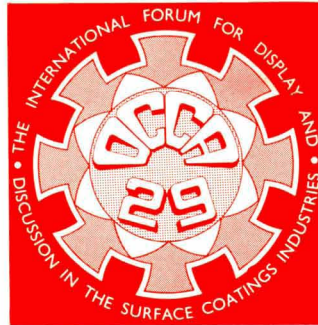


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**Good support  
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See page 384

# JOURNAL OF THE IL & COLOUR CHEMISTS' ASSOCIATION

A comparison of the DC and AC methods for measuring the electrical resistance of polymer films *M. Buller, J. E. O. Mayne and D. J. Mills*

Autoxidation and antioxidants *D. N. Rampley and J. A. Hasnip*

Blast cleaning in inflammable atmospheres *D. W. Singleton*

The photo-oxidation of normal primary alcohols by anatase titanium dioxide *A. D. Buss, M. A. Malati and R. Atkinson*

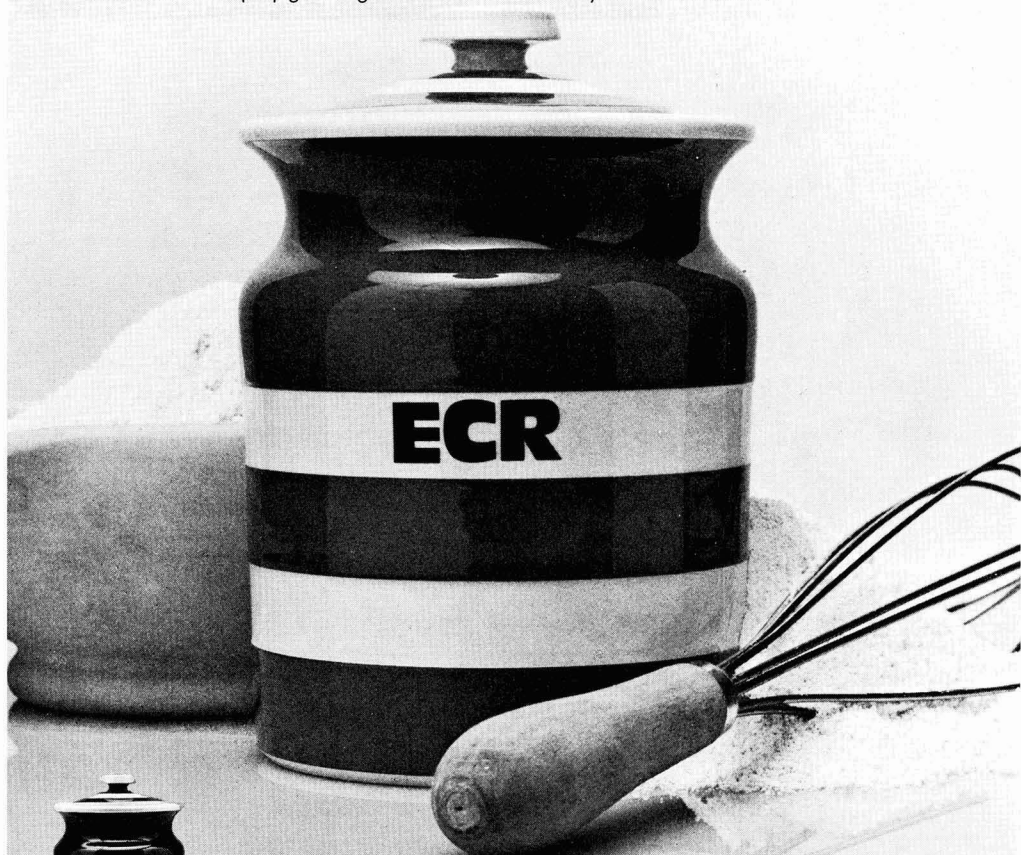
The role played by water-soluble polymers in paint performance. Part III: Molecular weight and concentration effects in mixed thickener studies *W. C. Arney Jnr and J. E. Glass*

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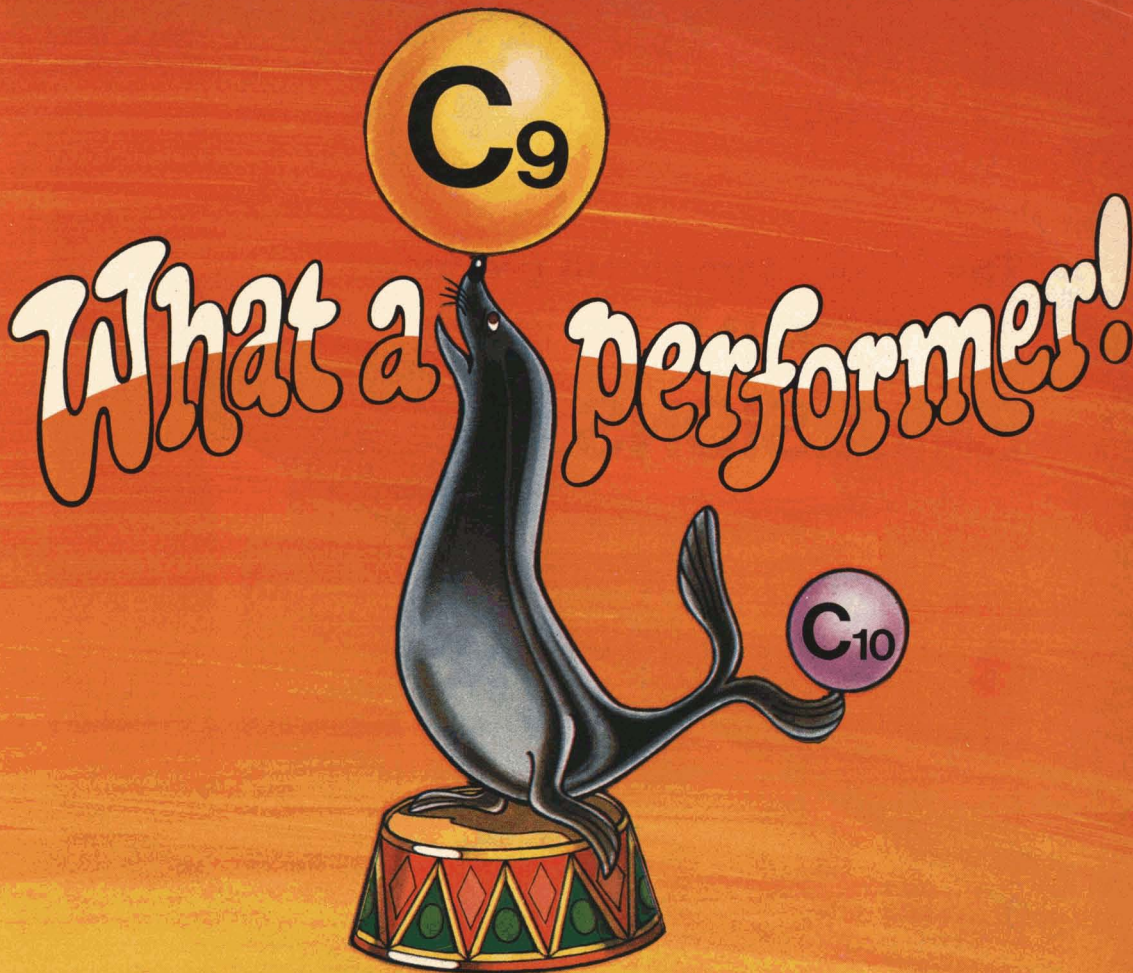
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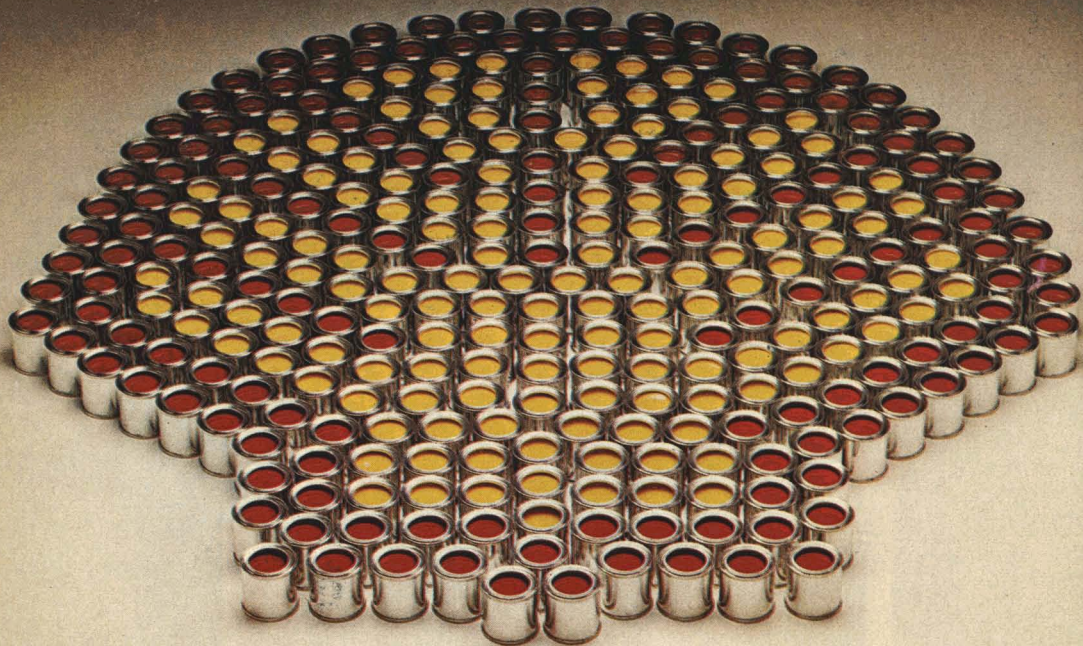
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The optional Professional Grade for Ordinary Members of OCCA was instituted by Council in 1971. Since that time, over 400 candidates have been successful in their applications to join the Professional Grade and a full list was last published in the December 1975 issue of the *Journal*. The various routes to the three Grades (see above) in diagrammatic form and the full regulations for admission are published in the July 1976 issue.

A reprint of the full regulations for admission to the Professional Grade and application form may be obtained by sending a stamped, self-addressed envelope, marked "Professional Grade leaflet" in the top left-hand corner, to the Association's offices at the address on the Contents page of this issue. It is felt that some overseas Members, in particular, might encounter difficulties contacting the required number of sponsors and any applicant who finds himself in this position is advised to write to the Director & Secretary of the Association in the first instance.

## OCCA-29 Exhibition

The Association's twenty-ninth Technical Exhibition will be held at Alexandra Palace, London N22, from 22 to 25 March 1977. Further details regarding the arrangements for OCCA-29 and the many facilities offered at Alexandra Palace appear on page 384 of this issue of the *Journal*.

The Exhibition Committee emphasises on this occasion the quality of the OCCA Exhibitions in providing a *focus* for all those connected (either as suppliers of raw materials and equipment, or as buyers or in some other capacity) with the many and varied coatings markets throughout the world. The exhibition has long been known as the annual international forum for display and discussion in the surface coatings industries, and the motif for 1977 draws attention to the concept of the annual "focal point" for the industries (see advertisement on the front inside cover of this issue).

Intending exhibitors are reminded that their completed application forms and remittance for stand space must be returned to the Director & Secretary of the Association as soon as possible after **Friday 1 October 1976**.

Any organisation which has not previously exhibited and wishes to obtain an Invitation to Exhibit should contact the Association's offices immediately. The address is given on the Contents page of this issue.

### "Official Guide"

The Exhibition Committee offers advertising space in the "Official Guide" to the Exhibition, which has proved to be a very popular advertising medium, not only for exhibitors but also for companies who were not showing at a particular Exhibition.

For details of advertising in this and other Association publications, write to the Assistant Editor at the address on the Contents page of this issue.

OIL & COLOUR



CHEMISTS'

ASSOCIATION



TECHNICAL EXHIBITION

22-25 MARCH 1977

The motif, designed by Robert Hamblin, uses red arrows to symbolise how exhibitors and visitors are drawn from all points of the compass to the Exhibition. The heads of the red arrows form white arrows in the opposite direction showing the subsequent spreading of knowledge of technical advancements from this unique annual focal point for the surface coatings industries.

TRAVEL ARRANGEMENTS FOR VISITORS TO OCCA-29

In recent years, travel arrangements have been improved by the addition of the Victoria Line to the Underground system, which now links Victoria Station to the Piccadilly Line at Finsbury Park. The building of the extension of the Piccadilly Line from Hounslow to the Airport terminal at Heathrow is now well advanced and when this is completed it will give a direct link with Turnpike Lane Station on the Piccadilly Line. In the meantime, a bus service operates from Heathrow Airport to Hounslow West Station. Those travelling by the Piccadilly Line should alight at Turnpike Lane Station and the Association will be running a bus shuttle service from this station to and from Alexandra Palace. The journey from central London to Turnpike Lane takes approximately 18 minutes.



# JOURNAL of the OIL AND COLOUR CHEMISTS' ASSOCIATION

Hon. Editor: S. R. Finn, BSc, FRIC, FTSC

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Vol. 59 No. 10

October 1976

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## Transactions and Communications

# A comparison of the DC and AC methods for measuring the electrical resistance of polymer films

By M. Buller, J. E. O. Mayne and D. J. Mills

Department of Metallurgy and Materials Science, Cambridge University, Pembroke Street, Cambridge CB2 3QZ

### Summary

The resistance of polymer films has been measured by means of DC and AC current over the frequency range 0-20 000 Hz.

In the case of free films, the DC resistance is always higher than the AC resistance and the difference in the case of films at high frequencies is four to five orders of magnitude. Similar results are obtained with films supported on mild steel and platinum, although the difference is not always so great.

It is found that the AC bridge yields results which cannot be interpreted in terms of a conductance and capacitance in parallel, since they vary with frequency. A more complicated equivalent circuit is required and the calculations will probably require the use of a computer.

### Keywords

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

*Raw materials: binders (resins, etc)*  
alkyd resin  
amide cured epoxy resin

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

## Une comparaison des méthodes à courant continu auprès de celles à courant alternatif pour mesurer la résistance électrique des films polymères

### Résumé

La résistance des films polymères a été déterminée sur une gamme de fréquences entre 0 et 20 000 Hz.

Dans le cas des feuillets libres, la résistance à courant continu est toujours plus élevée que la résistance à courant alternatif, et où il s'agit des hautes fréquences, la différence atteint à quatre ou cinq ordres de magnitude. Des résultats semblables sont obtenus à

l'égard des films sur acier doux et sur platine, bien que la différence ne soit pas toujours d'une telle importance.

On a trouvé que le pont à courant alternatif rend les résultats que l'on ne peut pas expliquer sous termes d'une conductance et une capacité en parallèle, puisque toutes les deux dépendent de la fréquence. On a besoin d'un réseau analogue mais plus évolué et le calcul fera probablement appel à un ordinateur.

## Ein Vergleich zwischen Gleich- und Wechselstrommethoden zur Messung des elektrischen Widerstandes von Polymerfilmen

### Zusammenfassung

Der Widerstand von Polymerfilmen wurde mit Hilfe von Gleich- und Wechselstrom über einen Frequenzbereich von 0 bis 20 000 Hz gemessen.

Im Fall freier Filme ist der Gleichstromwiderstand stets höher als der Wechselstromwiderstand, und der Unterschied im Fall der Filme bei hohen Frequenzen beträgt vier bis fünf Größenordnungen. Ähnliche Ergebnisse lassen sich mit auf Flussstahl oder Platin

befindlichen Filmen erzielen, obwohl der Unterschied hier nicht immer so gross ist.

Es lässt sich feststellen, dass die Wechselstrombrücke Ergebnisse mit sich bringt, die sich nicht aus Leitwert und Kapazität erklären lassen, da sie frequenzabhängig sind. Eine kompliziertere gleichwertige Schaltung ist daher erforderlich, und die Berechnungen machen wahrscheinlich den Einsatz eines Computers erforderlich.

### Introduction

Ref. 1

In a previous paper<sup>1</sup> an examination was made of the electrolytic resistance of polymer films when attached to and detached from their substrates. It was found that films on a corroding substrate had resistance similar to those for free films whereas if the substrates were inert (that is, platinum or iron passivated by chromate ions), then the resistances of the films were several orders of magnitude higher.

Throughout that investigation, the resistances of the films were measured by means of DC current. Claims have been made that measurements made with DC current are misleading owing to polarisation, and that AC current should be used. The object of this investigation was to examine the basis of such claims.

### Experimental

#### Preparation of films

Refs. 2, 3

Three varnishes were used in this investigation: a pentaerythritol alkyd, a phenol formaldehyde tung oil and a polyamide cured epoxide. Details have been published<sup>2</sup>.

Films were cast by means of a spreader bar on to glass plates, dried at room temperature in a glove box for 48 hours and then for a similar period in an oven at 65°C. The dried films were then soaked in water, carefully removed and mounted in small glass cells, which were filled with potassium chloride solution and immersed in a water thermostat maintained at 25°C.

Mild steel, of published composition<sup>3</sup>, was abraded with 00 grade emery, degreased in benzene, followed by acetone, and stored in a grease-free desiccator. Sheets, 20 × 10 cm, were coated with varnish by means of a spreader bar. In the case of platinum, 4 × 3 cm foil was used, and this was coated by immersion and slow withdrawal at a constant rate of 0.2 cm/sec. The coated metals were dried in a glove box for 48 hours and then stored at 65°C for the same period.

### Measurement of resistance

Refs. 4, 5, 2

In order to measure the DC resistance of a detached film, the glass cell was connected in series with a standard resistor of similar value and a potential of one volt applied to the combination. The drop in potential across the standard resistor was then measured by means of a vibrating reed valve voltmeter and from the reading obtained the resistance of the film was calculated. A diagram of the apparatus has been published<sup>4</sup>.

Previous work<sup>2</sup> showed that when samples of about 1 cm<sup>2</sup> were taken from a single cast film, 20 × 10 cm, of the varnishes used in this investigation, and their resistances measured in 3.5M and 0.001M potassium chloride, then either the resistances followed that of the external solution (this was classified as "Direct" or *D*-type conduction), or the resistances ran counter to that of the solution and were, in fact, controlled by its osmotic pressure (this type of conduction being called "Inverse" or *I*-type conduction).

For the AC measurements, a Wayne-Kerr Autobalance universal AC bridge was used, operating at 1592 Hz. In later work, the frequency range was extended by the use of a wide range oscillator operating in the range 20-20 000 Hz. This equipment enabled the total impedance of the film to be calculated from conductance and capacitance terms. Its

balancing arm contained a parallel combination of resistance and capacitance, which could be varied to obtain a point of balance, and it is similar to the apparatus suggested as most suitable for paint films by Rosenfeld, Zhigalova and Buryanenko<sup>5</sup>. Although the oscillator provided voltage at low frequencies, however, these were not used because the electrical noise so produced would obscure low conductances at the limit of the bridge's accuracy; thus the lower frequency limit tended to be 200-300 Hz.

### Procedure

In the preliminary experiments, the DC resistances of detached films mounted in cells were measured in 0.001M and 3.5M potassium chloride solution, using standard calomel electrodes. This enabled the films to be classified as a *D* or *I* type. The films were then left for 18 hours in molar potassium chloride solution at 25°C, after which further DC measurements were made. The calomel electrodes were then replaced by platinum electrodes and balance points obtained for resistance and capacitance using the AC bridge at 1592 Hz.

In later experiments, the DC resistances of detached films mounted in cells containing 0.001M potassium chloride solution, were measured using two standard calomel electrodes. The calomel electrodes were then replaced by two platinum electrodes and balance points obtained over a wide frequency range by means of the AC bridge. The dilute potassium chloride solution was subsequently replaced by one of 3.5 molarity and further readings were taken. It was important to ensure that the film and the solution had reached equilibrium; this was found to occur within two to four hours.

Difficulties were experienced in measuring the resistances of films supported on metal substrates. The apparatus finally used is shown in Fig. 1. Two metal specimens, each coated on one side only, were clamped on to a glass T-piece mounted in

Table 1  
Resistances of detached films of two unpigmented varnishes, measured with both DC and AC (1592Hz) current

Unpigmented epoxy-polyamine (thickness of films: 89μm)						
<i>D</i> films			<i>I</i> films			
DC resistance (ohms)	AC resistance (ohms)	Capacitance (pF)	DC resistance (ohms)	AC resistance (ohms)	Capacitance (pF)	
3.0 × 10 <sup>8</sup>	1.0 × 10 <sup>8</sup>	31.3	5.0 × 10 <sup>12</sup>	2.0 × 10 <sup>8</sup>	30.0	
3.0 × 10 <sup>7</sup>	1.5 × 10 <sup>7</sup>	31.6	7.0 × 10 <sup>12</sup>	2.0 × 10 <sup>8</sup>	29.2	
5.0 × 10 <sup>7</sup>	3.0 × 10 <sup>7</sup>	37.2	8.0 × 10 <sup>12</sup>	2.0 × 10 <sup>8</sup>	32.5	
2.0 × 10 <sup>7</sup>	1.1 × 10 <sup>7</sup>	31.9	5.0 × 10 <sup>12</sup>	2.3 × 10 <sup>8</sup>	30.8	
5.0 × 10 <sup>8</sup>	1.1 × 10 <sup>8</sup>	29.9	5.0 × 10 <sup>12</sup>	1.7 × 10 <sup>8</sup>	37.2	
1.0 × 10 <sup>9</sup>	1.5 × 10 <sup>8</sup>	33.3	8.0 × 10 <sup>12</sup>	1.9 × 10 <sup>8</sup>	31.0	
			3.0 × 10 <sup>12</sup>	1.7 × 10 <sup>8</sup>	35.4	
			5.0 × 10 <sup>12</sup>	1.8 × 10 <sup>8</sup>	31.6	
			1.0 × 10 <sup>13</sup>	2.2 × 10 <sup>8</sup>	31.1	
Average values 10 <sup>8</sup>	5.0 × 10 <sup>7</sup>	32.5 ± 1.0	7.0 × 10 <sup>12</sup>	2.0 × 10 <sup>8</sup>	31.9 ± 1.0	
Unpigmented pentaerythritol alkyd (thickness of films 63.5μm)						
<i>D</i> films			<i>I</i> films			
DC resistance (ohms)	AC resistance (ohms)	Capacitance (pF)	DC resistance (ohms)	AC resistance (ohms)	Capacitance (pF)	
5.0 × 10 <sup>8</sup>	3.0 × 10 <sup>7</sup>	73	3.0 × 10 <sup>12</sup>	6.0 × 10 <sup>7</sup>	44	
2.0 × 10 <sup>7</sup>	2.0 × 10 <sup>7</sup>	48	2.0 × 10 <sup>12</sup>	6.0 × 10 <sup>7</sup>	51	
			1.0 × 10 <sup>12</sup>	4.0 × 10 <sup>7</sup>	60	
			2.0 × 10 <sup>12</sup>	6.0 × 10 <sup>7</sup>	—	
			3.0 × 10 <sup>12</sup>	5.0 × 10 <sup>7</sup>	54	
Average values			2.0 × 10 <sup>12</sup>	5.0 × 10 <sup>7</sup>	52	
2.6 × 10 <sup>8</sup>	2.5 × 10 <sup>7</sup>	61				



a "Perspex" block. The glass T - piece had rubber washers attached to its end and the internal diameter of the glass tube was selected to give a 1cm<sup>2</sup> exposed area of painted metal. The benefit of this method was that no standard electrode was necessary; electrical contact was made either directly to the metal specimens or to the brass screws.

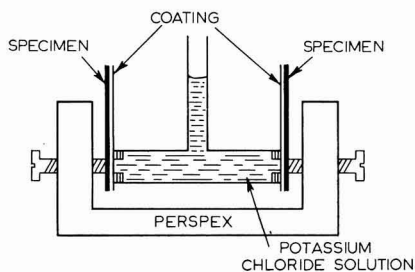


Fig. 1. Apparatus used to measure the resistances of films supported on metal substrates

**Results**

The results obtained in the preliminary experiments, when the resistances of detached films of an epoxy-polyamine and of an alkyd varnish were measured with both DC and AC current, at 1592 Hz, are given in Table 1. It can be seen that the DC resistances were always higher than the AC resistances, particularly in the case of *I* films; however, when standard carbon resistors of 10<sup>8</sup> and 10<sup>10</sup> ohms were used, the DC and AC values were the same. It was decided, therefore, to measure the AC resistances over a wide range of frequencies.

The results obtained with *D* and *I*-type alkyd films are shown in Figs. 2 and 3, in which the logarithm of the resistance (*R*) has been plotted against the frequency of the AC current.

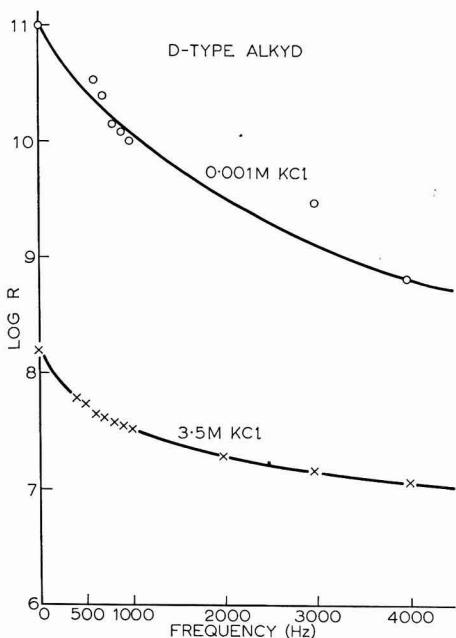


Fig. 2. Resistance (*R*) of a D-type alkyd film versus frequency of the AC current (detached film)

The values of the DC resistances have been plotted at zero frequency. The different behaviour of *D* and *I* films of an epoxy-polyamide varnish is shown in Figs. 4 and 5.

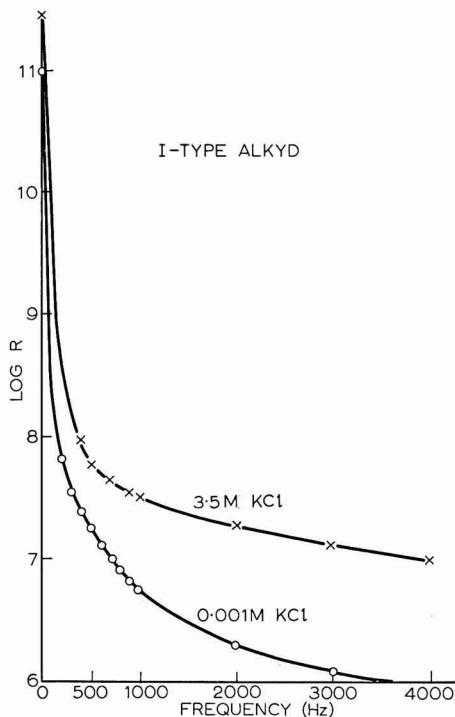


Fig. 3. Resistance (*R*) of an I-type alkyd film versus frequency of the AC current (detached film)

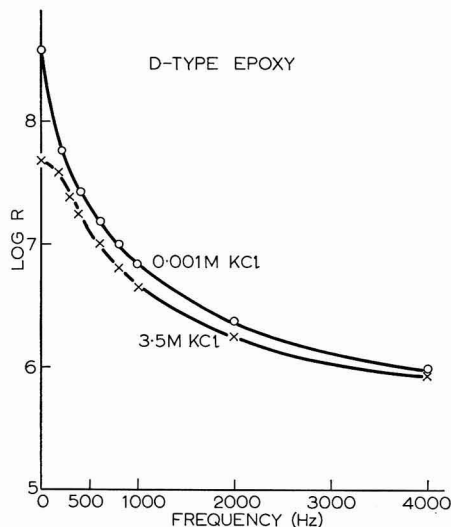


Fig. 4. Resistance (*R*) of a D-type epoxy-polyamide film versus frequency of the AC current (detached film)

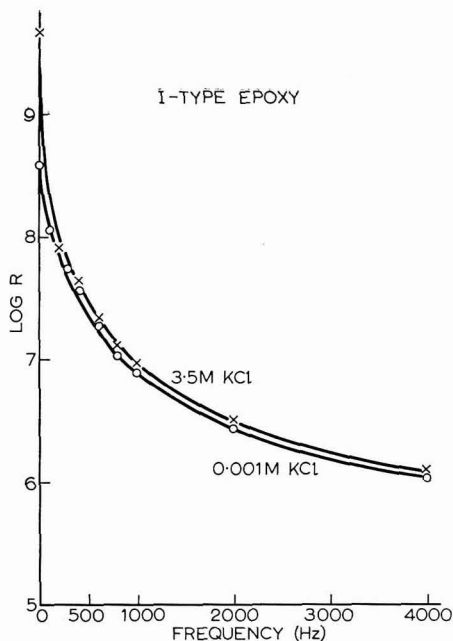


Fig. 5. Resistance (R) of an I-type epoxy-polyamide film versus frequency of the AC current (detached film)

The results obtained with alkyd films supported on mild steel are given in Figs. 6 and 7, and on platinum in Fig. 8.

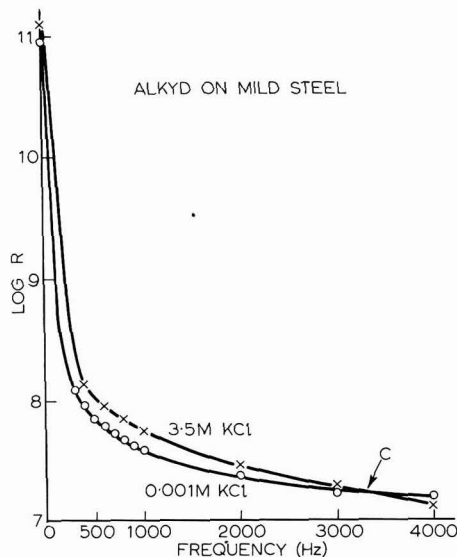


Fig. 7. Resistance (R) of an alkyd film cast on mild steel substrate versus frequency of the AC current, showing a cross-over point (C) indicating the differing behaviour of D and I-type films

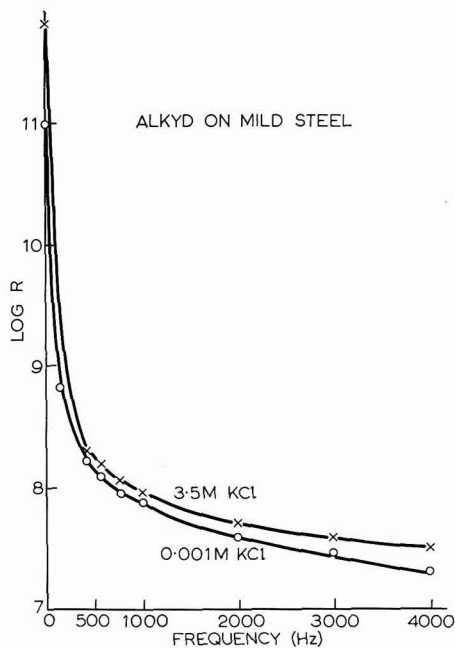


Fig. 6. Resistance (R) of an alkyd film cast on mild steel substrate versus frequency of the AC current (film exhibiting I-type behaviour)

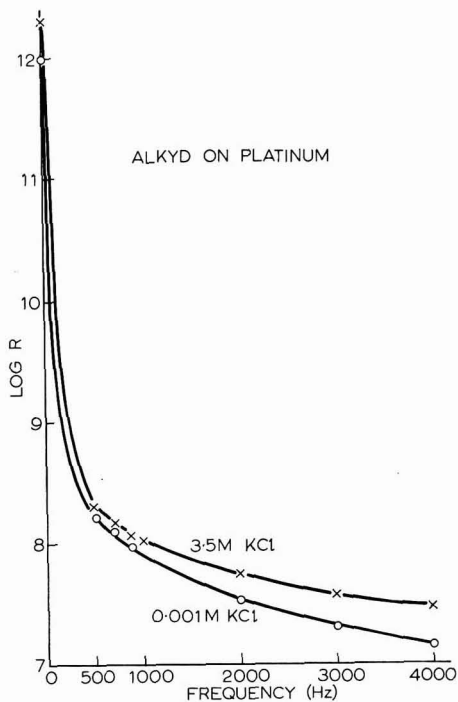


Fig. 8. Resistance (R) of an alkyd film cast on platinum substrate versus frequency of the AC current, showing the effect of the substrate (compare Fig. 3)

## Discussion

Refs. 1, 5-7

An AC bridge measures both conductance and capacitance, and the results obtained must be interpreted in terms of an equivalent circuit. In the case of continuous polymer films, previous workers<sup>5,6</sup> have used a simple equivalent circuit of a capacitance and resistance in parallel and the results obtained in this investigation have been interpreted in a similar manner.

Table 1 gives the values obtained with unsupported films of an epoxy-polyamide and an alkyd varnish. In the Table, the samples of film have been divided into two classes depending upon whether they exhibit *D* or *I*-type behaviour. It can be seen that with *D* films, the resistances are of similar magnitude whether they have been measured by DC or AC current, although the DC resistances are always slightly higher; in the case of *I* films, the DC resistances are always higher by three to four orders of magnitude. In contrast, there was little difference in the capacitances of *D* and *I* films for a particular type of polymer. This preliminary investigation raised the question of the significance of AC measurements and in order to obtain further information it was decided to carry out measurements over a wide range of frequencies.

The effect of frequency on resistance is shown in Figs. 2-5, in which the logarithm of the resistance of the polymer film has been plotted against the frequency of the AC current. It can be seen that all four films yielded curves of the same shape; thus, there was a fall in resistance between 0 and 300 Hz of about three orders of magnitude, after which the fall became more gradual. In the case of the alkyd films (Figs. 2 and 3), it was possible to differentiate between *D* and *I* type films, but with the epoxy-polyamide films (Figs. 4 and 5), no clear difference could be observed between the two types.

The results obtained with supported films are shown in Figs. 6-8. The shape of the curves is similar to that observed with detached films, but here the measurements were made with two films in series, so there were three possible combinations: *DD*, *II* and *DI*. It follows that two of these combinations will appear to be *I* and only one *D*, since the resistances are in series. Fig. 6 shows a typical result obtained for an alkyd varnish, the films of which exhibited *I* type behaviour. Frequently the curves were found to cross (e.g. as in Fig. 7), and it was concluded that in these cases, one of the films had acquired *D*-type behaviour. The films used in both experiments were, therefore, stripped from their substrates and mounted in cells, and their resistances measured in concentrated and dilute potassium chloride solutions. It was found that the films in Fig. 6 were both *I*-type; in Fig. 7, one was *D* and the other *I*-type. The cross-over (Fig. 7) may be due to the fact that the resistances of *D* and *I*-type films do not vary with frequency in the same manner.

The effect of the substrate is shown in Fig. 8; comparison with Fig. 3 shows that the resistances of films on platinum were higher at most frequencies than those cast on steel. A similar result was obtained with mild steel coated with red lead dispersed in the alkyd varnish. These observations fall in line with earlier work<sup>1</sup> in which films were supported on platinum or on iron passivated by chromate ions (that is to say, on a "passive" substrate). The higher DC resistance was attributed to the fact that when the substrate was passive then ionic diffusion occurred only from one side of the coating. As the values of the DC resistance tend towards  $10^{12}$ , the accuracy of the measurements decreases, since the resistance of the polymer film approaches the input impedance of the

voltmeter, which had a value of  $10^{13}$  ohms in the early DC measurements. Consequently, the difference in the measured DC resistance between coated steel and coated platinum was not as great as that observed in previous work.

It has been claimed by various workers that because of polarisation at the metal surface, the resistance of the coating should be measured with an AC current. It has been found here that the resistance of unsupported coatings is always higher when measured by a DC current and that supported coatings behaved in a similar manner. However, when the alkyd films (Figs. 6 and 7) were removed from their mild steel substrates and their DC resistances determined, very little change was observed. These measurements indicate that when the resistance of films is high (greater than  $10^8$  ohms/cm<sup>2</sup>), then the polarisation resistance is negligible. Moreover, they suggest that the lower resistance, often measured by AC, is not due to the elimination of the polarisation term.

AC measurements at 1592 Hz in molar potassium chloride solution failed to differentiate satisfactorily between *D* and *I*-type films, yet it has been shown that these films can give very different degrees of protection to a mild steel substrate<sup>1</sup>. It is concluded that if resistance measurements are made with the object of predicting coating performance, then DC current should be used.

This conclusion is in agreement with that of Bacon, Smith and Rugg,<sup>7</sup> who examined the behaviour of over 300 paint systems under conditions of total immersion and concluded that the condition for protection was that the coating, after immersion, should have a resistance of at least  $10^8$  ohms/cm<sup>2</sup>.

Throughout this investigation the conductance of the films varied with frequency. The capacitance term was also recorded and found to vary with frequency, but the values have not been included in this paper. If the equivalent circuit were a simple parallel combination of resistance and capacitance, then the reciprocal of the conductance term could not be regarded as a resistance, and the interpretation of the results would depend on the evolution of an equivalent circuit before the resistance portion of the impedance could be calculated: these calculations are complicated and frequently require the use of a computer.

## Acknowledgments

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# Autoxidation and antioxidants

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## Summary

The mechanism of hydrocarbon autoxidation is considered with particular reference to the degradation of polymers under the action of heat and light; it is shown that the first step is the formation of a hydroperoxide, which initiates a chain reaction.

## Keywords

### Raw materials:

binders (resins, etc)  
vinyl resin

### catalysts, accelerators, inhibitors

antioxidant  
hydroperoxide  
peroxide

### miscellaneous paint additives

sequestering agent  
ultraviolet absorber

The chemistry of antioxidants is reviewed with reference to four modes of action: ultraviolet absorbers, metal scavengers, chain terminators and peroxide decomposers.

Special consideration is given to the protection of polyvinyl chloride against degradation by heat and light.

### Processes and methods primarily associated with:

manufacturing or synthesis  
autoxidation

drying or curing of coatings  
drying mechanism

service or utility  
film degradation

## Autoxydation et antioxydants

### Résumé

On considère le mécanisme de l'autoxydation des hydrocarbures à l'égard particulier de la dégradation de polymères par l'action de la chaleur et de la lumière; on démontre que la première étape est la formation d'un hydroperoxyde, qui amorce une réaction en chaîne.

On passe en revue la chimie des antioxydants à l'égard de quatre

modes d'action: des adsorbants de lumière ultra violette, des agents qui dépistent les traces des métaux, des agents qui rompent des réactions en chaîne, et des agents qui décomposent les peroxydes.

On accord une considération particulière à la protection du chlorure de polyvinyle contre la dégradation provoquée par la chaleur et par la lumière.

## Autoxidation und Antioxidantien

### Zusammenfassung

Untersucht wird der Mechanismus der Kohlenstoffwasser-Autoxidation mit besonderem Bezug auf die Degradation von Polymeren unter der Einwirkung von Wärme und Licht; es lässt sich zeigen, dass der erste Schritt die Bildung eines Hydroperoxydes ist, was eine Kettenreaktion einleitet.

Das chemische Verhalten von Antioxidationsmitteln wird unter

Bezug auf vier Einwirkungen untersucht: UV-Absorber, Metall-Entionisierer, kettenabbruchbewirkende Mittel und Peroxid-zersetzer.

Besonderes Interesse gilt dem Schutz von Polyvinylchlorid vor Degradation durch Wärme und Licht.

## Introduction

Refs. 1, 2

Many organic substances suffer changes on exposure to air or oxygen and these changes are frequently accelerated by heat, ultraviolet light, metal ions and peroxides. Sometimes these changes are exploited, as in the case of paints formulated with unsaturated media, but more usually interaction of the substance with oxygen produces undesirable changes in properties. The oxidation of petrol and mineral oils increases their viscosity and can produce gums, whilst the oxidation of food oils and fats can cause rancidity. The oxidation of paint films and polymers involves chain scission, crosslinking or both, with consequent changes in the molecular weight, polymer structure and mechanical properties.

Many vegetable oils contain naturally occurring materials, termed "antioxidants", which retard the rate of oxidation of

the oil: for example, the tocopherols in soya bean oil<sup>1</sup>. The deliberate addition of small quantities of antioxidants to industrially important organic substances in order to extend their life and usefulness is a common practice and is the subject of many patents. Examples of antioxidants include phenols, amines, chelating agents, phosphorus and sulfur compounds, and metal salts. The purpose of this paper is to review the phenomenon of autoxidation and the mode of action of antioxidants; for a more detailed account the reader is referred elsewhere<sup>2</sup>.

## Autoxidation of unsaturated hydrocarbons

Refs. 3-18

The absorption of oxygen by films of drying oils and unsaturated synthetic media has been investigated by Bevan, Heavers and Moon<sup>3</sup> and has been shown to reach a steady level, generally somewhat short of theoretical requirements

and dependent on the degree of unsaturation of the oil. The reaction of oxygen with linseed oil and hydrocarbons is initially an auto-accelerating process<sup>4</sup>, and is generally preceded by an induction period, which can be reduced by the addition of oxidised turpentine or benzoyl peroxide. From this, it may be concluded that the peroxide compounds behave as catalysts for the autoxidation process.

The nature of the oxidation products obtained during the early stages of the reaction of oxygen with unsaturated organic compounds has been reviewed by several workers<sup>5-7</sup>. The autoxidation of cyclohexene yields a hydroperoxide retaining the original unsaturation<sup>8-10</sup> and the same appears to be true generally of mono-olefins, 1 : 4 dienes and hydroaromatics, oxygen addition taking place at the  $\alpha$ -carbon atom. The mechanism of autoxidation for unsaturated compounds has been discussed by Bolland<sup>5</sup> and Bateman<sup>11</sup>, and their views are similar to those of Chien and Boss<sup>12,13</sup> regarding the autoxidation of polypropylene.

The view that the liquid-phase autoxidation of olefins proceeds via a chain mechanism is well supported by both the influence of traces of initiators and inhibitors on the reaction rate and the fact that if the reaction is accelerated photochemically the quantum yield may exceed unity. Bolland<sup>5</sup> in his review analysed the mechanism in three stages: firstly he identified the contributing elementary reactions from the dependency of reaction rate on experimental variables; secondly he considered the efficiencies (rate constants) of the composite reactions; and finally he considered the efficiencies of the individual contributing reactions.

The rate of oxidation  $r_o$  may be expressed as:

$$r_o = r_1^{0.5} [RH] \frac{[O_2]}{k' ([RH] + [O_2])} \dots\dots(1)$$

where  $r_1$  = rate of formation of chain initiating species

[RH] = hydrocarbon concentration

[O<sub>2</sub>] = oxygen concentration

$k'$  = experimental constant

Three specific forms of this general equation are obeyed by systems employing benzoyl peroxide (unimolecular decomposition), hydroperoxides (bimolecular decomposition) and the energy of light as initiators.

The general relationship is consistent with the scheme:

#### Initiation

Production of  $R\cdot$  or  $RO_2\cdot$  radicals; overall reaction rate  $r_1$

	Rate constant	Reference number for the reaction
$(C_6H_5COO)_2 + h\nu \left. \begin{array}{l} \text{or ROOH} \\ \text{or 2ROOH} \end{array} \right\} \rightarrow R\cdot \text{ or } RO_2\cdot$	$k_7$	R7
	$k_1$	R1
<b>Propagation</b>		
$R\cdot + O_2 \rightarrow RO_2\cdot$	$k_2$	R2
$ROO\cdot + RH \rightarrow ROOH + R\cdot$	$k_3$	R3
<b>Termination</b>		
$R\cdot + R\cdot \rightarrow$ Inert products	$k_4$	R4
$R\cdot + RO_2\cdot \rightarrow$ Inert products	$k_5$	R5
$RO_2\cdot + RO_2\cdot \rightarrow$ Inert products	$k_6$	R6

The rate of oxidation according to the above scheme is related to the velocity coefficients of the various elementary reactions by the general relationship:

$$-d[O_2]/dt = r_1^{0.5} (k_3/k_6^{0.5}) [RH] \left( \frac{k_2 k_6^{0.5} [O_2]}{k_3 k_4^{0.5} [RH] + k_2 k_6^{0.5} [O_2] + [k_4 k_6 r_1]^{0.5}} \right) \dots\dots\dots(2)$$

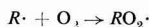
which at high chain lengths, when the term  $(k_4 k_6 r_1)^{0.5}$  becomes negligible, reduces to the experimental equation (1). The chain carriers  $R\cdot$  or  $RO\cdot$  are formed either directly or indirectly from the initiating agency. Chain propagation proceeds by a two-step cycle in which an oxygen molecule adds to the  $R\cdot$  type radical and the resulting peroxide chain carrier abstracts an  $\alpha$ -methylene hydrogen atom from a second olefin molecule to complete the hydroperoxide radical and regenerate a hydrocarbon radical ready for the next cycle. Chain termination occurs through the binary combination of the chain carrying radicals.

The addition of oxygen molecules to atoms and radicals is in general an extremely facile reaction<sup>5</sup> and although the term  $k_2 k_4^{-0.5}$  has been shown to be approximately constant for a number of olefins of different structure, it has unfortunately not been possible to isolate the two rate constants. It is believed that the rate controlling step in the above system is the abstraction of a hydrogen atom by a peroxide radical (reaction R3), and measurements of  $k_3$  by Bateman and Gee<sup>14</sup> have shown that this rate constant is dependent on the nature of the olefin.

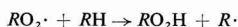
For long chains, when  $k_2 k_6^{0.5} [O_2]$  in equation (2) is negligible, then:

$$r_o = r_1^{0.5} k_3 / k_6^{0.5} [RH] \frac{k_2 k_6^{0.5} [O_2]}{k_3 k_4^{0.5} [RH] + k_2 k_6^{0.5} [O_2]} \dots\dots(3)$$

At high oxygen pressures, the reaction



may be regarded as fast relative to



so that the termination reaction involving  $RO_2\cdot$  radicals (reaction R4) may be disregarded, and equation (3) becomes:

$$r_o = r_1^{0.5} k_2 / k_6^{0.5} [RH] \dots\dots\dots(4)$$

The oxygen pressure at which the conditions implied in equation (4) prevail depends upon both temperature and the reactivity of the olefin; the more reactive the olefin the faster is the reaction R3.

The autoxidation of ethyl linoleate at 45°C, for example, proceeds at a rate independent of oxygen pressure at pressures greater than about 26 kPa, whilst the autoxidation of hexadiene is independent of [O<sub>2</sub>] at pressures greater than about 0.26 kPa.

An early review of the mechanisms of autoxidation of drying oils has been given by Hilditch<sup>15</sup> and later by Hutchinson<sup>16,17</sup>. The latter discussed the thermal polymerisation of oils and also the nature of the volatile products. Information on the effect of heat and hydroperoxides on the polymerisation of selected mono-unsaturated fatty acids and their esters and on the nature of the volatile products has been given by Skellon<sup>18</sup>. The general picture to emerge regarding autoxidation of non-conjugated systems is the development of dimer structures linked by  $-C-C-$ ,  $-C-O-C-$ , or  $-C-O-O-C-$  bonds. The linkage between connected chains in structures derived from conjugated systems is probably  $-C-C-$ , and the number of inter-connected units is almost certainly quite high.

## Phenolic and amine antioxidants

Refs. 19-28

When primary and secondary aromatic (including phenolic) amines are present in a system in small amounts, they provide an alternative and easier route for the removal of RO· radicals, without yielding a product of the R· type, so that termination by R4 can be ignored; in these cases, auto-oxidation is frequently independent of pressure. Bolland and ten Have<sup>19</sup> have studied the influence of quinol on the auto-oxidation of ethyl linoleate initiated by benzoyl peroxide and by ethyl linoleate hydroperoxide. The oxygen pressure was 4 kPa and the temperature 45°C. Under these conditions, the oxidation rate was independent of pressure. For inhibitor concentrations sufficiently high to ensure that all growing chains were terminated by inhibitor molecules, it was found that:

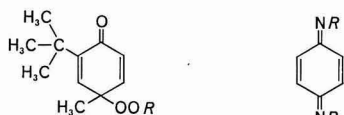
$$r_0 = K_c \frac{[(C_6H_5CO)_2O_2][RH]}{[H_2]} \quad \dots\dots(5)$$

$$r_0 = K_a \frac{[RO_2H]^2[RH]}{[H_2]} \quad \dots\dots(6)$$

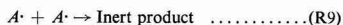
These equations are similar in form to equation (4). The same authors examined ten phenolic antioxidants to measure their efficiency in diminishing the oxidation rate of ethyl linoleate under standard conditions and showed that the efficiency was inversely related to the oxidation/reduction potential; that is, the most effective phenols were the more readily oxidised ones. They (and other workers) postulated the reaction:



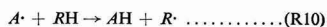
in which the peroxy radical chain propagating species A· is removed from the system with the termination of the chain sequence. Confirmation of this reaction has been obtained by the identification of pure compounds of the type:



Bolland and ten Have also postulated the reaction:

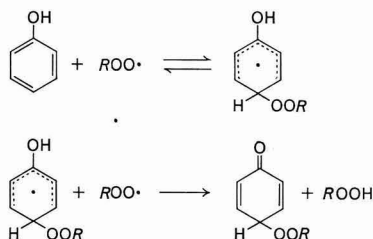


and stated that for the phenolic compound to be of practical value as an inhibitor, it should not be destroyed by direct reaction with oxygen. They pointed out that if the reaction:



could occur, this would limit the usefulness of the inhibitor since one chain propagating species would simply be replaced by another. Whether this last reaction will be important will depend on the minimum energy value of ( $E_A - E_{AH}$ ) consistent with R10. The authors showed that with the materials under investigation, this reaction could be discounted. Bickel and Kooyan<sup>20</sup>, working with aromatic amine antioxidants and with dihydroanthracene, found several types of reaction kinetics, which they interpreted on the assumption that aromatic amines behave in the same way as do alkyl phenols. It was concluded that the efficiency of the amines was defined by the ratio of the reaction rates for R8 and R9. The antioxidant efficiencies of the two classes of compound were similar, and the presence of large N-naphthyl groups completely prevented the chain transfer reaction R10.

Labile hydrogen atoms are removed from phenolic and amine antioxidants during inhibition reactions, but it has been suggested<sup>21, 22</sup> that the termination reaction for some antioxidants is second order with respect to alkyl peroxy radicals. For example:

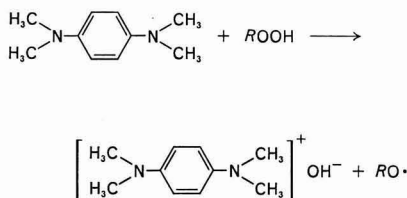


This view is now thought to be incorrect<sup>23</sup> and the anomalous kinetics which are sometimes encountered are now attributed to chain transfer reactions (see R10 and also R11 below) between the substrate or the alkyl hydroperoxide and the inhibitor radical:

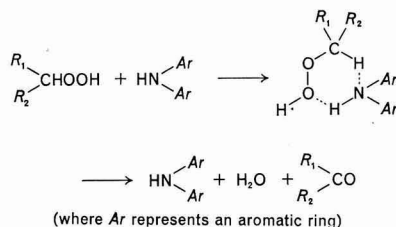


The observation that tertiary aromatic amines (which, of course, possess no labile hydrogen atoms) show antioxidant activity<sup>21</sup> appears to be not strictly true<sup>23</sup>.

N,N,N',N'-tetramethyl-*p*-phenylenediamine, for example, shows initial pro-oxidant behaviour, followed by a period of antioxidant behaviour. It is believed that the blue Wurster cation, positively identified from its colour and its electron spin resonance spectrum, is the species responsible for inhibition:



Another explanation for the behaviour of amine antioxidants is the formation of a hydrogen bonded complex between the amine and the hydroperoxide, followed by decomposition of hydroperoxide into inert products and regeneration of the amine:



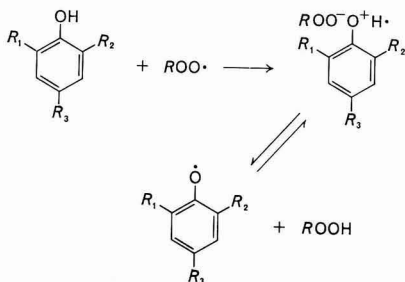
It is well recognised that in carbon black reinforced stocks, amines are more efficient antioxidants than the hindered phenols. This may be explained by the postulate that carbon black increases the effectiveness of the amine in causing induced decomposition of the peroxide into stable products according to the above mechanism. Conversely, hindered phenols are more effective than aromatic amines in gum



rubber stocks, which carry no carbon black reinforcement, indicating that the phenols may be less prone to take part in transfer reactions.

Fukuzumi and Ibika<sup>24</sup> have proposed, on the basis of evidence from infrared spectrophotometry, that the effect of phenolic antioxidants when used at low concentrations is steric in nature and arises from the formation of a hydrogen bond between the  $\pi$ -electrons of the olefin and the labile hydrogen atom of the phenol.

The relationship between chemical structure and the efficiency of phenolic and amine antioxidants has been considered by many workers<sup>19,20,25,26</sup> and this aspect has been reviewed by Scott<sup>28</sup>. The presence of electron releasing (for example, alkyl and alkoxy) groups in phenols increases the rate of the radical capturing reaction R8 relative to the rate of oxidation of the substrate R3. Electron attracting substituents, such as nitro, carboxyl and halogen, have the opposite effect. These effects have been correlated in common series with the energy of the most loosely held mobile electron (calculated from molecular orbital theory), which gives a measure of the rate at which R8 proceeds<sup>25</sup>, and the ease of electron release from the phenolic oxygen atom<sup>28</sup>. Thus, since the alkyl peroxy radical is an electrophilic agent, any substituents in a phenol which favour electron release will increase the stability of the electron transfer component of the transition state.



Mahoney<sup>27</sup> has recently investigated the oxidation of 9-10 dihydroanthracene and 2,2,3,3-tetraphenyl butane in the presence of non-hindered phenols, namely: phenol, 1,3 dihydroxy benzene, 4 methoxyphenol, 4 phenyl phenol, 2 hydroxy naphthalene and 3 hydroxy pyrene. He concluded that abstraction of the labile hydrogen atom by the alkoxy peroxide radical (reaction R3) is relatively insensitive to variations in the structure of the phenol, but observed large variations in the rate of the bimolecular termination reaction R9 which could be explained by polar and resonance factors.

## Degradation of polymers and plastics

Refs. 2, 28-33

It is well known that oxygen and ultraviolet light in combination have a greater destructive effect on most polymers than has either of these agencies by itself. Yamasaki<sup>29</sup> has investigated the degrading effect of various agencies on linseed oil films, using a special cell and infrared spectroscopy. The effectiveness of the various treatments in causing degradation was found to be:

Oxygen and UV radiation

Oxygen, water vapour (high concentration) and UV radiation

Oxygen

Oxygen and water vapour (high concentration)

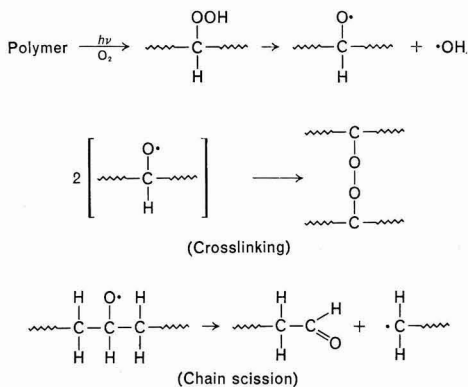
Nitrogen and UV radiation

Nitrogen

in order of decreasing severity.

The acceleration of polymer degradation due to water vapour has been noted by Hoffman and Saracz<sup>30</sup>, who used a xenon arc weatherometer to study the chalking behaviour of emulsion paints containing zinc oxide and anatase titanium dioxide. These authors suggested that water played some direct role in the degradation reaction by reacting with oxygen to produce, under radiation, hydrogen peroxide at the surface of the pigment particles. Other workers<sup>31,32</sup> have also proposed that formation of hydrogen peroxide is catalysed by titanium dioxide. Whether or not ultraviolet radiation will interact with a polymer depends upon the frequency of the radiation and the bond strengths of the constituent groupings within the polymer molecules<sup>33</sup>. The interactions of the radiation are randomly scattered throughout the polymer; in the presence of oxygen (which is not normally excluded) these can lead to both chain scission and crosslinking reactions.

For example:



Many of the possible reactions and radicals responsible for the autoxidation of organic polymers by heat, light, oxygen, metallic cations and ozone, have been discussed by Scott<sup>2,28</sup>, who states that heat and light, alone or in combination, have a degrading effect on saturated polymers. The action of light is particularly important for those polymers which contain UV absorbing groups, such as the polyesters and the polyamides, and the most important consequences of light absorption are the production of carbonyl radicals and the decomposition of hydroperoxides to give radical products, which participate in further chain reactions.

## UV absorbers

Ref. 34, 35

The purpose of UV absorbers for the protection of polymers and plastics during their service life is to limit the formation of free radicals and, more particularly, the radical decomposition of hydroperoxides. This objective can be met by pigments which scatter or absorb UV radiation when their colour is no objection, but for clear plastics or lacquer films recourse may have to be made to low molecular weight



behaviour and flavour of soya bean oil on exposure to the atmosphere and accelerate gum formation in petrols. Iron, which is added to the polymerisation mixture, stimulates the autoxidation of GR-S rubber.

There is some evidence<sup>44,45</sup> that the catalytic metal ions form co-ordination complexes with alkyl hydroperoxides and that, in the case of the more efficient catalysts at least, this is followed by electron transfer between the hydroperoxide and the central metal ion. The catalytic influence of the pro-oxidant metal may be suppressed, therefore, by combining it with a competing chelating agent<sup>44-49</sup>, preferably one which forms a strong complex utilising the ion to its maximum co-ordination number. However, because the reaction:



(where  $M$  represents a metal of valency  $n$  complexed with species  $Y$ ) is reversible, the efficiency of the blocking effect is dependent on the concentration of the alkyl hydroperoxide.

The replacement of a metal ion in one valence state by a different ion in another state provides additional stability by interrupting the sequence of catalysed reactions for the decomposition of hydroperoxide into radicals. However, the mere formation of a metal co-ordination complex cannot guarantee inhibition. Chalk and Smith, in their work on the autoxidation of cyclohexene in the presence of copper, manganese, iron and cobalt ions<sup>45</sup>, found that many chelating agents gave rise to an enhanced pro-oxidant effect, and this was attributed to a change in the redox potential to a value more favourable for the decomposition of the alkyl hydroperoxide into radicals. The same workers also found that the zinc complex of 1:2-bis (salicylideneamino) ethane caused rapid decomposition of the initiating peroxide (tertiary butyl hydroperoxide) into oxygen and inert products, with an inhibiting effect on the overall oxidation process. Typical chelating agents which have proved of value include bis-salicylidene diamines, hydroxy acids, oxamides and hydroxy- or mercapto-heterocyclics. These and other agents have been explored and proposed for use in great many systems: for example, citric acid for scavenging copper and other trace pro-oxidant metals from edible oils<sup>46,47</sup> and petrol; and ethylene diamine tetraacetic acid for the heat stabilisation of liquid polybutenes to protect against changes in viscosity and colour during processing<sup>48</sup>. Donor compounds, such as organo phosphines and phosphites, have been used as metal scavengers for the protection of GR-S rubber against catalysed degradation.

## Degradation of polyvinyl chloride

*Refs. 2, 49-51*

It is commonly accepted that the thermal deterioration of polyvinyl chloride (PVC) proceeds by a radical initiated mechanism, involving stepwise elimination of hydrogen chloride in a zipper like reaction to produce strongly coloured, conjugated poly-ene structures<sup>2, 49, 50</sup>. Initiation probably occurs at the site of activated chlorine atoms attached to tertiary carbon atoms or those which are  $\alpha$ -bonded with respect to unsaturated chain endings. Degradation under the action of light affects mainly the physical properties of the polymer, which becomes brittle and less extensible<sup>51</sup>. It is probable that a radical initiated mechanism is again involved, with crosslinking and/or scission reactions superimposed on dehydrohalogenation. Both the heat and light activated processes are modified in the presence of oxygen, which gives rise to the formation of carbonyl and hydroperoxide

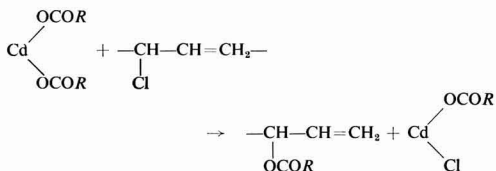
groups with the possibility of peroxide initiated autoxidation reactions of the type discussed previously.

The stability of PVC can be improved by the addition of small quantities of materials which fall into fairly well defined classes, although sometimes the chosen stabiliser may exercise its control by more than one mechanism. It is common practice to use composite stabiliser mixtures, the components of which function, or are believed to function, by different mechanisms. Such mixtures show synergistic behaviour. UV absorbers, such as phenyl salicylate, are recommended when light stability is important and conventional antioxidants, such as phenols and phosphites, are also used; one of the problems with the latter class of materials is the choice of an antioxidant which does not form a coloured reaction product.

Dieneophilic compounds, for example dibutyl tin diacetate and maleates, which are capable of reacting at the double bond in the degrading polymer and thus destroying its activating influence, offer another method of protection. Mercaptans, which undergo an addition reaction at the double bond, have been recommended for breaking up the poly-ene structure and reducing colouration.

It is frequently stated in the literature that the successive elimination of hydrogen chloride from PVC is catalysed by the acidic reaction product and whilst there is some doubt as to the general truth of this statement, acid acceptors, such as epoxides, mercaptides and basic salts of lead (for example, carbonate and phosphite), have been used for stabilisation.

The metal salts of stearic, ricinoleic and other carboxylic organic acids form another industrially important class of stabilisers for protection against both heat and light<sup>51,52</sup>. The metal constituent is responsible for the stabilising properties of the additive, and the organic radical for its compatibility with the polymer. Frye and Horst<sup>49,50</sup> have put forward convincing evidence, based on infrared and radio-active labelling techniques, for the displacement of labile chlorine atoms by carboxylate groups of greater thermal stability:



The same authors have shown that the addition of cadmium, barium or zinc chloride to PVC drastically impairs its thermal stability, and they suggested that the metal salts which are generated in the polymer by the reaction given above might function as Friedel Crafts catalysts in cross-linking reactions. It was demonstrated that in the presence of triphenyl phosphite there are no harmful effects from cadmium, barium and zinc chlorides, and that triphenyl phosphite by itself is without action on the polymer.

## Antioxidants in decorative surface coatings

*Ref. 53*

This review has shown that a large number of antioxidants exist, which are capable of protecting organic polymers against the worst effects of heat and light. Many of these compounds are used by the plastics and rubber industries but,



with the exception of PVCl plastisols and organosols and the incorporation of UV absorbers in transparent finishes, little use seems to have been made of these materials to confer improved stability on coatings which are subjected to a stoving process or which are to be exposed to the weather.

Volatile antiskinning agents, such as oximes and dimethyl hydrazine, have been used for some time to prevent the surface oxidation of unsaturated, oil modified vehicles in the can, but the problem of identifying additives which do not interfere excessively with the initial drying stage, yet exert a useful antioxidant action during the subsequent life of coatings formulated with unsaturated oils or vehicles prepared from them, would appear at first sight to be insuperable. One approach to the problem would involve a search for materials which are initially inert but which develop the required properties on oxidation. O'Neill<sup>18</sup> has examined the action of a great many antioxidants on the initial drying behaviour and subsequent oxygen uptake of thin films prepared from treated unsaturated oils. The study shows that long chain tertiary aliphatic mercaptans suppress oxygen uptake without interfering with the drying process. It was not possible to establish any effect of the mercaptan on the properties of the film after periods of natural and accelerated weathering which might be attributed to the decomposition of additive under the action of UV light.

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# Blast cleaning in inflammable atmospheres

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## Summary

Grit blast cleaning is accepted as the best method of preparing rusted steelwork for painting and this can easily be carried out on ships' hulls in dry docks. The grit blasting of areas of ships' decks is more difficult; it can cause considerable disruption of other maintenance operations and has to be carried out in whatever weather conditions prevail. In view of this, it is logical to consider whether grit blast cleaning can be regarded as part of a ship's maintenance programme to be carried out at sea.

Sparks are generated during the grit blasting of rusted steel, and this paper first investigates whether these sparks are capable of igniting inflammable liquids or gases of the type which might be

present on the deck of a laden tanker. The results indicate that whilst the sparks produced are numerous, they are dull and on no occasion have they ignited inflammable gas mixtures. A brief literature review indicates that other workers have reported similar findings.

Following this work, a full-scale grit blasting trial has been carried out at sea on a lubricating oil tanker. Details of this work and the safety procedures followed are given. It is concluded that grit blasting can be employed successfully on board vessels whilst they are at sea, provided that all normal safety precautions, and some additional ones given in this paper, are taken.

## Keywords

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

steel

*Processes and methods primarily associated with surface preparation before coating*

abrasive blasting

shot blasting

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

flammable vapour concentration

*Miscellaneous terms*

fire hazard

safety

## Nettoyage par jet de sable effectué dans les atmosphères inflammables

### Résumé

On considère que le nettoyage par jet de sable est la meilleure méthode pour enlever la rouille des structures en acier avant de leur repeindre à neuf, et dans le cas des coques de navire on peut l'effectuer facilement en bassins de redoub. Plus difficile est le sablage en partie des ponts; il peut entraîner de graves interruptions aux autres opérations d'entretien, et il doit être effectué en dépit du temps qui regne. A cause de cela, il est logique de considérer où le nettoyage par sablage peut être inclus dans le programme d'entretien du vaisseau que l'on entreprend pendant le voyage.

Les étincelles sont produites au cours du sablage d'acier rouillé, et en premier lieu cet exposé comporte une investigation sur la possibilité que ces étincelles peuvent enflammer les liquides ou gaz inflammables du type qui peut se trouver sur le pont d'un bateau-

citerne en charge. Les résultats indiquent qu'étant donné les étincelles produites sont nombreuses, elles sont tristes et n'enflamment jamais les mélanges gazeux inflammables. Une brève revue de la littérature indique que d'autres chercheurs ont mis en évidence des résultats semblables.

A la suite de cette étude une épreuve de sablage à grande échelle a été effectuée en mer sur un bateau-citerne chargé d'huile de graissage. On donne les détails de cette épreuve et des mesures de sécurité mises en vigueur. On conclut que l'on peut utiliser avec succès le sablage à bord des vaisseaux sur mer, pourvu que l'on prenne toutes les précautions normales de sécurité et certaines d'autres que l'on mentionne dans cet exposé.

## Strahlreinigen in entflammbaren Atmosphären

### Zusammenfassung

Putzstrahlen mit Strahlkies wird als die beste Methode der Präparierung von verrostetem Stahl zum Anstreichen angesehen, und dies lässt sich mühelos an Schiffskörpern im Trockendock ausführen. Das Kiesputzstrahlen von Flächen auf dem Deck auf Schiffen ist schwieriger; es kann andere Wartungsarbeiten erheblich stören und muss unter allen Wetterbedingungen ausgeführt werden. Es ist daher logisch, die Frage zu erörtern, ob Kiesputzstrahlen als Teil eines Schiffswartungsprogramms angesehen werden kann, das auf hoher See ausgeführt werden kann.

Während des Kiesputzstrahlens von verrostetem Stahl werden Funken erzeugt, und diese Abhandlung befasst sich daher zuerst mit der Frage, ob diese Funken entflammbare Flüssigkeiten oder Gase entzünden könnten, wie sie auf dem Deck eines beladenen

Tankschiffes vorhanden sein können. Die Ergebnisse zeigen, dass Funken zwar in grossen Mengen erzeugt werden, sie jedoch harmlos sind und keineswegs entflammbare Gasmischungen entzünden würden. Eine kurze Literaturübersicht zeigt, dass andere Untersuchungen zu ähnlichen Ergebnissen geführt haben.

Im Anschluss an diese Arbeit wurde ein Kiesputzstrahlversuch in grossem Rahmen auf hoher See auf einem Trägerschiff für Schieröl ausgeführt. Einzelheiten dieser Arbeit und die angewendeten Sicherheitsverfahren werden erörtert. Man kommt zum Schluss, dass Kiesputzstrahlen erfolgreich an Bord von Schiffen angewendet werden kann, wenn diese auf hoher See sind, sofern alle normalen Sicherheitsmassnahmen und einige zusätzliche, die in dieser Abhandlung angegeben werden, getroffen werden.

## Introduction

Grit blast cleaning of rusted steelwork to remove all traces of paint, rust and corrosive salt contaminants is now accepted as the best method for steel preparation prior to recoating with protective systems. Experience has shown that it is now possible to clean even the most severely corroded steel surfaces to very high standards.

Grit blasting of the outer hull of a ship is a comparatively easy operation in dry dock and, provided local regulations permit, can take place at most times during the dry docking without undue interference with other activities. However, the grit blasting of the deck area, pipework and flying bridge is difficult: in order to isolate these areas for grit blast cleaning, considerable disruption of other maintenance operations is involved. Thus, before deck maintenance can be carried out

in a dry dock most other work on the ship has to be completed. The docking period sometimes has to be extended by several days solely for the purpose of deck maintenance, and this can be very costly. A further complication is that the whole cleaning operation must be carried out in whatever weather conditions prevail at the time. Faced with these difficulties, it is logical to consider whether grit blast cleaning can be regarded as part of a maintenance programme, which could be carried out at sea.

It has been observed during grit blasting at night that streams of sparks are generated by the abrasive particles impinging on to the rusted steel surfaces. Before any blast cleaning was attempted at sea, it was considered essential to know whether the sparks produced during grit blasting could ignite inflammable liquids or gases of the type which might be present on the deck of a laden tanker. On tankers, especially around the hatches and vents, the gases given off by crude oils or oil products can, under certain conditions, be within the explosive limits for gas/air mixtures.

## Experimental

### Design of test rig

In order to study the ignition capability of the sparks produced by grit blasting, a test chamber 0.75 metres in diameter and one metre high was constructed from 9.5 mm mild steel plate. The chamber was closed at the top, open at the bottom, and mounted on a 0.6 m high stand to allow the grit blasting air-and-gas mixture to escape and to prevent a build up of abrasive within the chamber. A Hodge Clemco 14-40 "Ship-blaster" grit blasting pot fitted with a 9.5 mm diameter nozzle was used for the tests. This unit is designed for use on board ships and is slightly smaller than the one favoured by contractors for land-based grit blasting. The blasting nozzle could be clamped in such a way that the distance between the test plate and the nozzle could be varied. The test plate was fixed into position in the top of the chamber at an angle of 45° to the grit blasting stream. In preliminary tests, with a blasting air pressure of  $7 \times 10^5$  Pa (7 bar), sparks could be produced by the grit hitting a rusty steel plate even when the nozzle was up to two metres away from the plate (Fig. 1a-c). A gas inlet pipe was fitted into the chamber top near to the test plate in such a way that the stream of gas was directed into that part of the chamber where sparks would be produced. An automotive sparking plug, coupled externally to a coil and battery, was fitted into the top of the tank. This was used to produce sparks which could ignite the atmosphere within the chamber and so check that explosive conditions existed within it. A sketch of the test chamber is given in Fig. 2.

An examination of the ullage space gas (Table 1) present in a tanker carrying Middle East crude oil indicated that the gas had an explosive range very similar to that of propane. Because propane is readily available, it was decided to use this gas in all experiments.

Table 1

Comparison of the properties of propane and ullage space vapour

Property	Propane	Ullage space gas from a typical Middle East crude oil
Low inflammable limit, % volume in air	2.2	2.25
Upper inflammable limit, % volume in air	9.5	9.71
Vapour density (air = 1.0)	1.55	1.59

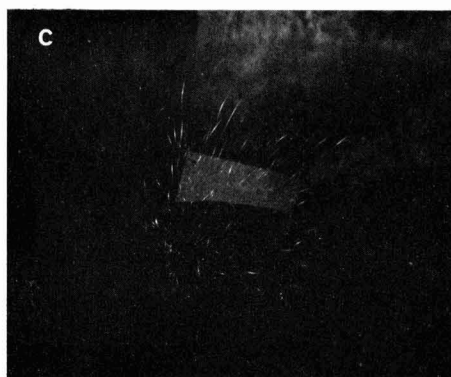
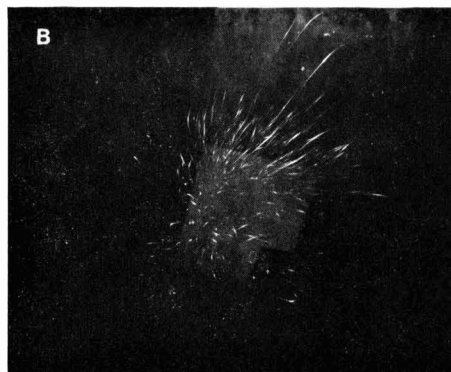
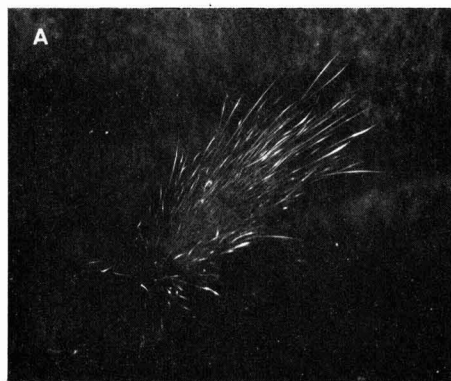


Fig. 1. Sparks produced by grit blasting—nozzle angled at 45° to the test plate: (a) at 0.6m, (b) at 1.3m, and (c) at 2.0m

The propane gas had to be supplied to the chamber at rates of up to 30 dm<sup>3</sup> per minute. To obtain this flow rate, liquid propane was fed through a heat exchanger and was monitored



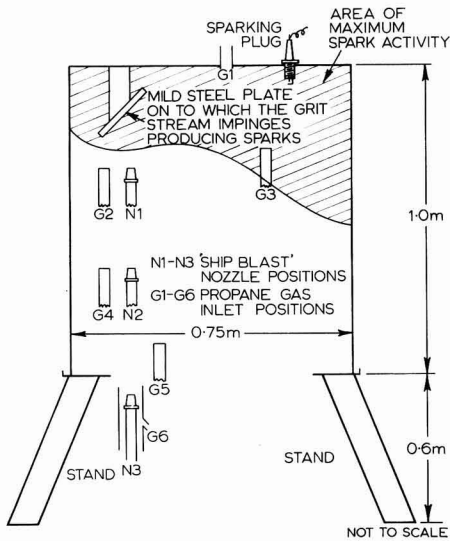


Fig. 2. Sketch of cross-section of blast chamber showing nozzle positions (N) and gas inlet positions (G)

as it passed into the chamber through a control valve and rotameter (Fig. 3).

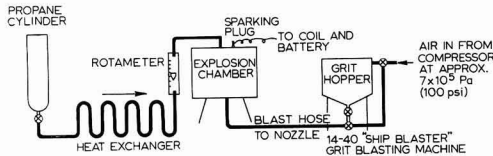


Fig. 3. Diagram of explosion rig

Test explosions were induced using different air/grit/gas mixtures fired by the sparking plug. In this way, the optimum conditions for maximum detonation (approximating to stoichiometric proportions) were established. Although it is possible to predict explosive limits and to measure gas flow accurately, it is not easy to measure the air flow through a blasting nozzle with any degree of accuracy. The reason for this is that although the air flow through the nozzle can be calculated if the pressure and nozzle diameter are known, the reduction in air volume resulting from the bulk volume of the entrained abrasive cannot be established easily. The air flow/grit ratio was kept as constant as possible throughout the experiments and was set for maximum grit blasting efficiency.

**Abrasives**

Two copper slag abrasives, representing a coarse and a fine grade, and an S170 steel shot abrasive were used in the tests.

**Test procedure and results**

The blasting nozzle was fitted into the chamber in the desired position and the blast air was turned on whilst the grit valve remained closed. Propane gas was then introduced into the chamber and a test firing made using the sparking plug. The

gas flow was gradually increased until detonations of what appeared to be maximum violence occurred. Abrasive was then introduced into the blast stream to the required amount and the gas flow was adjusted to compensate for the volume of grit until explosions of similar intensity were obtained. When the experimental conditions had been established, the tests were commenced and continued for several hours until either the grit or the propane gas was exhausted. Firings with the spark plug were made at regular intervals throughout, and at the end of each experiment, to ensure that explosive conditions prevailed at all times.

In addition to those tests carried out with the blasting nozzle 0.25m from the steel plate (N1 in Fig. 2), some tests were carried out with the blasting nozzle and the gas inlet in other positions (N1 to N3 in Fig. 2); these included fitting a sleeve around the blasting nozzle and introducing the gas at that point. The tests lasted for several hours and were carried out in a variety of atmospheric conditions (still and moving air, dry and warm, cool and wet).

The atmosphere in the vicinity of the chamber contained so much gas that normal manual blasting would have been impossible without the provision of breathing apparatus for the operator. During each test firing, the flame front spread for several metres around the chamber (Fig. 4).

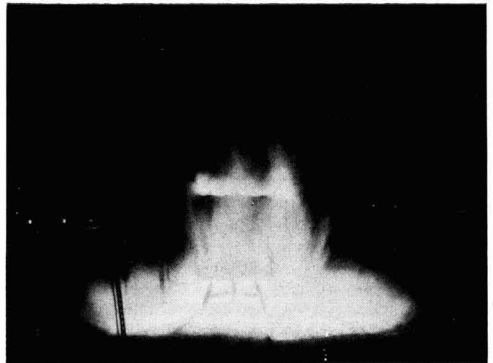


Fig. 4. Flame front produced during a test firing

The sparks produced by the grit streams were numerous but dull and they could be observed only in darkness. On no occasion did they ignite the inflammable gas mixture present in the test chamber. It is considered that this might be because the sparks are of low energy and are cooled by the surrounding air before they fly into the potentially explosive atmosphere.

**Discussion**

Refs. 1, 2

Casdorph<sup>1</sup> has reported similar findings to those reported here, (that is, no ignitions occurred) when he carried out tests in the USA using sand blasting equipment. He examined the problems of sand blasting in chemical plant in the presence of a range of inflammable materials, including acetaldehyde, kerosene and gasoline. Some of the physical properties of these materials are given in Table 2.

Table 2  
Properties of materials used in the tests reported by Casdorff

	Flash point (°C)	Ignition temperature (°C)	Boiling point (°C)	Lower explosive limit (LEL) (Volume %)	Upper explosive limit (UEL) (Volume %)
Acetaldehyde	-38	140	21	4.1	55.0
Kerosine	38-74*	227	210-260	1.16	6.0
Gasoline	-43	240-400	40-200	1.3	6.0

\*Closed cup

His tests were carried out using an iron table with a steel backing plate. The blasting jet was directed on to a test plate at various angles. Inflammable test liquids were fed under pressure into the jet stream as well as on to the table top and backing plate.

Further tests were reported in which the table and back-plate were wetted with the test liquid and ignited (in the case of kerosine the table and backplate were preheated facilitate evaporation). Additional fuel was pumped into the area to feed the fire. The sand blasting was then started and in each case the fire was extinguished and no re-ignition occurred even though the liquids were still evaporating or boiling.

Bradley<sup>2</sup> reported further tests in which a 0.6 m (3 ft) length of 0.66 m (26 inch) diameter pipe was welded to a 1 m × 1.3 m × 4.75 mm (3 ft × 4 ft × 3/16 inch) plate. Two pipes were fitted into this tank, one for the introduction of gasoline and the other as a take-off sampling pipe, which led to an explosion-meter test instrument. Test firings were made using sparks produced from a remotely operated welders' friction lighter. Gasoline was fed into this tank and the gas/air mixture in the tank was monitored, using the explosionmeter, whilst the sandblasting jet impinged on the bottom plate inside the tank. His tests covered the whole range from the over-rich down to lean gasoline/air mixtures and no ignitions associated with the sandblasting occurred during any of the experiments.

All these tests support the view that the sparks produced during abrasive blasting operations, using air as propellant, are incapable of causing explosions in inflammable atmospheres. However, there is the possibility of sparks being generated by static build-up during the blasting operation and if so, these could constitute a hazard.

Bradley has reported static build-up test results<sup>2</sup>. In these tests, a steel strip 8 × 24 cm (3 × 9 inch) was sand blasted whilst being insulated from earth by a wooden post. A voltage in excess of 16 kV built up on the steel strip. A spark produced by this voltage would be expected to ignite an inflammable gas/air mixture. When the same strip was properly earthed no voltage build-up occurred.

The tests described here, together with the work of other investigators, indicate that grit blasting may be carried out without hazard in inflammable atmospheres, provided the normal safety precautions are observed. With this knowledge, it was decided that grit blasting trials should be carried out at sea, and that the initial work should be carried out on a lubricating oil tanker, which would represent a low fire hazard. The details are given below.

#### Deck grit blasting trials at sea

A Hodge Clemco 1452 grit blasting pot, a 7.5m<sup>3</sup> per minute (265 cfm) compressor, a Jet-Vac industrial vacuum cleaner and

a CA 100 airless spray unit, together with all auxiliary hoses and equipment, were loaded on board an 18 000 tonne, 12 year old tanker. The compressor was installed in a "safe" area on the poop deck and was supplied with sufficient hose to enable blasting to take place on any area of the deck. It was essential that all the hoses and pipework to be used were of the anti-static type. All the blasting and painting was carried out by the ship's crew members after an initial one-day training session at the beginning of the voyage. The author acted as an observer throughout the trial. During the grit blasting operations, it was decided that in addition to all normal fire regulations and precautions being observed, any points where gas or liquid leaks might occur (vents, sampling points, sight gauge apertures, etc.) should be adequately blanked off; this precaution also prevented the ingress of abrasive into those areas. The structure being cleaned, the compressor, blasting pot and nozzle, and the operators were all electrically bonded together.

The port area of the foredeck immediately forward of the centre castle was chosen for the initial trial, and blasting commenced as soon as practicable once the ship was at sea. After blasting for several hours, the bulk of the spent grit was removed by brush and shovel and the residue was blown off with an air jet. This proved to be the most satisfactory method in the open areas of the deck. The Jet-Vac industrial vacuum cleaner was found to be the most efficient way of removing the grit from the cluttered spaces around decklines and valves. After removal of spent grit and dust, the area was primed using airless spray equipment. In the first two days of the trial, approximately 90 m<sup>2</sup> (110 square yards) were completed; this included all above-deck projections, such as tank lids, valve casings, sighting ports, ullage plugs, deck lines and a ladder (Figs. 5-7). Most areas were consistently blasted to an Sa 2.5 standard and only occasionally, in difficult or heavily scaled areas, did the standard of surface preparation fall to Sa 2.

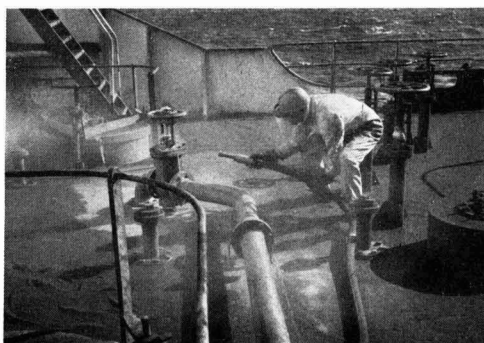


Fig. 5. Grit blasting in progress on foredeck during a sea voyage

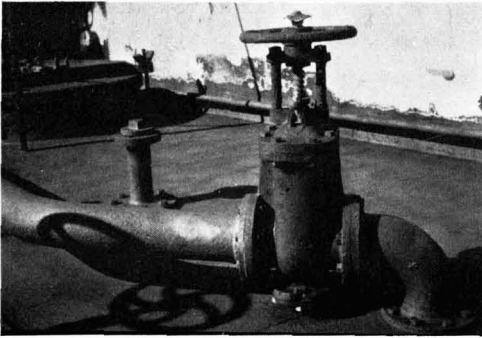


Fig. 6. Deck valve, showing the effectiveness of grit blasting. Note deep corrosion pitting in the valve casing

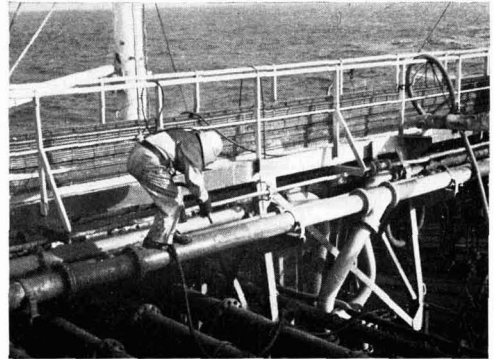


Fig. 9. Blasting pipework alongside the flying bridge during a sea voyage

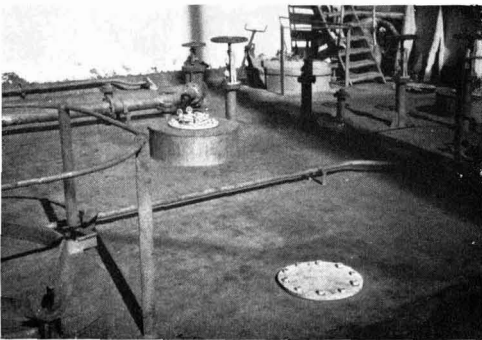


Fig. 7. Area of foredeck after grit blasting

As areas of the deck were cleaned, so that blasting operation was transferred to different sections in order that the painting could be carried out without grit particles getting on to the freshly painted area. The most difficult areas to clean were the flying bridge and supports and the associated piping of the loading and discharge manifold. This was because of the proximity of these pieces and their consequent inaccessibility (Figs. 8 and 9). The flying bridge supports and pipes were in



Fig. 8. Pipework in the manifold area, illustrating the difficulties facing maintenance teams

poor condition, coated with heavy rust and scale, which had resulted from years of neglect because the awkwardness and clutter of the area had made maintenance by conventional methods almost impossible. The flying bridge was roped off and the grills were removed to give access to the upper surfaces of the pipes and the angles of the flying bridge supports. The blasting programme was carried through as a continuous exercise for six days, each area cleaned receiving a primer coat at the end of each day's blasting.

During all this work, "J Blast Supa" abrasive was used and was found to remove adequately even the thick tenacious scale present on the deck steam lines. On the dry decks much of the grit was recoverable and was re-used after sieving through a 3 mm sieve. This used abrasive was mixed with new grit in the pot in the ratio of three bags of new grit to two bags of reclaimed abrasive. The total consumption of new abrasive for 293 m<sup>2</sup> (350 square yards) of cleared steel was 10 668 kg (210 cwt), and at the end of the trial approximately 4064 kg (80 cwt) of reclaimed grit remained. Throughout the trial, the compressor produced nozzle pressures in excess of  $5.7 \times 10^5$  Pa (80 psi).

## Conclusions

The experiments carried out in Thornton Research Centre and by other workers have shown that grit blast cleaning of rusty steel may be conducted safely in inflammable atmospheres. In addition, it has now been shown that grit blasting can be carried out successfully on board a vessel at sea. Whilst the trial described was carried out on a relatively "safe" ship—a lubricating-oil carrier with a low fire risk—it is believed that there are no reasons why grit blast cleaning should not be carried out with safety on board oil tankers in inflammable atmospheres, provided that all normal safety precautions and the additional ones given in this paper are taken.

It is stressed that the author was concerned only with the transportation of crude petroleum and petroleum products. With other cargoes, there may be different hazards not considered here, and it is essential that the degree of danger from these be ascertained before any blasting is attempted, especially in atmospheres other than those dealt with in this paper.

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**Acknowledgment**

The author wishes to thank Mr P. B. Wharton and Mr G. A. Hulley of Hodge Clemco Ltd for their helpful advice and co-operation throughout the trials.

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# The photo-oxidation of normal primary alcohols by anatase titanium dioxide

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## Summary

When a suspension of anatase titanium dioxide in n-butanol, ethanol or methanol is irradiated with ultraviolet rays in a nitrogen atmosphere, the alcohol is partly oxidised to the corresponding aldehyde, as may be shown by infrared and by ultraviolet spectrophotometry. The concentration of butyraldehyde in the distillate

from such reaction mixtures has been determined by gas chromatography. Titanium (III) ions, formed simultaneously, have been determined by adding excess iodine solution in methanol, followed by potentiometric back-titration with sodium thiosulfate solution. A tentative mechanism is suggested for the photo-induced reactions.

## Keywords

### Raw materials:

prime pigments and dyes  
anatase titanium dioxide

solvents  
alcohol

Processes and methods primarily associated with  
service or utility

photo-oxidation

Miscellaneous terms

ultraviolet light

## La photo-oxydation des alcools primaires normaux par dioxyde de titane du type anatase

### Résumé

Lorsqu'une suspension de dioxyde de titane du type anatase en n-butanol, éthanol ou méthanol est irradiée par des rayons ultraviolets dans un atmosphère d'azote, l'alcool est oxydé en partie à l'aldéhyde qui correspond, ce que l'on peut démontrer par la spectrophotométrie à l'infrarouge ou à l'ultra violet. On peut déterminer par chromatographie en phase gazeuse la concentration

de butyraldéhyde dans le distillat à partir de tels mélanges de réaction. Les ions de titane (III) formés simultanément ont été déterminés un ajoutant un excédent d'iode dissout en méthanol, suivi par titrage potentiométriquement en retour avec une solution d'hydrosulfite de soude. On propose un mécanisme tentatif des réactions photo-amorcées.

## Die Foto-Oxidation normaler primärer Alkohole durch Anatas-Titaniumdioxid

### Zusammenfassung

Wenn eine Suspension von Anatas-Titaniumdioxid in n-Butanol, Äthanol und Methanol mit ultravioletten Strahlen in einer Stickstoffatmosphäre bestrahlt wird, wird der Alkohol teilweise zum korrespondierenden Aldehyd oxidiert, wie sich anhand von Infrarot- und Ultraviolet-Spektrofotometrie nachweisen lässt. Die Konzentration von Butyraldehyd im Destillat aus solchen

Reaktionsgemischen wurde mittel Gaschromatographie bestimmt. Titanium (III)-Ionen, die gleichzeitig gebildet werden, wurden durch Zusetzen eines Überschusses von Jodlösung in Methanol, gefolgt von potentiometrischer Rücktitration mit Natriumthiooxulfatlösung bestimmt. Ein provisorischer Mechanismus für die fotoinduzierten Reaktionen wird vorgeschlagen.

## Introduction

Refs. 1-4

The oxidation of organic compounds by titanium dioxide on irradiation with ultraviolet light has been known for some time<sup>1</sup>. A weatherability test for titanium dioxide samples is based on irradiation of a paste of the powder and mandelic acid, followed by measurement of the reflectance<sup>2</sup>. The photo-oxidation of alcohols by titanium dioxide has been reported recently<sup>3, 4</sup>. Boehm and co-workers found that, in an oxygen-free atmosphere, an irradiated mixture of a primary alcohol and anatase titanium dioxide produced aldehyde and  $Ti^{3+}$  ions in a solution which was titrated with a solution of iodine<sup>4</sup>. The preliminary results reported here are in agreement with Boehm's results.

## Experimental

Refs. 5, 6

The pigment "Anatase P25" (Degussa, Frankfurt) was used in the form supplied ( $Al_2O_3 < 0.3\%$ ,  $SiO_2 < 0.2\%$ ) unless otherwise stated. Many of the characteristics of P25 have been reported by Boehm and co-workers<sup>5</sup>. A one per cent W/W suspension of P25 in normal primary alcohol was magnetically

stirred whilst being irradiated with unfiltered radiation from a Hanovia 100W medium pressure mercury lamp. The volume of alcohol used (240 cm<sup>3</sup>) surrounded the length of the arc to ensure the maximum utilisation of lamp output. The suspension was kept in a cylindrical vessel through which oxygen-free nitrogen was passed and the outlet stopper carried a micro-burette containing 0.05M iodine solution in methanol. After irradiation, a known excess of iodine solution was added and the suspension was filtered through GF/C paper. The excess iodine in the filtrate was back-titrated potentiometrically against standardised 0.05M sodium thiosulfate solution.

As a second procedure, the irradiated suspension was fractionally distilled and the appropriate fraction of the distillate weighed prior to examination by UV or IR spectrophotometry or by gas chromatography. (Due to the small amount of aldehyde produced, attempts to obtain derivatives with 2,4-dinitrophenylhydrazine or with dimedone were unsuccessful.) For the gas chromatography, a Porapak Q-S support column and a Perkin Elmer F11 flame ionisation unit were used. The flow rate was 60 cm<sup>3</sup> minute<sup>-1</sup> and the temperature was 453°C (180°C). Butyraldehyde was determined by comparison with a one per cent standard solution in butanol.

Attempts to determine butyraldehyde by absorbance measurements<sup>6</sup> at 280 nm were abandoned. Both the standard solution and the distillate after irradiation showed more intense absorption at approximately 235 nm, which became more pronounced on ageing. This may be due to the formation of a hemiacetal.

## Results and discussion

Refs. 1, 3, 5, 7-11

In the present investigation, the unfiltered radiation from the lamp was mainly in the region 248-1367 nm. No attempt was made to study the effect of wavelength on the oxidation process since the use of filters would have reduced the small amounts of oxidation products formed. The absorption cross-section of rutile pigment is slightly sensitive to wavelength<sup>1</sup> in the spectral region 300-370 nm. However, the photo-catalysed oxidation of mercury by the anatase grade<sup>7</sup> is most pronounced on irradiation at 390-420 nm, which corresponds to the absorption edge of titanium dioxide.

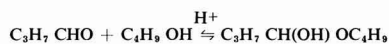
A summary of the results obtained is given in Table 1, which contains results when one of the alcohols methanol, ethanol or n-butanol was used. The use of the last of these is advantageous since the difference in boiling point between the alcohol and aldehyde is 43°C. Two batches of P25 were tried and one anatase sample "CLDD/881A" (BTP Tiocide Ltd, London) which had received no surface treatment and which was not calcined. Table 1 shows the amount of Ti<sup>3+</sup> ions determined in solution and in some cases the amount of butyraldehyde, produced in a parallel run and determined by gas chromatography.

The photo-adsorption of isopropanol by rutile titanium dioxide has been demonstrated recently<sup>3</sup>, and it may be assumed that the alcohols used in the present work were photo-adsorbed by the anatase pigment prior to oxidation. The energetics of photo-adsorption are usually discussed in terms of the theory of semiconductivity. A recent review includes a section on the band structure of rutile pigments<sup>1</sup>, but little is known about the band structure of the anatase grade<sup>8</sup>.

It is visualised that the irradiation of anatase titanium dioxide with UV quanta produces an electron and a "positive hole" at the surface. The electron would reduce Ti<sup>4+</sup> to Ti<sup>3+</sup> ions, which might become solvated by the alcohol. The partial formation of Ti<sub>2</sub>O<sub>3</sub> on the surface of the irradiated anatase grade is suggested by the blue/grey colour of the powder after filtration. A similar colour change for vacuum-heated rutile powder has been ascribed to organic surface contaminants<sup>9</sup>.

The positive holes formed by the irradiation of anatase pigment are likely to react with surface (OH)' ions and produce ·OH radicals, which would then oxidise alcohol molecules to aldehyde. Acidic and basic (OH)' ions have been identified on the surface of irradiated anatase pigments<sup>5</sup>. The marked decrease in the yield of the reaction products when a preheated anatase pigment was used, may be ascribed to dehydroxylation of the pigment's surface<sup>7</sup>. The distillate obtained from the irradiated suspension (anatase pigment/methyl alcohol or anatase pigment/n-butyl alcohol) showed an infrared absorption band at 1640 cm<sup>-1</sup>, which is characteristic of the carbonyl group. The band was not detected during experiments with blank samples, in the absence of either the anatase pigment or the UV source.

Any quantitative correlation which might exist between the Ti<sup>3+</sup> ions and the aldehyde found in solution was obscured, possibly by the formation of hemiacetal<sup>10</sup> according to:



A shift in the UV spectrum of a standard butyraldehyde solution in butanol was observed on acidification and was presumably due to hemiacetal formation. A similar shift was exhibited by the spectra of the distillates obtained from the irradiated suspensions.

The amounts of Ti<sup>3+</sup> ions determined in solutions of different alcohols oxidised by P25 (batch 2) were similar (Table 1), reflecting similar solvation of Ti<sup>3+</sup> ions.

The differing behaviour of the anatase pigments in the samples tested is not surprising and may be ascribed to

Table 1  
The yield of photo-oxidation products of alcohols by anatase titanium dioxide

Sample	Mass (g)	Alcohol	Volume (cm <sup>3</sup> )	Time (minutes)	Ti <sup>3+</sup> produced (10 <sup>-4</sup> mol.)	Aldehyde produced (10 <sup>-4</sup> mol.)
P25 (1*)	2.5	CH <sub>3</sub> OH	250	90	2.2	—
P25 (1)	2.4	nC <sub>4</sub> H <sub>9</sub> OH	240	135	2.4	—
P25 (1)	2.4	nC <sub>4</sub> H <sub>9</sub> OH	240	180	9.0 (av.)	6.2
P25 (1)	2.4	nC <sub>4</sub> H <sub>9</sub> OH	240	180	0.9	2.9 <sup>a</sup>
P25 (1)	1.2	nC <sub>4</sub> H <sub>9</sub> OH	240	180	1.4	—
P25 (2)	2.4	CH <sub>3</sub> OH	240	180	2.3 (av.)	—
P25 (2)	2.4	C <sub>2</sub> H <sub>5</sub> OH	240	180	2.7 (av.)	—
P25 (2)	2.4	nC <sub>4</sub> H <sub>9</sub> OH	240	180	2.9 (av.)	—
CLDD	2.4	nC <sub>4</sub> H <sub>9</sub> OH	240	180	9.4	0.4 <sup>b</sup>

\*Figure between brackets gives the batch number; av. denotes the figure is from an average of two runs.

<sup>a</sup>Sample heated to 500°C for 4 hours; <sup>b</sup>sample heated to 200°C for 4.5 hours.

differences in the surface area, the degree of hydroxylation and the level of impurities in the test specimens. Surface impurities were found to affect photo-oxidation by titanium dioxide<sup>11</sup>. No quantitative data are available for the characteristics of pigment sample CLDD/881A, which gave a very low yield of butyraldehyde.

### Acknowledgment

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# The role played by water-soluble polymers in paint performance. Part III: Molecular weight and concentration effects in mixed thickener studies

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## Summary

The influences which the molecular weight and the quantity of a thickener have on the rheological and performance characteristics of a cost-efficient, water-borne latex paint formulation are discussed. In particular, the study examines a broad spectrum of chemically different synthetic water-soluble polymers (SWSPs) in combination with a high molecular weight hydroxyethyl cellulose thickener and in a coating formulation which includes a high percentage of extender. The high shear viscosities (HSVs) of the paints are influenced only by the total amount of thickener present. The chemical composition of non-branched SWSPs does not effect the HSV, although amongst chemically similar compositions, a discontinuity in HSV is noted when the thickener's molecular weight is in the vicinity of, or below, the transition region observed in intrinsic viscosity molecular weight analyses. The HSVs observed with low (on average less than  $4 \times 10^4$ ) molecular weight polymers (that is, with "macro-oligomeric" thickeners) fall substantially below those extrapolated from data obtained with high molecular weight, SWSP thickened paints.

A coating's flow and levelling response to thickener variations is more complex than that noted in the HSV studies. The flow-out, which may be related to low shear strain elastic moduli, is influenced by both the amount of SWSP employed and its chemical composition. Contrary to the results of HSV studies, the use of

macro-oligomeric thickeners does not effect a discontinuity in flow-out characteristics. A comprehensive interpretation of coating flow and levelling is complicated by the amount of hydroxyethyl cellulose used in the mixed thickener studies. In paints employing a low percentage of hydroxyethyl cellulose, the effects observed with increasing SWSP concentration are related to the thickener's chemical structure, and a coating's flow-out is characterised by one of three responses: a marked retarding influence with increasing thickener concentration; a moderate retarding influence, until large quantities of macro-oligomers are used; or no noticeable effect, regardless of the amount or molecular weight of the thickener employed.

The linear proportionality between the HSVs and the quantities of chemically different thickeners of high molecular weight indicates that there are no significant intercomponent associations under high shear stress in the paints studied. Variations in flow and levelling with differing SWSP concentrations can be explained generally by the macromolecular interassociation mechanism, which has been proposed in an earlier part of this paper to explain the behaviour of formulations employing less extender, when strong component interactions are not evident. Significant component interactions are observed in the mixed thickener studies of cheaper formulations, and these are discussed.

## Keywords

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

### Raw materials:

*binders (resins, etc)*

polyvinyl alcohol  
styrene resin

*surface active and rheological agents*

hydroxyethyl cellulose  
thickening agent  
viscosity control agent

*Properties, characteristics and conditions primarily associated with:*

*materials in general*  
viscosity

*coatings during application*

flow characteristics  
levelling  
sagging

## Le rôle, dans le domaine du rendement des peintures, joué par les polymères solubles dans l'eau. 3ème Partie : Les effets de la masse moléculaire et de la concentration des mélanges d'épaississants

### Résumé

On discute les influences qu'exercent la masse moléculaire et la concentration de l'épaississant sur les caractéristiques rhéologiques et sur le rendement d'une peinture-émulsion à base d'eau et efficace au point de vue du prix. En particulier, l'étude comprend l'examen d'un large éventail de polymères synthétiques, solubles dans l'eau et de différente composition chimique (SWSP), ainsi qu'un épaississant à base d'hydroxyéthyl cellulose de haute masse moléculaire, la peinture contient également un pourcentage élevé de matière de charge. Les viscosités aux hautes vitesses de cisaillement (HSV) des peintures sont influencées seulement par la quantité totale d'épaississant dans la peinture. La composition chimique des polymères non ramifiés, solubles dans l'eau, n'exerce aucune influence sur la viscosité à haute vitesse de cisaillement, bien que parmi les compositions chimiquement semblables on note une discontinuité où la masse moléculaire se trouve à peu près de la région de transition que l'on observe dans les analyses de la viscosité intrinsèque et de la masse moléculaire. Dans le cas des polymères à faibles masses moléculaires (en moyen moins de

$4 \times 10^4$ ), c'est-à-dire, les épaississants macro-oligomères, les viscosités aux HSV observées, sont sensiblement plus faibles que celles obtenues au moyen de l'extrapolation des données à partir des peintures contenant des épaississants à base des polymères synthétiques, solubles dans l'eau, et de masse moléculaire élevée.

La réponse d'un revêtement, en ce qui concerne les caractéristiques d'étalement et de nivellement, aux variations de l'épaississant est plus complexe que celle mise en évidence par les études HSV. L'étalement d'un revêtement, qui peut être lié au module d'élasticité à faible vitesse de cisaillement, est influencé par la quantité de SWSP utilisée et également par sa composition chimique. Au contraire des résultats mis en évidence par les études HSV, l'emploi des épaississants macro-oligomères ne provoque aucune discontinuité dans les caractéristiques d'étalement et de nivellement. Une interprétation compréhensive de l'étalement est rendue plus difficile par la quantité d'hydroxyéthylcellulose utilisée dans ces études sur les mélanges d'épaississants. Dans le cas des peintures à faible

pourcentage d'hydroxyéthylcellulose, les effets que l'on observe en fonction d'une augmentation progressive de la concentration de SWSP sont liés à la structure chimique de l'épaississant. De même, l'étalement d'un revêtement est caractérisé par une sur trois réponses: une influence retardatrice bien définie en fonction de l'augmentation de la concentration d'épaississant; une influence retardatrice modérée, jusqu'au point où l'on utilise les quantités importantes d'épaississant; ou enfin, aucun effet sensible, n'importe quelle quantité ou quelle masse moléculaire de l'épaississant que l'on utilise.

La proportionalité linéaire entre les HSV et les quantités des

épaississants de haute masse moléculaire et de différente composition chimique indique que, dans les peintures étudiées et sous les hautes vitesses de cisaillement, il n'y a aucune association interconstituante importante. En général, le mécanisme d'interassociation macro-moléculaire proposé dans une partie précédente de cet exposé pour expliquer le comportement des peintures à teneur en matière de charge plus faible, saurait expliquer également, pourvu que les réactions interconstituantes fortes soient absentes, les variations d'étalement et de nivellement en fonction des différentes concentrations de SWSP. On discute les réactions interconstituantes importantes que l'on observe dans le cas des études sur les mélanges d'épaississants en peintures moins chères.

## Die Rolle wasserlöslicher Polymere bei der Leistungsfähigkeit von Farben. Teil III: Einwirkungen von Molekulargewicht und Konzentration in Mischverdickerstudien

### Zusammenfassung

Es werden die Einflüsse diskutiert, die Molekulargewicht und Menge eines Verdickungsmittels auf die rheologischen und Leistungsmerkmale einer kostenwirksamen Latexfarbenrezeptur auf Wasserbasis ausüben. Im besonderen untersucht die Studie ein breites Spektrum chemisch unterschiedlicher synthetischer wasserlöslicher Polymere (SWSPs) in Verbindung mit einem Oxyäthylzelluloseverdickungsmittel mit hohem Molekulargewicht und in einer Beschichtungsrezeptur, die einen hohen Prozentsatz an Streckmitteln einschließt. Die hohen Scherviskositäten (HSVs) der Farben werden nur durch die Gesamtmenge an vorhandenem Verdickungsmittel beeinflusst. Die chemische Zusammensetzung nicht-verzweigter SWSPs hat keinen Einfluß auf die HSV, obwohl unter chemisch ähnlichen Zusammensetzungen eine Diskontinuität in der HSV zu bemerken ist, wenn das Molekulargewicht des Verdickungsmittels nahe bei oder unter dem in spezifischen Viskosität/Molekulargewicht-Analysen beobachteten Übergangsbereich liegt. Die bei Polymeren mit niedrigem (durchschnittlich weniger als  $4 \times 10^4$ ) Molekulargewicht (d. h. mit "makro-oligomeren" Verdickungsmitteln) beobachteten HSVs liegen wesentlich niedriger als die, die aus Daten extrapoliert worden sind, die sich bei SWSP-verdickten Farben mit hohem Molekulargewicht ergaben.

Die Fließ- und Egalisierreaktion einer Beschichtung auf Verdickungsmittelvariationen ist komplizierter als die, die in den HSV-Studien bemerkt wurde. Das Ausfließen einer Beschichtung, das mit Elastizitätsmodul niedriger Scherspannung zusammenhängen mag, wird sowohl von der angewandten Menge SWSP als auch von ihrer chemischen Zusammensetzung beeinflusst. Im Gegensatz zu den Ergebnissen von HSV-Studien beeinflusst die

Verwendung makro-oligomerischer Verdickungsmittel eine Diskontinuität in den Ausfließmerkmalen nicht. Eine umfassende Interpretierung von Beschichtungsfluß und -egalierung wird durch die Menge an Oxyäthyl-zellulose kompliziert, die bei den Mischverdickungsmittelstudien verwendet wird. Bei Farben, die einen geringen Prozentsatz an Oxyäthylzellulose enthalten, stehen die bei steigender SWSP-Konzentration beobachteten Auswirkungen in Zusammenhang mit der chemischen Struktur des Verdickungsmittels, und das Ausfließen einer Beschichtung wird durch eine von drei Reaktionen charakterisiert: deutlicher Verzögerungseinfluß bei steigender Verdickungsmittelkonzentration; bescheidener Verzögerungseinfluß, bis große Mengen von Makro-Oligomeren verwendet werden; oder kein merklicher Effekt, unabhängig von der Menge oder dem Molekulargewicht des verwendeten Verdickungsmittels.

Die lineare Proportionalität zwischen den HSVs und den Mengen chemisch unter-scheidlicher Verdickungsmittel mit hohem Molekulargewicht zeigt an, daß es bei den untersuchten Farben bei hoher Scherspannung keine Assoziationen von Bedeutung zwischen den Komponenten gibt. Variationen in Fließen und Egalisieren bei unterschiedlichen SWSP-Konzentrationen lassen sich im allgemeinen durch den makromolekularen Interassoziationsmechanismus erklären, von dem in einem früheren Teil dieses Aufsatzes gesagt wurde, er erkläre das Verhalten von Rezepturen, die weniger Streckmittel enthalten, wenn starke Wechselwirkungen der Komponenten nicht zu verzeichnen sind. Komponentenwechselwirkungen von Bedeutung lassen sich in den Mischverdickungsmittelstudien an billigeren Rezepturen beobachten, und diese werden diskutiert.

### Introduction

Ref. 1

The present investigation is a continuation<sup>1</sup> of studies designed to elucidate the role of water-soluble polymers (WSPs), used as paint thickeners, in coating performance. The current study records observations made in an examination of a broad spectrum of WSPs, varying in molecular weight, in combination with a high ( $8.0 \times 10^5$ ) molecular weight hydroxyethyl cellulose. In all cases, the paints were prepared to an equivalent Stormer viscosity, which is a common formulation practice, and the effect of molecular weight on high shear viscosities (HSVs) and levelling were determined, for several chemically different types of WSP.

### Experimental

Refs. 1-6

A relatively cost-efficient interior flat paint based on a vinyl acetate/acrylic latex ("UCAR-360"—Union Carbide Corp.) in Formulation I-1215<sup>2</sup> was employed throughout the study. The samples were formulated to a Stormer viscosity of 92 KU whilst maintaining a constant PVC (60 per cent), so that the only differences were the type and concentration of the thickener system. Viscosity profiles as a function of shear rate were determined with the Ferranti Shirley viscometer<sup>3</sup>, and

values recorded at a shear rate of  $14\,000\text{ sec}^{-1}$  were chosen to approximate application conditions in practice. Levelling performance was evaluated using the draw-down bar and profilometer techniques employed previously<sup>1, 6</sup> and originally discussed by Dodge<sup>4</sup>. Sagging characteristics were quantified with the Leneta anti-sag meter<sup>5</sup>.

### Results

Refs. 2, 6, 7

The current studies utilised the excellent thickening efficiency of a high molecular weight hydroxyethyl cellulose ("Cellosize QP-52M", Union Carbide Corp.) to produce a part of the required viscosity in a relatively low cost formulation<sup>2</sup>. Simple, well-characterised WSPs could then be used to achieve the final viscosity, whilst maintaining a reasonable total cost for the system. The aim was to determine whether high quality performance characteristics could be obtained in formulations employing a high proportion of extender, and to relate performance with the amount and molecular weight of the SWSP employed. Specifically, paints were formulated with 25, 50 and 75 per cent of the amount of hydroxyethyl cellulose (HEC) necessary to produce 92 KU viscosity when it is the only thickener used. WSP and water were then added to produce the desired final viscosity and total formulation weight. By varying the molecular weight of the SWSPs, it was

possible to obtain families of paints for comparative studies at either the same or different levels of HEC.

A similar approach<sup>6</sup> has been employed to study HEC as the sole thickener. Formulations containing high molecular weight HEC in combination with lower molecular weight HEC materials were prepared. The levelling characteristics of these paints were found to be independent of the total HEC content; however, high shear viscosities (HSVs) were proportional to the amount of thickener employed. The formulation in this earlier work was based on the same latex vehicle used in the present study; however, the previous paints were lower in extender concentration and total PVC, to yield higher quality paints<sup>7</sup>. With these results as background, it was anticipated that the influence of the synthetic polymer would be detected easily.

#### Poly(ethylene oxide) (PEO)

A series of paints were prepared as described above using several molecular weight grades of PEO ("Polyox WSRN-10, WSRN-750, WSRN-3000 and WSR-301", Union Carbide Corp.). The HSV results are illustrated in Fig. 1. The data suggest possible secondary effects may result from the PEO/HEC ratio at a given total thickener concentration, but the primary effect is clearly due to the total amount of thickener in the formulation.

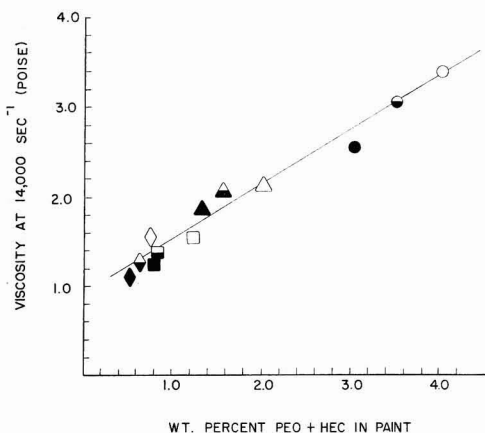


Fig. 1. High shear viscosity dependence on blended thickener concentration in Formulation I-1215 paints

Synthetic WSP: Poly(ethylene oxide) (PEO)

Mean molecular weight of poly(ethylene oxide) synthetic WSP:

Circles	$1.0 \times 10^5$
Triangles	$3.6 \times 10^5$
Squares	$6.2 \times 10^5$
Rhomb	$12.0 \times 10^5$

Mean molecular weight of hydroxy ethyl cellulose (HEC):  $8.0 \times 10^5$ . Weight per cent HEC used:

Closed symbol	0.21%
Partially open symbol	0.14%
Open symbol	0.07%

Fig. 2 presents a quantitative analysis of the profilometer traces from the levelling tests. When the peak height is recorded, a number of peaks are measured and averaged. As an aid to visualising these values, typical traces, measuring 4.0, 2.0 and 1.0 cm, are displayed in the illustration. The data indicate that levelling is retarded as the PEO content in the paint increases. Furthermore, this decrease in performance is independent of the HEC level until very high levels of PEO are used.

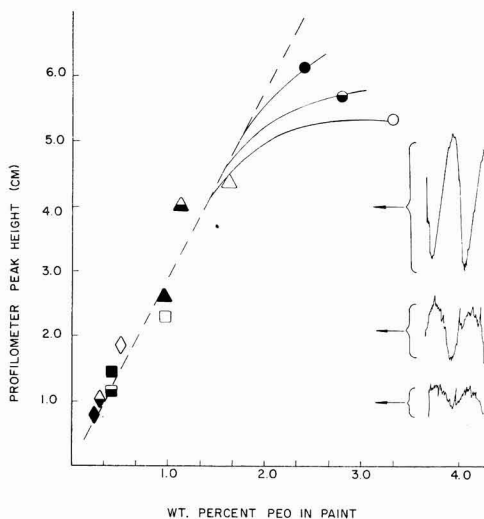


Fig. 2. Draw-down bar surface profile dependence on synthetic WSP concentrations in I-1215 paints thickened with WSP-cellulosic blends

Synthetic WSP: Poly(ethylene oxide) (PEO)

Mean molecular weights of poly(ethylene oxide) synthetic WSP, mean molecular weight of HEC, and weight per cent HEC used are the same as in Fig. 1.

#### Vinyl alcohol/vinyl acetate copolymers (PVAl)

As with the PEO/HEC mixed thickener studies it was found that an almost totally hydrolysed (99 per cent) vinyl alcohol/vinyl acetate copolymer in combination with HEC would provide paints with HSVs proportional to the total amount of thickener present (Fig. 3). In addition, the flow-out character-

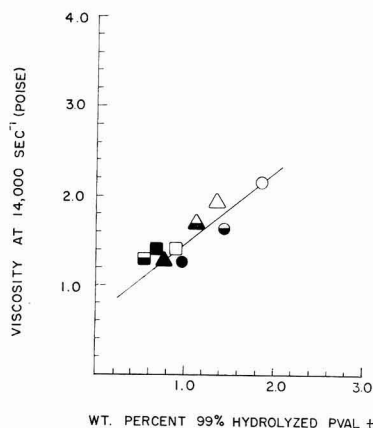


Fig. 3. High shear viscosity dependence on blended thickener concentration in I-1215 paints

Synthetic WSP: 99% hydrolysed vinyl alcohol/vinyl acetate copolymers (99% PVAl)

Mean molecular weight of synthetic WSP:

Circles	$0.87 \times 10^5$
Triangles	$1.2 \times 10^5$
Squares	$10.0 \times 10^5$

Mean molecular weight of HEC and weight per cent HEC used are the same as in Fig. 1.



istics (Fig. 4) were inhibited with increasing concentrations of 99 per cent PVA1.

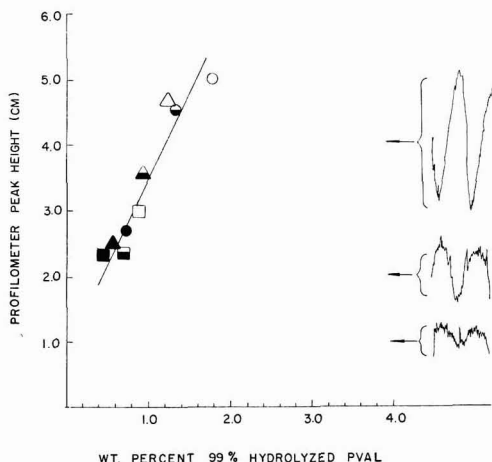


Fig. 4. Draw-down bar surface profile dependence on synthetic WSP concentration in I-1215 paints thickened with WSP-cellulosic blends Synthetic WSP: 99% hydrolysed vinyl alcohol/vinyl acetate copolymers (99% PVA1)

Mean molecular weights of synthetic WSP and of HEC and weight per cent HEC used are the same as in Fig. 3.

The less hydrolysed analogues of this chemical series (89 per cent PVA1) provided marked departures from the trends established in HEC combinations with PEO and 99 per cent PVA1. HSVs are linearly dependent upon the total thickener concentration (with a similar slope dependence—Fig. 5) provided that the copolymer's molecular weight is greater than  $4 \times 10^4$ . The lower molecular weight or "macro-oligomeric" copolymers provide substantially lower HSVs

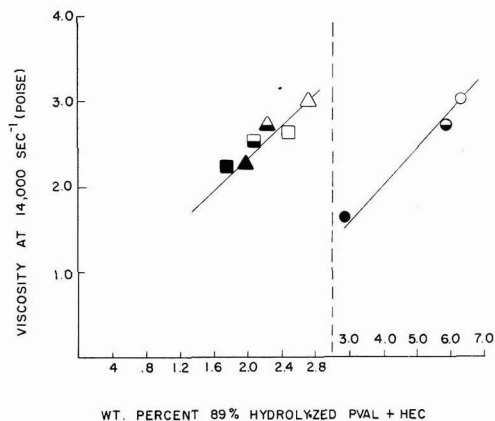


Fig. 5. High shear viscosity dependence on blended thickener concentration in I-1215 paints

Synthetic WSP: 89% hydrolysed vinyl alcohol/vinyl acetate copolymers (89% PVA1)

Mean molecular weight of synthetic WSP:

Circles	$0.1 \times 10^5$
Triangles	$0.96 \times 10^5$
Squares	$1.3 \times 10^5$

Mean molecular weight of HEC and weight per cent HEC used are the same as in Fig. 1.

than would be expected from extrapolated values obtained with higher molecular weight 89 per cent PVA1 polymers used in combination with HEC.

The flow and levelling characteristics of the 89 per cent PVA1 thickened paints are illustrated in Fig. 6. Little change in flow-out is noted as the concentration of the 89 per cent PVA1 is increased, which marks a total departure from previous trends. It is immaterial whether the higher level of PVA1 is achieved by decreasing the relative amount of HEC or by employing more of a lower molecular weight PVA1 at a given HEC concentration. The flow-out of the 99 and 89 per cent hydrolysed PVA1-thickened paints is consistent with what is already known, and previously discussed<sup>1</sup>, with respect to vinyl alcohol/vinyl acetate copolymer inter-associations through the supermolecular order phenomenon.

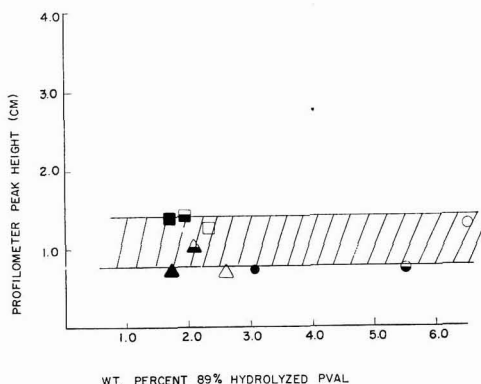


Fig. 6. Draw-down bar surface profile dependence on synthetic WSP concentration in I-1215 paints thickened with WSP-cellulosic blends Synthetic WSP: 89% hydrolysed vinyl alcohol/vinyl acetate copolymers (89% PVA1)

Mean molecular weights of synthetic WSP and of HEC and weight per cent HEC used are the same as in Fig. 5.

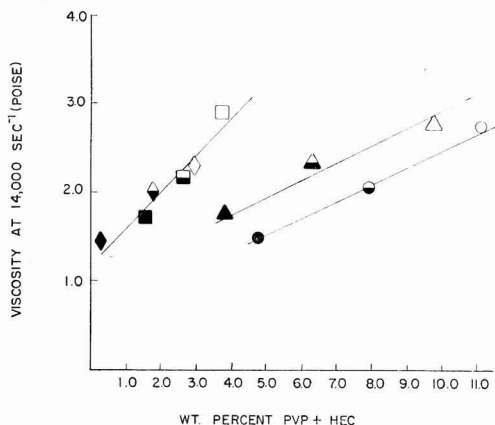
#### *Poly(vinyl pyrrolidone) (PVP)*

Commercial PVPs (GAF Corp.), ranging in molecular weight from about  $1.0 \times 10^4$  to  $3.6 \times 10^5$ , were studied. The HSV data are illustrated in Fig. 7. The previously observed linear dependence of HSV on total thickener concentration was found with the higher molecular weight PVP; however, as noted in the 89 per cent PVA1 series (Fig. 5), the low molecular weight polymers ( $10^4$  to  $4 \times 10^4$ ) were far less efficient, on a weight basis, in producing high HSVs.

The levelling behaviour proved to be even more unique. A decrease in performance as the concentration of PVP increased was not unusual, but a pronounced dependency on the HEC level (Fig. 8) is a departure from the trends established with other synthetic thickeners. Specifically, levelling performance was adversely affected by increases in both PVP and HEC concentrations.

#### *Disodium maleate/styrene copolymer (SMAc)*

A series of styrene/maleic anhydride copolymers of varying molecular weight were prepared by standard procedures<sup>8</sup>. Water-soluble styrene/maleic acid copolymers, used for preparation of the various families of paint, were produced by hydrolysis of the anhydride groups in aqueous sodium



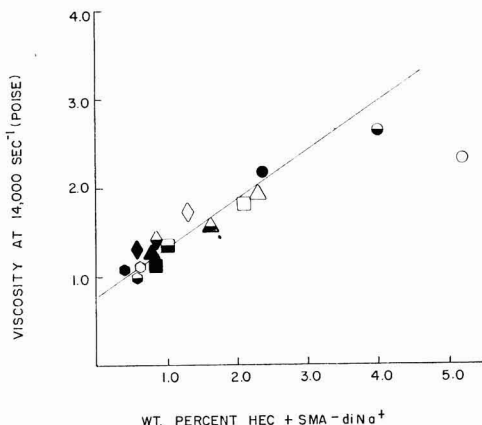
**Fig. 7.** High shear viscosity dependence on blended thickener concentration in I-1215 paints

Synthetic WSP: poly(vinyl pyrrolidone) (PVP)

Mean molecular weight of synthetic WSP:

- Circles  $0.10 \times 10^5$
- Triangles  $0.40 \times 10^5$
- Squares  $1.60 \times 10^5$
- Rhombos  $3.60 \times 10^5$

Mean molecular weight of HEC and weight per cent HEC used are the same as in Fig. 1.



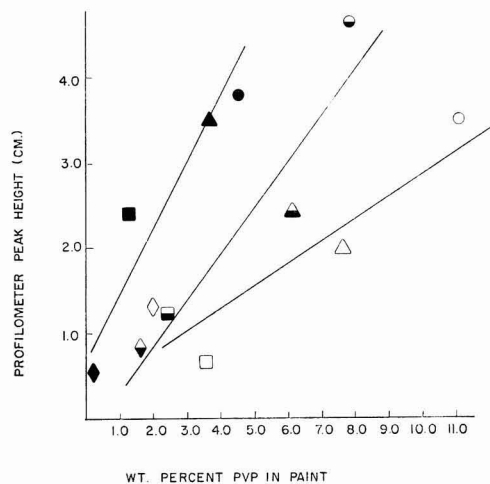
**Fig. 9.** High shear viscosity dependence on blended thickener concentration in I-1215 paints

Synthetic WSP: NaOH hydrolysed styrene-maleic anhydride copolymer

Mean molecular weight of synthetic WSP:

- Circles  $0.23 \times 10^5$
- Triangles  $1.5 \times 10^5$
- Squares  $2.4 \times 10^5$
- Rhombos  $2.7 \times 10^5$
- Hexagons  $3.6 \times 10^5$

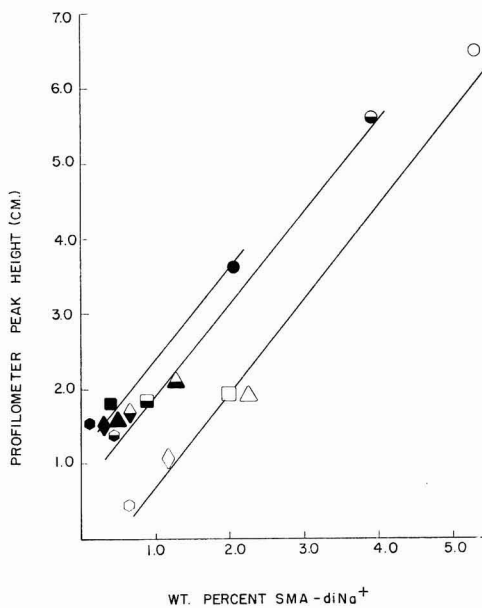
Mean molecular weight of HEC and weight per cent HEC used are the same as in Fig. 1.



**Fig. 8.** Draw-down bar surface profile dependence on synthetic WSP concentration in I-1215 paints thickened with WSP-cellulosic blends

Synthetic WSP: poly(vinyl pyrrolidone) (PVP)

Mean molecular weights of synthetic WSP and of HEC and weight per cent HEC used are the same as in Fig. 7.



**Fig. 10.** Draw-down bar surface profile dependence on synthetic WSP concentration in I-1215 paints thickened with WSP-cellulosic blends

Synthetic WSP: NaOH hydrolysed styrene-maleic anhydride copolymer

Mean molecular weights of synthetic WSP and of HEC and weight per cent HEC used are the same as in Fig. 9.

hydroxide. The HSV data (Fig. 9) again indicate a linear dependence upon total thickener concentration with the higher molecular weight products. The behaviour of the low molecular weight material was somewhat different from the corresponding macro-oligomeric 89 per cent PVA1 and PVP materials in that the HSV concentration curve deviated only at low HEC levels. The levelling characteristics of the paints were found to be similar to those observed with PVP in that performance was inversely related to both HEC and synthetic polymer content (Fig. 10).

## Discussion

Refs. 6, 1, 9

High shear viscosities (HSVs) at a constant hydroxyethyl cellulose (HEC) concentration are linearly dependent upon the amount of high molecular weight SWSP present. A similar effect has been observed<sup>6</sup> in variable molecular weight HEC studies. Thus, in non-branched, water-soluble polymers, the chemical composition of the thickener does not effect differences in HSVs, as is noted in low shear viscosity studies<sup>1</sup>.

The linear dependence of HSV upon the amount of thickener in the formulation is illustrated in Fig. 11 for chemically different SWSPs in combination with a small, constant amount of HEC. The relatively inefficient contribution of the low (less than  $4 \times 10^4$ ) molecular weight polymers, regardless of their chemical composition, is also evident. Since the paints (and so their HSVs) were tested under comparative conditions (that is, pigment particle deformations, etc. are the same in each test), the observed HSVs may be simply viewed in terms of additive effects, that is the thickener's total volume fraction plus the (constant) volume fraction of the other ingredients, as in the Einstein and similar equations. Thus, the relatively inefficient contribution to HSV of the macro-oligomers may be understood in terms of the differences in their hydrodynamic volume. A hydrodynamic volume change, reflected in molecular weight/intrinsic viscosity relationships<sup>9</sup>, occurs at a critical degree of polymerisation, which varies with the polymer's chemical composition, but is generally in the molecular weight range 2 to  $4 \times 10^4$ . This may be observed as a discontinuity in the HSV data. The currently accepted explanation of this molecular weight phenomenon is that at a critical chain length, intramolecular interactions give rise to a larger effective volume than is expected on the basis of random flight statistics, applicable to volume calculations for short-chain polymers<sup>9</sup>.

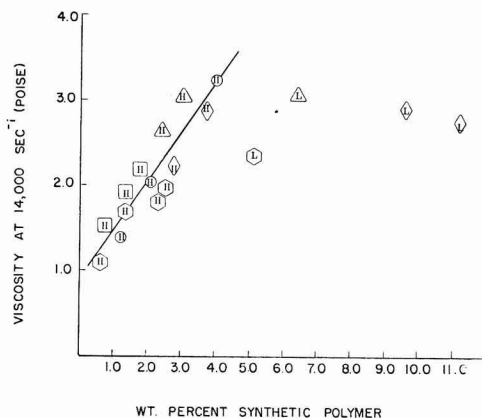


Fig. 11. High shear viscosity dependence on SWSP chemical structure and molecular weight in I-1215 paints containing 0.07 wt. % HEC, average molecular weight  $8.0 \times 10^5$

Synthetic polymers:

Circles	PEO
Triangles	89% PVAI
Squares	99% PVAI
Rhombs	PVP
Hexagons	SMA—diNa <sup>+</sup>

Mean molecular weight of synthetic WSP:

H	greater than	$0.4 \times 10^5$
L	less than	$0.4 \times 10^5$

The relationship between SWSP/HEC combinations and flow-out is not always as straightforward as the linear relationship noted in HSV analysis. A linear relationship is apparent between flow-out and the total amount of SWSP present when the synthetic polymer is PEO, 99 per cent PVAI or 89 per cent PVAI (Figs. 2, 4, 6 and summarised in Fig. 12), but more complex patterns appear with SMAc and PVP (Fig. 8 and 10). Previous studies employing mixtures within a comparatively narrow molecular weight range of HEC as the sole thickener did not reveal a relationship between thickener concentration and flow and levelling. Thus, the linear increase in profile peak height with SWSP concentration (observed in Figs. 2, 4 and 6) may be attributed to effects produced by the synthetic thickener. This behaviour is consistent with the relative trends predicted as a result of the interassociation concept<sup>1</sup>.

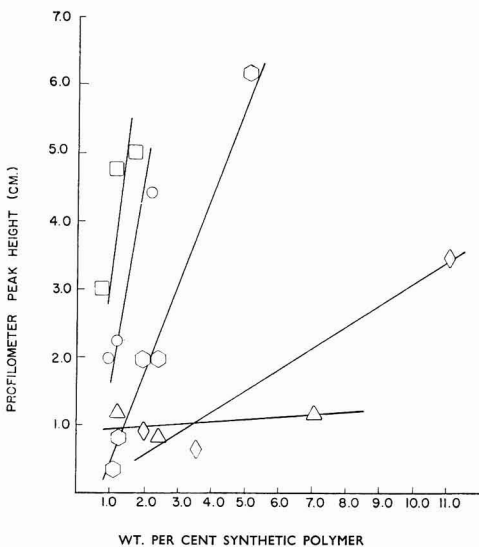


Fig. 12. Draw-down bar surface profile dependence on SWSP chemical structure and molecular weight in I-1215 paints containing 0.07 wt. % HEC, average molecular weight  $8.0 \times 10^5$  (Key for symbols as in Fig. 11).

The complex flow-out behaviour noted with SMA and PVP (Figs. 8 and 10) appears to result from a dependence on both SWSP and HEC concentrations. A flow-out value of 5 is observed for formulation I-1215 when a Stormer viscosity of 90KU is obtained using only HEC as thickener. An extrapolation of the flow-out profiles as functions of decreasing HEC concentration in Figs. 8 and 10 gives a prediction of good flow-out with either PVP or SMA alone, which is observed in practice in the lower PVC formulation I-1212. On the basis of these considerations, it is proposed that the complexities noted are the result of interactions between SMA and PVP with the cellulosic ether, although the nature of these interactions cannot be defined at the present time.

## Conclusions

Ref. 1

The HSVs of mixed thickener formulations are simple to predict. They are related in a linear fashion to the total amount of thickener present and appear to be related also to the total volume fraction of thickener. The discontinuities



noted with lower molecular weight macro-oligomers, regardless of their chemical composition, may be understood in terms of the comparative hydrodynamic volume contributions at high shear stresses.

A single concept does not serve to predict the flow-out behaviour of mixed thickener formulations. In some cases, the solubilisation and interassociation concept<sup>1</sup> is sufficient, but marked complexities are evident with other combinations. In the latter systems, flow-out appears to be a function of the concentration of the individual thickeners. It is proposed that there are significant molecular interactions in such thickener combinations. On the basis of the data presented, the nature of these proposed interactions cannot be defined; a more thorough examination is needed, and this should prove to be a very rewarding area of research if it advances the understanding of coating flow and levelling behaviour.

[Received 16 June 1976]

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## Next month's issue

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

**Optical properties of films** by *W. Carr*

**Preparation and properties of paint films with special morphological structure** by *W. Funke*

**The effect of wet time on accelerated outdoor exposures** by *J. L. Scott and T. E. Anderson*

**Thermal cure of acrylic finishes in a laboratory gradient stove** by *J. F. A. Hazenberg*

# Natal

### Hydroxyethyl cellulose

A meeting of the Section was held at the Elangeni Hotel, Durban on 24 May 1976 when 37 members and guests attended to hear a lecture entitled "Hydroxyethyl cellulose: a protective colloid for latex paints", presented by Mr A. C. Soldatos of Union Carbide, Europe.

The speaker explained the need for thickeners in latex paints—*viz*, the resin was not dissolved in the water, thus the liquid phase was mostly pure water. Unthickened paints were too fluid—hence the need for a thickener. The principal types of thickener included vegetable gums, casein, alginates, starches, poly(ethylene oxide), poly(vinyl alcohol), polyacrylates and cellulose derivatives. The last three were the more important types. The cellulose derivatives constituted the most important class, acting as both protective colloid and thickener.

A description was given of hydroxyethyl cellulose produced by Union Carbide and this included an outline of the chemistry and how variations in substitution affected the properties.

The advantages of the use of the various molecular weight grades of hydroxyethyl cellulose in paints were discussed. Before it was possible to arrive at a practical paint formulation, a number of factors had to be compromised. The viscosity behaviour was one of the most important considerations to ensure pourability, flow, non-sagging, pigment suspension, and so forth.

Because of its versatility, hydroxyethyl cellulose was widely used: it promoted effective thickening in the presence of high concentrations of soluble salts, and this was unimpaired over a pH range from 2 to 12; in addition, paints did not "gel" on storage nor were they degraded at high rates of shear; moreover, hydroxyethyl cellulose was compatible with many other modifiers, surfactants, and dispersions. Pigment dispersion and suspension were maintained during prolonged storage and water layering was eliminated. Other favourable properties included ease of solution, good colour stability, reliable thickening action, reduced foaming and freedom from insoluble particles.

Latex stabilisation techniques were described and the role of protective colloids in paints was discussed. A singular feature of hydroxyethyl cellulose was its ability to initiate and promote polymerisation. The effects of several hydroxyethyl cellulose variables (molecular weight, ratio of oxyethyl to anhydroglucose units and type and amount of salt present) on the compound's performance as a protective colloid were mentioned. Notes on the use of this material as a protective colloid were given.

The lecture was well illustrated with slides of structures, graphs and tables.

L. F. S.

# Ontario

### Psychology of colour

A joint meeting with the Toronto Society for Coatings Technology was held on 10 May 1976 at the Town and Country, Toronto. The meeting was arranged by OCCA, and the audience of over 150 heard a fascinating lecture by Dr Thornton of the Department of Psychology, University of Toronto, on "The psychology of colour".

Dr Thornton described in depth the basic mechanism of normal and abnormal colour vision and outlined the recent developments in the measurement of colour behaviour. The lecture was amply illustrated with graphs and slides.

This joint meeting was the first such meeting of the two Associations and it is expected that it will become an annual event.

E. S. McD.

# Transvaal

### Bitumenous coating materials

A lecture was delivered to a meeting of the Section at Shell House, Braamfontein, Johannesburg on 15 July 1976. Mr D. G. Green, of Shell Oil South Africa (Pty) Ltd, gave a talk entitled "Innovations in bitumen coating materials". Afterwards a vote of thanks to the speaker was proposed by Mr A. Shephard. A synopsis of the lecture is given below.

Three recently developed applications which used a coating of bitumen were described and the properties of the coating materials detailed. These applications, of widely differing nature and purpose, were:

#### *Pile coating*

In situations where structures have to be erected on ground subject to settlement, they are frequently supported on piles driven into the ground to such a depth that either they bear on bedrock or the friction between the pile and the soil surrounding it is sufficient to support the load on the pile. As settlement of soil occurs, an additional load is transmitted to the pile—so-called "negative friction"—thus effectively reducing the bearing capacity of the pile. By coating with bitumen that portion of the pile which passes through the layers expected to settle, the effect of negative friction can be largely eliminated, thus the number of piles required to support the structure is reduced at only a small extra cost per pile.

The speaker set out the conditions and forces to which the piles are subjected during storage, whilst the pile is being driven and whilst the soil is settling. A guide to the choice of coating type was given.

#### *Blends of bitumen and thermoplastic rubbers*

Many attempts to alter the rheological properties of bitumen in directions not possible by conventional petroleum refining techniques, have been made over the years by the addition of polymers. Shell Research's Amsterdam laboratory has produced blends of bitumen and styrene-butadiene-styrene or styrene-isoprene-styrene block copolymers which go a long way towards achieving the most desirable properties. The nature of these thermoplastic rubbers and the improvements in properties which they effect, were described.

One of the most attractive uses of this type of bitumen blend is as a coating compound in the manufacture of roofing felt. This and other uses to which these blends are being put were given, together with limitations imposed by the thermoplastic rubbers.

#### *Shellgrip*

The "Shellgrip" system is a road surface treatment (a coating applied to the road surface) consisting of a bitumen-extended epoxy resin binder in which are embedded chippings of calcined bauxite. This has proved eminently successful in reducing the accident rate at accident black spots where,

because of heavy traffic, a conventional road surface tends to become polished and slippery in a short time. Calcined bauxite has been shown to retain its exceptionally high skid resistance for over 6 years under extreme conditions of wear due to traffic.

The properties of the components of the system, the method of application and the economic justification for use of comparatively expensive materials for this purpose were described.

P. A. J. G.

## West Riding

### Exports

On 24 and 25 June this year, the Section held a symposium at the Crown Hotel, Harrogate; it was entitled "Exporting paints and similar materials". Although the support was numerically less than had been anticipated, those who did attend adjudged the range of subjects covered and the quality of the papers to be of a very high standard and of considerable benefit. The speakers and summaries of the papers are given below.

#### *Government services to exporters*

Mr J. Lister, Director (Exports) British Overseas Trade Board, presented an excellent film which showed how an exporter could gain considerable useful information, practical help and even financial assistance from the BOTB. Mr Lister also provided a preprinted summary dealing with exporting to Poland, together with a comprehensive selection of BOTB hand-out material.

#### *The "Chambers of Commerce" and exporting*

Mr R. G. Taylor, Director of Leeds Chamber of Commerce, outlined the many services available to exporters through the Chambers. The heart of these services lay in the Chambers' position as the issuing authority for Certificates of Origin, Certified Invoices etc. They had developed into organisations able to provide a whole range of documentary requirements placed by foreign governments on exporters.

Chambers could also provide useful contacts for finding agents, market reports, letters of introduction, overseas addresses etc. They were also responsible for about half of the missions going abroad under the BOTB scheme.

#### *The role of the shipping company*

Mr R. L. C. Charvet, Director of Killick, Martin & Co. Ltd, explained the role of shipping agents, shipping lines and the relationship which existed between them. He went on to forecast a big increase in the utilisation of container ships and a subsequent decrease in the availability of conventional vessels, and made the point that in future manufacturers should increasingly design their products and packaging with containerisation in mind.

Mr Charvet also made the point that the marketing departments of shipping lines were able and prepared to help find trade through their contacts in foreign markets.

#### *Export credit guarantee department*

Mr P. A. Dawson, Managing Director of Stewart Wrightson (Credit Management) Ltd, discussed all aspects of the "Comprehensive short term guarantee", including basic cover, risks covered, types of cover, premiums, credit-limits, claims payments, conditions of cover and extensions of basic cover. Mr Dawson also described the other types of guarantee

available, as well as financial facilities available under ECGD guarantees.

#### *Marine insurance*

Mr R. S. Horner, Director of Stewart Wrightson (North Eastern) Ltd, explained the difference between the various marine cargo policy options. He advised exporters which policy to take out according to the various terms of sale, and also gave advice on the formulation of claims.

#### *Services provided by banks to exporters*

Mr W. K. Skelton, Chief of the Overseas Department of the Midland Bank, Leeds, talked about the current world trading situation, and how this had meant that exporting companies were increasingly in need of the specialist services provided by the UK clearing banks. He went on to discuss in some detail, the three main services in question: information; means of settlement; and finance pending settlement.

Mr Skelton concluded by stressing the importance of scrupulous accuracy in the documentation required of exporters, as well as the need to seek advice from their banks before starting to export.

#### *The decorative paint market in Western Europe*

Mr J. R. L. Whiteley, Paint Marketing Manager, Metal Box Ltd, said that because of time limitations, he would deal only with six important paint using countries: Holland, France, Sweden, Italy, Germany and Belgium. He named the major manufacturing companies and their share of the market, and also gave the breakdown of the various markets into the trade, retail and export sectors.

#### *Exporting chemicals*

Mr W. L. Alldis, a Director of Durham Raw Materials Ltd, concentrated on giving advice to new exporters, based on his many years of experience in the business. He stressed the importance of "in depth" market research, and praised the help which was available from the BOTB, Chambers of Commerce and other organisations.

#### *Exporting printing inks*

Mr G. H. Hutchinson, Technical Director of Croda Inks Ltd, opened his paper by stressing the absolute necessity for Britain to export if she were to survive. He said that any company expecting to export successfully must have a clear idea of the function of its export department, and went on to enumerate five principles on which it was necessary to concentrate.

Agents, markets and marketing, objectives, visits, profitability and staff were all discussed. Mr Hutchinson concluded his paper by stating that the fundamental and governing factor of export was "Planning ahead". Exports could be the growth area of any company, so long as it had commitment and involvement was complete.

#### *Selling consumer products in Africa*

Mr R. L. Sommers, Director of Planning and Development, Reckitt and Colman (Overseas) Ltd, talked about his company's marketing experiences in the Nigerian market, showing colourful slides of typical retailing situations.

#### *Exporting paint*

Mr L. H. Silver, Managing Director of the SPL Group of Companies, apologised for initially digressing from his nominated subject and went on to discuss exports generally.

He strongly criticised successive governments for not providing a long-term policy on investment and industrial growth, saying that what was needed was industrial investment by either better regional grants or, preferably, low interest government loans, to be repaid out of profits as new plant and equipment came on stream.

Returning to the subject of exporting paint, Mr Silver said that whilst Britain had been the largest exporter of paint until the mid 1950s, the country had now slipped back to third in the league. Even so, there had been a considerable increase in tonnage exported. If insurable business only had been taken, however, the figures would have been considerably less. He criticised the constraints placed by government on ECGD, saying that a more entrepreneurial approach should be taken if the volume of exports were to keep growing.

The principal guest at the symposium dinner was Mr S. D. Wilks, Chief Executive of the Overseas Trade Board, who told the delegates that exports in terms of volume were expected to be about 11 per cent higher than last year; there were indications of a strong continuing expansion. This, he said, would help to offset the slack home market, ease the unemployment situation, and have a substantial effect upon the country's balance of payments.

Mr Wilks also discussed the forthcoming, "Export Year", and explained how it was hoped to involve the Government, CBI, TUC and all sectors of industry down to and especially including the shop floor, in a co-operative effort to boost exports.

M. G. B.

## Reviews

### Basic metal finishing

By J. A. Von Fraunhofer

London: Paul Elek (Scientific Books) Ltd, 1976.

Pp. 191 + bibliography and index. Price £4.95

To deal with the subject of metal finishing in 191 pages demands a basic text. It follows therefore that this book gives only the facts, and that there is no padding. Were this always the case!

The first 100 or so pages deal with electrodeposition, the theory underlying this and ancillary activities, such as surface treatment, equipment and testing. Further chapters deal with diffusion coatings (sherardising), galvanising and cladding, and sprayed metal coatings. This last-mentioned subject is given a chapter to itself and is well dealt with in the context of a book of this type. Conversion coatings are described adequately, but no mention is made of the silicate treatment for galvanised steel—a small omission.

Chapter 14 onwards will be of most interest to the paint technologist, although the reviewer feels that the attempt to compress the subject of paint technology into 40 pages of text is not one that he would relish. Suitable binders are discussed in 16 pages of text, and this section illustrates very clearly the problems faced by the author in trying to deal with a diverse subject in a limited space. There would, for instance, seem to be no reason why condensation polymerisation should be honoured by an equation demonstrating the reaction between phenol and formaldehyde, and also that between urea and formaldehyde, whereas epoxy/polyamide and urethane reactions are given a verbal treatment. Pigments and solvents are dealt with in tabular form, and pigment volume concentration is briefly mentioned.

Methods of application are surveyed concisely, with sufficient detail for the reader to appreciate the techniques available, and test methods are briefly described.

The last chapter deals with other coating processes, such as vitreous enamelling and the vacuum deposition of coatings, plastics and rubbers.

There is finally a good bibliography and an adequate index.

Remembering that it is based on lectures given by the author for a given "standard" of student, the reviewer feels that this book will serve its purpose in giving a survey of

metal finishing techniques in almost synopsis form. Some specialists might criticise that it does not go into sufficient detail in their own particular field, but the reviewer considers it to be a useful publication.

D. S. NEWTON

### Coatings—Recent developments

By W. Rannay

Park Ridge, New Jersey and London, England,

Noyes Data Corporation, 1976. Pp. xii + 313

Price US \$39.00

This book abstracts and interprets 240 patents granted in the United States since 1972. The author suggests that the US patent literature is the largest and most comprehensive source of technical information in the world. He has made a commendable effort to select and describe those patent developments which make a contribution to the saving of energy and have a significant effect on reducing environmental problems.

The bulk of the patents selected relate to systems designed to meet air pollution regulations and they cover water-borne, powder and high solids coatings and materials designed for ultraviolet and electron beam curing. There is also a section on specific applications of solvent based coatings.

So often when a title like "Recent developments" is given, the references are anything but recent. This cannot be said of this book, in which many of the patents to which reference is made were granted as recently as 1975. Making a patent search is a tedious business and there is always the risk that some important development is overlooked. The author of this work seems to have covered the field in an admirable way and provided a digest of information that should prevent interested readers from pursuing "blind alleys" in which patents have already been granted.

The book is well indexed and well produced. It is, perhaps, a little expensive but it has clearly involved a good deal of time in the search for and selection of material.

For technologists operating in the areas which are considered, the book should prove a useful reference work particularly as the author has phrased his descriptions with a minimum of patent jargon.

A. T. S. RUDRAM



# Information Received

READER ENQUIRIES: Any reader who wishes to obtain further information regarding articles published in the Information Received section of the *Journal* is advised to contact the Association's offices at the address given on the Contents page of this issue.

## Agent in France for BIP

APC (Azote et Produits Chimiques) of rue Jeanne d'Arc, Paris, has taken over the agency for a number of British Industrial Plastics thermostat resins and moulding materials in France. The products are all manufactured by the Chemicals Division of BIP at Oldbury, West Midlands and at Whiston on Merseyside. BIP is Europe's largest manufacturer of urea and melamine moulding materials.

## Building with chemistry

It has been common practice in recent years for Hoechst AG to prepare a film for showing at the company's annual meeting of shareholders. The film for 1976 has the title "Building with chemistry" and is concerned with the partnership Hoechst has maintained with the building industry in Germany for the past 100 years or so. The film with English commentary is now available for hire free of charge from either Hoechst (UK) Ltd or Guild Sound & Vision.

## Donald MacPherson agreement with Unerman

The directors of Donald Macpherson Group Ltd, of Unerman Holdings Ltd and of Rexmore Ltd, which holds 66.65 per cent of the issued ordinary capital of Unerman, have announced that agreement has been reached on the terms of an offer to be made by Donald MacPherson for the whole of the issued ordinary share capital of Unerman.

Unerman is the largest supplier of fixtures and fittings to the UK furniture industry—this activity accounting for approximately 65 per cent of its business—and has recently built up a significant export trade, now contributing approximately 10 per cent to total sales. Among other markets which Unerman supplies are the "Do It Yourself" market and the building industry. Donald MacPherson already has substantial sales of surface coatings in both these sectors, and three years ago began to market a range of components to the furniture trade; sales of these are currently running at an annual rate in excess of £1 million. Market research indicates that "brought in" components are accounting for an increasing proportion of the cost of manufactured furniture. In view of this, and of encouraging industry projections for furniture demand, Donald MacPherson Group has been actively exploring opportunities for expanding its involvement in the components field.

The proposed acquisition of Unerman will represent for Donald MacPherson an important development which will broaden the base of its commercial operations in fields which it knows well.

## Handling chemical emergencies

New and up-dated procedures for handling major emergencies in and around chemical plant have been published recently by the Chemical Industry Safety and Health Council of the Chemical Industries Association. The procedures cover major emergencies resulting from fire, explosion or

large scale release of hazardous or toxic material.

## Spelthorne Metals Ltd

Agreement has been reached in principle for Associated Lead Manufacturers Ltd, a wholly owned subsidiary of Lead Industries Group Limited, to acquire for cash the powdered lead paste business of Spelthorne Metals Ltd. Spelthorne Metals Ltd, whose parent company is Berger Jensen & Nicholson Ltd, will thereafter cease trading on its own account. The value of the assets being acquired is less than one per cent of the net assets of Lead Industries Group Ltd.

## Thor expands microbiocide capacity

Thor Chemicals plans to double production capacity for its "Acticide THP" microbiocide by a DM 2.5 million expansion at its site in Speyer, West Germany. Production capacity of the new plant will be 8000 tonnes per annum. The company's present manufacturing facility is located at Margate in England.

## Literature

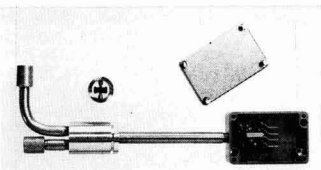
### Degradable plastics

Yarsley Research Laboratories (a division of Fulmer Research Institute), has recently published a special report on degradable plastics.

The current methods of rendering plastics photo- or bio-degradable are described. The importance of these materials in relation to the overall subject of plastics waste disposal is discussed.

The general conclusions are that the possible disadvantages associated with the widespread use of degradables appear to outweigh their marginal advantages. For example, special additives incur a risk of contamination of water supplies. The widespread use of degradables could encourage the general public into thinking that all plastics wrapping could be discarded, aggravating rather than alleviating the litter problem. There is a need to consider alternative starting materials for the manufacture of "disposal plastics" based on naturally occurring materials rather than oil. Biological recycling of discarded and buried materials would then occur without the need to incorporate special additives.

## New products



Litre Meter Ltd has produced a new flowmeter, "Model SS" (shown above). Features include a stainless-steel body to withstand high pressures and corrosive fluids, a specially curved inlet tube to normalise flow, and the latest integrated

circuitry to send the correct information to the recording instrument.

## Linear indicator



The new Series 700 linear indicator pictured above is available from Chessell Ltd, Worthing, Sussex. The instrument will accept virtually any input signal, according to the choice of plug-in amplifier, and can be mounted either vertically or horizontally.

## Non-mercurial fungicides and additives for water thinnable coatings

Cole Chemicals Ltd, UK distributor for Troy Chemical Corporation, can now supply two new fungicidal additives and also a new flow control additive and a new defoamer for general use:

"Troysan Polyphase Anti-Mildew" is designed for incorporation into aqueous paints which are intended for use in areas where fungal growth on the final paint film must be prevented. It is also applicable in aqueous dip tanks where fungal contamination may be a problem. For oil and alkyd paints, "Troysan Anti-Mildew O" is recommended. Both products have a low order of toxicity and are completely free from mercury.

Additive "Q148" is primarily a flow control and substrate wetting agent and "Q154" is generally effective as a defoamer. These two products are mutually compatible and have often been used in combination to achieve optimum properties.

## Two new pigments for plastics

Two new pigments, "Cromophthal Yellow AGR" and "Microlith Yellow 3R-K", have been added by the Pigments Division of Ciba-Geigy Plastics and Additives Company to its range of pigments for plastics.

Cromophthal Yellow AGR is an anthraquinonoid yellow pigment with a strong, bright red shade and very good lightfastness. Its heat stability is much better than that normally associated with organic yellow pigments and compares favourably with that of cadmium yellow pigments and the better yellow solvent-soluble dyes. It is recommended where high processing temperatures rule out most conventional pigments. At high processing temperatures it dissolves in the polymer, which means that excellent transparency can be obtained in selected polymers.

In ABS Systems, Cromophthal Yellow AGR can be used in combination with titanium dioxide as a replacement for cadmium yellow and is stable in this polymer at the highest processing temperature normally used. In polystyrene it gives an attractive transparent yellow and may be processed up to 280°C. It is equally suitable in styrene-acrylonitrile and polymethyl methacrylate, and can also be used for colouring methyl methacrylate monomer before polymerisation.

Polymers processed above 300°C, such as polymethyl pentene, polycarbonate and polysulfone can all be coloured with Cromophthal Yellow AGR. Conventional organic yellow pigments do not meet the very demanding processing requirements.

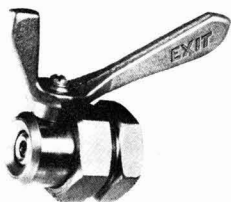
With high density polyethylene it is suitable for use in articles produced by sheet and blown film extrusion and rotational mouldings, and also in injection-moulded products, except large articles where deformation problems may occur. It can also be used in polypropylene and to colour polypropylene fibres.

Microlith 3R-K is an addition to Ciba-Geigy's range of specially prepared pigments predispersed in a vinyl copolymer resin. It is based on the high quality tetrachloro-isoindolinone pigment, "Irgazin Yellow 3RLTN".

It is a red-shade transparent yellow pigment and has good all-round fastness

properties. Its good dispersibility and excellent fastness properties make it suitable for the coloration of certain plastics, particularly rigid, semi-rigid and flexible PVC, polyurethane fabric coating and polymethyl methacrylate.

#### Airless-spray nozzle



Exit S.A. has introduced a new, high pressure, self-cleaning, airless-spray nozzle to the UK market. The device is claimed to meet and in many cases exceed the requirements of the high pressure (airless) paint spraying industry. Its designed working pressure is 50 MPa.

#### Courses, symposia etc.

##### London College of Printing Open Week

The London College of Printing Open Week this year is from 18 to 22 October. It is

planned to coincide with the National Caxton Celebrations and a special exhibition, the History of Printing Education in London, will reflect this theme. A one-day conference on "Careers in printing" will be held on Tuesday 19 October, and there will be a Careers exhibition running through the week.

#### Protection of materials in the sea

Marine corrosion and fouling and the protection of materials against deterioration in sea water is the subject of a symposium to be held on 25 and 26 February 1977 in Bombay under the auspices of the Indian government's Ministry of Defence.

#### Wood preservation

The ninth annual meeting of the International Research Group of Wood Preservation will take place in Noordwijk aan Zee, Holland from 26 to 30 September 1977.

#### Competition

##### Galloway Medal

The award of the Institution of Corrosion Science and Technology Galloway Medal for 1977 will be based on the results of a competition with the title "Corrosion and pollution". The competition is open to all students under the age of 25, who will be asked to submit an essay or project report before the closing date of 1 March 1977.

## Correspondence

### Theories—laboratory investigations—practical performance

SIR—Referring to the letter by Mr F. B. Stieg (*JOCCA*, 1976, 59, 153) I would like to present the following comments.

The motivation for my paper on paint film durability was to provide a general knowledge about those evaluation instruments (techniques) and weatherometer types (cycles) available at the Scandinavian Paint Research Institute. Our "arbitrary exposure cycles" (Mr Stieg's expression) have given the Institute considerable information and knowledge about our new weatherometer (with exchangeable lamps and filters) and also about the weathering mechanism as such.

The changes in film properties of a large range of building paints under the influence of different weatherometer parameters have been studied. Not only the usefulness but also the limitation of evaluation methods has been illustrated: for example, the deterioration of a flat latex paint cannot be followed by gloss measurements, but loss of weight may be an excellent technique. When we started the investigation, we did not expect to find any final answer to the problem of durability correlation between exterior exposures and laboratory weatherometer exposures. In the international literature and in practical sales work, reference is often made to exposure in Florida. Thus, it was natural to compare (or correlate) Florida exposures with two typical Scandinavian climates in our investigation.

Mr Steig refers to results obtained by Hoffman and Saracz based on outdoor exposure in Australia with typical Australian paint formulations, but their findings may differ substantially from facts valid in Scandinavian climates and with "Scandinavian" paints. Furthermore, Hoffman and Saracz are perhaps not quite as negative in their approach to

"correlation" as stated by Mr Stieg. Thus, in 1969 in the *Journal (JOCCA)*, 1969, 52, 1142), they write:

"The chalking of paint films at varying humidities in a xenon arc weatherometer has provided data from which valid conclusions can be drawn as to chalking of similar coatings exposed at Highett and Lae."

Moreover, Mr Stieg suggests that one should attempt to "match" the outdoor climate as closely as possible in laboratory weathering testing. This is very difficult as the natural climate is not at all constant (perhaps it might be in Florida, but certainly not in Scandinavia). How would it be possible simultaneously to include in weathering machines such deterioration factors as, for example, biological attack, dirt pick-up, freeze/thaw cycles and perhaps even the influence of snow? The degradation process is always a complex and continuous interaction between many elements. Thus, even if it is possible to study the influence of these elements separately, the complex and often arbitrary variation of natural deterioration processes cannot be imitated completely in laboratory testing. This fact is also expressed in the conclusion of my paper: "The question of correlation between outdoor exposures and laboratory testing in weatherometers is very complex and difficult to answer."

On the other hand, I fully agree with Mr Stieg, that statistical analysis of the results is of value in order to express more exactly (mathematically) the "correlation", for example by correlation coefficients and variance analysis.

Yours faithfully,

B. LINDBERG

Scandinavian Paint and Printing Ink  
Research Institute,  
Odensegade 14,  
2100 Copenhagen, Denmark

30 July 1976



# OCCA-29 Exhibition

22-25 March 1977 at Alexandra Palace, London

**Good support for OCCA-29 from organisations in many countries**

## The continuous dialogue between suppliers and manufacturers

### General

The twenty-ninth annual exhibition of raw materials, plant and equipment for the paint, printing ink, colour and allied industries organised by the Association will take place at Alexandra Palace, London N22 from 22 to 25 March 1977. Alexandra Palace was the venue for the exhibition held in March 1976 and for the series of exhibitions from 1965 to 1969.

Six weeks before the closing date for OCCA-29, deposits for more than four times the stand space at a comparable date in 1975 had been received from organisations in the United Kingdom and abroad, including both exhibitors at OCCA-28 and from previous exhibitions. This support demonstrates the value which companies place on this unique annual event for the surface coating industries.

### The international forum for the surface coatings industries

The exhibition provides an excellent annual opportunity for the technical personnel in the supplying industries to meet their counterparts in the manufacturing industries and to discuss their common technical problems. The advantage both to exhibitors and visitors of meeting in an informal atmosphere needs hardly be stressed, since the cost to exhibitors sending representatives to all the countries from which the visitors are drawn might well be prohibitive, particularly to smaller companies. In pursuance of the idea of an informal atmosphere the Committee has amended the rule which had previously prohibited the serving of alcoholic refreshments to visitors on the stands. It is felt that the opportunity now afforded to exhibitors to offer alcoholic refreshments if they so wish will not detract in any way from the technical content of the exhibition.

### Facilities at Alexandra Palace and travel arrangements

The facilities at Alexandra Palace, which the Association's exhibition will occupy on its own, include 2 licensed Restaurants, 2 bars, a Cafeteria and an Exhibitors' bar. Exhibitors have commented that an advantage of Alexandra Palace is that visitors tend to spend longer at the exhibition as all facilities are provided under one roof. Ample free car parking facilities are available for both exhibitors and visitors and Alexandra Palace is within easy access of the M1 Motorway and the flyover at the junction of the M1 and the North Circular

Road was opened earlier this month. The Association organises a free bus service to and from Turnpike Lane Station on the Piccadilly Underground Line. The journey by Underground from Central London takes approximately 18 minutes and in due course the Piccadilly Line will be extended to Heathrow Airport terminal, which will give a direct link for visitors arriving at the Airport. In the meantime, a bus service operates from Heathrow Airport to Hounslow West Station. Visitors who prefer to travel from Heathrow Airport to the West London Air Terminal in order to leave their luggage at hotels, can board the Piccadilly Line trains at Gloucester Road Station.

### "Official Guide"

This unique publication will contain descriptions of all exhibits and advertising space is available both to exhibitors and those organisations not able to show at the 1977 Exhibition. The "Official Guide" will be published at the end of January 1977, so that intending visitors can obtain copies and plan their itineraries.

**Each Member of the Association, at home and abroad, will be sent a copy of the "Official Guide" and free season admission ticket.**

Members are asked to ensure that they bring their tickets to the Exhibition since

otherwise the charge for admission will be made and no refund will be applicable in these cases.

As for the 1976 exhibition, copies of the "Official Guide" and season admission tickets will be available several weeks in advance of the exhibition (prepayment only) from the Association's office and they will also be available for purchase at the entrance to the Exhibition Hall.

For the last two exhibitions, it was decided that a small charge should be made both for the "Official Guide" and for season admission tickets to the exhibition. This policy undoubtedly deterred casual visitors who might otherwise be attracted to exhibitions for which no admission charge was made and who gathered quantities of technical literature from the stands. The innovation was welcomed by many exhibitors and in no way acted as a deterrent to visitors to this exhibition. A similar charge will be made for the "Official Guide" to OCCA-29.

### Information in foreign languages

As in previous years, the Association will be circulating information leaflets in six languages, which will contain application forms for those wishing to purchase copies of the "Official Guide" and season admission tickets before the exhibition.

## News of Members

Mr T. Bowerman, an Ordinary Member attached to the London Section, and formerly the Products Manager of the pigment division of Bush Beach & Segner Bayley Ltd, has been invited to join the rapidly expanding USA subsidiary, Degussa Incorporated, based in New Jersey.

Mr F. J. Rafferty, an Ordinary Member attached to the Manchester Section, has joined the United Kingdom sales organisation of Sachtleben Chemie GmbH, one of Europe's leading manufacturers of white pigments and extenders.

Mr Rafferty was previously with Anchor Chemical Co. Ltd as a technical representative in the United Kingdom and Eire. In his new post he will be responsible for sales and technical liaison with Sachtleben

Chemie customers in the North of England and Scotland.



Mr F. J. Rafferty

Amongst the new Members elected and attached to the Transvaal Section is Mr Antoni Z. Poklewski-Koziell, whose father Mr W. Z. Poklewski-Koziell has been a Member since 1963.



# Forthcoming Events

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

## October

### Friday 1 October

*Hull Section:* Annual Dinner Dance to be held at the Willerby Manor Hotel, Willerby, Hull, commencing at 8.00 pm.

### Monday 4 October

*Hull Section:* "Safety and pollution effluent disposal" by Mr J. Alexander, PD Pollution Control Ltd. Joint meeting with the Institution of Chemical Engineers at the Haven Inn, Harrow Haven, Lincs, commencing at 6.30 pm.

### Thursday 7 October

*London Section:* "Water repellent preservative stains" by a speaker from the British Wood Preserving Association. Evening meeting at the Royal Society of Tropical Medicine & Hygiene, 26 Portland Place, London W1 commencing at 7.00 pm.

*Midlands Section—Trent Valley Branch:* "North Sea oil—inspection" by Mr J. D. Griffiths, RJP Nicklin & Co, to be held at the Crest Hotel, Pastures Hill, Littleover, Derby at 7.00 pm.

*Newcastle Section:* Joint Meeting with the Institution of Corrosion Science and Technology. Two papers will be presented: "The integration of the protection function when building a ship", by Mr J. P. Jemitus, Cammell Laird Shipbuilders Ltd, and Mr A. N. McKelvie, Paint Research Association and "Steel cleaning standards—a case for their reappraisal" by Mr McKelvie. To be held at Newcastle Polytechnic.

*Scottish Section:* "Recent developments in polyurethanes" by Mr R. M. Entwistle, Bayer (UK) Ltd, to be held at the Beacon's Hotel, 7 Park Terrace, Glasgow G3 at 6.00 pm

*Thames Valley Section:* "Health and Safety at Work Act". A panel meeting and discussion with speakers from Government and industry, to be held at the Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Bucks at 6.30 for 7.00 pm.

### Friday 8 October

*Manchester Section:* "Films from particles" by Mr M. J. Waghorn, ICI Paints Division, to be held at the Manchester Literary & Philosophical Society, George Street, Manchester commencing at 6.30 pm.

### Tuesday 12 October

*West Riding Section:* "Water-based stoving finishes" by Dr K. Sellars, Harlow Chemical Co Ltd, to be held at the Griffin Hotel, Board Lane, Leeds commencing at 7.30 pm.

### Wednesday 13 October

Reunion Dinner for past and present Members of Council. To be held at the Piccadilly Hotel, London W1 at 6.30 for 7.00 pm. *Informal dress.*

### Friday 15 October

*Irish Section:* "Implementation of EEC directives on the packaging in paint,

printing ink and adhesive industries" by Mr F. Shaughnessy, Industrial Inspector, Department of Labour, to be held at the Clarence Hotel, Dublin at 8.00 pm.

*Scottish Section—Eastern Branch:* Annual skittles match vs Student Group. To be held at the Murrayfield Club, Edinburgh, commencing at 7.00 p.m.

### Wednesday 20 October

*Ontario Section:* "Optimistic outlook for the future of the coatings industry" by Mr E. Barry, Vice-President of the Canadian Paint Manufacturers Association.

### Friday 22 October

*Manchester Section:* Annual Dinner Dance to be held at Peacock Suite, Hotel Piccadilly, Manchester.

### Thursday 28 October

*Midlands Section:* "The Health & Safety Act", by Mr M. Kelly, University of Aston. Joint meeting with the *Trent Valley Branch* to be held at the Birmingham Medical Institute, 36 Harbourne Road, Birmingham.

### Friday 29 October

*London Section:* Annual Dinner Dance at the Piccadilly Hotel London, W1.

*Midlands Section—Trent Valley Branch:* Social Buffet and Dance at the Cross Keys Inn, Turnditch, commencing at 7.30 pm.

## November

### Monday 1 November

*Hull Section:* "The fundamentals of UV curing" by Mr R. G. Smith, Arthur Holden & Sons Ltd. To be held at the George Hotel, Land of Green Ginger, Hull, commencing at 6.30 pm.

### Thursday 4 November

*Newcastle Section:* "The use of microvoids as pigments" by Mr J. Clark, Tioxide International Ltd. To be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, commencing at 6.30 pm.

### Friday 5 November

*Bristol Section:* "North Sea oil and gas—their effect on industry" by Mr J. Tooke-Kirby, FTSC, Chairman of the London Section. Joint meeting with the Birmingham Paint, Varnish and Lacquer Club to be held at the Royal Hotel Bristol at 7.15 pm.

### Tuesday 9 November

*West Riding Section:* Lecture by a speaker from SCC Colours Ltd. To be held at the Griffin Hotel, Board Lane, Leeds, commencing at 7.30 pm.

### Wednesday 10 November

*Scottish Section—Eastern Branch:* "Industrial solvents" by Mr C. Smith of Carless Solvents Ltd. To be held at 7.30 pm, in the Carlton Hotel, North Bridge, Edinburgh.

### Thursday 11 November

*Midlands Section—Trent Valley Branch:* "Inflation accounting" by Mr S. Turner,

Mebon Ltd. To be held at the Crest Hotel, Pastures Hill, Littleover, Derby at 7.00 pm.

*Scottish Section:* *New subject and speaker to be announced.* Joint meeting with the Society of Dyers and Colourists. To be held at the Beacon's Hotel, 7 Park Terrace, Glasgow G3 at 6.00 pm.

*Thames Valley Section:* "Zinc coatings" by Mr F. C. Porter, Zinc Development Association. To be held at the Beaconsfield Crest Motel (White Hart) Aylesbury End, Beaconsfield, Bucks at 6.30 for 7.00 pm.

### Friday 12 November

*Hull Section:* Disco-Dance to be held at the Cricket Club, Anlaby Road, Hull.

*Manchester Section:* "Possibilities and prospects for metal coatings with polyurethanes" by Dr. Sonntag, Bayer AG. To be held at the Woodcourt Hotel, Sale, Cheshire, commencing at 6.30 pm.

*Midlands Section:* "Paint manufacture" by Mr B. Lucas, Joseph Mason Paints Ltd. To be held at the Birmingham Medical Institute, 36 Harbourne Road, Birmingham.

### Monday 15 November

*Hull Section:* "Synthetic clays—their properties and uses" by Mr B. J. R. Mayes, Laporte Industries Ltd. *Student lecture.*

### Tuesday 16 November

*London Section:* "New approaches to the development of specific properties in paint films" by Prof H. P. Schreiber, Department of Chemical Engineering Ecole Polytechnique, University of Montreal. To be held in the Colnbrook Room, Sheraton-Heathrow Hotel, commencing at 11.00 am. and to include luncheon.

### Wednesday 17 November

*London Section:* "Water thinned anti-corrosive coatings". Joint day meeting with the Institution of Corrosion Science & Technology and in association with Thames Polytechnic, commencing at 10.00 am.

*Ontario Section:* "The ultraviolet screening behaviour of pigments" by Dr R. J. Kennedy of Hilton-Davis, Cincinnati, USA. Venue Skyline Hotel, Toronto.

### Friday 19 November

*Irish Section:* Annual Dinner Dance commencing at 8.30 pm.

### Friday 26 November

*Bristol Section:* "Waste disposal in the surface coatings industries" by Mr H. G. Pullen, Redland Purle Ltd. To be held at the Royal Hotel, Bristol at 7.15 pm.

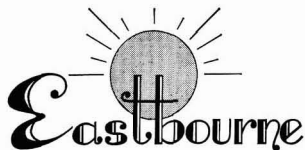
## December

### Wednesday 15 December

*Ontario Section:* Informal Ladies' Evening with a talk on cosmetics by Miss H. Hamley of Yardley of London (Canada) Ltd. To be held at the Skyline Hotel, Toronto.



## Biennial Conference 1977



The next biennial Conference of the Association will be held at the Grand Hotel, Eastbourne, from Thursday 16 to Sunday 19 June 1977 and the theme for the Conference will be:

### The conservation of energy, materials and other resources in the surface coatings industry

It is intended that as on previous occasions, full preprints will be published

for despatch to delegates in advance of the Conference.

It will be recalled that it is the custom at the Association's Conferences for the authors merely to outline their papers, highlighting points of interest, and for a general discussion of the paper to follow. The author will not be expected to deliver the paper *in toto* since the object of sending out the preprints in advance is that delegates may read these thoroughly before the Conference.

Eastbourne was the venue for the Association's Conference held in 1953, 1969 and 1973, and has always proved a most popular centre for delegates. Forms for registration will be despatched to all Members of the Association attached to the Sections in the United Kingdom, Ireland and the General Overseas Section early in 1977 and any non-member wishing to receive the registration form should write to the Director & Secretary at the Association's offices before the end of this year.

## Sixtieth Anniversary celebrations

In May 1978 the Association will celebrate the sixtieth anniversary of its foundation and it is felt that Members (and others who wish to take part in the celebrations) would like to have as much notice as possible of the dates. Following the pattern successfully used at the Association's Fiftieth Anniversary in 1968, the main events will be on two consecutive days. On the evening of Thursday 11 May it is planned to hold at a City Livery Hall a Commemorative Lecture, followed by a Dinner to which Past Presidents, Past Honorary Officers of the

Association, Honorary Members and the surviving Founder Member will be invited as guests. On Friday 12 May the Association's Dinner and Dance will be held at the Savoy Hotel, London WC2 and Presidents of other societies, together with their ladies, will be invited to attend. Full details will be published in the *Journal* from time to time and forms of application for the celebrations will be sent to all Members (and others who have made application to the Director & Secretary) at the beginning of 1978.

## Jordan Award

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

The rules of the Award are:

1. The Award will be made for the best contribution to the science or technology of surface coating by a Member of any nationality working in either the academic or industrial field who is under the age of 35 at the date of application.
2. The final date for submission of applications will on this occasion be 31 December 1976 and it is hoped to present the award at the 1977 Association Conference.
3. The selection of the recipient of the Award will be made by a Committee under the chairmanship of the Association's Hon. Research and Development Officer.
4. There will be two methods of application. First, by the submission of a paper describing original work by the candidate which is offered for publication in the *Journal* or has been so published during application. The alternative method will be by recommendation by a superior for work which for reasons of commercial secrecy cannot be published; in this case the candidate will be expected to submit a dissertation on a topic relating to his work and demonstrating his superior knowledge of the principles thereof. The Award is for individual merit and clear evidence of the candidate's own contribution will be required if a paper is offered under joint authorship.
5. Applications should be addressed to the Director & Secretary at the Association's offices.

## Register of Members

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

### Ordinary Members

- DUNN, RAYMOND, 6 Ellesmere Avenue, Thornton Cleveleys, Lancs FY5 5JD. (*Manchester*)
- HARRIS, JOHN MADDERN, MSc, DSc, 16 Sophia Street, Rotorua, New Zealand. (*Auckland*)
- LEES, FREDERICK, CIBA-GEIGY (Pty) Ltd, PO Box 92, Isando 1600, Transvaal, South Africa. (*Transvaal*)
- McLAUGHLIN, HENRY JAMES, Titanium Paints Ltd, PO Box 927, Ndola, Zambia, Africa. (*General Overseas*)
- McLEOD, ROSS DAVID, BSc, 21 Elizabeth Avenue, Papatoetoe, New Zealand. (*Auckland*)
- MISKOWICZ, ERIC LYNN, BSc, 139 Landscape Road, Mt. Eden, Auckland, New Zealand. (*Auckland*)
- PEACE, LEONARD, CIBA-GEIGY (Pty) Ltd, PO Box 92, Isando 1600 Transvaal, South Africa. (*Transvaal*)
- PENDERIS, HENRY, BSc, National Chemical Products (Pty) Ltd, PO Box 344, Germiston 1400, South Africa. (*Transvaal*)
- SYKES, DAVID CHRISTOPHER, MA, Rohm & Haas (UK) Ltd, 2 Masons Avenue, Croydon, Surrey CR9 3NB. (*London*)
- VERGHIS, GEORGE, BSc, ICI (Paints), PO Box 2158, Jakarta, Indonesia. (*General Overseas*)

### Associate Members

- ALLAN, RICHARD JOHN, 97 Avondale Road, Auckland 7, New Zealand. (*Auckland*)

- CLINNING, DAVID JOHN, PO Box 369, Pinetown 3600, South Africa. (*Cape*)
- DICKINSON, MICHAEL STEWART, 11 Pangbourne Avenue, Davyhulme, Urmston, Manchester M31 3GN. (*Manchester*)
- GEMMELL, WAYNE, 21 Battle Place, Glenfield, Auckland, New Zealand. (*Auckland*)
- JOHNSON, ROLAND EMANUEL GEORGE, PO Box 3843, Salisbury, Rhodesia. (*Transvaal*)
- METS, WILLEM ANTON, CIBA-GEIGY (Pty) Ltd, PO Box 224, Eppindust 7475, South Africa. (*Transvaal*)

### Registered Students

- BOOTH, MICHAEL JOHN, 9 Firwood Drive, Swinton, Manchester M27 1QY. (*Manchester*)
- BROUGH, PAUL, 14 Tooley House, Barton Lane, Eccles, Manchester M30 0HU. (*Manchester*)
- GORTON, HAROLD, 55 Magnolia Court, Salford M6 5AN, Lancs. (*Manchester*)
- HORRIDGE, STEPHEN, 34 Delamere Avenue, Salford M6 7WS, Lancs. (*Manchester*)
- McGUINNESS, ROBERT ANTHONY, 51 Lichfield Road, Radcliffe, Manchester. (*Manchester*)
- SMELTING, PETER JOHN, CIBA-GEIGY (Pty) Ltd, PO Box 92, Isando 1600, Transvaal, South Africa. (*Transvaal*)
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# UV polymerisation

The twelve papers in this volume were originally published in the *Journal* earlier in 1976. They are based on lectures given at a Symposium of the Newcastle Section of the Association, held at Durham University on 10 and 11 April 1975. Titles and authors are listed below:

**Photochemical excitation and its consequences—a review** by R. B. Cundall

**The application of UV-curing materials and technology to packaging** by A. D. Lott.

**Photoinitiation by aromatic carbonyl compounds** by A. Ledwith.

**The technological literature relating to polymerisation photoinitiators** by A. Pryce.

**Photopolymerisation: the kinetics of a-type photopolymerisation** by F. C. de Schryver and N. Boens.

**The use of polyfunctional monomers in UV curing** by J. R. Younger.

**Sensitisation and stabilisation in monomer/polymer systems** by D. Phillips.

**Photodegradation of polymers** by I. C. McNeill.

**UV-drying equipment, design and installation** by R. E. Knight.

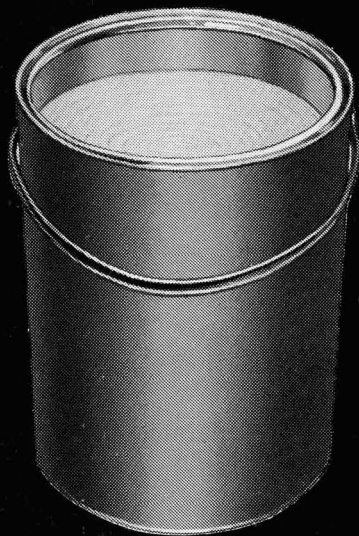
**Ultraviolet curing inks** by A. A. Gamble.

**Some aspects of the pigmentation of UV-curable systems** by B. E. Hulme.

**Some aspects of the formulation of UV-curable polyester based systems** by A. Laws, S. Lynn and R. Hall.

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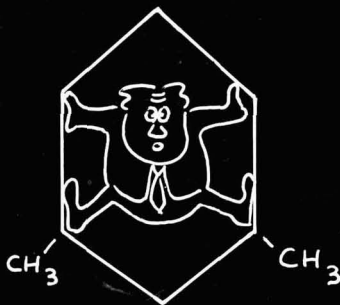


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