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Transactions and Communications———————————————

The effect of the substrate on the electrical resistance of polymer films

By J. E. O. Mayne and D. J. Mills

Department of Metallurgy and Materials Science, University of Cambridge, England

Summary

Mild steel coated with three different varnishes has been exposed to 3.5M potassium chloride. It is found that when corrosion occurs, the film at that point has a low resistance and is D type; whereas, when corrosion is absent, the film in that region has a high resistance and is I type.

The resistances of D areas on platinum are one to two orders of magnitude higher than those on mild steel, which are found to be the same order of magnitude as those of detached films. However, the resistance of I films is independent of the presence and nature of the substrate. When zinc chromate is used as a pigment, the steel substrate is passivated and behaves in a similar way to platinum.

It is concluded that the higher resistance of films on an inert substrate is due to the fact that ionic diffusion occurs only from one side and that the protective value of coatings, with or without inhibitive pigments, can be predicted from resistance measurements, provided that the coatings will be used under immersed conditions and not subjected to ultraviolet radiation.

Keywords

Raw materials: chemically active pigments

corrosion inhibiting pigment

Properties, characteristics and conditions primarily associated with:

materials in general
electrical resistivity

structures or surfaces being coated
corrosion

L'influence qu'exerce le subjectile sur la résistance électrique des feuils de polymères

Résumé

On a exposé l'acier doux revêtu de trois vernis différents à une solution 3,5M de chlorure de potassium. Dans le cas où la corrosion se met en évidence, on a trouvé que la résistance du feuil aux zones affectées est à la fois faible et du type D; tandis que la résistance des zones du feuil exemptes de corrosion est élevée et du type I. La résistance des zones D sur platine est d'un ou deux ordres de grandeur supérieur à celle sur acier doux, qui est en même temps semblable à celle des feuils détachés. Toutefois, la résistance des feuils I est independante de la présence et de la nature du subjectile. Lorsqu'on se sert du chromate de zinc en tant que pigment, le subjectile en acier devient passivé et se comporte dans une manière semblable à celle du platine. On conclut que la résistance élevée des feuils déposés sur un subjectile inerte est due au fait que la diffusion ionique ne se produit qu'à partir d'une seule côté et que la valeur protectrice des revêtements, avec ou sans pigments inhibitifs, peut être prédite en vertu des mesures de résistance, pourvu que les revêtements soient utilisés dans un état d'immersion totale et qu'ils ne sont pas assujetis à la radiation ultra violet.

Die Wirkung des Substrats auf den elektrischen Widerstand von Polymerfilmen

Zusammenfassung

Mit drei verschiedenen Lacken beschichtetes Schmiedeeisen wurde der Einwirkung von 3,5M Kaliumchlorid ausgesetzt. Dabei wird gefunden, dass der Film zu dem Zeitpunkt, an welchem Korrosion auftritt, einen niedrigen Widerstand besitzt und vom Typ D ist; wenn hingegen keine Korrosion vorkommt, leistet der Film an dieser Stelle einen hohen Widerstand und ist vom Typ I. Die Widerstände von D Stellen auf Platin liegen ein bis zwei Grössenordnungen höher, als solche auf Schmiedeeisen, welche als der gleichen Grössenordnung zugehörig befunden werden, wie die von abgelösten Filmen. Der Widerstand von I Filmen ist unabhängig von dem Vorhandensein eines und der Art des Sub-strates. Wen man als Pigment Zinkchromat verwendet, wird das eiserne Substrat passiviert und verhält sich ähnlich wie Platin.

Es wird gefolgert, dass der höhere Widerstand von Filmen auf einem inerten Substrat darauf zurückzuführen ist, dass ionische Diffusion nur von einer Seite her vor sich geht, und dass der Schutzwert von Anstrichen mit oder ohne inhibierende Pigmenten aus Widerstandsmessungen vorausgesagt werden kann. Dies gilt jedoch nur, wenn die Anstriche untergetaucht verwendet und keiner ultravioletten Bestrahlung unterworfen werden.

Introduction

Refs. 1-3

In order for a polymer film to protect a metallic substrate against corrosion, the film should possess low permeability to ions, that is to say it should have a high electrolytic resistance[1].

Bacon, Smith and Rugg[2] examined the behaviour of over 300 paint systems under conditions of total immersion and concluded from resistance measurements, carried out on coated mild steel specimens, that good protection was obtained when the resistance exceeded 10^8 ohms/cm², that in the region 10^6—10^8 ohms/cm², the behaviour was variable, but when the resistance fell below 10^6 ohms/cm², corrosion always occurred.

Work in the present authors' laboratory has been concerned with the effect of electrolytes on the resistance of polymer films and in order to eliminate complications due to reactions

C

at the metal/polymer interface, the behaviour of free films has been studied. It has been found that the films investigated were not homogeneous in their resistance behaviour. Thus, when samples of about 1cm² were taken from a single cast film, 20 × 10 cm, and their resistances measured in dilute and concentrated potassium chloride solution either the resistances followed that of the external solution, "Direct" or D-type conduction, or the resistance of the film ran counter to that of the solution, "Inverse" or I-type conduction[3].

The work has now been extended to attached films and in the first part of this paper it is shown that when corrosion occurred the film at that point had a low resistance and was of D type; whereas, when corrosion was absent the area had a high resistance and was of I type. The second part describes measurements of the resistances of clear varnish films when attached to mild steel or platinum and also of films pigmented with zinc chromate attached to mild steel and in the free form. It was concluded that when corrosion occurred the resistance of the film in that area was low and the value was typical of that of a detached film, but that on an inert substrate, that is platinum or iron passivated by chromate ions, the resistances of D films were two to three orders of magnitude higher than those of detached films.

Experimental

Preparation of polymer films

Refs. 3, 4, 2

Three varnishes were used in this investigation: a pentaery-thritol alkyd, a phenol formaldehyde tung oil and a polyamide cured epoxide. Details have been published[3].

Films were cast, by means of a spreader bar, on 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.

In order to measure the resistance of the films, the cells were immersed in a water thermostat, 25°C, and a DC potential of one volt was applied to the films, which were placed in series with a standard resistor of similar value. The drop in potential across the standard resistor was measured by means of a high input impedance valve voltmeter; from this reading the resistance of the film was calculated. The apparatus is shown in Fig. 1.
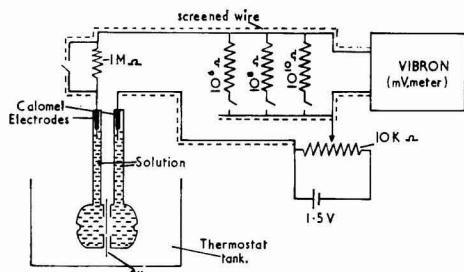
Fig. 1. Method used for DC resistance measurement of detached films

Mild steel, the composition of which has been published[4], was abraded with 00 grade emery, degreased in benzene, followed by acetone, and stored in a grease-free dessicator. Sheets, 20 × 10cm, were coated with varnish by means of a spreader bar. In the case of platinum, foil was used, 4 × 3cm,

and this was coated by immersing the sample and withdrawing it at a constant rate of 0.2cm/sec. The coated metal was dried in a glove box for 48 hours and then stoved at 65°C for the same period.

The method of measuring the resistances of attached films is shown in Fig. 2 and is similar to that used by Bacon, Smith and Rugg[2]. It is based on the standard method of measuring the internal resistance of a battery. The potential difference between the coated specimen and a calomel electrode was measured, a standard resistance was then introduced into the circuit, the potential again measured and the resistance of the paint film calculated from the standard formula. The cell containing the electrolyte was then moved to another area and the resistance again measured.
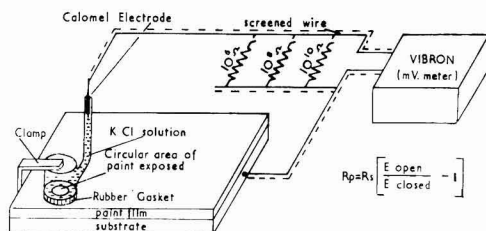
Fig. 2. Method used for resistance measurement of small areas of paint in situ

Both systems were calibrated and checked from time to time by means of standard resistances, whose accuracy was known.

The relation between corrosion and resistance of polymer films

Coated mild steel sheets were incorporated into the "Perspex" cell shown in Fig. 3, which was then filled with 3.5M potassium chloride to a depth of about 2cm. A silicone rubber gasket was used to prevent escape of the solution and the cell was clamped on to the steel by means of four bolts with butterfly nuts. In this way about 64cm² of coated surface was exposed to the solution.
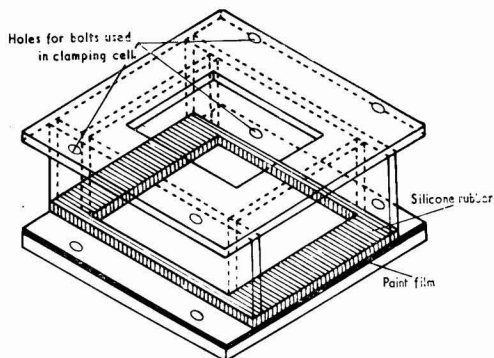
Fig. 3. Perspex cell used to expose area of painted mild steel to corrosive solutions

The films were left for one week in contact with the solution at 22-23°C and the areas of corrosion and of loss of adhesion were recorded by means of tracings, which are shown in Figs. 4, 5 and 6. In all three cases there were areas of adhesion loss, which were generally associated with blue, or brown, blisters.

● — Dark blue blisters
∴ — Small blue or brown blisters
▨ — Area of adhesion loss
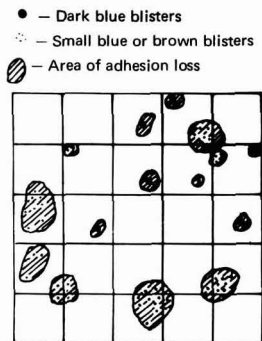
Appearance of specimen (alkyd on mild steel) after exposure to 3·5M K Cl for 1 week (20°C.)
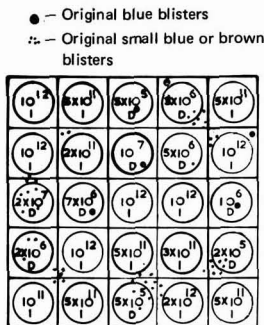
● — Original blue blisters
∴ — Original small blue or brown blisters

Resistance behaviour of same film when detached from mild steel and cut into squares.

Fig. 4.

● — Dark blue blisters
○ — Small colourless blisters
▨ — Area of adhesion loss
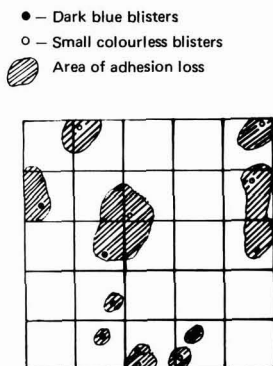
Appearance of specimen (thick tung oil on mild steel) after exposure to 3·5M K Cl for 4 days (20°C.)
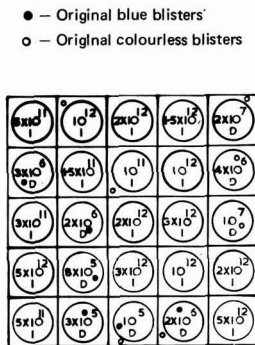
● — Original blue blisters
○ — Original colourless blisters

Resistance behaviour of same film when detached from mild steel and cut into squares.

Fig. 5.

● — Dark blue blisters
▨ — Area of adhesion loss
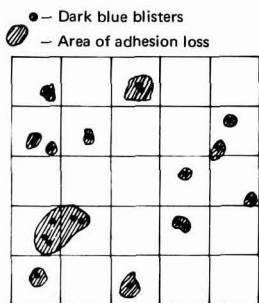
Appearance of specimen (thick epoxy on mild steel) after exposure to 3·5M. K Cl for 1 week (22°C.)

● — Original blue blisters
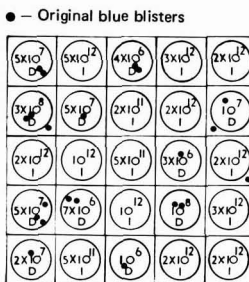
Resistance behaviour of same film when detached from mild steel and cut into squares.

Fig. 6.

The films were then stripped from the substrate by means of a razor blade—this was found to be fairly easy owing to the thickness of the films (75-100µm)—and cut into squares 1.5 × 1.5cm, which were mounted in glass cells. The films' resistances were measured in 0.001M and 3.5M potassium chloride as indicated in Fig. 1. The relationship between the distribution of corrosion and the resistances of the small

pieces of film, after immersion in 3.5M potassium chloride, are shown for the three vehicles in Figs. 4, 5 and 6.

It can be seen that there was good correlation between the resistances of the stripped films and the distribution of corrosion. Thus, all areas where corrosion occurred had resistances of 10^6-10^8 ohms/cm^2 and exhibited D-type behaviour when

removed from the metal; in contrast, where no corrosion was observed, the films had resistances of the order of 10^{12} ohms/cm².

Similar results were obtained with grit blasted and with abraded mild steel immersed in 0.5M potassium chloride and 0.5M potassium sulfate. This suggested that the results were independent of the roughness of the steel surface and the nature and concentration of the electrolyte.

Since in the case of clear varnish films on abraded mild steel there was a relationship between the distribution of corrosion and D areas, it followed that either innate D areas in the polymer film were leading to corrosion, or corrosion occurred underneath the film and this led to D areas.

In order to resolve this point, the percentage of D-type samples for a free film, previously cast on glass, was compared (Table 1) with the percentage for a similar film on mild steel and with an estimate of the percentage distribution of corrosion shown in Figs. 4, 5 and 6. The figures for glass were taken from twenty samples from a single casting and those for mild steel from a similar number of samples taken from films stripped from an area of mild steel adjacent to that used in the corrosion experiments.

Comparison of columns one and two in Table 1 shows that the percentage of D samples for free films cast on glass is not very different from that obtained from films cast on mild steel. This indicates that the process of casting and stripping,

Table 1
Percentages of D-type areas on various samples

Nature of films			% D samples Free film	% D samples Mild steel	% area corroded
Alkyd	..	..	14	17	25–30
Tung oil	..	..	15	10	20–25
Epoxy	..	..	55	50	35–40

in the case of mild steel, did not affect the results. Moreover, the relationship between the percentage of D samples and the distribution of corrosion is reasonable and it is concluded that it was the initial breakdown under the D areas which led to the observed corrosion.

The effect of the substrate on the resistance of polymer films

Mild steel sheets, similar to those used in the previous experiments, were abraded, coated with alkyd varnish and exposed to 0.001M potassium chloride for two days in the cell shown in Fig. 3. The resistance of the whole area was measured periodically and was found to be steady after two days. The solution was removed and a small movable cell containing 0.001M potassium chloride was temporally fixed in position by means of a pressure clamp and rubber gasket and the resistance measured as shown in Fig. 2. The cell was then moved to another area and a further reading taken; in all, six measurements were made. The small cell was then removed and the large cell was filled with 3.5M potassium chloride. After a further 48 hours, the solution was removed and another set of six readings taken from the same areas, but this time the small cell contained 3.5M potassium chloride. The results obtained are shown in Table 2, which also records the corrosion.

Table 2
Results of experiments to determine the effect of substrate on the resistance of polymer films (thickness of films 40-50 microns temperature 22-23°C)

1. Alkyd on mild steel

Resistance of films (ohms/cm²) 0.001M KCl	3.5M KCl	Corrosion	Type
10^{10}	2×10^5	Yes	D
10^{10}	10^7	Yes	D
3×10^{10}	2×10^6	Yes	D
3×10^8	10^6	Yes	D
10^{10}	10^{11}	No	
10^{11}	10^{10}	No	

2. Alkyd on platinum

Resistance of films (ohms/cm²) 0.001M KCl	3.5M KCl	Type
5×10^9	5×10^8	D
5×10^9	10^{11}	I
7×10^8	5×10^8	D
10^{10}	10^9	D
10^{10}	10^{11}	I
10^9	3×10^9	I

3. Alkyd removed from platinum

Resistance of films (ohms/cm²) 0.001M KCl	3.5M KCl	Type
10^8	10^7	D
10^{12}	2×10^{12}	I
10^8	4×10^6	D
10^9	3×10^7	D
3×10^{11}	10^{12}	I
8×10^9	3×10^7	D

Platinum foil, 4×3cm, was coated with the alkyd varnish and completely immersed in 3.5M potassium chloride for two days. It was then removed from the solution and the resistance at six areas was measured in the same way. The coated foil was then immersed in 0.001M potassium chloride for a further two days and further measurements made of the resistances of the same six areas. The film was then stripped from the platinum, cut into pieces, mounted in cells and the resistances of the respective samples measured in 0.001M and 3.5M potassium chloride. In this case equilibrium was attained in under two hours. The results obtained are shown in Table 2. Similar results were obtained with the tung oil and epoxy varnishes.

It can be seen from Table 2 that in the case of the measurements made on mild steel, four of the areas were of D type and all four showed some signs of corrosion under the film within two days of immersion in 3.5M potassium chloride. Two areas were free from corrosion and were of high resistance. It proved difficult to measure resistances greater than 10^{10} ohms/cm² by the method shown in Fig. 2, so that whether the last two areas showed true I-type behaviour was not certain. However, from the work in the previous section it seems likely that these two areas would have been I type had they been detached.

When platinum was used as the substrate, the resistances of the films *in situ* could be directly compared with those of the detached films. It can be seen that, in general, the values of the resistances of D-type films on platinum were one to two orders of magnitude higher than when the same film was detached; in contrast, I-type films retained their high resistance even when detached.

The effect of inhibitive pigments on the resistance of polymer films

Ref. 5

In order to examine the effect of inhibitive pigments on the resistance of polymer films some measurements have been made on films produced from a styrene-butyl acrylate emulsion, pigmented with zinc chromate; in some cases a sealing coat pigmented with titanium oxide was applied. The composition of these paints has been published[5].

The films were prepared by spraying the emulsion paint on to mild steel and glass using a standard compressed air gun. The films were dried in a glove box for 48 hours and then heated for a further 48 hours at 65°C. They were then stoved at 110°C for half an hour. Portions of the film were detached from the glass and the percentage D type determined in the usual way; the value was found to be 100 per cent D type with a very uniform resistance behaviour, probably owing to the lack of crosslinking.

The resistance was measured of single and two-coat systems after immersion in 0.005M potassium sulfate, both attached to mild steel and in the form of free films and the results are shown in Table 3. The values quoted are the

Table 3
Results of experiments to show the effect of inhibitive pigments

	Thickness (μm)	Average resistance of detached films (3 hours) (3 days) (ohms/cm^2)		Average resistance of attached films (3 hours) (3 days) (ohms/cm^2)	
Two-coat 1 Inhibitive 1 Sealing	75	5×10^7	10^7	10^{11}	10^{10}
One-coat 1 Inhibitive	38	3×10^6	10^6	5×10^{10}	3×10^9

average of four or five cells; the scatter in the readings was small.

It can be seen that the resistances of the attached films are two-three orders of magnitude higher than those of the free films.

Conclusions

Ref. 2

An examination has been made of the effect of the substrate on the electrolytic resistance of polymer films.

It has been found that when the films were attached to iron and immersed in a corrosive solution, corrosion occurred at the areas of low resistance in the films and that at these areas the films had similar resistances to those of detached films.

In contrast, when the films were supported on an inert substrate (platinum or passivated iron), then their resistances were several orders of magnitude higher than those of free films.

These results can be explained in terms of the penetration of ions into the film, a process occurring more easily if ions are available from both sides.

In the case of a supported film, on an inert substrate, ionic penetration can occur only from one side and then only after the film has taken up water, thereby lowering the film's dielectric constant. This uptake of water is retarded in the case of an attached film, as opposed to a free one, by the forces of cohesion and adhesion to the substrate.

These observations provide support for the claim by Bacon, Smith and Rugg[2] that prediction of coating performance can be made from measurements of electrolytic resistance. It should be noted that this conclusion is limited to the behaviour of immersed paint films—conditions under which the coatings are not exposed to degradation by ultraviolet light. Furthermore, throughout this paper all measurements were made with DC current and polarisation resistance has been neglected. The reasons for this will be discussed in a later paper.

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Organotin-based antifouling systems

By C. J. Evans and P. J. Smith

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Summary

The unique combination of chemical, physical and biological properties displayed by the tri-organotins, particularly the tributyl- and triphenyl-tin derivatives, coupled with the fact that they leave no long-lasting harmful residues in the environment, has led to a considerable increase in their use in marine antifouling paints.

Recent research efforts have been aimed at incorporating these biologically active tri-organotin moieties into either polymeric networks or elastomeric substrates, in order to increase the antifoulants' effective lifetime.

Keywords

Types and classes of coatings and allied products

  antifouling coating

  marine finish

Raw materials:

binders (resins etc.)

  polymer

biologically active agents

  microbiological agent

  organotin

Les systèmes "antifouling" à base des composés organostanniques

Résumé

L'unique ensemble des caractéristiques chimiques, physiques et biologiques met en évidence par des tri-substitués composés organostanniques, en particulier les dérivés tributyle et triphényle, et d'ailleurs le fait qu'ils ne laissent à l'environnement aucune reste nocive et persistante, ont favorisé un essor important de leur utilisation en peintures "antifouling." Les tentatives de recherche récentes ont eu pour but l'incorporation de ces dérivés organostanniques ayant une certaine activité biologique aux réseaux polymères ou aux supports elastomères, afin de prolonger .eur vie utile.

Antifouling Systeme auf Organozinnbasis

Zusammenfassung

Die einzigartige Kombination von chemischen, physikalischen und biologischen Eigenschaften der Tri-Organozinnverbindungen, insbesondere der Tributyl-und Triphenylzinnderivate, führte in Verbindung mit der Tatsache, dass sie in der Umwelt keine langlebigen, harmvollen Rückstände hinterlassen, zu beträchtlich erhöhter Verwendung in Antifoulingfarben für Seeschiffe.

Neuere Forschungsexperimente zielten darauf hin, diese biologisch aktiven Triorganozinnbestandteile in polymere Vernetzungen oder elastomere Träger zu incorporieren, um die Dauer ihrer Wirksamkeit zu verlängern.

Introduction

Refs. 1-5

World-wide consumption of organotin compounds is currently touching at least 25 000 tonnes[1]. Although there are a wide number of uses for these compounds[1, 2], their applications broadly divide between the use of di-organotin compounds[3] in association with plastics and the biocidal uses of tri-organotin compounds[4]. The histogram (Fig. 1) shows the rapid increase in recent years in the consumption of organotins, which stems largely from advances in the technology of their use.

At the present time the biocidal applications account for some 10 000 tonnes of organotins (representing 2 000-3 000 tonnes of tin) and this figure is expected to increase rapidly over the next few years. Ship-owners are becoming increasingly aware of the advantages (in running efficiency) to be gained by the use of antifouling systems. Tri-organotin compounds are proving themselves to be highly effective toxicants in these coatings and, moreover, have the advantage that they constitute no long-lasting environmental hazard. There is a current trend away from the use of
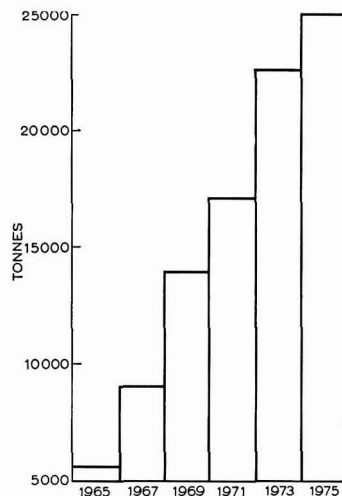
Fig. 1. The approximate annual world consumption of organotins

organolead and organomercury biocides due to their high mammalian toxicity and their relatively adverse effect on the environment. In contrast, organotin compounds are eventually degraded in nature to give non-toxic inorganic tin residues.

This article reviews the use of tri-organotin compounds in antifouling compositions and discusses recent developments in the field. For a more general discussion of the topic of marine fouling, reference should be made to an excellent review[5] published recently.

The fouling problem

Refs. 6-8

Marine fouling results from the attachment of marine organisms, whether animal or plant types, to a surface immersed in sea water. The known number of fouling species is now in the region of 4 000 to 5 000[6], with sea grass and barnacles being the most common forms. Others which cause trouble to shipping include molluscs (especially mussels and oysters), tubeworms, hydroids and sponges. Fouling increases hull friction as a vessel moves through the water, fuel consumption goes up and the maximum speed is decreased. It has been estimated that marine fouling can cut speeds by 0.5 to 1.0 knots, which can represent a serious loss in efficiency. One estimate of the world-wide cost to shipping of marine fouling puts the figure at about 1 000 million dollars a year[7]. Removal of the fouling from hulls means long periods out of service and may even result in paint damage when tenacious shell attachments are present.

The most realistic method of dealing with this fouling problem is to protect the surface of the vessel which comes into contact with the water by providing it with an antifouling coating system. This functions by releasing chemicals poisonous to marine organisms and thus prevents their attachment to the ship's hull. The two vital components of such an antifouling system are: a toxicant which will effectively deal with a wide range of fouling species at low concentrations, which will constitute only a minimum toxic hazard during application to a vessel, and which will not contribute significantly to environmental pollution; and a coating medium which will release the toxicant at a slow, but steady, rate and preserve its film integrity on the hull surface. The problems in finding a suitable toxicant are increased by the fact that new coastal and industrial developments and changing environmental conditions are constantly modifying the fouling situation.

One of the most common forms of fouling consists of barnacles, which, as free-swimming larval forms, attach to the hull by secreting tiny droplets of cement and then grow into the conical adult form with calcareous shells (Fig. 2).

This type of fouling arises when vessels are stationary for a day or two, as when moored in a harbour. They also constitute a problem in seawater piping, ships' condensers and in desalination and power plants. The advent of large oil tankers has created further difficulties. These are seldom stationary long enough to pick up mollusc and barnacle attachments, but their hull configuration and trading routes make them very susceptible to grass fouling, particularly *Enteromorpha* or green "ribbon grass" (Fig. 3).

Although the latter problems can be dealt with, it should be noted that bacteria, diatoms and other micro-organisms

Fig. 2. Marine fouling by barnacles (Courtesy: Schering AG, Bergkamen, West Germany)
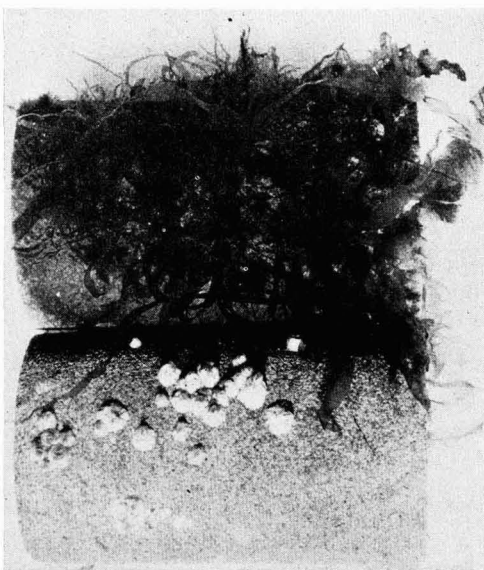
Fig. 3. The upper panel shows typical fouling by Enteromorpha. The lower panel is fouled by barnacles only (Courtesy: International Red Hand Marine Coatings, Gateshead, England)

can cause micro-fouling[8]—the formation of a slime film on existing antifouling coatings—and this may affect the performance of any antifouling agent.

Organotin compounds as toxicants

Ref. 9

As early as 1943, a patent taken out by Tisdale[9] had suggested that organotin compounds were effective for antifouling systems. However, this patent aroused no commercial interest and it was not until 1950, when the Tin Research Institute sponsored research at the Organisch Chemisch Instituut TNO, Utrecht, Holland, that the possibilities of organotin compounds began to be realised. The commercia-

lisation of organotin antifouling systems dates from the 1960s and today they are used extensively all over the world.

In view of the increasing concern with ecology, it is important to examine firstly the toxicology of tri-organotin compounds.

Toxicity pattern of organotin antifoulants

Refs. 1, 10-15, 19, 23, 24

In any organotin series, R_nSnX_{4-n} (R = carbon-bonded organic group; X = inorganic substituent), it is now well established that the maximum toxicity to all types of living species (for example, rats[10], insects[11], fungi[12, 13] and bacteria[13]), occurs with the tri-organotin compounds, R_3SnX. As the length of the carbon chain is progressively increased within a particular series of tri-n-alkyltin salts, R_3SnX, the mammalian toxicity reaches a maximum value when R is an ethyl group[10, 14] and then falls off rapidly with further lengthening of the alkyl chain (Table 1); the tri-n-octyltin derivatives are essentially non-toxic[1, 15].

Table 1
Mammalian toxicity of tri-n-alkyltin compounds (R_3SnX)

Compound	Acute oral LD_{50} (rats, mg/kg)	Ref.
$Me_3SnO.CO.Me$	9.1	14
$Et_3SnO.CO.Me$	4.0	14
$Bu_3SnO.CO.Me$	125-136	16
$Bu_3SnO.CO(CH_2)_9Me$	205	15
$Bu_3SnO.CO.(CH_2)_7CH:CH(CH_2)_7Me$	195	15
$Bu_3SnO.CO.Ph$	132 (505*)	15
$Bu_3SnOSnBu_3$	112-148 (605*)	15
,,	190	17
,,	193	16
,,	148-194	18
,,	234	19
Bu_3SnF	200	17, 19
$Oct_3SnO.CO.Me$	>1,000	14

Me = methyl; Et = ethyl; Bu = butyl; Ph = phenyl; Oct = octyl

*Dermal

The tributyltin salts $(C_4H_9)_3SnX$, which show acute oral LD_{50} values in the approximate range 100–200 mg/kg (rats), lie between the two extremes of mammalian toxicity. Their biological activity is almost entirely due to the $(C_4H_9)_3Sn$ moiety, since, in common with other tri-alkyltin compounds, variation of the inorganic substituent X does not usually have a significant effect on the toxicity (Table 1).

Acute dermal toxicities have also been determined for tributyltin oxide[15, 18], fluoride[19] and benzoate[15] and these are considerably lower than the oral toxicities.

The acute mammalian toxicities of the common triphenyltin biocides (Table 2) are generally very similar to, and often lower than, those of their tributyltin analogues. It is also interesting to note that the anionic group appears to have an effect on the toxicity in these compounds.

Tributyl- and triphenyl-tin compounds have been used industrially as biocides for many years—the former as wood preservatives[10, 23], the latter as agricultural fungicides[13]—and, apart from skin[10, 19, 24] or eye[19] irritations which can

occur when concentrated solutions are handled, there have been no reports of serious toxic effects among operatives.

Table 2
Mammalian toxicity of triphenyltin compounds (Ph_3SnX)

Compound	Acute oral LD_{50} (rats, mg/kg)	Ref.
$Ph_3SnO.CO.Me$	136 (450*)	15
,,	125-150	11
,,	429-491	20
Ph_3SnOH	500-600	21
Ph_3SnF	1170	19
Ph_3SnCl	125	22
$Ph_3SnSSnPh_3$	680-1470†	11

*Dermal. †Mice
Me = methyl; Ph = phenyl

Biocidal activity

Refs. 5, 7, 11-14, 20, 25-37

Although tributyl- and triphenyl-tin compounds are not unduly hazardous to humans, as discussed above, they are nevertheless very effective biocides against a wide range of marine fouling organisms. Information on the activities of various tributyl- and triphenyl-tin derivatives against marine algae (*Enteromorpha*[25, 26], *Ectocarpus*[25], and *Ulothrix*[27]), barnacles[7], shrimps (*Artemia salina*[28]) and tubeworms (*Tubifex tubifex*)[29] has been published. In Table 3, the activities of the R_3SnX compounds against marine algae and barnacles are compared[7] with those of other antifouling agents and it can be seen, for example, that the amount of organotin compound required to prevent fouling is usually five to ten times less than that of cuprous oxide.

Table 3
Comparison of marine biocidal activities of common antifoulants[7]

Antifoulant					Range of activity (ppm)	
					Algae	Barnacles
R_3SnX ..	..	..	..	..	0.01-5	0.1-1
Cu_2O ..	..	..	..	..	1-50	1-10
R_3PbX ..	..	..	..	..	0.1-1	0.1-1
$RHgX$ ..	..	..	..	..	0.1-1	0.1-1

Although the tributyl- and triphenyl-tins appear to be less effective against algae than against other marine fouling species[5, 7, 30], their activity spectrum may be widened by (a) adding other toxicants, such as cuprous oxide[30]; or (b) incorporating a biologically active anion X into the tri-organotin molecule (for example, tributyltin pentachlorophenoxide[31]); or (c) chemically binding two R_3Sn groups of different biological activities into a polymeric network, as discussed later.

The exact mechanism by which the tri-organotins exert their lethal effect on marine organisms is still not completely clear, although extensive studies in mammals have established[10, 32] that the trialkyltins—at least up to the tributyltins—inhibit the vital process of oxidative phosphorylation and thereby depress general metabolism; the triphenyltin compounds produce a similar depression of metabolic activity[10, 20]. Since the trialkyltins appear to be

relatively non-specific in their action[10], it is likely that they are able to depress metabolism in the cells of marine plants and animals also. For example, recent studies[33] of the effects of tri-ethyltin sulfate on the metabolism of the barnacle *Eliminius modestus* do not preclude a toxic action on respiration.

Histological studies on Ram's Horn snails (*Planorbis* spp.) have indicated[34] that tributyltin oxide combines with amino acids in proteinaceous tissue. In the case of two animal proteins (rat haemoglobin and a protein from guinea-pig liver supernatant), it has been suggested[35] that a tri-alkyltin-histidine complex (Fig. 4a) is formed, in which the tin atom is pentacoordinate with a trigonal bipyramidal geometry.

(a)

(b)
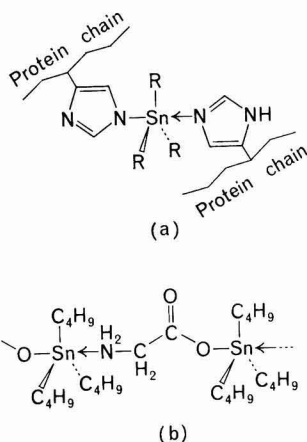
Fig. 4. Proposed structures for (a) tri-alkyltin-protein complex and (b) tributyltin glycinate

The original anionic group of the R_3SnX molecule is not directly involved in the bonding in this complex, which explains the anion-independence of the biological activity.

A number of tri-alkyltin complexes of α- and β-amino acids and dipeptides have also been synthesised[36] and these include tributyltin glycinate, which probably has a closely related polymeric type of structure (Fig. 4b).
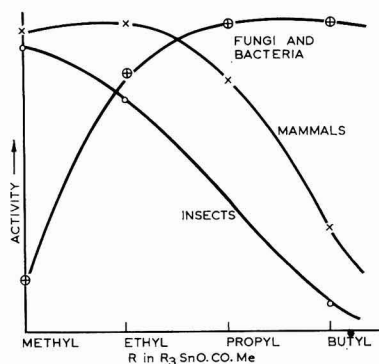
Fig. 5. Dependence of the biological activity of tri-n-alkyltin acetates on the nature of the alkyl group for different species (based on data in refs. 11-14)

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The activity maxima for different types of living species are found to be dependent upon the length of the alkyl chain in the tri-n-alkyltin compounds: for insects, the trimethyltins are usually most toxic[11]; for mammals, the tri-ethyltins[10, 14, 32]; for gram-negative bacteria the tripropyltins[13]; whilst for gram-positive bacteria and fungi, the tributyltins are found to show the highest activity[12, 13] (Fig. 5).

Since the formation of tri-alkyltin-amino acid complexes of the type described above is unlikely to be affected dramatically by the alkyl chain length (*cf.* ref. 36), the dependence of the biological activity on the nature of the alkyl group for different species is probably due to variations in the ease with which the toxic R_3Sn moiety is able to penetrate the different cells to reach the site of toxic action[13, 37] (Fig. 4a).

Environmental considerations

When examining the environmental aspect of organotin-based anti-foulants, it is necessary to consider, firstly, the conditions under which these coatings are applied to vessels, and secondly the effect on the marine environment of the small amounts of toxicant continuously released in service.

Sheldon[19] has examined the effects of organotin antifouling coatings on both man and his environment. He indicates that the main hazards in handling relate to potential contact with eyes and with the skin, and he outlines general safety considerations to be adopted when handling tri-organotin antifoulants. He stresses that chemicals, such as tri-n-butyltin oxide and triphenyltin fluoride, are being safely used in shipyards around the world, and their safe handling has been demonstrated over five years. Airless spraying is recommended, with full provision for protection of the operator and nearby workmen from spray. Similar precautions should be taken in sandblasting, welding or burning operations on ships' hulls coated with paints containing organotins. Whilst mixing coatings, care should be taken to avoid both eye and skin contact.

The amount of toxicant released to the world's oceans by antifouling coatings might seem to be insignificant, but, with the growing use of these systems, this factor has to be taken into consideration on the grounds of ecology. As an example, it has been estimated that about 5 000 tonnes of copper is released into the sea every year from copper-based antifouling systems[7]. In the case of the more toxic organomercury compounds, this contamination is, of course, more serious. Recent work with organotin derivatives, described in the following sections, has enabled the release rate of organometallic toxicant into the marine environment to be controlled at a very low level.

In the long term, tri-organotin derivatives have the advantage of producing no harmful residues in sea water since they are eventually broken down to non-toxic inorganic tin compounds (probably stannic oxide), by successive cleavage of the three tin-carbon bonds. Although there are no specific studies on the rate of degradation of organotins in the marine environment, the triphenyltin derivatives are known to be broken down fairly rapidly on crops and in the soil by the combined action of light[38-40] and micro-organisms[40]. Tributyltin compounds behave similarly on exposure to ultraviolet[41] and γ-irradiation[42]. although no work has yet been conducted on their microbial decomposition. Bollen and Tu found[43] that levels of tributyltin oxide of up to 100 ppm in soil do not appear to have any detrimental effects on the soil micro-organisms.

In 1973, the Tin Research Institute, in collaboration with the Organisch Chemisch Instituut TNO, Utrecht, Holland, organised a cooperative research project to obtain data on the behaviour of organotin compounds in the environment. This project has been dubbed "ORTEP", an acronym for Organotin Environmental Project[44]. Major producers of primary organotin compounds from the USA, Germany, the UK, Switzerland and Japan have joined the project and studies have commenced at TNO.

Antifouling coatings containing organotins

Conventional paint systems

Refs. 2, 5, 7, 16, 19, 30, 45-53

Antifouling paints can be made by incorporating the toxicant in standard paint formulations, such as thixotropic polyure-thane media or vinylite VAGH/rosin systems.

In 1966 Bennett and Zedler[45] described the development of suitable paint vehicles for tributyltin oxide, and provided experimental data on their effectiveness. There have been many further developments since this paper was published, and it is now possible to exert more effective control over the leaching rate of the toxicant. The rate of uncontrolled release of tri-alkyltin groups from antifouling paint films can be either too rapid or too slow[30]; the optimum release rate required for an organotin compound such as tributyltin oxide or tributyltin fluoride is about 10-12 mg/m^2 of surface per day[5, 7]. Mor and his co-workers have recently reported[46] a method for determining small amounts of tributyl- and triphenyl-tin compounds in sea water due to leaching from marine paints. Using synthetic sea water and an extraction technique with carbon tetrachloride followed by spectro-photometry, as little as 0.01 to 0.2 μg/ml of organotins can be determined reproducibly. Vernon has also described[47] a sensitive fluorimetric technique for the determination of triphenyltin residues, using the reagent 3-hydroxyflavone.

Various methods have been adopted to approach an ideal release rate in practical terms. Mearns[16] has looked closely at the factors influencing the formulation of vinyl-based systems. High-performance and long life must be based upon a non-saponifiable resin system, which will provide a skeleton, or sound framework, in the exhausted film. The leaching rate is controlled by the total volume of material which is soluble in sea water, by the pigment packing and by the solubility of the constituents. Satisfactory results were obtained in trials using tributyltin fluoride in vinyl media. Lorenz[48] tested the effectiveness of tributyltin oxide and tributyltin tetrachlorophthalate in vinyl and chlorinated rubber coatings. Tributyltin oxide behaves like a solvent and migrates from a film, so that after an initial period of effectiveness, its activity falls off with time; the tetrachlorophthalate behaves as a plasticiser and its smaller leaching rate keeps it effective over a longer period.

The inclusion of between 0.1 and 10 weight per cent colloidal silica in a paint formulation containing tributyltin oxide has been patented[49] as a means of overcoming possible incompatibility of the organotin with the paint binder. Advantages claimed include better adhesion of the paint film, and a slower leaching rate of the toxicant, hence a longer antifouling effectiveness.

The triphenyltin compounds, although very similar in mammalian toxicity and biocidal activity to the tributyltins, are not used quite as extensively in antifouling coatings at the present time. This may be due partly to difficulties involved in their formulation[45]. Triphenyltin oxide[50], fluoride[49, 50] and tetrachlorophthalate[51] have been described as antifouling toxicants and in Japan, for example, tri-phenyltin chloride, acetate and hydroxide are all in common use[52].

The inorganic group X of the compounds R_3SnX will affect the solubility and consequently the release rate of organotin toxicant. Most of the effective tri-organotin antifoulants—with the exception of tributyltin oxide and triphenyltin chloride, which are simple monomeric species—are self-associated polymeric molecules, due to intermolecular coordination by the X groups to tin. Included in this category are tributyl- and triphenyl-tin fluoride (Fig. 6a; R = butyl or phenyl) and many of the tri-organotin carboxylate anti-foulants, such as tributyltin acetate (Fig. 6b; R = butyl, R' = methyl).

(a)

(b)
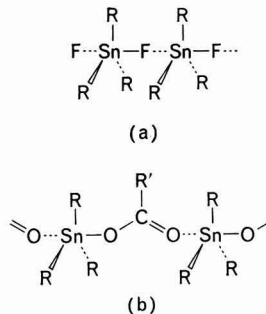
Fig. 6. Solid state structures of some simple organotin antifoulants (a) tri-organotin fluorides and (b) tri-organotin carboxylates

The tendency for the R_3SnX compounds to form these self-associated polymeric structures in the solid state is known to be very marked[2].

For the majority of merchant ships, which dry dock at intervals of about 12 to 18 months, the ordinary paint formulations containing simple tri-organotin additives of the above types are quite satisfactory, and provide adequate protection over this period. However, giant tankers involve capital investment which runs into millions of pounds[53]. Their economical operation requires that they spend a high proportion of their time at sea and with a period of at least 2 to 2.5 years (preferably 4 to 5 years) between dry-docking periods. A long-term coating is even more essential for naval vessels, and many of the more recent developments have originated in the laboratories of the US and Australian navies, whose ships spend considerable periods in tropical environments conducive to marine fouling.

Elastomeric systems

Refs. 5, 7, 14, 32, 54-63

The first approach has been to incorporate the tri-organotin toxicant into an elastomeric matrix. The precursor for these systems was the "Nofoul" antifouling rubber (marketed by the US company, B. F. Goodrich) and a full account of the development of this product has been given by Cardarelli[54]. Originally developed as a protective coating for sonar buoys and later extended to other applications, Nofoul contains tributyltin oxide and tributyltin sulfide incorporated in chloroprene rubber, and 100 per cent effectiveness over long periods has been demonstrated[55]. Cardarelli[56] considers

that the tributyltin oxide crosslinks, or "cures" the chloro-prene, and that the active agent is thought to be only partly tributyltin oxide, the main constituents being tributyltin chloride and various tributyltin-fatty acid combinations, resulting from the vulcanising reaction.

Woodford and co-workers have published work on similar systems carried out at the Australian Defence Standards Laboratories[57, 58]. The compounds studied were tributyltin oxide, acetate and fluoride and the elastomers, in the form of sheet, were natural rubber, nitrile rubber and polychloro-prene, containing conventional curing agents, antioxidants and carbon black. Effective antifouling was observed with all the systems over 12 months' immersion at Port Jackson, NSW. Tributyltin fluoride, which has low solubility in water and elastomer, was considered the most promising toxicant for further work. The sheet rubber systems were restricted to simple low surface area applications because of the practical difficulties in applying them; high-build polychloroprene solution coatings containing organotins are considered a possible answer to this problem. Wake[59] has reported further results obtained with nitrile rubber containing 2 to 10 parts per 100 of tributyltin oxide, acetate or fluoride, immersed in sea water for 636 days at a sub-tropical site, and for 365 days at a tropical location. The degree of dispersion of the organotin within the rubber matrix is found to be of significance for antifouling effec-tiveness. For this reason, the less mobile acetate proved less effective than the other organotins. This author suggested that incorporation of compounds, such as the tripropyltin derivatives, which are active against gram-negative org-anisms, might help prevent the traces of organisms and algae which still occurred on the rubber surface. However, the higher mammalian toxicity of the tripropyltins[14, 32] should be borne in mind. The usefulness of impregnated rubber systems for coverage of sonar domes has also been pointed out[60].

When organotins are incorporated in elastomers, the curing may be retarded, so that more than 10 per cent of toxicant may have an adverse effect on the mechanical properties of the rubber. Dunn and Oldfield[61] have reported a new technique which overcomes this limitation. They have produced vulcanisates containing active organotin groups, by adding an unsaturated organotin monomer, such as tributyltin acrylate, to an uncured elastomer, such as chloro-sulfonated polyethylene, natural rubber or polychloroprene, and curing the systems with peroxides. Three reactions can occur: cross linking of the elastomer, homopolymerisation of the organotin monomer or, finally, co-vulcanisation of the elastomer and the organotin compound. Since the cure rate is not retarded, it should be possible to incorporate up to 50 per cent by weight of tributyltin acrylate without impairing the mechanical properties. This was borne out by mechanical testing, which showed good properties even after long periods of marine immersion. Antifouling trials with immersion tanks or raft tests confirmed the effectiveness of these vulcanisates, from which active organotin groups are released at a slow, steady rate as sea water diffuses into the system.

Phillip has reviewed the progress of this work at the Australian Defence Standards Laboratories[5, 7]. He points out that the leaching rate of the toxicant depends to some extent on the nature of the elastomeric matrix. With natural rubber, tributyltin oxide is released more rapidly with increasing concentration in the rubber, whereas tributyltin fluoride is released at a constant rate, which suggests the latter behaves as an inert filler. In polychloroprene coatings both toxicants show a dependence of leaching rate on initial concentration, so that for this system the effective antifouling life cannot be extended merely by increasing the loading of organotin.

Workers at Mond Division of ICI Ltd have also investiga-ted the antifouling properties of chlorinated rubbers containing various toxicants[62]. Steel plates coated with experimental formulations were exposed for two years in raft tests and afterwards examined for evidence of marine fouling. Best results were obtained with a chlorinated rubber containing a mixture of toxicants: tributyltin oxide, tributyltin fluoride and cuprous oxide. Accelerated storage trials were also conducted to determine the factors influencing the long-time stability of the formulations.

Ginsberg and Stevens[63] have reported on the development of high-build vinyl compositions for marine coatings. Their use as anti-fouling coatings is described, and a three-coat system consists of a wash primer, a high-build anticorrosive primer and one high-build coat of antifouling paint. Tests have been conducted on such coatings, some of which con-tained 29 per cent tributyltin fluoride as toxicant, and results are considered promising.

Organotin polymer systems

Refs 5, 7, 30, 64-69

Even with these elastomeric substrates, the release rate of organotin may still be up to sixteen times higher than the ideal level[30], and Phillip shows[5, 7] how attention has turned to organometallic film-forming polymers for use as anti-fouling coatings. Attempts had been made[64, 65] since 1958 to produce polymeric films in which a tri-organotin group is chemically bound to the polymer backbone, but practical difficulties arose from the poor film-forming properties of such polymers. At the Australian Defence Standards Labora-tories[5, 7, 30], tributyltin acrylate (Fig. 7a, $R = H$) or metha-crylate (Fig. 7a, $R = $ methyl) has been copolymerised with appropriate ratios of co-monomers, such as vinyl chloride (Fig. 7b) or methyl methacrylate.

(a)

(b)

Fig. 7. (a) Tributyltin acrylate (methacrylate) monomer, and (b) tributyltin acrylate (methacrylate)/vinyl chloride copolymer

A large number of such copolymers has been synthesised and studied to determine the degree of polymerisation, molecular weight, tin content and presence of functional groups. Suitable polymers are then formulated into marine coatings with appropriate pigments, plasticisers and toxic materials, and used in immersion trials at marine sites. Bocks-teiner has reported[30] results with such systems. The organotin polymers studied included tributyltin acrylate copolymerised with vinyl polymers or with methyl methacrylate and acrylic acid polymers. The percentage of organotin polymer varied from 30 to 50 per cent by weight of the total polymer, and a herbicide such as ametryne was often present at the 5

to 10 per cent level. Film thickness was between 100 and 120 μm. The higher contents of organotin polymer gave the longest effective lives, and sea water immersion and removal did not seem to affect the antifouling properties. An effective lifetime of up to three years is thought within the capabilities of these systems.

Concurrent with this work, researchers at the US Naval Ship R & D Centre, Annapolis, Md., have studied organotin copolymers for antifouling systems. Results have been reported by Dyckman and his co-workers[66]. Part of the motivation for this work was the need to reduce the ecological impact of toxic coating components being released into the aqueous environment. A large number of organotin polymers has been synthesised and tested; these include tributyltin, tripropyltin, tribenzyltin, triphenyltin and trimethyltin groups chemically bonded to acrylic, vinyl, polyester, epoxy, and polyurethane resins. Copolymers of tri-n-butyltin methacrylate with methyl methacrylate and styrene polymers have also been tested. Test panels coated with these polymers have exhibited excellent antifouling performance after 28 months of immersion. A rotating cylinder apparatus has been used to simulate ships' hull behaviour in accelerated tests, and selected organisms have been exposed to a leachate to determine an LD_{50}. Using these data as a guide, organometallic polymers are chemically modified to reduce leaching to a minimum consistent with long-term antifouling effectiveness. Leaching occurs by hydrolysis of the polymer at the surface by contact with sea water. The best antifouling performance was obtained with those polymers containing tributyltin and/or tripropyltin groups, and the incorporation of two R_3Sn units of different biological activities widens the "kill" spectrum of the polymer. The authors anticipate that use of these systems should result in long-term protection, whilst reducing the pollution hazards by a factor of 10.

Some work on organotin polymers has also been conducted in the UK. Tributyltin methacrylate and methyl methacrylate have been copolymerised to incorporate 20 to 60 per cent by weight of organotin monomer; an appreciably water-soluble pigment with toxic action, such as cuprous oxide, and a plasticiser, are also present[67]. Several other patents cover similar systems[68, 69].

It is of interest to compare these polymeric structures with those of the simple R_3SnF and $R_3SnO.CO.R'$ antifoulants (Fig. 6). In the latter case the toxic R_3SnX groups are only weakly held together by intermolecular association, which explains their generally higher release rate.

The future for organotins in antifouling systems

Refs. 70-73

At the present time, organotin compounds are in commercial use in many antifouling paints and this use is growing as ship owners seek longer protection for their vessels to minimise dry-docking costs. Fig. 8 shows the hull of a large ocean-going vessel being protected with a four-part paint system, which includes a 50μm thick coating of an organotin-containing paint (A/F Oceanic 7640-5140, from Hempel's Marine Paints), applied over A/F Oceanic 7640-2193 (also 50μm thick) as secondary protection. In the lower photograph, the same hull is shown after 16 months in continuous service. The top protective layer has more or less leached out, leaving the secondary layer for further protection. Only a little *Enteromorpha* is present as fouling species, indicating the long-term effectiveness of this coating system.
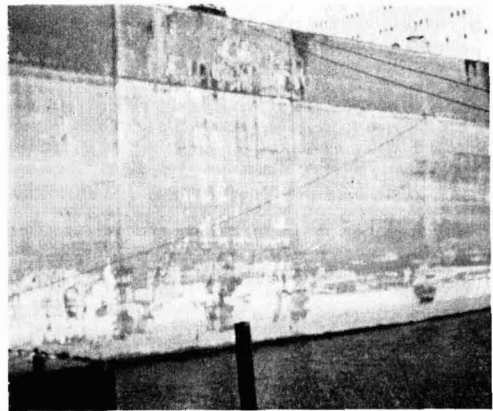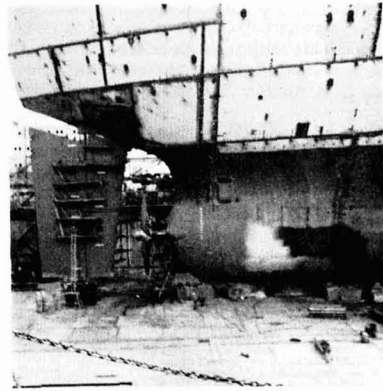
Fig. 8. (a) Applying an organotin-based antifouling system to the hull of a large vessel, and (b) the same hull, practically free of fouling after 16 months' service (Courtesy: Hempel's Marine Paints, Lyngby, Denmark)

International Red Hand Marine Coatings has employed organotin-based systems for a number of years. Its "Wide Spectrum" antifouling paint was originally developed to overcome the problem of the fouling of huge ocean-going tankers by *Enteromorpha* and *Ectocarpus*[70]. Meanwhile, the system itself was being continually improved by researchers at the company. In the form of "Speedcote", it has been used successfully on many tankers and other vessels. The latest antifouling system to come from the firm is known as "SPC" (self-polishing copolymer). This system also incorporates an organotin toxicant[71]. The coating, it is claimed, becomes smoother with passage of time since turbulent flow of sea water selectively removes the "peaks" of the antifouling coating where it covers roughness in the underlying hull surface. As the toxicant is an integral part of the resin matrix, the length of time during which it is active depends on the thickness of the layer applied. Up to 100μm can be applied in one coat, and the number of coats can be selected to give the requisite lifetime. The company estimates that the owner of a 250 000 DWT tanker can save £130 000 during the two-year interval between dry-docking periods[72]. In this way an antifouling system developed for one application has gradually extended its scope and coverage.

Similarly, it is to be expected that the work currently under way at Naval Laboratories in Australia and the USA with a view to improving antifouling effectiveness on naval ships will ultimately benefit the commercial ship owner. Another significant development is the use of a number of toxicants together in order to widen the spectrum of effectiveness. In this respect the use of polymeric organotins allows the incorporation of groups, such as tripropyltin, which have wide-ranging effectiveness but would otherwise prove too toxic for general use.

Little has been said about protection of smaller boats and yachts, yet here the organotin-based systems demonstrate other important advantages. Their colourless nature allows the use of light pastel shades in the paints, and they are not subject to the bimetallic corrosion problems encountered with copper-based antifouling formulations on lightweight aluminium hulls. Several commercial yacht paints are now available for use by the small boat owner, and many famous racing yachts have been protected by organotin-based antifouling paints during their record cruises. An example is "Pegasus III" which recently won the Lloyd's Register yacht trophy[73].

In a relatively small number of years, tri-organotin compounds have reached a significant usage in antifouling systems. All the signs are that this will extend still further, as developments now in hand come to fruition.

Acknowledgments

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The role played by water-soluble polymers in paint performance*

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Summary

The influence of water-soluble polymers (WSP) on paint rheological characteristics is discussed. The effect of a paint's surface tension, high shear viscosity and instantaneous low shear viscosity recovery on a coating's flow and levelling and hiding power are examined. An extensive study of WSP in formulations encompassing three latex vehicle types defines the rate of instantaneous viscosity recovery at low shear rates, after cessation of high shear conditions, as the primary factor in a coating's flow and leveling performance. The paint's surface tension and high shear viscosity are not primary factors. The chemical structure of the water-soluble-polymer determines the rate of viscosity recovery in a paint containing a latex of intermediate viscosity at low shear rates. With an increasing solvation capability of the WSP, improved flow and levelling is noted. The weight per cent of the WSP used as thickener is significant in defining viscosities at high shear rates. In a paint formulated to a constant Stormer viscosity, the weight per cent is defined by the thickener's molecular weight. The use of WSP in mixed thickener combinations, i.e. their synergistic influences on the properties of paint films, and the use of Lissajous analysis in low shear strain oscillatory measurements to determine yield stress values directly are discussed.

Keywords

Types and classes of coatings and allied products

  emulsion paint

Raw materials: paint additives
Surface active and rheological agents

  thickening agent

  viscosity control agent

Properties, characteristics and conditions primarily associated with:

  materials in general

  surface tension

  viscosity

  coatings during application

  flow characteristics

  levelling

  sagging

L'importance des polymères hydrosolubles pour la fabrication de peintures-dispersions

Résumé

On discute l'influence de polymères hydrosolubles sur les propriétés rhéologiques de peintures-dispersions. On étudie l'influence de la tension superficielle, de la viscosité sous des contraintes de cisaillement faibles et élevés, ainsi que de l'élévation immédiate de la viscosité (mesurée pour une faible vitesse de cisaillement) après une contrainte de viscosité élevée, sur les propriétés rhéologiques, sur l'étalement et sur le pouvoir couvrant d'une peinture-dispersion. Les essais étendus, effectués sur des polymères hydrosolubles utilisés dans des formules contenant trois dispersions de polymères de types différents, ont démontré que la vitesse d'élévation de la viscosité (mesurée pour une faible vitesse de cisaillement) immédiatement après cessation d'une contrainte de cisaillement élevée est un facteur déterminant des propriétés rhéologiques et des propriétés d'étalement. La tension superficielle et la viscosité sous une forte contrainte de cisaillement ne constituent pas des facteurs déterminants. La structure chimique des polymères hydrosolubles détermine la vitesse de rétablissement de la viscosité d'une peinture contenant une dispersion de polymères de viscosité moyenne sous faible contrainte de cisaillement. Avec l'augmentation du pouvoir de solvatation du polymère hydrosoluble, on observe une amélioration des propriétés rhéologiques et des propriétés d'étalement. La proportion de polymères hydrosolubles employés comme épaississants est importante pour l'explication de la viscosité à une haute vitesse de cisaillement. Si l'on formule une peinture d'une viscosité Stormer constante, la proportion d'epaississant dépend de son poids moléculaire. On examine en outre l'influence de polymères hydrosolubles utilisés en combinaison avec d'autres épaississants et on discute notamment les effets synergistiques sur les propriétés des films. On décrit une méthode de détermination directe des seuils d'écoulement par l'analyse de mesures de vibrations sous de faibles contraintes de cisaillement.

Die Bedeutung wasserlöslicher Polymere für die Herstellung von Dispersionsfarben

Zusammenfassung

Es wird Einfluß wasserlöslicher Polymere auf rheologische Eigenschaften von Dispersionsfarben diskutiert. Untersucht werden an einer Dispersionsfarbe Einflüsse von Oberflächenspannung, Viskosität bei niedrigem und hohem Schergefälle, sowie des unmittelbaren Viskositätsanstieges (gemessen bei niedriger Schergeschwindigkeit) nach hoher Scherbeanspruchung auf Fließeigenschaften, Verlauf und Deckvermögen. Aus der ausgedehnten Untersuchung wasserlöslicher Polymere in Formulierungen, die drei Polymerdispersionen unterschiedlichen Typs enthalten, ergibt sich als wesentlicher Faktor für Fließ- und Verlaufseigenschaften die Geschwindigkeit des Viskositätsanstieges (gemessen bei niedriger Schergeschwindigkeit) unmittelbar nach Beendigung der hohen Scherbeanspruchung. Oberflächenspannung und Viskosität bei hohem Schergefälle sind keine wesentlichen Faktoren. Die chemische Struktur der wasserlöslichen Polymeren bestimmt die Geschwindig-keit des Viskositätsaufbaus der Farbe, die eine Polymerdispersion mittler Viskosität bei niedrigem Schergefälle enthält. Mit steigendem Solvatationsvermögen des wasserlöslichen Polymeren wird eine Verbesserung der Fließ- und Verlaufseigenschaften registriert. Der prozentuale Anteil an wasserlöslichen Polymeren, die als Verdickungsmittel benutzt werden, ist von Bedeutung für die Erklärung der Viskosität bei hoher Schergeschwindigkeit. Formuliert man eine Farbe mit einer konstanten Stormer-Viskosität, dann wird der prozentuale Anteil des Verdickers durch sein Molekulargewicht bestimmt. Ferner wird der Einfluß wasserlöslicher Polymere, die in Kombination mit anderen Verdickungsmitteln verarbeitet werden, untersucht und z. B. synergistische Einflüsse auf Filmeigenschaften diskutiert. Es wird beschrieben, wie aus der Analyse von Schwingungsmessungen bei niedrigen Schubspannungen die Fließgrenzen direkt bestimmt werden können.

Introduction

Refs. 1-7

There are several mathematical treatments[1-6] which relate the flow characteristics of a coating to fundamental parameters. The analysis given below (Equation 1) is available to the reader in a general textbook form[7].

$$t = 0.036 \, \lambda^4 \log \frac{Z_0}{Z_t} \frac{\eta'}{(\sigma-\sigma')X^3} \quad \ldots\ldots(1)$$

In this equation, only four variables are determined by the properties of the coatings being applied: σ the surface tension of the paint; X^3 the coating's film thickness (which is approximated in these studies by the viscosity at 14 000 $\sec^{-1}$ shear rate; σ' the yield stress of the paint; and η' the non-Newtonian viscosity characteristics of that paint. The parameter λ is the wavelength, Z_0 the initial amplitude at time zero and Z_t the amplitude at time t of the brush marks. These latter parameters are held constant in comparative studies. For the reader with additional interest, Orchard[2] provides one of the most comprehensive mathematical analysis of this type. In the present experimental study, the non-Newtonian viscosity, is studied in low oscillatory shear strain measurements. Analysis of typical data (Fig. 2) reveals that the storage modulus, G'—generally related to an elastic function of the paint—is the variable that exhibits substantial changes during the instantaneous recovery. This observation is consistent with the analysis by Biermann[4], who theoretically deduced that "the elasticity of the fluid thus has a reducing effect on the levelling velocity". Noting this agreement, the recovery responses after Fig. 5 are recorded as the complex modulus. In this article, the surface tension of the paint, high shear viscosity (which reflects film thickness) and the viscosity recovery after cessation of the high application shear rates are examined for their contribution to the coating's properties. In addition, a procedure for determining the yield stress value of a paint by Lissajous analysis is discussed.

Experimental

Refs. 8-11

The surface tensions of commercial paints containing variations in both thickener and vehicle were determined by the pendant drop method[8]. The viscosity profiles of the thickened paints as a function of shear stress and shear rate were determined with the Weissenberg rheogoniometer and the Ferranti Shirley viscometer[9]. Utilisation of the Weissenberg rheogoniometer to approximate high shear brushing conditions, followed by low shear strain oscillatory measurements and the actual performance rating of flow and levelling characteristics of a coating using the draw-down bar and profilometer techniques were all in accord with the procedures described by Dodge[10]. The usual formulation procedures for paint preparation[11] were followed in the comparative studies; only the concentration of the water-soluble polymer (WSP) was varied. All paints were made to an approximate Stormer viscosity of 90KU*, except those noted otherwise in Table 4.

Surface tension

Ref. 8

A fully formulated paint usually contains excess amounts of surfactant. Therefore, it might be considered that the surface tensions of all paints are equal. It was envisaged that because

*Krebs Units (empirical)

of the high-energy surfaces present (titanium dioxide, calcium carbonate, etc.), the surface tension of various paints could change with variations in formulation ingredients (higher PVC values and lower surfactant concentrations). This possibility is indicated in Table 1 using a vinyl acetate/acrylic latex vehicle (UCAR 360-Union Carbide Corp) in an interior paint formulation (I-1212).

In order to quantify the relationship between PVC and surfactant levels, the surface tension of UCAR 360 latex was measured. UCAR 360 is synthesised in the presence of a surfactant. The addition of excessive surfactant which would be included in the interior paint formulation does not lower the surface tension of the latex. However, UCAR 360 in the interior I-1212 formulation without the addition of the formulation surfactant (Tergitol NPX-Union Carbide Corp) shows a higher surface tension (Table 1). If the amount of surfactant used in any particular paint formulation were not excessive, it would be conceivable that the surfactant could preferentially be adsorbed on the high energy surfaces in the formulation and this could allow the WSP to contribute to the overall surface tension of the paint.

Table 1
Pendant drop surface tension data

Sample	Surface tension (dyn/cm) 30 minutes	60 minutes
Vinyl acetate: acrylic latex TS54.8	33.3	33.2
Vinyl acetate: acrylic latex with Tergitol NPX	33.6	33.1
I-1212 Formulation without Tergitol NPX	35.8	35.7

The influence of water-soluble polymers on the flow and levelling characteristics of a paint was determined with a series of paints differing only in the type and amount of thickener necessary to produce a paint with a Stormer viscosity of 90KU. The surface tension data are presented in Table 2. The various thickeners represent a wide range in

Table 2
Surface tension-variable thickening agent study: interior I-1212 formulation

Sample	Surface tension (dyn/cm) 30 minutes	60 minutes
I-1212: Poly(ethylene oxide)	34.0	34.4
I-1212: Hydroxyethyl cellulose M. S. = 2.0	34.2	34.2
I-1212: Hydroxyethyl cellulose M. S. = 2.5	34.1	34.1
I-1212: Hydroxypropyl methyl cellulose	33.1	33.3
I-1212: Hydroxyl cellulose	33.6	33.5
I-1212: Propyl/acrylic acid copolymer	32.5	33.0

I-1212 density range: 1.414—1.434
Mean value = 1.426 with std. dev. = 0.00621
used in surface tension calculations

surface activity[8]. All paints, except one, exhibit intermediate flow and levelling characteristics. The one vinyl/acrylic latex vehicle which levelled well was thickened with the acrylic acid copolymer thickener (Acrysol G–110—Rohm and Haas). This paint had the lowest surface tension, giving a preliminary indication that this parameter is not a dominant factor in

controlling the rate of flow and levelling. Similar studies with other latex vehicles in different paint formulations are summarised in Table 3. The vinyl acetate latex (UCAR 130-Union Carbide Corp.) was chosen in an interior formulation (I-1174) because it exhibited excellent flow and levelling. The all-acrylic formulation (UCAR 370-Union Carbide Corp.) in an exterior paint (E-1206) was chosen because it exhibited poor flow and levelling. The all acrylic exterior paint possesses a high surface tension even with the addition of excess surfactant required in the formulation. This gives additional insight into the minor role of surface tension in determining the rate at which levelling is accomplished.

Table 3

Surface tension—variable thickening agent study

Sample	Surface tension (dyn/cm) 30 minutes	60 minutes
I-1174: Poly(ethylene oxide)	33.4	33.5
I-1174: Hydroxyethyl cellulose	33.3	33.4
I-1174: Hydroxypropyl methyl cellulose	34.2	34.3
E-1206: Acrylic acid copolymer	37.8	37.8
E-1206: Poly(ethylene oxide)	37.9	38.3
E-1206: Hydroxyethyl cellulose	36.0	36.0
E-1206: Hydroxypropyl methyl cellulose	38.0	38.0

Film build

The viscosity at high shear rates (14 000 sec^{-1}) was used as an approximate guide to film thickness (Equation 1). A summary of the studies in this area are shown in Table 4. Cellulose ethers are very efficient in their ability to thicken a paint to a 90KU value. Two types of studies are noted in Table 4: in one the WSPs were employed in amounts sufficient to thicken the paint to 90KU; in the other, a weight percentage equivalent to that required for cellulose ethers was used. The data indicate that viscosities at high shear rate as a guide to film thickness do not constitute one of the primary variables in the flow and levelling characteristics of paint.

Low shear oscillatory measurements

Refs. 10, 12

The procedure of shearing a paint at approximately 3 000 sec^{-1} for 30 seconds to break down the paint's structural components and then studying the viscosity recovery at low oscillatory shear strains, instantaneous with cessation of the steady state shearing force, has been described by Dodge[10]. In Fig. 1,
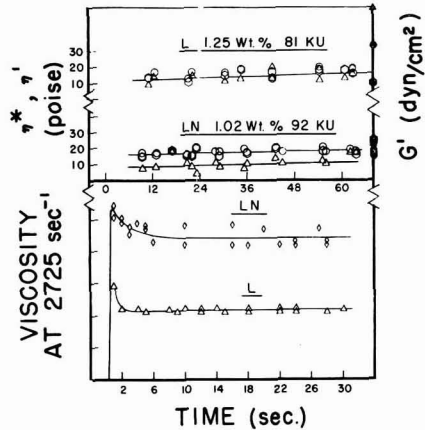

Fig. 1.

this procedure is illustrated in one graph for the I-1212 formulation thickened with a maleic acid/methyl vinyl ether copolymer (Thickeners L and LN-GAF Corp.). The paint takes six minutes to recover its initial viscosity; because of the slow viscosity recovery the paint flows well and it also exhibits sagging characteristics. In Fig. 2 a similar analysis (showing only the oscillatory data) on a semi-gloss paint formulation, thickened with hydroxyethyl cellulose (Cellosize QP-52 000 and QP-09-Union Cardibe Corp) is illustrated. In low oscillatory shear strain measurements, recovery can be analysed in terms of a complex viscosity or modulus (η^* or G^*, respectively), a dynamic viscosity (η') and a storage modulus (G')[12]. The responses shown in Fig. 2 are

Table 4

Paint formulation studies

Form: thickener	Concentration (weight %)	Stormer (KU)	Viscosity High shear (poise) 14 000 sec^{-1}	Application tests Levelling[1]	Sagging[2]
I-1174: Poly(vinyl alcohol) ca. 11% Acetate	0.40	58	0.23	1	4
Acrylic acid copolymer	0.40	61	0.31	1	5
Poly(ethylene oxide)	0.40	63	0.67	2	1
I-1212: Acrylic acid copolymer	1.18	89	1.29	2	1
I-1174: Acrylic acid copolymer	3.00	88	1.96	3	1
Hydroxyethyl cellulose	0.40	98	0.85	4	1
Hydroxypropyl methyl cellulose	0.40	104	0.98	4	1
I-1212: Hydroxypropyl methyl cellolose	0.36	90	0.88	4	1
Poly(ethylene oxide)	1.16	90	1.50	4	1
E-1206: Hydroxyethyl cellulose	0.40	88	0.42	5	1
Acrylic acid copolymer	0.40	67	0.32	5	1
Poly(ethylene oxide)	0.40	64	0.33a	5	1
Poly(vinyl alcohol) ca. 11% Acetate	0.40	60	0.13	5	4
Hydroxypropyl methyl cellulose	0.40	88	0.46	5	1

[1]Visual rating: 1 equals excellent, 5 represents poor levelling.

[2]Visual rating: 1 indicates no sagging, 5 is excessive.

representative of most paint formulations. The most pronounced recovery with time is noted in the storage modulus (G'), generally related to an elastic function of the paint; the dynamic viscosity (η') shows relatively little change in comparison. A discussion of the various rheological parameters and the utility of low oscillatory shear measurements under various experimental conditions will be the subject of a future paper. In this study, a displacement amplitude of $\pm28\mu m$ was employed. Using a 1° cone angle of 7.5 cm diameter, a shear strain of 0.04 was obtained which, as an approximation at 0.3Hz, gives a shear rate value of 0.08 sec⁻¹. This is, generally, accepted as the approximate shear rate during levelling in a paint after it has been applied by brush or roller.
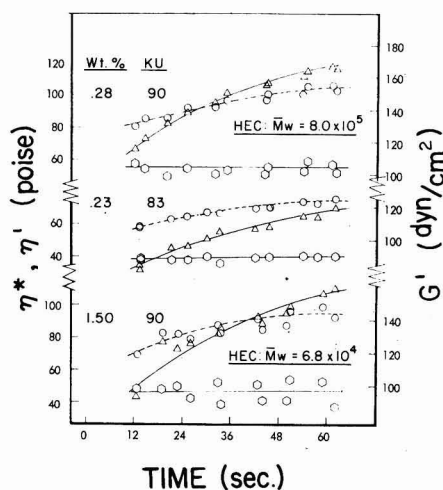

TIME (sec.)

Fig. 2

The data shown in Fig. 2 indicate that although varying amounts of the same chemical structure are required for different molecular weight thickeners to produce an equivalent KU, there is no substantial variation within the limits of experimental error in their viscosity or modulus recovery responses. The magnitudes of the rheological responses decrease with lesser amounts of thickener, i.e. with decreasing Stormer viscosities. The data shown in Figs. 1 and 2 summarise a systematic study of commercial and experimentally synthesised WSPs. This study utilising a chemical modelling approach will be detailed in a later publication. The study

demonstrates that the flow and levelling characteristics of a paint are related to its viscosity recovery after shear and that this recovery is influenced, in a latex paint of intermediate viscosity, by the solvation characteristics of the WSP.

Mixed thickener studies

Molecular weight variations. The effect of molecular weight of the WSP on paint rheological properties was studied in a hydroxyethyl cellulose (HEC) series (Cellosize QP-52 000, QP-300 and QP-09, representing weight-average molecular weights of *ca.* 8.0×10^5, 3.0×10^5 and 6.8×10^4 in turn. Using the same paint grind, percentages of the high molecular weight material were used to thicken partially different paints. By cutting the percentages of the higher molecular weight HEC to 75, 50 and 25, greater amounts of the lower molecular weight hydroxyethyl cellulose materials were required to reach a constant Stormer value of 90KU. The amounts required are shown in Table 5.

The steady state viscosities at shear rates approximating brushing application conditions (14 000 sec⁻¹), and at lower shear rates possibly reflecting roller application conditions (1 800 sec⁻¹), are plotted in Fig. 3 against the percentage of high molecular weight HEC used; that is, as a function of
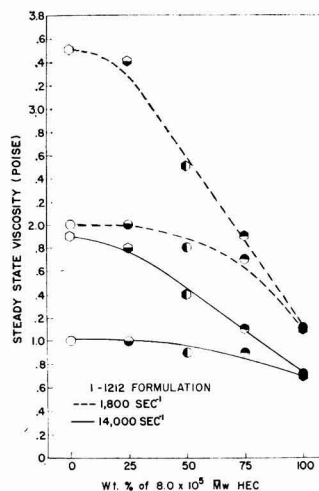
Fig. 3

Table 5

Hydroxyethyl cellulose, molecular weight mixture study: I-1212 formulation

Thickener molecular weight, $\overline{M}_w$	Concentration (weight %)	Secondary thickener molecular weight, $\overline{M}_w$	Concentration (weight %)	Stormer KU (24 hours)
8.0×10^5	0.36			92
	0.25	3.0×10^5	0.25	91
	0.17		0.42	90
	0.08		0.50	91
			0.71	90
	0.25	6.8×10^4	0.50	91
	0.17		1.00	92
	0.08		1.41	91
			1.91	90

the thickener's molecular weight distribution. The greater amounts of lower molecular weight HEC increase the high shear viscosities. As the shear rate is decreased, the influence of the molecular weight becomes more pronounced. The relationship of steady state viscosities to the total weight percentage of hydroxyethyl cellulose (and consequently the molar concentration) is presented in a more quantitative form in Fig. 4. The data are grouped into two linear relationships defined by the shear rate.
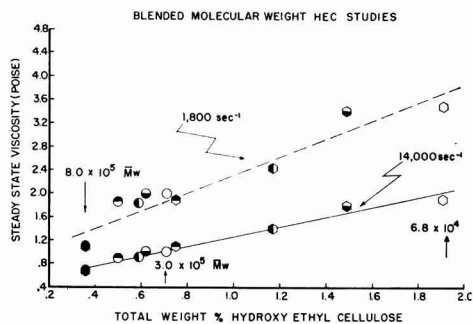
BLENDED MOLECULAR WEIGHT HEC STUDIES

Fig. 4

After cessation of steady state shear conditions, the recovery response as reflected by the complex modulus (G^*) does not distinguish (within experimental error) a molecular weight influence (Fig. 5). A study of the surface profiles of the films obtained from threaded draw-down bars shows no significant flow and levelling differences within the limits of experimental error (Fig. 6). In the draw-down measurements, the film thickness is kept constant ($X = 0.762$mm). In multiple coat brushouts, the surface profile data demonstrate minor differences (Fig. 7). The data in Fig. 7 (in the 6.8×10^4 $\overline{M}_W$ blend series) cover progressive film thicknesses from 0.058 to 0.081mm. In agreement with the data in Table 4, film thickness does not appear as important a parameter in flow and levelling as does the complex modulus recovery.
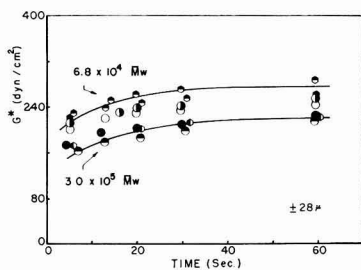

Fig. 5

Chemical structure variation. By increasing the solvation characteristics of the WSP, improved flow and levelling in a coating can be obtained. A study of mixed thickeners was undertaken in order to obtain flow and levelling without sagging. The amounts of materials employed in this series to produce an approximate 90KU paint are shown in Table 6. As before, the amount of HEC was decreased in 25 per cent steps and additional amounts of synthetic thickener added to reach a 90KU Stormer value. The synthetic thickener used in this particular study was a maleic acid/methyl vinyl ether

PAINT (I-1212) DRAWDOWN BAR SURFACE PROFILES
HEC MOLECULAR WEIGHT BLENDS

CLEVITE BRUSH SURFANALAZER 150
THREADED DRAWDOWN BAR
0.762mm DEPTH, 60° THREADS

Fig. 6

PAINT (I-1212) BRUSHOUT SURFACE PROFILES
HEC MOLECULAR WEIGHT BLENDS
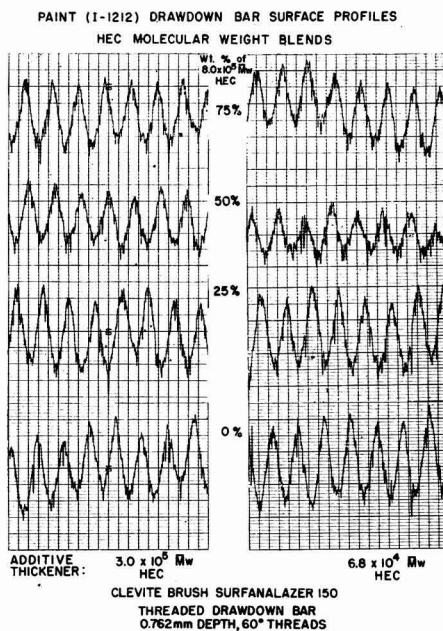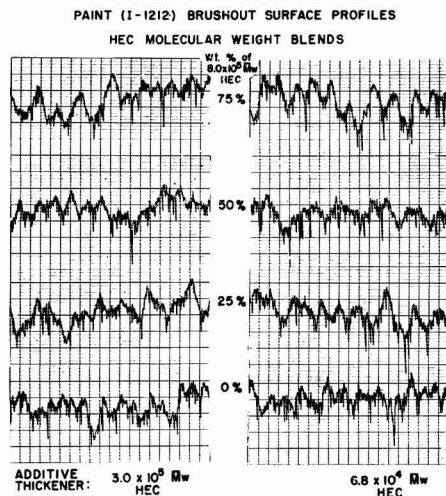
Fig. 7.

copolymer (Thickener LN (an ammonium salt)—GAF Corp). Unlike the mixed molecular weight studies, the mixing of chemically different WSPs, where one polymer has a high degree of solvation, does lead to changes in the complex modulus (G^*) with changes in the percentage of high molecular weight HEC (Fig. 8). The changes in the low shear modulus data are reflected in the surface analysis of the draw-down paint films (Fig. 9). Additional studies were conducted between the fifty and seventy-five per cent HEC intervals; the draw-down profiles are shown in Fig. 10. The data (Fig. 10)

Table 6

Chemical structure mixture study: I-1212 formulation

Thickener	Concentration (weight %)	Additional thickener	Concentration (weight %)	Stormer KU (24 hours)
HEC[1]	0.36			92
	0.25	MVE:MAAS[2]	0.36	93
	0.17		0.72	91
	0.08		1.02	90
			1.20	88

[1]Hydroxyethyl cellulose, $\overline{M}_W = 8.0 \times 10^5$
[2]Methyl vinyl ether/maleic acid copolymer

indicate that in the area of 60 to 65 per cent hydroxyethyl cellulose (mixed with a synthetic polymer of high solvation characteristics), a paint with excellent levelling characteristics
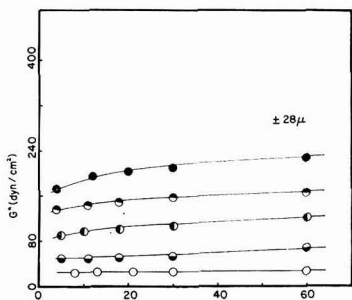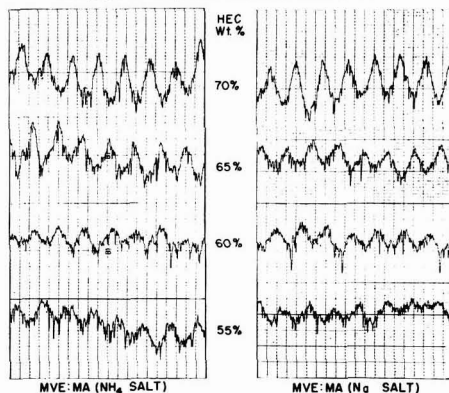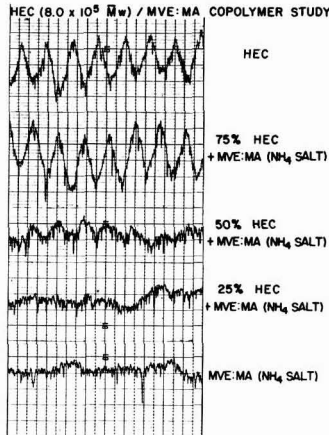

Fig. 8.

PAINT (I-1212) DRAWDOWN BAR SURFACE PROFILES
HEC (8.0 x 10⁵ M̄w) / MVE:MA COPOLYMER STUDY

CLEVITE BRUSH SURFANALAZER 150
THREADED DRAWDOWN BAR
0.762mm DEPTH, 60° THREADS

Fig. 9.

PAINT (I-1212) DRAWDOWN BAR SURFACE PROFILES
HEC (8.0 x 10⁵ M̄w) / MVE:MA COPOLYMER STUDY

CLEVITE BRUSH SURFANALAZER 150
THREADED DRAWDOWN BAR
0.762mm DEPTH, 60° THREADS

Fig. 10

is obtained, which does not possess the substantial sagging characteristics usually inherent in paints thickened with well-solvated synthetic polymers alone. The data refer to studies in an intermediate low shear viscosity latex paint system.

WSP-thixotropic agent mixtures. The use of an attapulgite clay (Attagel 50-Engelhard Corp.) imparts substantially different rheological characteristics in the instantaneous recovery response of a paint (Fig. 11). The amounts of materials required for a mixture study similar to those reported above are listed in Table 7. Unlike low molecular weight polymers, inorganic materials do not contribute to the high shear viscosity of a paint formulation (Fig. 12). Such materials are insoluble and do not contribute to the viscosity of the mixture on a basis of hydrodynamic volume. In accordance with the solvation concept, it would be anticipated that an increase in low shear strain recovery response would be noted, and this was in fact observed (Fig. 13). Changes in the low shear complex modulus (G^*) are reflected in the profilometer results for paint applied with a draw-down bar (Fig. 14).

Table 7

Thixotropic agent mixture study: I-1212 formulation

Thickener	Concentration (weight %)	Additional thickener	Concentration (weight %)	Stormer KU (24 hours)
HEC[1]	0.36			94
	0.27	Attapulgite clay	0.41	90
	0.18		1.28	88
			2.60	85

[1]Hydroxyethyl cellulose, $\overline{M}_w = 8.0 \times 10^5$

Fig. 11.

Fig. 13.

PAINT (I-1212) DRAWDOWN BAR SURFACE PROFILES

CLEVITE BRUSH SURFANALAZER 150
THREADED DRAWDOWN BAR
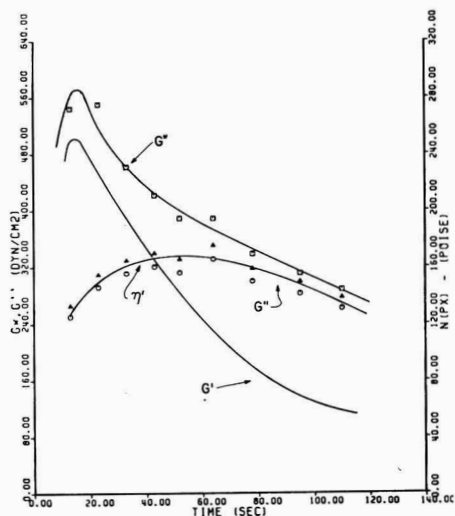0.762mm DEPTH, 60° THREADS

Fig. 14.
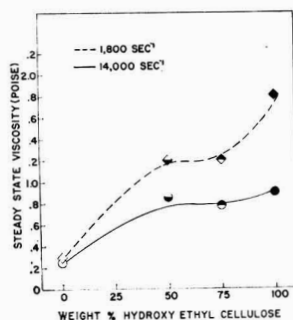
Fig. 12.

Yield stress values

Ref. 13

Lissajous analysis[13], using an oscilloscope to measure the strain and stress measurements, offers the possibility of determining directly the yield stress values. Examples of three different thickeners in two different formulations are illustrated in Figs. 15-17. The yield stress values can be obtained by calibrating the stress-strain curve, or by changing the amplitude of displacement until the Lissajous figures assume non-elliptical shapes. The examination of yield stress values and their interactions with the parameters affecting the flow and levelling properties of a paint as examined here will be discussed in a future paper.
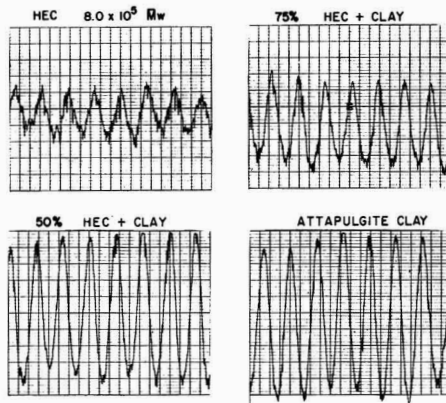
I-1212   FORMULATION
HYDROXY ETHYL CELLULOSE
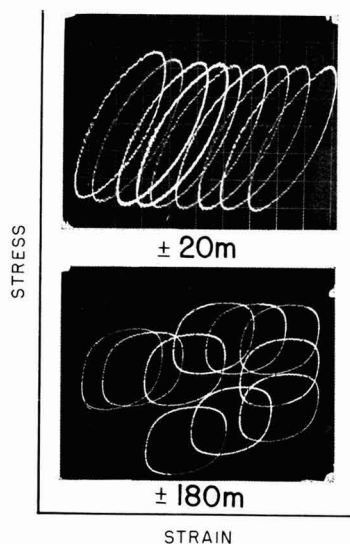
FORMULATION
CELLULOSE-CLAY GRAFT THICKENER
I-1174   I-1212

± 20m

± 180m

STRAIN

LISSAJOUS FIGURES TAKEN IN
TIME SEQUENCE

Fig. 15.

± 20m   ± 20m

± 180m   ± 180m

LISSAJOUS FIGURES TAKEN IN
TIME SEQUENCE

Fig. 17

E-1206   FORMULATION
POLY(ETHYLENE OXIDE)

± 20m

± 180m

STRAIN
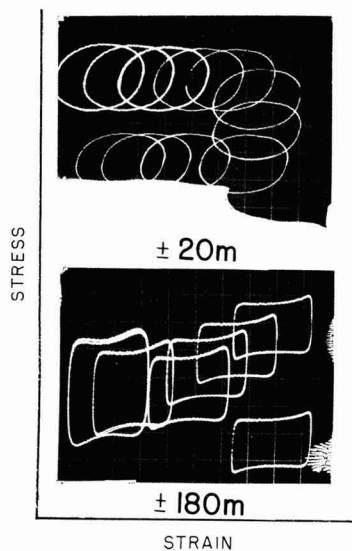
LISSAJOUS FIGURES TAKEN IN
TIME SEQUENCE

Fig. 16.

Conclusions

In latex systems possessing high viscosity or modulus charac-
teristic at low shear rates, a water-soluble polymer, functioning
as a thickener for the system, cannot improve the coating's
flow and levelling properties; however, in intermediate or low
viscosity latex systems, the thickener can influence those
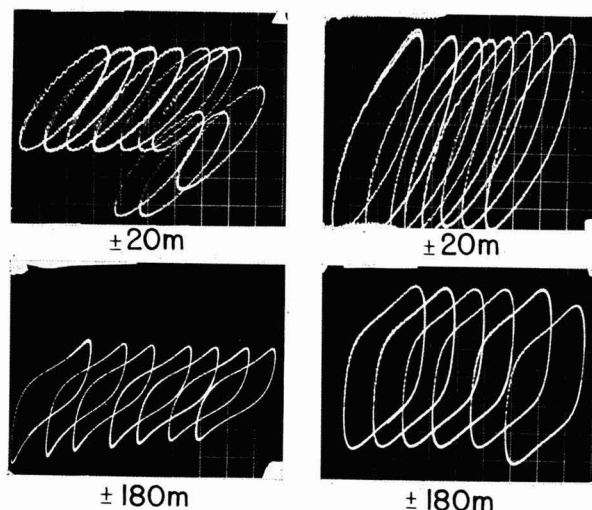characteristics substantially. The greater the solvation
properties of the water-soluble polymer—that is, the less the
inter-association of the polymer—the better will be the
coating's flow and levelling. By using mixed thickener
systems, it is possible to obtain adequate flow and levelling
without detrimental sagging of the paint film. By lowering the
molecular weight of the thickener, greater viscosities at high
shear rates can be obtained. Paint surface tensions, high
shear viscosities and the instantaneous complex viscosity or
modulus recovery characteristics have been examined. Only
the latter instantaneous parameters were observed to be
primary variables in determining a coating's flow and levelling
characteristics.

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Analysis of polyurethane resins: A co-operative IUPAC study*

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Summary

In order to assist the selection of the appropriate techniques for the analysis of modern synthetic resins, a co-operative exercise was carried out by five European laboratories, requiring the analysis of four polyurethane resins of undisclosed compositions using techniques chosen at their discretion. The results showed that there were satisfactory techniques for identifying the isocyanates, polyol and fatty acid components (provided these were not changed during manufacture of the resin) and estimating the phthalic and isocyanate content of urethane alkyds.

Keywords

Raw materials:

  binders (resins, etc)

    urethane resin

  used in manufacture or synthesis of ingredients for coatings

    fatty acid
    glycerol
    pentaerythritol
    phthalic anhydride

Processes and methods primarily associated with analysis, measurement or testing

  aminolysis
  gas chromatography
  hydrolysis
  infrared analysis
  Kjeldahl method
  nuclear magnetic resonance spectroscopy

L'analyse des résines polyuréthannes

Résumé

Afin de faciliter la sélection des techniques convenables à l'analyse des résines synthétiques modernes, une étude coopérative a été effectuée par cinq laboratoires européens dont chacun a choisi selon son gré les techniques pour analyser quatre résines polyuréthannes de composition inconnue. Les résultats montraient qu'il existe des techniques satisfaisantes pour identifier les constituants tels que les isocyanates, polyols et acides gras (pourvu qu'ils ne fussent pas transformés lors de la fabrication des résines), et pour doser les teneurs en radical phtalique et en isocyanate des alkydes uréthannes.

Polyurethanharzanalyse

Zusammenfassung:

Um die bestgeeigneten Techniken für die Analyse von modernen Kunstharzen ausfindig zu machen, wurde von fünf europäischen Laboratorien eine kooperative Untersuchung vorgenommen. In dieser waren vier Polyurethanharze, deren Zusammensetzung nicht bekanntgegeben worden war, unter Benutzung selbst gewählter Methoden zu analysieren. Die Ergebnisse zeigten, dass brauchbare Methoden zur Identifizierung von Isozyanaten, Polyol- und Fettsäurekomponenten bestehen (vorausgesetzt, dass diese nicht im Laufe der Herstellung des Harzes verändert worden waren), und der Gehalt an Phthalsäure und Isozyanat in Urethanalkyden bestimmt werden kann.

Introduction

Refs. 1-3

Early co-operative studies organised by the Organic Coatings Section of IUPAC resulted in Recommended Methods for the Analysis of Drying Oils[1] and Alkyd Resins[2], and a report on the efficiency of modern analytical techniques for the analysis of thermosetting acrylic resins[3]. A further study similar to the one last mentioned has now been carried out on a set of single-pack polyurethane resins, in some instances using methods from ref. 2. The same procedure was followed, namely, the resins whose compositions were not disclosed until the end of the work, were distributed to the individual laboratories to analyse by techniques chosen at their discretion. The laboratories taking part were:

Cray Valley Products Ltd.	(Gt. Britain)
Sadolin & Holmblad Ltd.	(Denmark)
Laboratoire Profession IVP.	(Belgium)
TNO, Verfinstituut	(Netherlands)
Paint Research Association	(Gt. Britain)

One of the polyurethane resins was of the moisture-curing and three were of the oil-modified oxidising type; their compositions are given in Table 1.

The techniques used by the laboratories included infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, gas chromatography, various hydrolytic procedures and chemical methods.

The findings of the laboratories and the techniques used are summarised in Table 2.

Table 1
Composition of the single-pack polyurethanes for the co-operative analysis (weight %)

	Resin *A*	Resin *B*..............(%)	Resin *C*............(%)		Resin *D*..............(%)
Oils		Safflower 68.0	Soya bean 48.5 Dehydrated castor 16.5		Linseed 70.0
Polyols	Polypropylene glycol ether Trimethylolpropane 1,4-Butane diol	Pentaerythritol 7.6	Pentaerythritol 12.4		Pentaerythritol 10.5
Isocyanates	Toluene diisocyanate	Dicyclohexyl methane diisocyanate 25.1	Toluene diisocyanate 11.9		Toluene diisocyanate 13.5
Dibasic acids	—	—	Phthalic anhydride 12.2		Phthalic anhydride 6.9

Table 2
Analysis of the single-pack polyurethanes. Results from the laboratories (weight %)

Laboratory	Methods used	*A*	*B*	*C*		*D*	
(i)	IR Saponification/ IR/TLC/ GLC Acid hydrolysis/IR Kjeldahl Other chemical methods	Polypropylene glycol ether Trimethylolpropane (Dipropyleneglycol?)* Toluene 31 diisocyanate	Linoleic rich oil 67–75 Pentaerythritol 6.8 Non-aromatic 20.1 diisocyanate	Soya bean oil Pentaerythritol Toluene diisocyanate Phthalic anhydride	62 11.9 16.7	Drying oil Pentaerythritol Toluene diisocyanate Phthalic anhydride	67 9.5 11.8 8.6
(ii)	IR Methanolysis/GLC Saponification Aminolysis/GLC Acid hydrolysis/IR Kjeldahl Other chemical methods	Polypropylene glycol ether Trimethylolpropane Toluene 53 diisocyanate	Safflower oil Pentaerythritol (Dipentaerythritol) Dicyclohexylmethane diisocyanate	Soya bean oil Pentaerythritol Toluene diisocyanate Phthalic anhydride	60 17.0 10.0 11.7	Linseed oil Pentaerythritol Toluene diisocyanate Phthalic anhydride	70 20.0 11.9 7.3
(iii)	Saponification IR/TLC/GLC Other chemical methods	1.4-Butane diol (2.3-Butane diol) (1.2-Butane diol) Toluene diisocyanate	(Polypropyleneoxide- polyester) (Hexane diisocyanate)	Soya bean oil (4.4-Diphenylmethane diisocyanate)		Linseed oil Toluene diisocyanate (4.4-Diphenylmethane diisocyanate)	
(iv)	IR Saponification Aminolysis/ GLC/TLC Kjeldahl	Polyetherpolyol Trimethylolpropane 1.4-Butane diol Toluene 29 diisocyanate	Oil 55 Pentaerythritol 5.7 (1.5-Naphthalene diisocyanate?)	Soya bean oil Pentaerythritol Toluene diisocyanate Phthalic anhydride	62 12.5 9.5 16	Linseed oil Pentaerythritol Toluene diisocyanate Phthalic anhydride	70 10.1 13.9 15
(v)	IR Methanolysis/GLC Saponification Aminolysis/GLC Acid hydrolysis/ NMR Kjeldahl	Polypropylene glycol ether Toluene diisocyante	Safflower oil Dicyclohexylmethane diisocyanate 22.5	Soya bean oil Pentaerythritol Toluene diisocyanate Phthalic anhydride	 11.5 11.5	Linseed oil Pentaerythritol Toluene diisocyanate Phthalic anhydride	 12.8 6.8

*A question mark indicates that the laboratory was in doubt and a bracket that the component should not have been present.

Infrared spectroscopy

Refs. 2, 4, 6

An infrared spectroscopic examination of the resins, (for example, as films on potassium bromide plates) was made by four of the laboratories. This showed clearly that resin *A* had a strong isocyanate band at 2270cm^{-1} and was likely to be a moisture-curing polyurethane; sample *B* was free from

moisture-curing polyurethane; simple *B* was free from aromatic bands and was, therefore, an aliphatic urethane oil; and resins *C* and *D* had bands characteristic of *o*-phthalic acid and an aromatic isocyanate and hence were aromatic urethane alkyds.

The nature of the aliphatic isocyanate used in resin *B* could not be deduced directly from the infrared spectrum and all

laboratories were not certain of the aromatic isocyanate in samples *C* and *D*. Laboratory (v) correctly identified the toluene diisocyanate (TDI) in these, giving the table of diagnostic bands shown in Table 3.

Table 3
Infrared spectroscopic bands from resins C and D

(cm⁻¹)	Characteristic
3005 2950 2920 2850	Fatty acids (when these bands are strong, with the 2920cm⁻¹ bands being the strongest or second strongest band in the spectrum)
1742	Urethane and ester C=0 stretch
1620	TDI ring stretch
1600	TDI ring stretch masks the much weaker *o*-phthalic ring stretch
1581	*o*-Phthalic ring stretch
1535	Urethane amide II
1275	*o*-Phthalic ester
1227	Aromatic urethane
1040	*o*-Phthalic ester
1001	TDI
815	TDI aromatic o.o.p. deformation
765	TDI urethane vibration
740	*o*-Phthalic o.o.p. deformation
723	Fatty acids CH₂ rock
704	*o*-Phthalic ring vibration

In resin *C*, the *o*-phthalic bands at 1040, 1275 and 1581cm⁻¹ appear as distinct bands, but in resin *D*, with less *o*-pthalic content, they appear as shoulders on the stronger urethane vibrations.

Infrared spectroscopy was also valuable in combination with other techniques. Examination of the unsaponifiable matter after saponification of resin *A* confirmed the presence of a polyol ether (see below) and trimethyl propane. The infrared spectrum of the amine obtained after acid hydrolysis indicated the nature of the aliphatic isocyanate in resin *B* (see "Acid hydrolysis" below) and could also confirm the presence of toluene diisocyanate in resins *C* and *D*.

Methanolysis/gas chromatography

Ref. 2

For identification of the acids, whether fatty acids or dibasic acids, most of the laboratories converted the acids in the resins directly to their methyl esters and subjected them to gas chromatographic analysis. Different procedures have been followed, but none of them gave better results than method No. 7—Qualitative analysis of carboxylic acids in alkyd resins by gas chromatography[2].

The safflower oil (linoleic rich oil) in resin *B* was identified by three laboratories, the soya bean oil in resin *C* by five laboratories, the linseed oil in resin *D* by four laboratories, and the phthalic anhydride in resin *C* and *D* by four laboratories. None of the laboratories was able to identify the dehydrated castor oil in resin *C*, the most reasonable explanation being that the characteristic conjugated fatty acids had been lost during preparation of the resin. All things considered, methanolysis followed by gas chromatography is a useful technique for identification of carboxylic acids in single-pack polyurethanes.

Saponification

Refs. 2, 4, 5

Quantitative analysis of the fatty acid content of resins *B*, *C* and *D* was carried out by only two laboratories, and analysis of the content of resins *C* and *D* by three laboratories; these laboratories used a saponification technique for determination of the fatty acid content. For resins *C* and *D* there is good agreement between the oil content found and the stated oil content. For resin *B*, one of the laboratories found much too low an oil content, but this result was obtained using a gelled sample.

The results obtained were checked in two of the laboratories by calculating the oil from the content of glycerol, assuming that glycerol was introduced only as oil. These laboratories used method No. 5—Fatty acids content[2].

Although the number of results reported here is limited, it seems justified to recommend the use of this method for determination of the fatty acids content in single-pack polyurethanes.

Determination of the phthalic anhydride content in resins *C* and *D* was carried out in four laboratories. The laboratories (i) and (iv) used a saponification method similar to method 4— Phthalic anhydride content[2]. This method gave too high results, probably because the potassium phthalic monoalcoholate is contaminated to varying degrees with undecomposed polyurethane. The undecomposed resin can give rise to error, either by contaminating the phthalate in the crucible, or by causing it to adhere to the sides of the reaction flask. These sources of error can be eliminated by using the ASTM-D 1306 method of estimation of the phthalic anhydride content as non-stoichiometric lead phthalates; this method has been used by the laboratories (ii) and (v) with good results.

Saponification of the moisture-curing polyurethane resin *A* was reported from laboratories (i) and (ii). This resin caused some trouble because it was partially gelled when the laboratories received the samples. Laboratory (i) used a normal absolute alcoholic (1N) KOH saponification resulting in an unsaponifiable fraction, the IR-spectrum of which showed a polyether-urethane. This fraction was hydrolysed with a 1:1 mixture by volume HCl:water at 150°C in a pressure tube for 18 to 21 hours, yielding polypropylene glycol ether, the mean molecular weight of which was determined as about 750 by vapour pressure osmometry. Laboratory (ii) carried out saponification with 40 per cent aqueous NaOH for several hours using a method given by David[4]. The IR-spectrum of the unsaponifiable portion revealed polyether polyol. This fraction was further analysed by gas chromatography of the TMS-derivative according to Corbett et al[5]. From the gas chromatogram, the mean molecular weight of the polypropylene-glycol ether was calculated to be about 900.

Aminolysis/chromatography

Ref. 6

For identification, and to some extent for semi-quantitative analysis of the polyols, different methods have been used. Since no method used gave better results than method No. 8— Identification and semi-quantitative determination of polyols in alkyd resins by gas chromatography[2], the results obtained by this combination of aminolysis and GLC on polyolacetates will be discussed in detail.

Three laboratories (ii), (iv) and (v) used this method in order to identify the polyols used in resins *B*, *C* and *D*. Glycerol was identified in all cases and pentaerythritol in eight out of nine cases. Two laboratories (ii) and (iv) tried this method for semi-quantitative analysis of pentaerythritol in resins *B*, *C* and *D*. Laboratory (iv) succeeded, as can be seen by comparison of Tables 2 and 1, but laboratory (ii) was not successful.

Two laboratories (ii) and (iv) used the method mentioned for identification of the polyols in resin *A*. Laboratory (iv) succeeded in finding both trimethylolpropane and 1,4-butanediol, but laboratory (ii) did not identify the latter because of lack of a reference material. On the whole, it seems justified to recommend the above mentioned method for identification of polyols in single-pack polyurethanes.

One laboratory used an aminolysis thin layer chromatographic procedure as described in the standard methods published by the Verfinstituut T.N.O.[6] using silica gel plates and tert- or iso-amyl alcohol solvents to identify the polyols, namely trimethylol propane in resin *A* and pentaerythritol and glycerol in resins *B*, *C* and *D*.

Acid hydrolysis/NMR spectroscopy or IR spectroscopy

The NMR spectra of the original polyurethanes are too complex for direct interpretation and this technique is best carried out on the amine hydrochlorides. The technique used by laboratory (v) is described in Appendix A.

Identical NMR spectra were obtained from the amine hydrochlorides from urethane resins *A*, *C* and *D*. The details are tabulated below:

Chemical shift (τ)	Multiplicity	Integration
2.49	Singlet	x units
5.28	Singlet	—
7.62	Two peaks	x units

The large peak at 5.28τ was assigned to the residual protons in the solvent and the labile protons of the sample. The chemical shift of the 2.49τ peak indicated the presence of aromatic ring protons, whilst the 7.62τ peaks indicated aliphatic substitution. Integration of the peaks showed that the sample contained equal numbers of aromatic and aliphatic protons. The spectrum suggested two possible structures, tolylene diamine dihydrochloride, or xylylene diamine dihydrochloride. The latter alternative was ruled out as the predicted chemical shift of the methylene protons would be much lower than 7.62τ. This chemical shift is, however, the expected value for a methyl group on an aromatic ring. The two peaks are due to the slightly different chemical shift of the methyl groups of the 2 : 4 and 2 : 6 isomers.

The isocyanates in *A*, *C* and *D* were identified, therefore, as tolylene diisocyanate. The NMR of the amine hydrochloride isolated from urethane *B* is tabulated below.

Chemical shift (τ)	Multiplicity	Integration
5.3	Singlet	—
6.0 –7.0	Broad hump	1 x units
7.85–8.90	Multiplet	10 x units

The 5.3τ peak once again corresponded to the labile and solvent protons. The chemical shift and the broad structure of the 6.0–7.0τ peak was characteristic of aliphatic protons adjacent to nitrogen atoms. The absence of any peaks below 5 showed that the compound does not contain any aromatic or unsaturation protons. The complex structure of the 7.85–8.90 multiplet suggested a cyclohexane ring structure. The integral measurements showed that the majority of protons in the compound were on the cyclohexane ring. Only one structure was found that would give such a spectrum. This was dicyclohexylmethane diaminedihydrochloride. The isocyanate in urethane *B* was identified, therefore, as dicyclohexylmethane diisocyanate.

The amine hydrochlorides obtained could also be identified from their infrared spectra provided reference spectra were available and laboratory (ii) identified the dicyclohexylmethane diisocyanate in resin *B* and toluene diisocyanate in resin *C* using this technique.

Chemical methods

Nitrogen analysis

Four laboratories carried out Kjeldahl nitrogen determinations and, knowing the nature of the parent isocyanate, the isocyanate content of the resin could be calculated. For resin *C*, nitrogen contents found were from 1.6 to 1.9 per cent giving toluene diisocyanate contents of 9.5 to 11.9 per cent (from formulation 11.9 per cent). For resin *D*, nitrogen contents varied from 1.9 to 2.2 per cent giving toluene diisocyanate contents of 11.8 to 13.9 per cent (from formulation 13.5 per cent).

Other analyses

Some laboratories determined acid, hydroxyl and saponification values of the resins by standard methods. No difficulties were reported, but the results were of no particular significance in characterising the resins.

Conclusions

Infrared spectroscopy distinguishes rapidly the moisture-curing and fatty acid modified urethanes and can identify the commoner isocyanate components. The best procedure for identifying the isocyanates is acid hydrolysis, followed by IR or NMR identification of the derived amine hydrochloride.

The polyols can be identified by aminolysis followed by gas chromatography.

The fatty acids can be identified by methanolysis followed by gas/liquid chromatography, but acids which have been modified in the process of making the urethane resin can be missed. A measure of the fatty acid content can be obtained gravimetrically after saponification.

The best method of obtaining the phthalic anhydride content is gravimetric determination as lead phthalate.

Having identified the parent isocyanate, the isocyanate content can be calculated from the nitrogen content obtained from a Kjeldahl determination.

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5. Corbett, G. E., Hughes, W., and Harris-Jones, R. G., *J. Appl. Polymer Sci.* 1969, **13**, 1297-1307.

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Appendix A

Procedure for acid hydrolysis and NMR examination of polyurethanes

Prior to NMR examination, the polyurethane was converted to the amine hydrochloride. The resin (2-3g) was dissolved in 25ml of dioxan, 10ml of concentrated hydrochloric acid were added and the solution refluxed for 2 hr. A further 10ml of acid were added and the solution refluxed again for 2 hr. The bulk of the solvent was then distilled off and the solution taken down to dryness in a stream of nitrogen and left to cool under vacuum. The contents of the flask were then transferred to a 100ml separating funnel with 50ml of H_2O and 25ml of diethyl ether. The aqueous layer was run off and shaken with successive 25ml portions of ether until a colourless ether layer was obtained. The aqueous layer was removed, evaporated to dryness, and the residue dissolved in a minimum volume of absolute ethanol. Dry acetone was then added slowly until the amine hydrochloride had all been precipitated. The precipitate was then filtered off, washed with a small quantity of dry acetone then dried on the filter paper under vacuum.

The solid (50mg) was then dissolved in 0.5ml of deuterium oxide. A trace of D.S.S. (Sodium 2,2-dimethyl-2-silapentane-5-sulfonate) was added as an internal standard and the nuclear magnetic resonance spectrum of the amine hydrochloride obtained using a Perkin-Elmer R10 60MHz NMR spectrometer.

Next month's issue

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

Some traffic paint compositions *by A. H. Kamel, M. A. El-Azmirly, A. M. Naser and A. Ramadan*

An investigation of the discrepancies in the determination of the solids content of stoving enamels crosslinked with nitrogen resins *by P. F. Sharp and G. Wright*

Optimum use of organic pigments *by F. M. Smith*

Deterioration of paint films by water *by P. Whiteley, G. W. Rothwell and J. Kennedy*

Corrigenda

The following corrections should be noted to the paper "Some aspects of the industrial application of the Egyptian rice germ oil in the field of surface coatings. Part II: Preparation and evaluation of rice germ and rice germ/linseed oil alkyds" by A. M. Naser, M. A. El-Azmirly and A. Z. Gomaa, published in the April 1975 issue:

1. Page 136, first line: for "Tahta" read "Tanta."

2. Page 138, Table 2: the units for the "Iodine Values" given should be cg I_2/g.

London

Painting metal bridges

The Section recently held a technical meeting at the East Ham College of Technology under the chairmanship of Mr R. H. E. Munn, and welcomed as speaker Mr P. Ferguson of MQAD, Woolwich, who presented a paper entitled "The painting of metal bridges—historical and current trends."

Mr Ferguson illustrated his talk with a series of very interesting slides. He outlined the methods which had been used to protect bridges during the past two hundred years or so. Some early protective systems included the immersion of the metal parts of bridges in boiling linseed oil, a fact noted by Lewis Carroll in "Alice Through the Looking Glass" when he wrote, "I heard him then for I had just completed my design, to keep the Menaii Bridge from rust by boiling it in wine."

The present anti-corrosion systems were discussed, and the use of Corten steel was mentioned; this steel forms a protective layer on ageing, and does not require painting.

Mr Ferguson also mentioned the Forth Rail Bridge. A section through the paint film of this bridge showed 29 coats to have been applied since 1890. Maintenance painters applied around 17 tonnes of paint per annum to this bridge, taking 3 to 4 years to complete a repainting operation. Maintenance painting of bridges was an important factor when it was considered that present motorway bridges had a design life of 120 years.

A lively discussion period followed the talk. Mr Sayer, a graduate student at East Ham, then made a short speech of thanks to Mr Ferguson for presenting such an interesting paper and illustrating it so superbly. Mr R. H. E. Munn then made a closing speech thanking East Ham College for such a warm welcome.

B.A.C.

Manchester

The energy situation and raw material supplies

A meeting was held at the Woodcourt Hotel, Brooklands Road, Sale, Cheshire, on Friday 14 February. The lecture was given by Mr A. L. Waddhams of BP Chemicals Limited, London, entitled "Some forward views on the energy situation and raw material supplies."

Mr Waddhams gave an interesting and informative lecture, concentrating on the relationship between worldwide energy requirements and availability of oil-based chemical feedstocks.

Slides showing the forecasts of various authoritative authors were shown, giving forecasts of oil reserves versus usage, the relative importance of various sources of energy in the year 2000, and similar predictions.

The audience found the talk very thought provoking and this was emphasised by the lively question period. The vote of thanks proposed by Mr G. Topham was well received.

After the lecture most members stayed to enjoy some refreshments, both solid and liquid, following which some brilliant solutions to the energy crises were overheard.

A.McW.

Midlands

Paint—past, present and future

The speaker at a meeting on 15 November at the Apollo Motor Hotel, Birmingham, was Mr H. J. Clarke, of Postans Limited and a member of the Section, whose lecture was entitled "An individual's views and reflections on paint—past,

present and future." This was the second in a continuing series of talks aimed particularly at the younger members.

The lecture commenced with a brief historical background to paints and varnishes, from origins now lost in antiquity to the dates of introduction of the more important raw materials currently in use. Only recently had the emphasis shifted from natural to synthetic raw materials. It was suggested that a study of the historical background of paint was a very worthwhile pursuit.

The speaker then turned to the recent developments brought about by the growing awareness of ecological and environmental problems, commenting briefly on non-aqueous dispersions, powder coatings and water-borne coatings. In the last category, it was ironic that coatings based on water as the solvent were likely to be very costly, despite the cheapness of water. A brief survey of recent commercial trends was made, and was developed to cover the implications of the current period of inflation. It was essential that R & D costs should not be reduced, and that short term projects should be actively promoted.

The effects of recent legislation were enumerated, and whilst compliance could give rise to difficulties it could also bring to light some most interesting facts.

The question of education within the industry required special attention, as recruitment was very much at stake. The final part of the lecture dealt with possible future trends. No technical revolution was forecast, and slow progress could be anticipated, at least in the short term. Ingenuity would be required when formulating, as it would probably be 1978 before the ethylene/propylene situation improved. Improvements in application methods were well under way, but there still remained a lot of work to be done in this direction.

A lengthy discussion followed, which reflected the wide-ranging content of the lecture, whilst the size and content of the audience was an encouraging indication of the general interest aroused by this type of subject. A vote of thanks was proposed by Mr R. King.

F.W.C.

Extenders—their present and future position
(Annual Dinner Lecture)

A talk on the subject of extenders was given by Mr R. T. Simpson and Mr D. J. Huxtable, English China Clays Limited, on Friday 17 January at Birmingham Chamber of Commerce and Industry. The lecture was preceded by an excellent dinner, and following this the first speaker was Mr R. T. Simpson.

The current raw material situation was outlined, reference being made to shortages and escalating costs as short term problems. In the case of extenders, long term security could be achieved if price levels were realistic, and there was an encouraging trend with both users and suppliers towards the recognition of one another's problems.

Britain was in a strong position with respect to indigenous extender minerals and these might be of great value in a future international financial situation.

The use of extender slurries in aqueous systems would save the energy expended in the drying process and slurries were already being utilised in the paper coating industry. Break-even costs, when considering transportation and storage of slurries, were calculated and 50 to 60 tonne bulk deliveries were considered economic. Some expertise in slurry utilisation existed and several large continental paint manufacturers were already showing great interest.

On the subject of dry extender powders, it was hoped to introduce at least two extenders showing improved dispersibility. Considerable improvements in whiteness were confidently expected.

The second speaker, Mr D. J. Huxtable, elaborated on various methods of improving dispersibility. High intensity milling methods produced the best overall results; however, a predispersed slurry, where appropriate, could offer considerable advantages. Amongst the disadvantages was the lack of availability of other extenders and pigments, notably titanium dioxide in slurry form. The idea appeared to be sound, however, and long-term developments were likely.

There next followed a discussion, illustrated by slides, on the properties of calcined and lamellar clays in both aqueous and non-aqueous media.

Future trends would be towards:

1. Improved dispersion.
2. Use of slurry extenders.
3. Use of opacifying extenders.
4. Increased brightness.
5. Increased awareness of the advantages of co-operation between user and supplier.

A prolonged question time had to be finally brought to a close by the chairman, and a vote of thanks by Mr R. McD. Barrett brought an enthusiastic response from the audience.

F.W.C.

Trent Valley Branch

Pollution

A meeting was held on the evening of Thursday 13 February 1975 at the British Rail School of Transport, London Road, Derby. The subject, "Pollution and its effect upon the surface coatings industry," was conducted as an open forum, chaired by Mr J. R. Bourne.

Two short films were run, the first showing something of the history of paint making and how modern epoxy systems could be used to prevent corrosion, so conserving structures, and the second demonstrating how solventless coatings reduced the amount of solvent vapour released into the atmosphere. The ensuing debate, in which all present participated, was chiefly concerned with the Government's plans for new anti-pollution legislaton to be introduced on 1 April this year. It was thought that the new regulations would have far-reaching effects on the "man in the street" in the near future and would stress his responsibilities for reducing hazards and so improving health and safety.

The work of the Chemical and Allied Products Industries Training Board was discussed, and the problems of controlling solvent emission and the release of products of chemical breakdown in stoving systems, were outlined.

The meeting concluded with the suggestion that a second forum could be arranged at some future date, in order that members might benefit from a further exchange of experiences.

J.R.K.

Thames Valley

Additives

The speaker at a meeting held at the Beech Tree Hotel, Beaconsfield, Bucks, on 23 January, was Mr Gozden of Rohm & Haas (UK) Limited.

Mr Gozden opened by giving the correct title of his talk as "Acrylic emulsions for maintenance paints" and apologised to any who may have attended to hear discussed the subject of gloss emulsions. Nevertheless, he undertook to deal with this interest later if the meeting so wished.

He proceeded to describe the use of acrylic emulsions for light-duty protection of exterior steelwork, for which purpose

there was a satisfactory comparison on a cost/performance basis with other types of coating. Both advantages and disadvantages were shown tabulated, and many other slides were shown to illustrate test results and also case histories of satisfactory industrial applications. The speaker went on to mention some principles of formulation and particularly referred to the preferred use of reactive pigments such as "Oncor M 50" and zinc molybdate.

A prominent disadvantage of maintenance coatings based on acrylic emulsions had been the phenomenon of "flash rusting" A newly-developed emulsion was now available which largely overcame this, and at the same time exhibited very good solvent and chemical resistance as well as good performance under salt spray and humidity exposure.

The speaker then invited questions and clarified many points raised by his audience. A vote of thanks was proposed by Mr Prigmore, who complimented the speaker on his most interesting talk and voiced his acknowledgment that industry should be aware of the need to reduce the use of solvents. The 34 members and guests present responded warmly in the usual manner.

R.H.W.

Protection of off-shore oil rigs

A meeting was held at the Beech Tree Hotel, Beaconsfield, on 27 February. The chairman welcomed the speaker Mr F. G. Dunkley, Technical Director of the British Inspection Engineering Co., and a founder member of the Trent Valley Branch of the Midlands Section.

Mr Dunkley, using a great many colour slides in illustration, gave a comprehensive review of the elements of his subject, detailing the constructional features of the rigs, and the inherent problems of protection due to the sheer size and difficult accessibility. Re-working due to engineering changes or postponement of the launch dates of the rigs created great problems with protection before completion of the construction work.

The different areas of the structure in relation to the waterline called for different protection specifications and a typical modern system was: cathodic protection for the jacket; solvent-free epoxy for the tidal zone; epoxy-pitch for the splash zone; and zinc-rich epoxy or zinc-silicate primer, with an epoxy, chlorinated rubber, vinyl acrylic or silicone/alkyd finish for the superstructure.

The main problem of maintenance was that of access. The suspended cradle was unsatisfactory and scaffolding was recommended. Another problem was the weather; during the season from April to September, almost half the number of working days could be lost for this reason. The speaker stressed his aim as quality for the whole job—not just the measure of film thickness—and described the many ways in which the inspector contributed to this end.

A lively question and answer session took up nearly as much time as the lecture and became almost controversial on the subject of reactive primers. Mr H. Bray proposed a vote of thanks to the speaker and members and guests showed their appreciation.

R.H.W.

West Riding

Packaging in the decorative paint industry

A meeting was held on Tuesday 11 February 1975, at the Griffin Hotel, Leeds. The lecture was presented by Mr Whiteley of the General Line Group of Metal Box Limited.

Mr Whiteley opened his talk by reviewing the market, mainly in the UK and Western Europe, for containers of

5 litres and below. In the UK there is a basic standard range from 50ml to 5 litres of standard diameters. In Europe the range was far from standard, with a wider range of capacities. So far as closures were concerned, the UK basically used the lever lid, although there were a few tapered pails with a plug lid. In Europe the triple-tight or double-tight closure was more popular, although there were some "easy open end" cans, with which the top peeled back and a plastic reclosure was used. Round containers were most popular in the UK, whilst in Europe and North America square and also tapered containers were fairly common.

So far as decoration was concerned, printing directly on to the tin was the most common, but in Europe more paper labelling was encountered than in the UK. Plastic pails were more commonly used outside the UK as were composite containers (that is with a cardboard body and metal or plastic ends). Composites tended to be lined with aluminium, which was relatively cheap in the USA.

Mr Whiteley then discussed the various aspects required of the container by those using it. Thus the paint producer was concerned with increasing the speeds of handling and filling, minimising the cost and standardising packages. Some of these requirements, particularly standardisation of packages, might conflict with the interests of the marketing man as well as those of the retailer and end user.

UK membership of the EEC could have a bearing on future packaging trends. Attempts were being made to cut down on the wide variety of capacities and diameters. Proposed capacities are no problem so far as the UK was concerned, but none of the diameters compared with those in the UK. Closures were also different. Transport regulations were also under review and containers would have to conform to certain minimum drop tests. No paint container currently in use would meet the proposed (but unadopted) standard being discussed in Europe. UK regulations were under review and although it was anticipated that they would not be as strict, they were still likely to be difficult to meet with present packages.

Looking to the future, Mr Whitely considered that future diameters would tend to be based on food can diameters where the volume production lay, particularly if a move to "easy open end" were required. Tapering offered good space saving in the warehousing of empties, whilst stackability also required some thought. So far as decoration was concerned, there was a suggestion that this could be more adventurous in design. Post-printing was an area for investigation where, for example, the colour of the contents could be post-printed on to a standard can. So far as materials were concerned, Mr Whiteley considered that plastic was not yet entirely satisfactory, either technically or aesthetically. So far as composites were concerned, strength was the problem at the present time.

Mr Whiteley's lecture gave rise to many questions and Mr M. G. Bentley expressed the thanks of all present for a most interesting and comprehensive presentation of the subject.

Advances in condensation polymers

A meeting was held on Tuesday 11 March 1975 at the Griffin Hotel, Leeds. Professor Goodman, Professor in Polymeric Materials at Bradford University, presented the lecture on the advances in condensation polymers. This particular field of research had sustained vigorous research for a number of years, only a little of which would lead to practical applications.

The broad range of present-day commercial polymers was outlined and the chemical formulae of newer polymers were discussed. Most of these were prepared by conventional chemical techniques. Much of the work had been prompted by the search for polymers possessing high temperature resistance. In general, this work proved largely fruitless but the ideas generated had proved very useful in more recent research.

Professor Goodman summarised typical syntheses which had been used over the past 10 to 15 years to produce a wide range of polycondensation polymers. Some recent effort had been directed towards producing useful polymers containing boron and phosphorous. Polymers based on decarborane and carborane had been developed. The carborane derivatives had proved to be of interest; they gave rise to polymers which were stable up to about 600°C. Mention was made of several recent developments in the field of polyester resins having poor hydrolytic stability, which had found outlets in surgery, for example, as absorbable surgical sutures. Finally, Professor Goodman discussed the newer polyamine/imides and polyamide/imides, which had useful properties in structural and electrical engineering appliances.

Mr M. J. Cochrane proposed the vote of thanks to Professor Goodman for a stimulating and interesting lecture.

R.A.C.

Scottish

Paint, pollution and possibilities

A meeting was held on Thursday 13 February at the Beacons Hotel, Glasgow. The lecture was entitled "Paint, pollution and possibilities" and was given by Mr R. H. E. Munn, Cray Valley Products Limited.

Mr Munn began by outlining the two problems normal in solvent-based systems, that is, pollution and cost. The American experience and Rule 66 were well known, but UK legislation was to be expected on the handling of various surface coating ingredients, for example acrylic and isocyanates.

Mr Munn outlined four systems which were contenders in this area of cost and pollution reduction:

1. Powder coatings

2. Radiation cured systems (UV and electron beams)

3. Water-based systems

4. High solid content, solvent systems, for example, non-aqueous dispersions and high concentration solution systems.

Mr Munn outlined the advantages and disadvantages of the various systems with the conclusion that no single system showed overall advantages in performance, ease of use and cost compared with existing alkyd-melamine type coatings.

An example of the complex factors involved was given by a consideration of the water-based coatings. The well-known advantages for water were its low cost and freedom from pollution, whereas a damaging disadvantage was the high energy required to remove the water (high latent heat) from the coating. Recent considerations on energy comparison had shown, however, that the circulation of air required for water removal was lower than that required for organic solvents due to the explosion hazard presented by the latter type. The energy requirement for air circulation was, therefore, in favour of water.

A lively discussion followed and a vote of thanks was expressed to Mr Munn for his comprehensive coverage of this very complex area.

G.H.R.

Information Received

Plastics and Rubber Institute

At Extraordinary General Meetings held on 20 February, members of the Institution of the Rubber Industry (founded 1921) and the Plastics Institute (founded 1931) voted overwhelmingly in favour of forming from their two organisations the "Plastics and Rubber Institute."

The headquarters will be at 11 Hobart Place, London, the former headquarters of the Plastics Institute.

BASF extends butanediol capacity

BASF is to expand its 1.4-butanediol capacity in Ludwigshafen, West Germany, by 40 000 to 110 000 tonnes per year, using BASF's own process at atmospheric pressure. This process is based on modern technology applied to the original work of Professor Reppe some 40 years ago, and will utilise acetylene, readily available from BASF's own capacity in Ludwigshafen.

Change of name—H. Warson Limited

H. Warson (Chemical Consultant) Limited, which operates a scientific advisory service with special reference to the resin manufacturing and allied industries and which also publishes specialised bulletins and reports, will in future operate under the title "Solihull Chemical Services." The organisation will continue under the technical directorship of Dr H. Warson, PhD, FRIC.

ICI ethoxylates plant

A 20 000 tonne/year capacity ethoxylates plant is due on stream in the third quarter of 1975 at ICI Petrochemicals Division, Wilton Works, Cleveland (formerly Teesside). It will produce alkylphenol and alcohol-based ethoxylates in the "Synperonic" and "Teefroth" ranges of general purpose and specialised surfactants, for sale in the United Kingdom and overseas. These ethoxylates are raw materials in the manufacture of household detergents, industrial detergents, oil slick dispersants, sophisticated wetting agents, emulsifiers and froth flotation agents.

The plant is being built by Engineering Services (Wilton) Ltd, using ICI design and engineering. It will be joined by pipeline to the ethylene oxide plant at Wilton, and alkylphenols and "Synprol" detergent alcohol will be supplied from Billingham.

New agent in Ireland for Diamond Shamrock

Diamond Shamrock (UK) Limited has appointed Reginald F. Clarke & Son Ltd as its official agent to handle sales of the "Nopco" and "Foamaster" speciality chemicals in Northern Ireland and Eire. The new agent's address is 50 University Street, Belfast BT7 1HD.

Synres in the USA

Chemische Industrie Synres BV has disclosed a number of projects to extend its activities to the USA. The synthetic resin plant in Kenilworth, New Jersey, which was acquired in 1973, will change its name to Synres Chemical Corporation. Through this subsidiary, a number of companies has now been acquired in the USA: Shanco Plastics and Chemicals, Tonawanda, NY, Custom Chemical Co., Elmwood Park, NJ, and the synthetic resin division of Stepan Chemical Co., Anaheim, California.

Synres is planning to relocate its East Coast operations to a new large tract of land in New Jersey, with an enlarged modernised plant, and to continue and extend production at Anaheim on the West Coast, so that a full range of products may be offered in the United States.

By acquiring Custom Chemical Co., Synres will enter a new field—that of pigments dispersions for plastics and printing inks, and of speciality products to be applied as top and intermediate layers in paper, textile and plastic combinations.

UK representative for Kohler

Wentworth Instruments Limited has announced its appointment as UK representative for H. Kohler KG of Lippstadt, West Germany, makers of the original Kesternich Corrosion Testing Apparatus.

New products

Acrylic monomers

Ultraviolet curing systems for printing inks and surface coatings are amongst the suggested uses for a range of acrylic monomers manufactured by the American Aniline & Extract Co. Inc., and available in the UK through its agent, British Chemical Products & Colours Limited. In addition to glycidyl acrylate and methacrylate, the range also includes cyanoethyl acrylate and the acrylate esters of tetraethylene glycol, pentaerythritol triethylene glycol and trimethylol propane.

Besides UV curing systems and their conventional uses, these products are also being evaluated for use in conjunction with peroxides in EPDM rubbers.

Inmont dispersions

Inmont Corporation has announced the introduction of a "991 RBH" series of industrial pigment dispersions specifically for use in water-based systems. The range comprises eighteen colours with additional single colours offered on a made-to-order basis.

Flow control agents

Victor Wolf Limited, Manchester, is now marketing a comprehensive range of acrylic based flow control and surface levelling agents to the paint and resin industry. The range, known as "Resimix," is at present manufactured by Mohawk Industries Inc., New Jersey, but production in the UK is under consideration.

Aqueous vehicle for inks

An aqueous vehicle of high molecular weight and low viscosity for inks and coating systems is now available in the United Kingdom from British Chemical Products & Colours Limited, the UK agent for the manufacturers, Ionac Chemical Company, a division of Sybron Corporation. The product is a styrene-shellac polymer with a 45 per cent solids content. British Chemicals Products & Colours Limited emphasises that use of this vehicle not only provides fast solvent release and ease of press-side clean up, but also eliminates fire hazard and minimises atmospheric pollution.

The new Graco EH 433GT portable electric airless spray unit, which the company recommends for applying high-build coatings.

Micronised polyethylene

Allied Chemical International SA has announced the addition of low molecular weight "Polymist B-12" to its range of micronised polyethylene products. The company recommends its new product for use as an anti-scuff agent for printing inks and as a scratch and mar resistant agent for various lacquers and paints, including powder coatings.

Polyamide resins from Italy

Jacobson van den Berg & Co. (UK) Limited has signed an agreement with Chem-Plast of Milan, Italy, suppliers of polyamide resins used in the surface coating and adhesive industries under the trade name "Reammide."

Specialised silicas

Joseph Crosfield and Sons Limited has developed three new specialised silicas for use in the paint resin and plastics industries: "Gasil EBC" and "EBN," for the matting of electron beam cured coatings, and "Silica SM111."

Suprapal LG

BASF United Kingdom Limited has announced the availability of a low viscosity soluble styrene polymer suitable for use as a binder for zinc-rich primers, luminous paints, electrical insulation lacquers and other speciality coatings. The new product is designated "Suprapal LG" and is supplied by BASF as a hard, crystal-clear thermoplastic. Its solutions dry in air to yield clear tack-free films that are not attacked by water, aqueous solutions of salts, alkalis, dilute inorganic acids, or alcohols.

Courses, symposia, etc

Colour

ICI has made available a new film "Colour." This replaces a film of the same title which

has been one of the most popular films in the ICI film library for many years. The new film is designed to appeal to a very wide audience, and runs for 22 minutes.

Electron microscopy

A two-year day release course, "Electron-microscopy Technicians", leading to eligibility to apply for the Royal Microscopical Society's Qualification in the Technology of Microscopy (Tech RMS) is currently being run at Southall College of Technology in co-operation with Brunel University. Enrolment dates for the new intake are 9 to 11 September.

Powder technology

The following short courses are being run between June and September at the University of Bradford School of Powder Technology: "Sampling, particle size measurement and surface area determination" (5 day course); "Flow and storage of particulate solids" (4 days); "Mixing in the process industries" (5 day course); "Solid-liquid separation" (4 days).

Literature

Accident prevention

The Air and Water Pollution Panel of the Paintmakers' Association has recently published a booklet "Accident prevention clearance certificate procedures" and copies are available from the PMA at 15p each plus postage and packing.

Electropainting

R. H. Chandler Limited has recently published "Advances in Electropainting 1973/74" giving 188 references and individual abstracts of 125 patents. A special section of the bibliography is devoted to the "cathodic" method of painting. Ultrafiltration and other advances are also covered with reference to the increasing quantity of research material from Russia.

British Standards Institution publications

The following two publications are now available:

BS 3416: 1975. Black bitumen coating solutions for cold application.

BS 5193: 1975. Zinc phosphate pigment for paints.

The BSI Sub-Committee PVC/10/4—Optical Tests (Paints) has issued a *draft* of British Standard 3900 "Methods of test for paints. Part D—Visual comparison of the colour of paints". The latest date for receipt of comments is 30 May 1975.

Filtration selection guide

A liquid filtration selection guide is available from Albany Engineered Systems Europe Limited of Slough. Eleven materials of construction and 115 of different liquids are covered in the compatibility chart. The guide also includes other data, such as recommended filters and a pressure drop table.

Bulk delivery and storage of polymer emulsions

Vinyl Products Limited, Carshalton, Surrey has published an entirely new edition of its booklet "Technical Service Report G1", which provides recommendations of storage conditions and equipment for large scale emulsion handling installations.

Mr L. H. Silver (extreme right), Chairman and Managing Director of the SPL Group and President of the Association, together with (from left to right) Mrs L. Beaumont (SPL), Mr R. O. Evans (Director General of the International Export Association), Mr C. Butterworth (SPL) and Sir Frank Marshall. The certificates were awarded by the International Export Association to the Silver Paint and Lacquer Company Limited for export achievements 1973-74.

Review

Uses of epoxy resins

By W. G. Potter

London: Newnes-Butterworths, 1975, Pp. 281. Price £6.50

This book claims to be the first comprehensive technical/economic assessment of epoxy resins. It is addressed to industrial designers, architects and production managers rather than to readers with extensive chemical knowledge. Dr Potter has already written on the technology in a Plastics Institute monograph, entitled "Epoxide resins". This monograph was reviewed in this *Journal* (1971, **54**, 796) and the reviewer commented that more should have been written about the uses of these resins. Dr Potter does this comprehensively in the present book.

An introductory section describes basic epoxy resin technology, the history, commercial background and an outline of properties making these resins so useful and versatile.

The varied uses of epoxy resins in the surface coatings field will be familiar to most working in that area, if only from the literature of efficient resin manufacturers. The author presents sound economic arguments for using epoxide resins where maintenance costs are high, as in marine paints, or where maintenance is not practicable as with pipelines. He predicts a large growth in the use of epoxy powder coatings, but with increasing pressure from acrylics and polyester powders.

Section III deals with electrical applications. Epoxy resins have revolutionised small electrical and electronic equipment. Poor weathering of existing resin types has prevented wider use in outdoor equipment but developments are being actively pursued.

The next section describes floorings, road surfaces, bridge protection, construction materials for buildings and grouts for levelling. Adhesives, composites, arts and crafts and tooling materials in production engineering are applications in the final section.

This is a fascinating and most readable account of the versatility of epoxy resins.

L. R. SEABORNE

Scarborough Conference 17 to 21 June 1975

Performance of surface coatings—does reality match the theory?

Registrations

The closing date for the registration for the Conference was given as 1 April 1975 primarily for the benefit of the Hotel managements who would be in a position to let any accommodation taken up by that date. Registrations have been received from delegates in the United Kingdom and eight overseas countries.

Applications can still be accepted, but delegates are reminded that VAT at the standard rate (8 per cent at the time of going to press) applies to all registrations. Copies of the full programme of technical and social events and registration forms can be obtained from the Association's offices (Tel. 01-908 1086; Telex 922670).

Preprints

Preprints of the papers are now being prepared and it is expected that these, together with details of accommodation, badges, programmes etc, will be sent to those who have registered at the end of this month. It is a feature of the Association's Conference that preprints are sent well in advance of the function, in order that delegates can read them before the Conference, at which the lecturers illustrate their topics, but do not read the papers in their entirety. This allows for a much longer discussion period than at any other conferences and has proved of immense value to those attending previous Association Conferences.

Dates and times of sessions

The Conference assembles on the evening of Tuesday 17 June when, in accordance with its usual tradition of hospitality, the Association will hold a reception for all those attending from overseas, which will be followed by a meeting of the lecturers and the chairmen of the sessions. The Conference sessions (which this year comprise 17 papers) will be held as follows:

Wednesday 18 June (9.30am-12.30pm)

Chairman: A. R. H. Tawn (Hon. Research and Development Officer).

"Quality control of painting in the construction industry—making reality match the theory" by Mr F. G. Dunkley (BIE Anti-Corrosion Ltd).

"Testing of surface coatings by the customer" by Mr D. A. Bayliss (Central Electricity Generating Board).

"Flocculation—its measurement and effect on opacity in systems containing titanium pigments" by Mr J. G. Balfour and Mr M. J. Hird (Tioxide International Ltd).

"Prediction of the corrosion protective properties of paint films by permeability data" by Dr H. Haagen (Forschungsinstitut für Pigmente und Lack EV) and Dr W. Funke (University of Stuttgart).

Wednesday 18 June (2.30pm-4.30pm)

Chairman: G. H. Hutchinson (formerly Chairman of the Eastern Branch of the Scottish Section)

"Why did it fail?" by Mr A. F. Sherwood and Mr A. N. McKelvie (Paint Research Association).

"Problems encountered in testing paint films" by Mr M. B. Kilcullen (British Steel Corporation).

"Prediction of the performance of surface coatings by accelerated testing under normal conditions" by Dr K. M. Oesterle (formerly Maderlack AG).

Thursday 19 June (9.30am-12.30pm)

Chairman: G. de W. Anderson (Director of the Paint Research Association).

"Implications of the paint film contraction theory for comparison of accelerated and natural weathering" by Mr T. W. Wilkinson and Mr J. Colling (Laporte Industries Ltd).

"Theories—laboratory investigations—practical performance" by Mr B. Lindberg (Scandinavian Paint and Printing Ink Research Institute).

"The theory and practice of film formation by co-ordination reactions involving aluminium compounds" by Mr J. H. W. Turner, Mr W. K. H. Lakin and Mr P. Womersley (Manchem Ltd).

"Practice makes perfect" by Mr A. E. Claxton (Inmont Ltd).

Thursday 19 June (2.30pm-4.30pm)

Chairman: A. G. Holt (Vice-President)

"Ecological coatings: the theory and the reality" by Mr A. G. North, Mr R. Little and Mr J. L. Orpwood (Cray Valley Products Ltd).

"Paints for buildings—the potential and the performance" by Mr P. Whiteley and Mr G. W. Rothwell (Building Research Establishment).

"The flow of epoxy powder coating films in relation to reactivity, rheology and wetting" by Mr S. Gabriel (Shell Delft).

Friday 20 June (9.30am-12.30pm)

Chairman: A. T. S. Rudram (President Designate)

"A new versatile lead free pigment" by Mr S. L. Davidson (NL Industries Inc.)

"Protection: from hypothesis to principle" by Mr P. J. Gay (formerly Storry Smithson & Co Ltd).

"Opportunities and constraints for the chemical industry" by Mr G. S. Galer (Shell Chemicals UK Ltd).

The Association's Annual General Meeting will take place at 2.15 p.m. on the afternoon of Friday 20 June and this will be followed by three Workshop Sessions which have proved very popular in the past. The subjects this year will be:

"How can we control over-speculation?", "What is the reality of toxic hazards for the surface coatings manufacturer?" and "The impact of non-impression processes on the printing ink industry". The number attending each workshop session is strictly limited and places will be allocated in order of receipt. Where the total places for a session have been filled, later applicants will be informed and, if possible, offered an alternative session.

There will be an Informal Reception for all delegates at lunchtime on Wednesday and a Civic Reception will be held, at which delegates will be welcomed by the Mayor and Mayoress of Scarborough, on the evening of the same day. The Association's Dinner and Dance will be the closing function of the Conference on the Friday evening. Other social activities, such as coach tours are being arranged for the benefit of ladies attending the Conference.

Obituary

G. N. Hill

With deep regret, it is announced that Mr G. N. Hill died at his home at the end of March, aged 87.

Mr Hill joined the Imperial Varnish and Colour Company in Toronto in 1911 as a chemist. He returned to England in 1923 to take up an appointment with Llewellyn & Ryland Ltd, Birmingham, and remained in the service of that company for 52 years.

He became a member of the Association in 1924, and served as a Council Member from 1931-33 and 1937/38, as a Vice-President of the Association from 1939 to 1942, and was Honorary Editor of the Association from 1939 to 1942, and was Honorary Editor of the Association's Journal from 1937 to 1947—the longest time this post has been held. In 1962 the highest award of the Association, that of Honorary Membership, was conferred upon him in recognition of his services as Honorary Editor.

Mr Hill was also an Honorary Member of the Federation of Societies for Paint Technology and was instrumental in the founding of the Birmingham Paint Club.

He leaves a widow, and our condolences are passed to her.

Scottish Section

Annual Dinner Dance

The annual Dinner Dance was held in the Albany Hotel, Glasgow, on Friday 10 January 1975. The guests were Mr and Mrs L. H. Silver; Mr and Mrs C. Finlay (Newcastle); Mr and Mrs D. Morris (West Riding); Mr and Mrs R. Munn (London); and Mr and Mrs J. Stewart (Scottish, Eastern Branch).

Mr A. McLean, Chairman of Scottish Section, welcomed the guests in original verse, which was competitive in style and language with the more traditional address to the haggis. Mr Silver's speech was, as expected, very interesting with comments from his world tour of the overseas Sections.

A very lively dance session followed the excellent meal. All present enjoyed renewing acquaintances and thanks were extended to Mr Davidson and his Social Committee for their excellent organisation.

Paint technology course

A course entitled "Paint technology" was organised by the Section at the Reid Kerr College, Paisley, during the 1973/74 session. The course consisted of two parts, an introductory series of ten lectures, and a second, more advanced course of a further ten lectures. The lecturers were chosen from industry and were recognised experts in their fields. Each two-hour lecture was accompanied by relevant preprints drawn up by the individual lecturers.

A short examination was held on both parts of the course and the following were successful:

Part 1	*Parts 1 and 2*
D. S. MacFarlane	W. Arnot
H. McIntosh	D. A. Frew
A. Stevenson	J. Oliver
J. Struthers	

Part 2

C. Crombie

Each successful student was presented with a certificate from the College signed by the Chairman of the Scottish Section and the Principal of the Reid Kerr College.

Students and lecturers were enthusiastic about the venture and it is hoped to repeat this type of course in the future, when the number of new students is considered sufficient.

All concerned expressed their thanks to Mr R. F. Hill (Scottish Section Education Officer) for his work in organising the course. Appreciation was also expressed to the Reid Kerr College and to, in particular, Mr R. McKinney, Head of the Chemistry Department, for making available the college facilities and for helpful comments on the course format.

Professional Grade

The following Ordinary Member has been admitted as an Associate in the Professional Grade:

Elizabeth Stretton (*Manchester Section*)

Newcastle Section

Annual Dinner Dance

The Section held its annual Dinner and Dance at the Five Bridges Hotel, Gateshead on 21 February, 1975. As usual this was a very successful evening and was attended by nearly 230 members and guests. Mr C. N. Finlay proposed the toast to the ladies and guests, who included Mr L. H. Silver, Mr F. E. Ruddick, Mr D. Morris, Mr D. E. Hopper, Mr A. Maclean, Mr J. K. Kaminsky and their ladies. The President, Mr Silver, responded on behalf of the guests. Music was provided by the Ballroom Five, who did much to ensure the success of the evening.

From left to right: Mr C. N. Finlay (Newcastle Section Chairman), Mrs Finlay, Mrs Silver and Mr L. H. Silver (President) at the Newcastle Section's annual Dinner Dance.

Forthcoming Events

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

May

Thursday 8 May

Thames Valley Section—Student Group: "Colour matching and measurement" by Mr B. Jeffs, ICI Ltd., Paints Division, to be held at 4.00 p.m. at Slough College in the main Lecture Hall.

June

Tuesday 17-Saturday 21 June

OCCA Biennial Conference "The performance of surface coatings—does the reality match the theory?" at the Grand Hotel, Scarborough, Yorkshire, England.

Friday 20 June

Annual General Meeting of the Association, to be held at the Grand Hotel, Scarborough, Yorkshire, at 2.15 p.m.

A view of the bay at Scarborough. On the right is the Grand Hotel, venue this year for the Association's Biennial Conference

Report of Council Meeting

A meeting of Council was held at the Great Northern Hotel, King's Cross, London N1, on 25 February 1975, when 28 members of Council were present. The President Mr L. H. Silver took the Chair.

The appointment of representatives to various BSI Committees was reported as follows:

PVC/1 Pigments—Mr H. G. Cook

PVC/1/9 Carbon Black—Mr V. G. Heffer

PVC/16 Ready Mixed Paints—
Mr A. T. S. Rudram

The Annual Report of Council for 1974 was adopted and the Agenda was agreed for the Annual General Meeting for 1975, to be held at the venue for the Conference at Scarborough at 2.15 p.m. on 20 June.

The Hon. Secretary reminded Council of the format for Council Reunion Dinners during the last two years. It was agreed that these arrangements had resulted in successful functions and that a further Reunion Dinner should be held on similar lines in October 1975.

Council was pleased to learn that the new Association tie (single gold motif on a dark maroon background) had met with approval and that some Sections had purchased quantities to sell to members at Section meetings. The blue tie was still available if required.

It was reported that forms for the 1975 Conference at Scarborough, as well as for two Section Symposia, had been despatched with the January issue of the Journal, and a number of registrations had been received.

Council was pleased to learn that by the end of January the number of stand units sold for the 1975 Technical Exhibition was well over 690 (from 15 countries including a late Australian applicant). The printing of the "Official Guide" had just been completed and it was expected that copies would be despatched to members, exhibitors and other organisations, such as the Paintmakers Association, in early March. A large number of requests for season admission tickets and copies of the "Official Guide" (accompanied by remittances on this occasion) had already been received from non-members at the Association's offices.

Membership subscriptions were discussed and it was unanimously agreed that new subscription rates for 1976 should be proposed for adoption at the Annual General Meeting. It was also agreed that any member whose 1975 subscription was three months in arrears would not receive any issues of the Journal after March and this year would not receive issues published during the period of arrears.

Council was reminded that the January issue of the Journal had contained summaries of the 17 papers and biographies of lecturers for the Scarborough Conference 1975. Three papers had been designated as being presented on behalf of the other members of the International Liaison to be presented as follows:

Mr S. L. Davidson on behalf of the Federation of Societies for Coatings Technology (FSCT); Mr B. Lindberg for the Scandinavian Federation of Paint Technologists (SLF); and Dr H. Haagen and Dr W. Funke for FATIPEC.

The Jordan Award Committee had considered the applications received and it was proposed that the Award should be presented at the AGM during the Scarborough Conference in June.

Since the last meeting a request had been received from the newly-appointed Scottish Technical Education Council to nominate a representative on the sub-committee—Chemistry. It was agreed that Mr R. Hill should be asked to take this appointment.

The Director & Secretary had prepared a paper on the possible development of the Sections overseas and it was decided that Council would discuss the proposals more fully at the April meeting when the views of the three present overseas Sections would be known.

Council was delighted to give its permission to the London Section to form a branch in Canada to be known as the "Ontario Branch of the London Section" and extended its best wishes for the success of this activity. Council was pleased to learn that the inaugural meeting of the Branch would be held in Toronto in May and that the incoming Chairman (Mr J. T. Tooke-Kirby) and the Hon. Secretary (Mr H. C. Worsdall) of the London Section planned to be present.

Section representatives then reported on the activities of their Sections; it was reported that many applications had been received for the forthcoming Symposia of the Newcastle and Thames Valley Sections.

There being no other business the President thanked the members for attending and declared the meeting closed at 3.25 p.m.

Register of Members

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

Ordinary Members

BRIDGEMAN, IAN, PhD, ARIC, 13 Riddings Road, Timperley, Altrincham, Cheshire.   (Manchester)

COWAN, MICHAEL HUGH, Crown Decorative Products Ltd., Hollins Road, Darwen.   (Manchester)

DARGE, REGINALD THOMSON, ARIC, Coates Bros. (Industrial Finishes) Ltd., Easton Street, London WC1X 0DP.   (London)

GOTO, MASAHIRO, Kansai Paint, 40 Basinghall Street, London EC2.   (London)

HADLEY, HARRY VANSITTART, 85 Avery Way, Allhallows-on-Sea, Rochester, Kent.   (Midlands)

HITCHINS, BRIAN, API, Coates Bros. (Industrial Finishes) Ltd., Easton Street, London WC1X 0DP.   (London)

KERR, WILLIAM ORR, Monsanto NZ Ltd., PO Box 347, Auckland, New Zealand.   (Auckland)

OGILVIE, ANGUS G., BSc, MPhil, 84 Walden Avenue, Chislehurst, Kent BR7 6EW.   (London)

PADAYACHIE, RADHAKRISHNA, BSc, 173 Jacobs Road, Clairwood, Durban, South Africa.   (South African)

PORTEOUS, BARRIE M., BSc, Inmont Canada Ltd., 303 Campbell Avenue, Toronto, Ontario, Canada.   (General Overseas)

RING, JOHN, BSc, 33 Gillett Avenue, East Ham, London E6 3AW.   (London)

RYCROFT, CHRISTOPHER PETER, 76 Dewhurst Road, Fartown, Huddersfield HD2 1BW.   (West Riding)

SCOTT, FRANK, 10 Vuurpyl Crescent, Thornton, Cape Province 7500, South Africa.   (South African)

SUTCLIFFE, MICHAEL, BSc, PhD, 1 Dalserf Crescent, Giffnock, Glasgow G46 6RB.   (Scottish)

VAN LONDEN, ANTON MATTIJS, Burkkardalen 2, Gadevang, 3400 Hillerod, Denmark.   (General Overseas)

VEITCH, THOMAS HOGARTH, 103 Fauldsworth Crescent, Paisley, Renfrewshire.   (Scottish)

WALKDEN, STEPHEN ANTHONY, LRIC, AC Hatrick (NZ) Ltd., PO Box 2359, Auckland, New Zealand.   (Auckland)

WIEGNER, PAUL FRITZ, BSc, MSc, PhD, PO Box 4918, Durban, South Africa.   (South African)

WILLIAMS, TREVOR JOSEPH, LRIC, Consolidated Chemicals Ltd., PO Box 15-104, New Lynn, Auckland, New Zealand.
(Auckland)

WINGFIELD, ELIZABETH SANDRA, Plascon-Evans Paints, PO Box 1386, Durban, South Africa.   (South African)

WOLLBRANDT, CHRISTIAN JOHANNES, PO Box 73093, Fairland, Johannesburg, South Africa.   (South Africa)

WRIGHT, RAYMOND HAROLD, 28 Bradfield Avenue, Buckingham, Bucks.   (Thames Valley)

Associate Members

PEDERSEN, KENNETH MICHAEL, Monsanto NZ Ltd., PO Box 347, Auckland, New Zealand.   (Auckland)

RADEMAN, CHRISTOFFE JOHANNES, PO Box 5010, Vaalreefs Mining & Exploration Co., Western Transvaal.   (South African)

VAN DER WAAG, UDO, Protea Chemical Services (Pty) Ltd., PO Box 4636, Cape Town, South Africa.   (South African)

WOODS, BRUCE MARTIN, Neill Cropper & Co. Ltd., Box 9, Auckland, New Zealand.   (Auckland)

Registered Student

CAMERON, MAUREEN, 4 Barra Place, Bourtreehill, Dreghorn, Ayrshire.   (Scottish)

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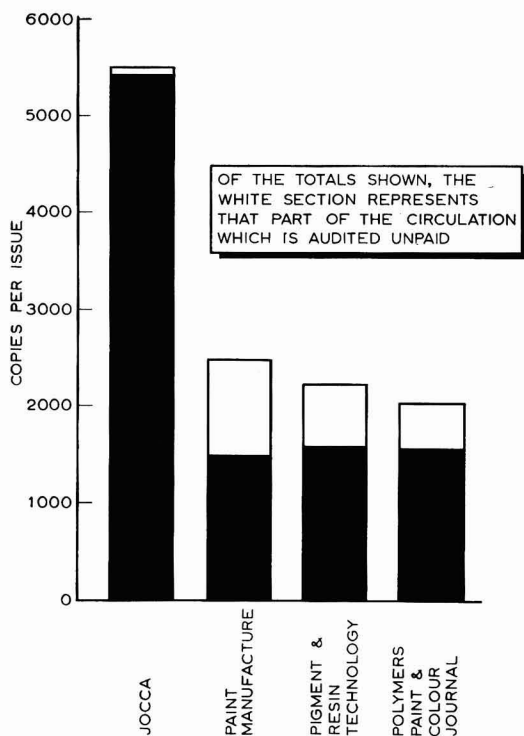
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