 am. It was universally agreed that the evening had been a tremendous success.

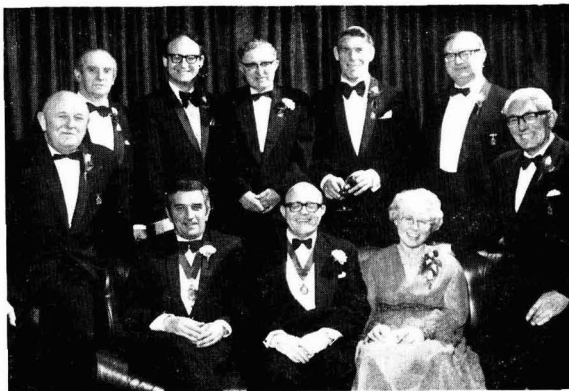
## Obituary

### R. E. Bradburn

Mr R. E. Bradburn, an Ordinary Member attached to the Manchester Section, died in Hospital on 30 October 1973 and was cremated at Altrincham Crematorium on 5 November.

Mr Bradburn was a well known and well liked figure in the Manchester area, having spent some 47 years with Isaac Bentley & Son Ltd., of Trafford Park. Following the closure of the firm's paint making activities, Mr Bradburn joined England, Hughes, Bell & Co. Ltd., where he worked for a further two years before becoming ill in July 1973.

He was an active member of the Association and served on the Manchester Section Committee 1957-1961.



From left to right: C. Butler, D. A. W. Adams, L. J. Watkinson, D. Grey, N. Cochrane, K. Hargreaves, S. Cass. Front: L. H. Silver (President and Section Chairman 1967-69) D. Morris (Section Chairman) and Mrs K. Driver (immediate past Chairman)

## Borough Symposium

### Long-life exterior coatings

The Borough Surface Coatings Association will be holding a One-Day Symposium on "Long-life exterior coatings" on 6 March 1973 at the Polytechnic of the South Bank, London.

Speakers have been drawn from CIBA-

GEIGY, ICI, Bakelite Xylonite Ltd., Inmont Ltd., Taylor Woodrow Construction Ltd., and BIE (Anti-corrosion) Ltd. The fee for the Symposium will be £7.50 (£7 to members of the Association) and will include lunch, coffee, tea and preprints. For further details apply to P. J. Barnes, Department of Chemistry and Polymer Technology, Polytechnic of the South Bank, Borough Road, London, SE1.

## Victor Terrell Crowl BSc, PhD, ARCS, DIC, FRIC, FTSC—1920-1973

### An Appreciation by Dr S. H. Bell

Dr Crowl was a true expert—trained by practice, skillful and knowledgeable in a difficult and complex area of surface coatings science and technology, namely pigment dispersion, about which so much has been done during many years and much more has been written and argued. He wrote and spoke only about what he knew from his extensive laboratory work at the Paint Research Association and from his critical appraisal of the work of others.

For many years, he will be remembered in OCCA for his outstanding contributions to the surface chemistry of pigments and media, particle size analysis, wetting and dispersion processes, dispersion stability and pigment flocculation and flotation. He published numerous papers at home and abroad and gave excellent lectures to OCCA Sections and at biennial conferences, and, on behalf of OCCA, in Denmark and at FATIPEC assemblies. There are many PRA reports to his credit and until only a few weeks before his death, he was a regular lecturer at the training courses at Teddington. He was a committee member of the Colloid and Surface Chemistry Group of the Society of Chemical Industry, and Secretary of the Particle Size Analysis Group of the Society for Analytical Chemistry.

His work was of special interest to me because my own laboratory initiation at Teddington many years ago was in the same subject. We had frequent discussions about his research results and their interpretation, and it gave me particular pleasure to collaborate with him in bringing together many findings and ideas in the chapter on "Assessment of Dispersion" in the book on "Dispersion of Powders in Liquids" edited by Professor G. D. Parfitt.

There were other activities however about which he did not speak very often. There was his quiet steady work for OCCA London Section as Honorary Publications Officer since 1965, his reporting of the OCCA Exhibitions in the Journal and his recent (1971-73) membership of Council. There was also his outstanding role in the PRA Staff Association of which he was a committee member from 1957 to 1967 and Chairman in 1958-60 and 1963-65, and was responsible for many social activities with memorable success.

He graduated in chemistry in 1939 from Imperial College, London, where he was a Royal Scholar, and completed his PhD in Physical Chemistry in 1941. Then followed a period on chemical plant

operations with ICI and a post-war responsibility as a senior technical assistant in the Control Commission in Germany. Later, after a period of ill health, he was introduced to me by Prof. H. V. A. Briscoe of Imperial College (then President of the PRA) who suggested that full recuperation would be assisted by some steady laboratory work as a research assistant. That was how he came to Teddington in 1954 and as his health improved his talents became increasingly apparent leading to his taking charge of the Physical Chemistry Section and to his gaining his international reputation.

In September 1970, he moved from the laboratories to assist Mr E. F. Redknapp, then the editor of World Surface Coatings Abstracts, where his technical experience and linguistic ability were of great value. He ceased full-time service in December 1972, continuing abstracting work from his home until his sudden death on 24 October 1973.

I shall remember him as a very active, friendly colleague with ready wit and good humour, who in spite of recurrent ill-health intensively applied his very considerable technical and social talents to the benefit of others.



## Forthcoming Events

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

### February

#### Monday 4 February

*Hull Section:* Ladies Evening. "Wallpaper design and manufacture" by Mr B. C. Callaghan of ICI Wallpapers Ltd., to be held at the Dorchester Hotel, Beverley Road, Hull at 7.00 p.m.

#### Thursday 7 February

*Newcastle Section:* "Profitability in the paint industry" by Mr L. H. Silver (SPL Group) to be held at the Royal Turks Head Hotel, Grey Street, Newcastle-upon-Tyne.

*Thames Valley—Student Group:* "The basic principles of Dispensymers" by Dr D. Pont of ICI Paints, to be held at the main Lecture Theatre, Slough College at 4 p.m.

#### Friday 8 February

*Manchester Section:* Instrument Evening to be held at the Manchester Literary and Philosophical Society at 6.30 p.m. (1) "The Gel Permeation Chromatograph" by Dr R. Ellis of The Walpamur Co. Ltd.

(2) "The Zeiss Goniophotometer" by Dr W. Carr, CIBA-GEIGY (UK) Ltd., Pigments Division.

*Scottish—Eastern Branch:* Burns Supper in the Lady Nairn Hotel, Edinburgh.

*Thames Valley Section:* Buffet Dance at Great Fosters, Egham.

#### Tuesday 12 February

*London Section:* "Recent developments in metal decorating" by Mr J. Holt and Mr M. Reid of the Research Division, Metal Box Company, to be held at Great Northern Hotel, King's Cross, London N1 9AN at 7.00 p.m.

*West Riding Section:* "Fast air drying vegetable oils" by Dr Gorke of Chemische Werke Huls AG, to be held at the Griffin Hotel, Leeds at 7.30 p.m.

#### Thursday 14 February

*Midlands Section—Trent Valley Branch:* "Developments at British Rail" by Mr D. M. Bishop to be held at British Rail School of Transport, London Road, Derby at 6.30 p.m.

*Scottish Section:* Talk on matters of topical interest by R. W. Kay of HM Factory Inspectorate, to be held in the St Enoch Hotel, Glasgow at 6.00 p.m.

#### Friday 15 February

*Irish Section:* "Works visit" to the Irish Glass Bottle Company.

*Midlands Section:* "We need paint" by R. J. King of Blundell Permoglaze Ltd., to be held at the Birmingham Chamber of Commerce and Industry PO Box 30, 75 Harborne Road, Birmingham B15 3DH at 6.30 p.m.

#### Saturday 16 February

*Scottish Section—Student Group:* "Communications" by Mr D. Glenn of CIBA-GEIGY (UK) Ltd., to be held at St. Enoch's Hotel, Glasgow at 10.15 a.m.

#### Tuesday 19 February

*London Section—Southern Branch:* Meeting postponed.

#### Wednesday 20 February

*Scottish Section—Eastern Branch:* "Computers in general" by Mr F. Lawry, Croda Polymers, to be held in the Carlton Hotel, North Bridge, Edinburgh at 7.30 p.m.

#### Thursday 21 February

*Thames Valley Section:* "Corrosion: the vulture of metallurgy" by Dr M. Clarke of Sir John Cass School of Science and Technology, to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks at 7.00 p.m.

#### Friday 22 February

*Bristol Section:* Details to be announced.

*Newcastle Section:* Ladies Night. Five Bridges Hotel, Gateshead.

#### Saturday 23 to Sunday 24 February

*London Section:* Weekend conference on "Colour" with participation from the French Association AFTPV at the Queen's Hotel, Hastings, Kent.

#### Wednesday 27 February

*Manchester Section—Student Group:* "Paint additives" by a lecturer from Byk-Mallinckrodt to be held at the Manchester Literary & Philosophical Society at 4.30 p.m.

### March

#### Monday 4 March

*Hull Section:* "Etch and blast primers" by H. F. Clay of Cromford Colour Co. Ltd., to be held at the Dorchester Hotel, Beverley Road, Hull at 7.00 a.m.

#### Thursday 7 March

*Newcastle Section:* "Coatings for plastics" by Dr Kutt, E. Wood Ltd., to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne.

*Thames Valley—Student Group:* Works visit.

#### Friday 8 March

*Bristol Section:* Annual Dinner Dance at the Mayfair Suite, New Bristol Centre.

*Manchester Section:* "Recent trends in wood finishing" by Mr K. Waddington of Donald Macpherson & Co. Ltd. to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester 1 at 6.30 p.m.

#### Tuesday 12 March

*London Section:* "Additives in paint." Half-day symposium at the Polytechnic of the South Bank, Borough Road, SE1 commencing at 2.00 p.m.

*West Riding Section:* "The forensic examination of inks and paints" by Mr R. M. Kevern to be held at the Griffin Hotel, Leeds at 7.30 p.m.

#### Thursday 14 March

*Midlands—Trent Valley Branch:* "Marketing" by Mr J. E. Fowles-Smith, Mebon Ltd., Sutton-in-Ashfield, Notts to be held at British Rail School of Transport, London Road, Derby at 6.30 p.m.

*Scottish Section:* "Paint and joinery" by A. Sherwood (Paint Research Association) to be held in the St. Enoch Hotel, Glasgow at 6.00 p.m.

#### Friday 15 March

*Irish Section:* "Dispersible pigments for printing inks" by Mr H. Bower BSC, Ciba Geigy (UK) Ltd. to be held at the Clarence Hotel, Dublin at 8.00 p.m.

*Midlands Section:* Annual J. Newton Friend Lecture 7.30 p.m. "Wines" by D. J. Smith (Seligman & Co. Ltd.) to be held in the Birmingham Chamber of Commerce and Industry, PO Box 30, 75 Harbourne Road, Birmingham B15 3DH.

#### Saturday 16 March

*Scottish—Student Group:* "Pigment elaborations" by Mr A. G. Able of Hoechst Cassella to be held at St. Enoch Hotel, Glasgow at 10.15 p.m.

#### Tuesday 18 March

*London—Southern Branch:* Meeting postponed.

#### Wednesday 20 March

*Scottish—Eastern Branch:* AGM at 7.00 p.m. followed by a lecture on coloured television by Mr L. Ashton, BBC, to be held in the Carlton Hotel, North Bridge, Edinburgh.

*Midlands Section:* Day Symposium 10.00 a.m. at Pavilion Suite, County Ground, Edgbaston, Birmingham "Atmospheric pollution—will the paint user overcome this problem."

#### Thursday 21 March

*Thames Valley Section:* "Dispersymer two years' production experience" by Mr M. Waghorn of ICI to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks at 7.00 p.m.

#### Friday 29 March

*Bristol Section:* "The new flashpoint regulations—flashpoint and combustibility tests" by Mr A. N. McKelvie of the Paint Research Association, to be held at the Angel Hotel, Cardiff.

## News of Members

Dr S. H. Bell, an Ordinary Member attached to the London Section and a Fellow in the Professional Grade, President from 1965 to 1967 and deputy Director & Secretary of the Paint Research Association, has been appointed an OBE in the New Year's Honours List. The warmest congratulations of the Association are offered to Dr Bell on this distinction.

Miss M. Searle, a registered student attached to the Trent Valley Branch of the Midlands Section, has been awarded the F. W. Clark Memorial Prize and Medal for 1973 for her results in the City

and Guilds of London Institute Part III Paint Technology Examination.

The following members were elected as Officers and to the Council of the British Colour Makers Association for the 1973-74 session at its annual general meeting held on 7 November 1973:

*Chairman:* Mr P. Perkin, an Ordinary Member attached to the Manchester Section.

*Hon. Treasurer:* Mr F. B. Mortimer-Ford, an Ordinary Member attached to the London Section.

*Council:* Mr G. K. Burrell (Associate Member, London Section.)

Mr H. G. Clayton (Ordinary Member, Manchester Section.)

Mr W. B. Cork (Ordinary Member, Hull Section.)

*Secretary:* Mr A. G. Wyatt (Ordinary Member, Manchester Section.)

Mr W. F. McDonnell, an Ordinary Member attached to the West Riding Section, has been appointed Works Director of Goodlass Wall & Co. Limited in succession to Mr J. B. Davis, an Ordinary Member attached to the Manchester Section, who is taking up a new appointment at Lead Industries Group Headquarters.

## Register of Members

The following elections to Membership have been approved by Council. The Section to which new Members are attached is given in italics.

### Ordinary Members

BOSSHARD, WERNER, Schurbungert 4, CH-8057 Zurich, Switzerland. (*General Overseas*)

ELBASHIR, GAAFER EL AMIN, BSc, London House, Mecklenburgh Square, London WC1. (*London*)

ESPEUT, KENNETH WILLIAM, BSc, 96 Green Dragon Lane, Winchmore Hill, London N21 2NJ. (*London*)

HARMAN, DENIS JOSEPH, BSc, 56 Muswell Road, Muswell Hill, London N10. (*London*)

HOOD, BERNARD KENNETH, The Grange, Little Waldingfield, Nr. Sudbury, Suffolk. (*London*)

HUDSON, ANDREW, 73 Beech Road, Wycombe Marsh, High Wycombe, Bucks. (*Thames Valley*)

JOHNSON, COLIN ANTHONY, 17 Newbury Close, Harold Hill, Romford, Essex. (*London*)

KHAN, ROBERT ULLAH, MSc, 34 Barley Lane, Goodmaye, Essex. (*London*)

PRICE, PAUL, Abbott Laboratories Chem. Div. North Chicago, Illinois 60064 USA. (*General Overseas*)

PROVAN, ANDREW WILSON, 235 Adelaide Road, Newton, Wellington, New Zealand. (*Wellington*)

SEVKET, DORUKER ALI, Etiler Gamlik, Mevki EVA apt. No. 5/1, Istanbul, Turkey. (*General Overseas*)

SNOWDEN, ANTHONY JOHN, 177 High Street, Walthamstow, London, E17. (*London*)

STAPLETON, REGINALD ROYSTON, MSc, "Oaklands" 4 Aislabie Close, Ripon, Yorks HGH 2DD. (*West Riding*)

### Associate Member

KERNICK, KEVIN JOHN, 34 Copeland Street, Lower Hutt, New Zealand. (*Wellington*)

### Registered Students

BELL, WILLIAM IVAN, Grad RIC, 30 Westmorland Crescent, Bangor Co. Down, N. Ireland. (*Irish*)

ELLIOTT, PETER, 95 Crescent Road, Plumstead, London SE18. (*London*)

MAGNALL, CHRISTOPHER JOHN, 58 Chapel Street, Brierfield, Lancs. (*Manchester*)

# print in practice

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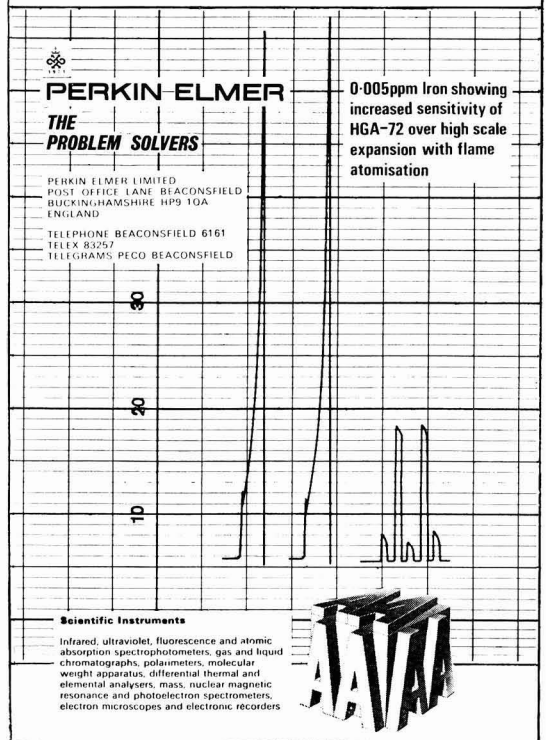
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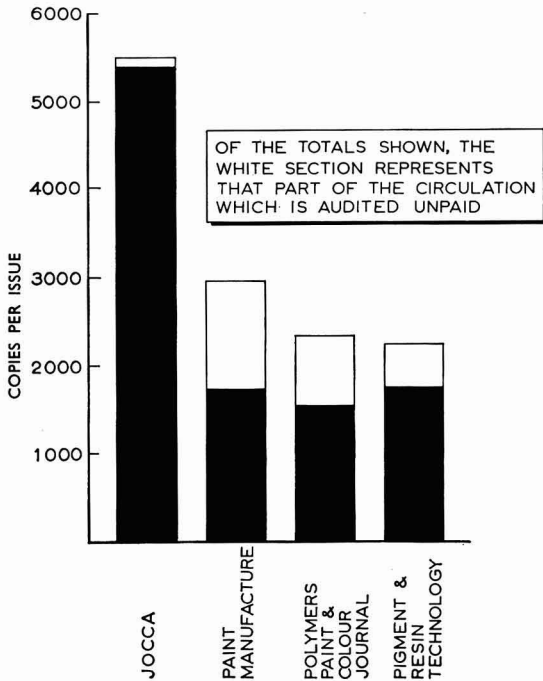
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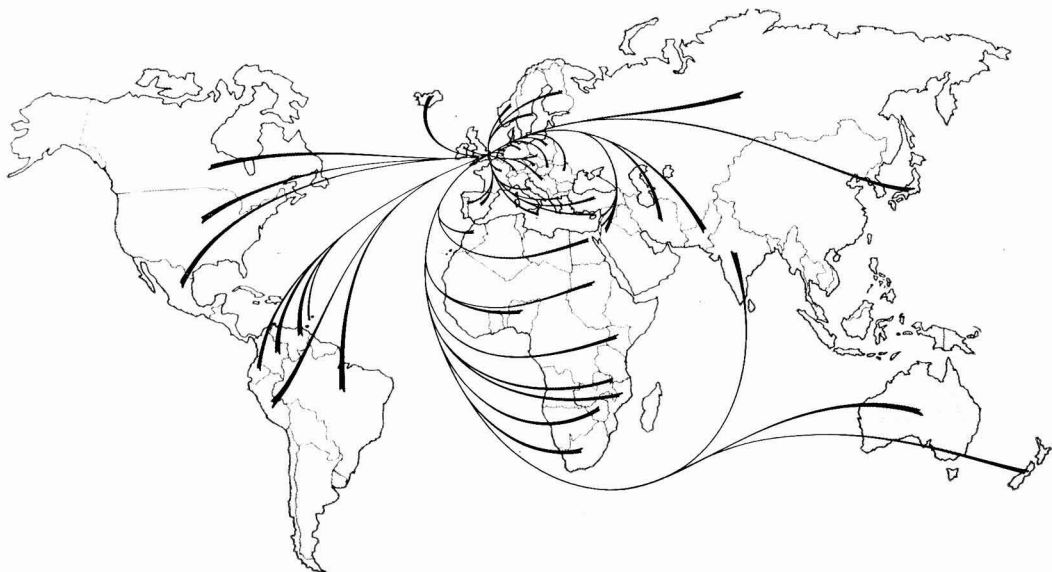
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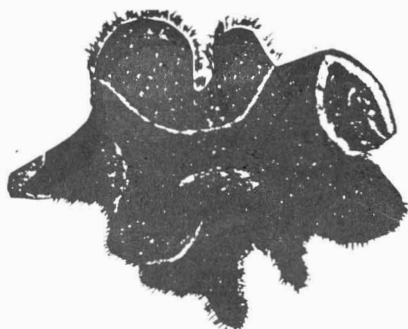
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