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Vol. 52 No. 7 **July 1969**

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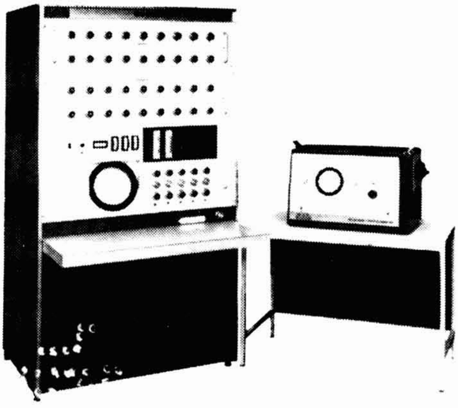

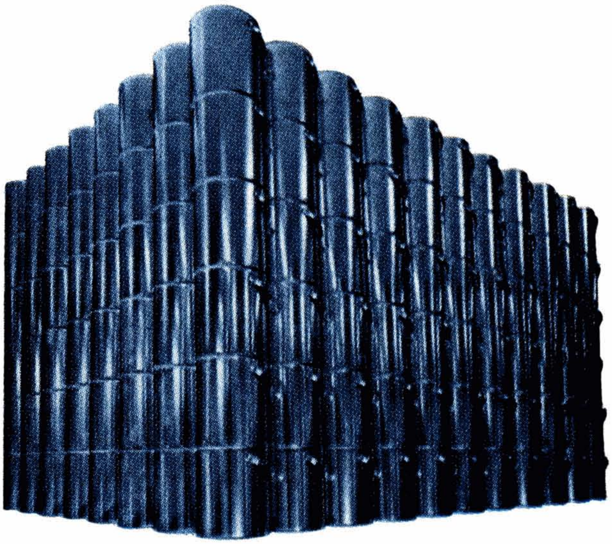

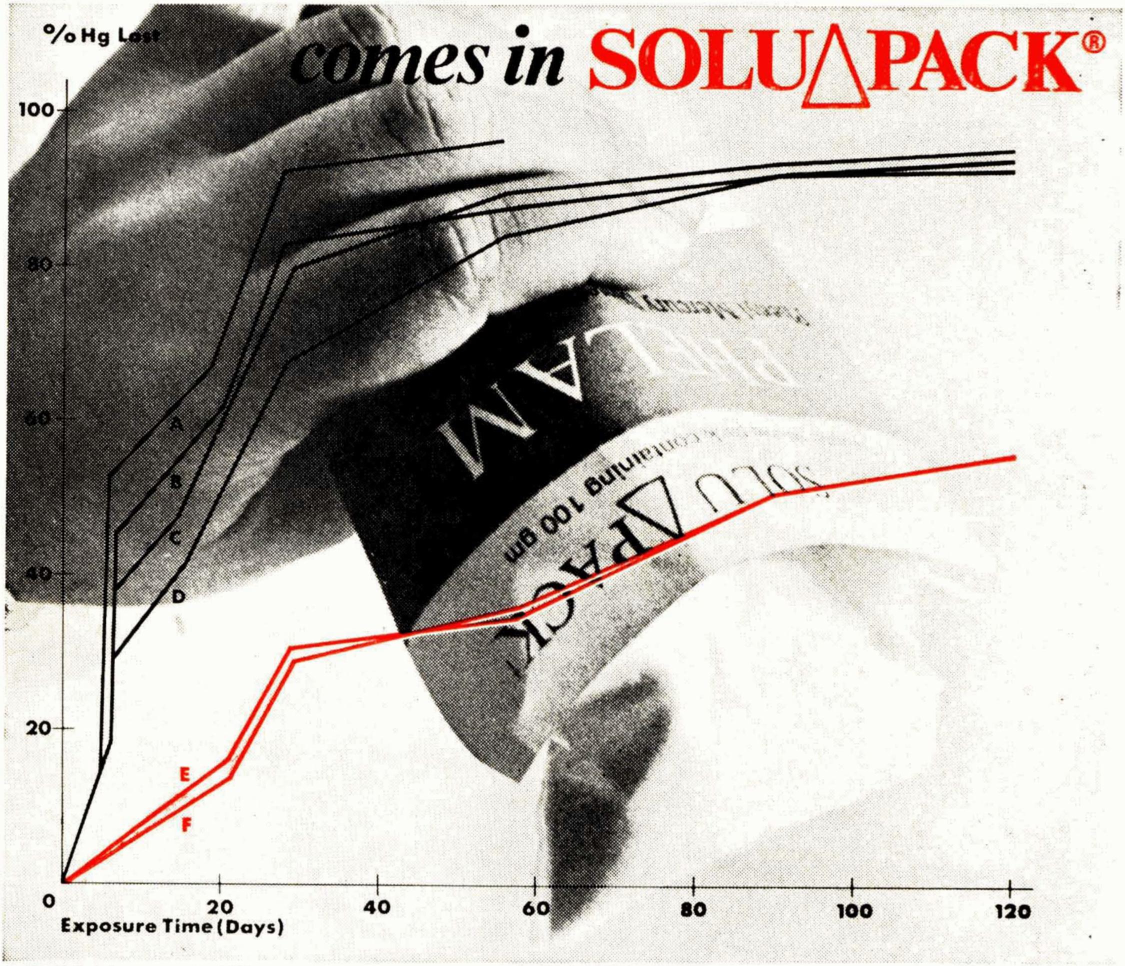

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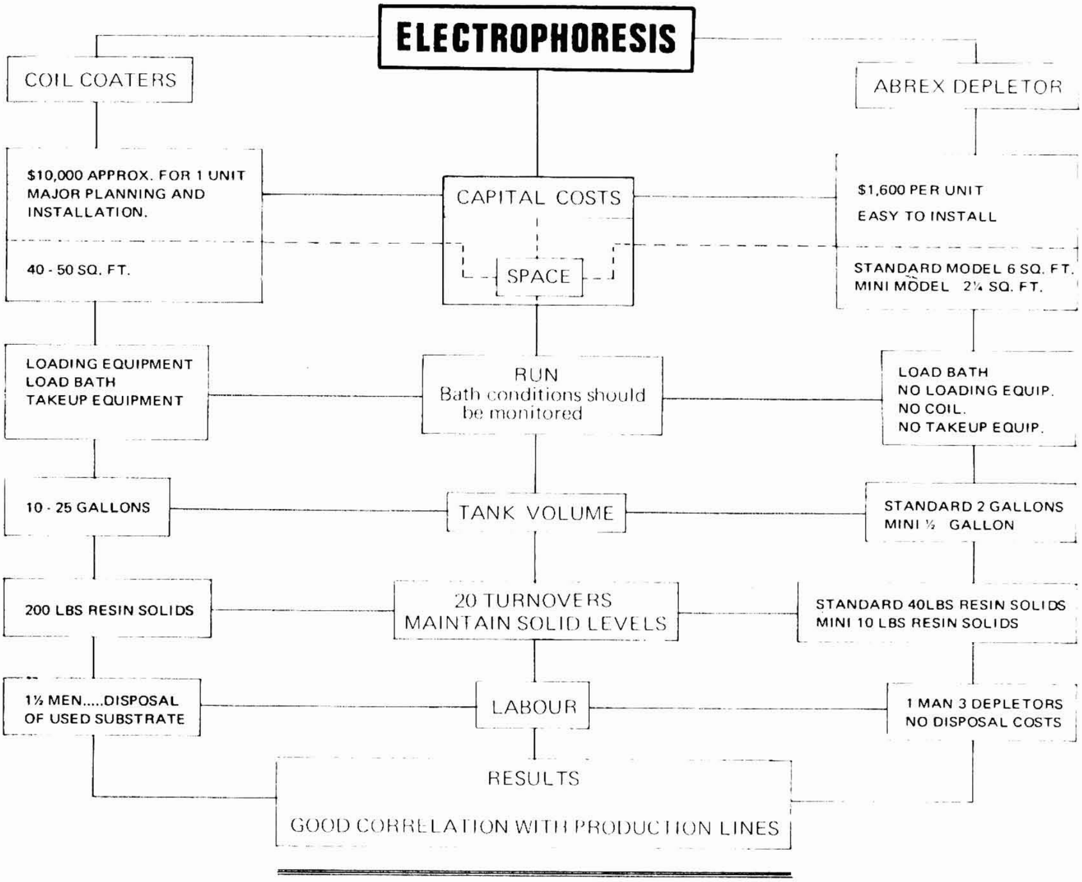

It is essential to have a knowledge of how the paint bath composition changes during deposition through a number of depletion cycles, or turnovers, in order to be able to formulate a suitable feedstock or to devise a means of controlling the unwanted buildup of non-depositing ingredients. To observe the effect of depletion (with or without simultaneous replenishment) it is necessary to coat large areas of substrate. Usually this involves either the repeated laborious coating and stripping of a large number of metal panels, or the coating of a continuous strip which is then discarded as waste. Both methods are expensive.

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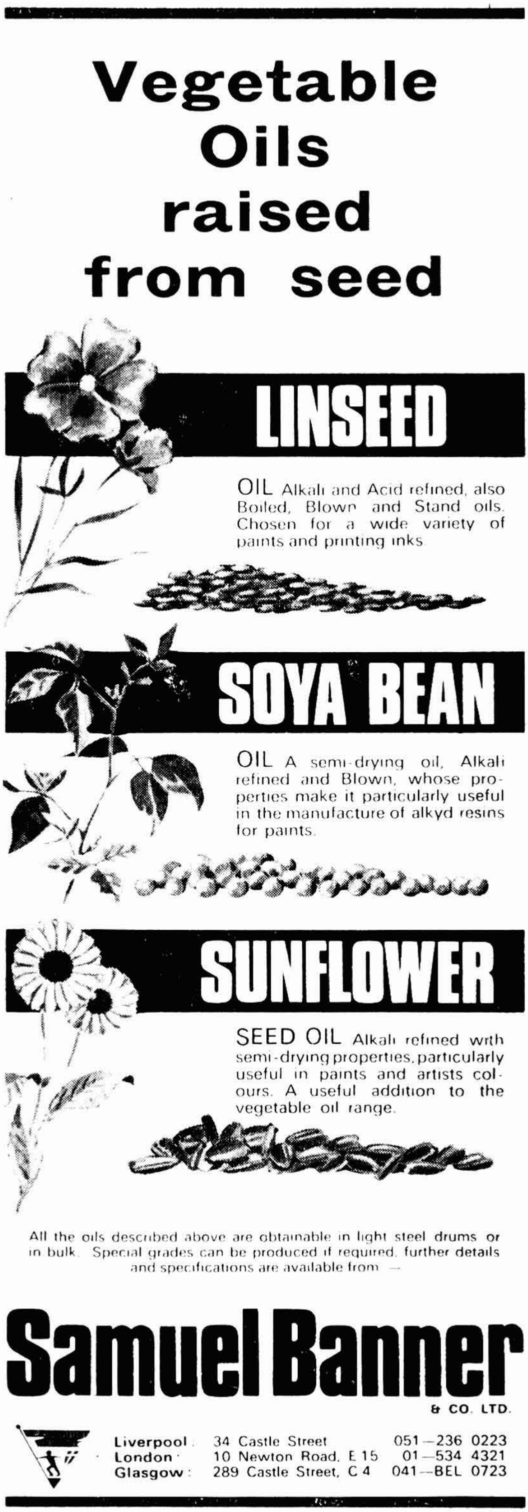

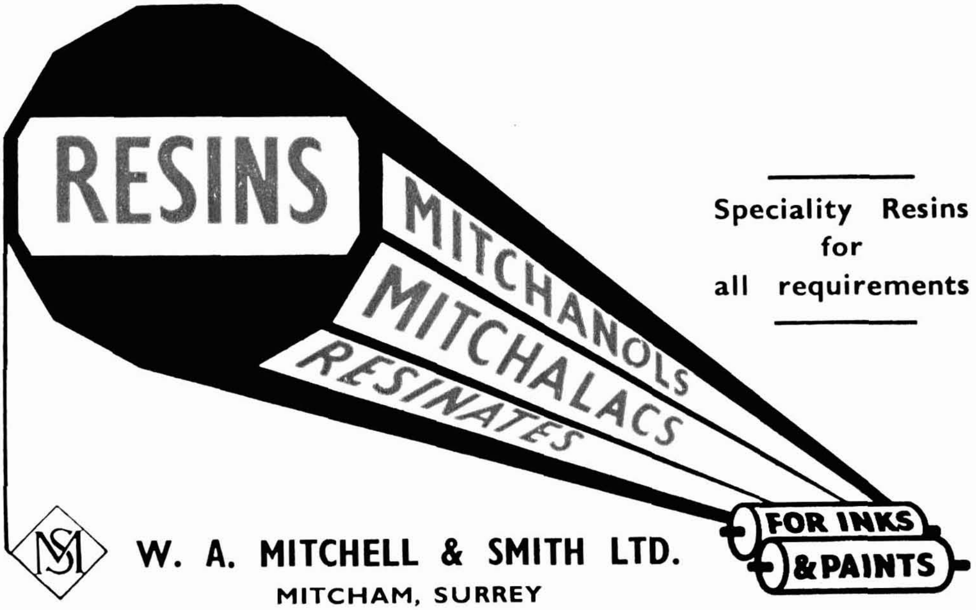
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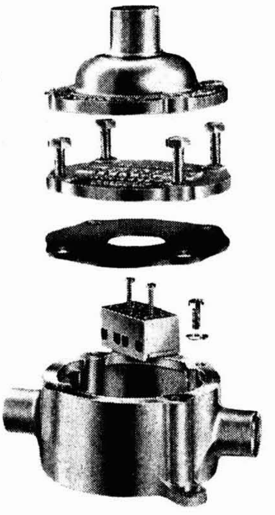


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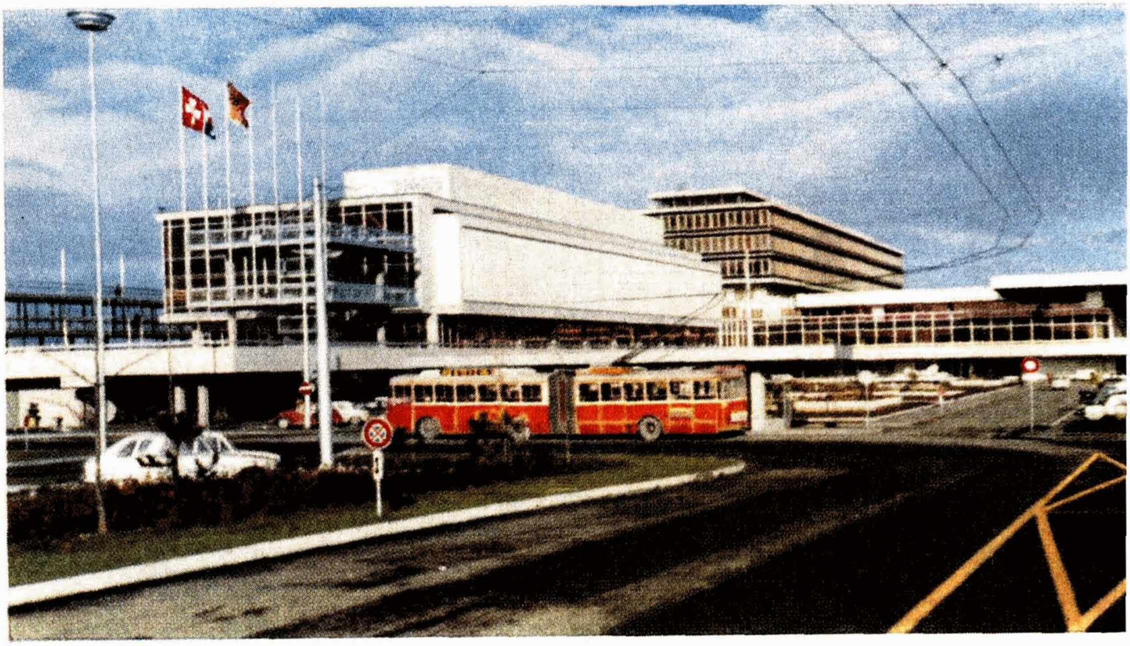

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Transactions and communications

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J. Oil Col. Chem. Assoc. 1969, 52, 587-592

Transactions and Communications

Freeze-drying of soft polymer dispersions for determining their particle size by electron microscopy

By F. H. de la Court and H. Vogt

Verfinstituut TNO, Delft, Holland

Summary

As is well known from the literature, the determination by electron microscopy of particle size and particle size distribution of film-forming dispersions, in particular when they comprise acrylic monomers, is still a difficult matter.

In this paper, a freeze-dry method is described in which the particles are kept in their spherical form by covering them with a carbon coating at temperatures far below their glass transition points.

In this way, excellent electron-micrographs have been made of dispersions containing a high amount of 2-ethylhexyl acrylate.

As the carbon coating has a controlled thickness, this method enables an exact calculation of particle sizes from the electron micrograph.

Key words

Processes and methods primarily associated with analysis, measurement or testing
electron microscopy
freeze drying

Properties associated with materials in general
particle size

Binders-resins etc
dispersion resin

Raw materials used in manufacture of ingredients for coatings
acrylic monomer

Le séchage par gelation des dispersions de polymères tendres au cours de la détermination de leur grandeur particulaire par microscopie électronique

Résumé

Il est bien établi dans la littérature que la détermination, par microscopie électronique, de la grandeur particulaire et de la granulométrie des dispersions filmogènes reste-elle un problème difficile, surtout dans le cas où elles contiennent des monomères acryliques.

Dans cet exposé on décrit un méthode pour séchage par gelation qui permet la retention de la forme sphérique des particules au moyens d'un revêtement de carbone effectué aux temperatures fortement au dessous de leurs pointes de transition vitreuse. Dans cette manière on a obtenue d'excellentes micrographies électroniques de dispersions contenant des quantités importantes de 2-ethyle hexyle acrylate.

Puisque le revêtement de carbone est d'un épaisseur contrôlé, cette methode permet le calcul exact des grandeurs particulaires à partir de la micrographie électronique.

Gefriertrocknung Weicher Polymerdispersionen Zwecks Bestimmung Ihrer Teilchengrösse Mittels Elektronenmikroskopie

Zusammenfassung

Aus der Literatur ist bekannt, dass die Bestimmung von Teilchengrössen und deren Grössenabstufung bei filmbildenden Dispersionen, vor allem, wenn diese Akrylmonomere enthalten, mit Hilfe der Elektronenmikroskopie noch immer schwierig ist.

In dieser Abhandlung wird eine Gefriertrocknungsmethode beschrieben, in der die Kugelform der Teilchen durch Bedeckung mit einer Kohlenstoffschicht weit unter ihren Glasübergangspunkten erhalten bleibt.

Auf diese Weise wurden von Dispersionen mit hohem Gehalt an 2-Äthylhexylakrylat ausgezeichnete Elektronenmikrographien angefertigt.

Da die Kohlenstoffschicht eine kontrollierte Dicke besitzt, ermöglicht diese Methode aus den Elektronenmikrographien Teilchengrössen genau zu berechnen.

Сушка замораживанием дисперсий мягких полимеров для определения величины их частиц при помощи электронной микроскопии

Резюме

Как хорошо известно из библиографических данных, электронно—микроскопическое определение величины частиц и распределения размеров частиц пленко-образующих дисперсий, в особенности когда они включают акриловые мономеры, все еще сопряжено с известными трудностями.

В настоящей статье описывается метод сушки замораживанием, в котором частицы сохраняются в своей сферической форме покрывая их слоем углерода при температурах намного ниже их точки стеклования. Этим путем были получены отличные электронные микроснимки дисперсий содержащих большое количество 2-этилгексилового акрилата. Так-как толщина углеродного покрытия поддается регулированию, этот метод дает возможность точного вычисления размеров частиц по данным электронного микрографа.

Introduction

Up to now, particle size determination of soft polymer dispersions by electron microscopy has been a difficult matter, because of the deformation of the particles on the substrate upon drying. The diameter of deformed particles can only be approximated, as described by Bradford and Vanderhoff[1]. For the purpose of keeping the particles in their spherical form, they may be hardened by bromination before preparation[2-4].

This method is not always usable, as certain types of polymers, *e.g.* those containing vinyl acetate, acrylate esters, vinyl chloride or vinylidene chloride, do not respond to bromination since they contain little or no residual unsaturation.

Other particle hardening methods are high energy irradiation, as also described by Bradford and Vanderhoff[5], and the addition of salts like uranyl acetate to the dispersion, a method developed in particular for polymers containing acrylic monomers and described by Mahl[6].

Both methods have their drawbacks. According to Bradford and Vanderhoff, several polymers (*e.g.* copolymers of ethyl acrylate and methyl methacrylate) degrade on being irradiated instead of being crosslinked[7]. It is not known if hardening with uranyl acetate is applicable to all types of dispersions.

Quite another method of hardening has been described by Vanzo and collaborators[8,9]. They add styrene monomer to the dispersion, which is absorbed by the dispersed particles. The styrene is then polymerised by γ -radiation by which process the particles are hardened.

This method was originally developed for polyvinyl acetate dispersions,[8] but has been used successfully for acrylics too[9]. This method may show the same disadvantage as does the high-energy irradiation technique mentioned above.

Furthermore, it is doubtful if all types of dispersions do absorb enough styrene monomer to be sufficiently hardened in this way.

In addition to their specific problems, the methods mentioned above show one disadvantage in common, *viz.* the uncontrolled change of particle size during the hardening process. It is the aim of this paper to describe a method free from all these drawbacks.

Its principle is in freezing the particles quickly at the temperature of liquid nitrogen (−180°C), after having applied the diluted dispersion to a microscope cover glass, and holding the particles at this temperature until the ice on the substrate has disappeared by sublimation under high vacuum and a carbon coating of controlled thickness has been applied.

The preparation can then be completed in the usual way, during which the particles are kept in their spherical form by the protecting layer of carbon.

Method of preparation

A drop of dispersion is thinned 10 to 20 times with distilled water. One or two drops of the thinned dispersion are smoothly spread over the surface of a microscope cover glass. The cover glass is then quickly plunged into liquid nitrogen. After that, the cover glass is put in a small copper tray situated under the bell jar of the vacuum coating unit (numbered 1 in Fig. 1) and which is cooled with liquid nitrogen.

The liquid nitrogen is fed to this copper tray through a conduit-pipe *via* an air-tight inlet and then *via* an air-tight outlet back to a reservoir outside the bell jar. The nitrogen is impelled through the conduit-pipe with compressed air.

To get a better heat exchange between the copper tray and the microscope slide the tray was smoothly polished on the inside and then painted black.

To avoid ice formation on cooling the copper tray before the microscope cover glass has been put in and vacuum has been applied, some liquid nitrogen is introduced. This obviates prolonged pumping later on.

During preparation, another copper tray of the same form (numbered 2 in Fig. 1), which is cooled by some liquid nitrogen, may be turned on top of the former. This tray prevents heating of the polymer particles by radiation from outside the bell jar. For that reason, only its under-surface has been painted black. During preparation, the temperature of the sample is controlled with a thermocouple. In most cases it does not rise above −120°C. To sublime the ice from the sample in a relatively short time, a quick decrease of the pressure to approximately 2.10^{-5} Torr is recommended. Then the upper copper tray

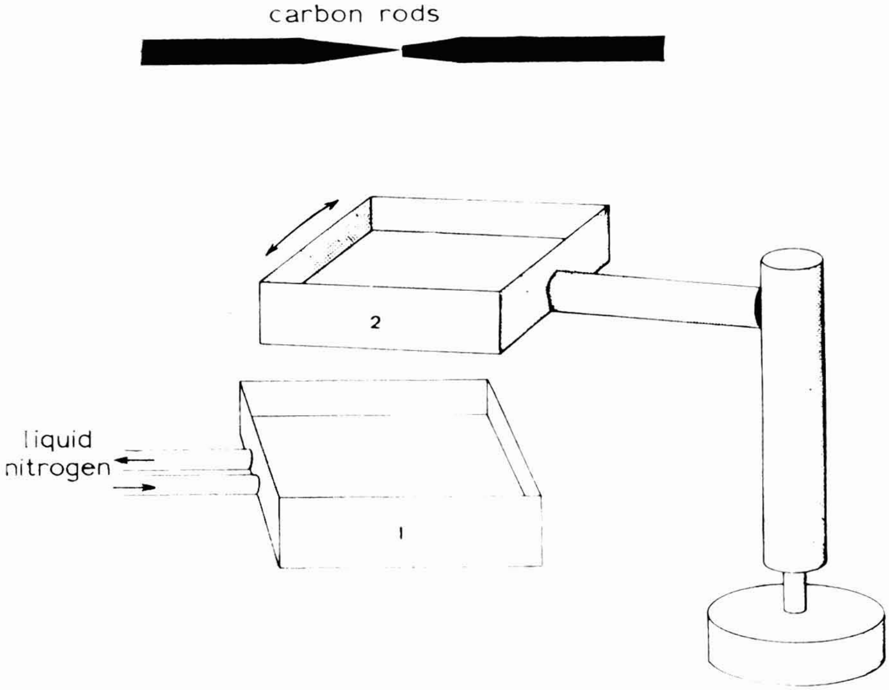

Fig. 1. Freeze-drying apparatus

is removed and the polymer particles are coated with carbon. The thickness of the carbon coating is controlled by measuring the blackness of a glass plate placed at the same distance from the evaporating source as the specimen. After coating, the liquid nitrogen stream is stopped, and the temperature is allowed to rise to ambient. Then air is admitted to the bell jar. Thereupon, the carbon film is detached from the microscope cover glass by etching with hydrofluoric acid. After having been washed with distilled water, the film is mounted on a number of copper grids.

The electron micrographs were made by means of a Philips EM 200 Electron Microscope (at the Technisch-Physische Dienst TNO-TH, Delft, Holland). To calibrate the microscope, after each series a diffraction grating replica was photographed as well. For determining the particle size distribution, a counting wedge was used, which permitted counting the particles in sixteen size classes.

Results

Fig. 2 shows the particles of a styrene : 2-ethylhexyl acrylate dispersion, prepared as previously described.

As can be seen, most particles are spherical and determination of particle size distribution by means of this picture appears to be relatively easy.

So far excellent photographs have been made from this type of dispersion in which the styrene : 2-ethylhexyl acrylate molecular ratio varied from 1 : 1 to 6:1.

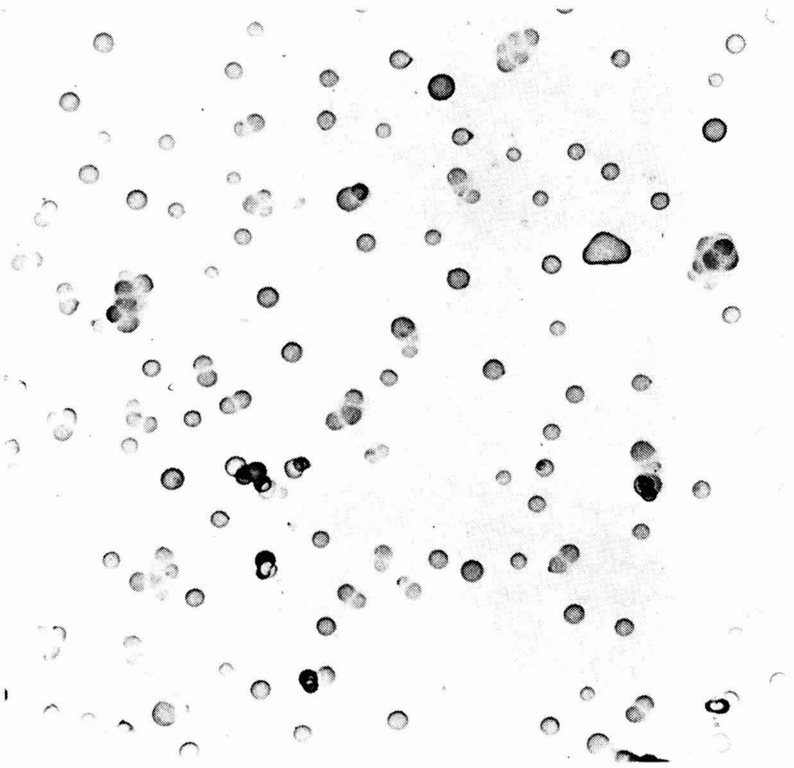

Fig. 2. Styrene:2-ethylhexyl acrylate emulsion mole ratio 1:1 (magnification × 14,000)

Good results have also been obtained with a polyvinyl acetate dispersion (externally plasticised), an acrylate copolymer dispersion, and a styrene/butadiene dispersion, all three having minimum film-forming temperatures below 0°C.

Accuracy of the method

Apart from the method of sampling and of counting the particles, there are two important factors which may influence the accuracy of particle size determination, *viz.*:

1. the calibration of the electron microscope magnification
2. the treatment of the particles during preparation.

When the magnification has not been calibrated, a variation of 10 per cent in it and, therefore, in particle size must be taken into account[10]. The authors used a diffraction grating replica for calibration, as a result of which the variation in the magnification decreases to 1 to 5 per cent, depending on particle size[11]. An equivalent method is calibration with a dispersion of exactly known particle size. The remaining variation in particle size between different micrographs of the same dispersion due to random errors, *e.g.* the way the specimen is placed in the sample holder, can only be decreased by calibrating each micrograph internally. Consequently, the dispersion must be photographed on a diffraction grating replica as a support, but this is a very time consuming and difficult procedure.

Internal calibration can also be achieved by photographing the dispersion together with another one of known particle size on the same grid. For this purpose the particles of the latter dispersion must be readily distinguishable from those of the former.

Errors in particle size determination may also arise from the method of preparation, in particular from hardening procedures, as pointed out in the introduction.

The authors carefully controlled the thickness of the carbon skin on the particles. Repeated coating of a dispersion of known particle size showed the thickness to be substantially constant.

The spherical form of the particles was checked by shadowing a styrene acrylate dispersion with platinum before applying the carbon coating and comparing the diameter of the particles, measured from the electron micrograph, with their height calculated from the length of the shadow and the tangent of the shadow angle. The result was found to be very satisfactory.

The repeatability of the method proved to be very good. With a 0.2 micron particle size dispersion, a standard deviation from the mean of 0.003 micron was found.

As for the absolute particle size value, a discrepancy was found between the size of Dow polystyrene dispersion LS-055-A determined according to the present method, but without applying the carbon coating, and the value given by Dow (0.188 micron). The authors' mean value was 0.013 micron lower.

[*Received 3 February 1969*

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Aircraft finishes*

By J. A. Scott

British Aircraft Corporation Limited, Weybridge Division, Weybridge, Surrey

Summary

The problems of providing protective coatings for aircraft are discussed in relation to the environmental conditions to which they are exposed. Reference is also made to interior and exterior decor painting. Coating systems preferred by British Aircraft Corporation are described.

Key words

Types of coating
- alkyd coating
- corrosion resistant coating
- corrosion resistant primer
- epoxy coating
- urethane finish

Types of surface
- aluminium
- steel

Chemically active pigments
- strontium chromate

Surface treatment before coating
- phosphate treatment

Finitions pour Avions

Résumé

On discute les problèmes de la mise au point des revêtements protecteurs à l'égard des conditions environnantes auxquelles sont-ils exposés. On fait référence d'ailleurs aux peintures décoratives pour l'intérieur et l'extérieur d'avions. On décrit les systèmes de revêtements préférés par la British Aircraft Corporation.

Flugzeuglacke

Zusammenfassung

Die Probleme werden besprochen, welche mit Flugzeugschutzlacken in Bezug auf die Bedingungen, denen die Flugmaschinen im Dienste ausgesetzt sind, in Zusammenhang stehen. Auch dekorative Anstriche für das Innere und Äussere werden erwähnt. Die von der British Aircraft Corporation bevorzugten Systeme werden beschrieben.

Отделка самолетов

Резюме

Обсуждается проблема обеспечения зашитных покрытий для самолетов, в зависимости от окружающих усиовий которым они подвержены. Рассматривается также внутренняя и внешняя окраска. Описываются защитные покрытия предпочитаемые Британской Корпорацией по Авиации.

Introduction

This discussion on aircraft finishes will be mainly concerned with structural protection, because it is in this field that most of the important problems lie.

Fig. 1 shows the BAC 1-11 airliner, a typical modern short/medium-haul jet. The majority of the fuselage is manufactured from aluminium alloy sheet, reinforced where necessary by machined components (Fig. 2). The main wing structure is machined from aluminium alloy planks (Fig. 3) and forms a sealed tank which contains the bulk of the fuel load. Major load-bearing components such as undercarriage legs (Fig. 4) and engine mountings are manufactured from high tensile steel.

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*Presented to the Southern Branch on 11 November 1968.

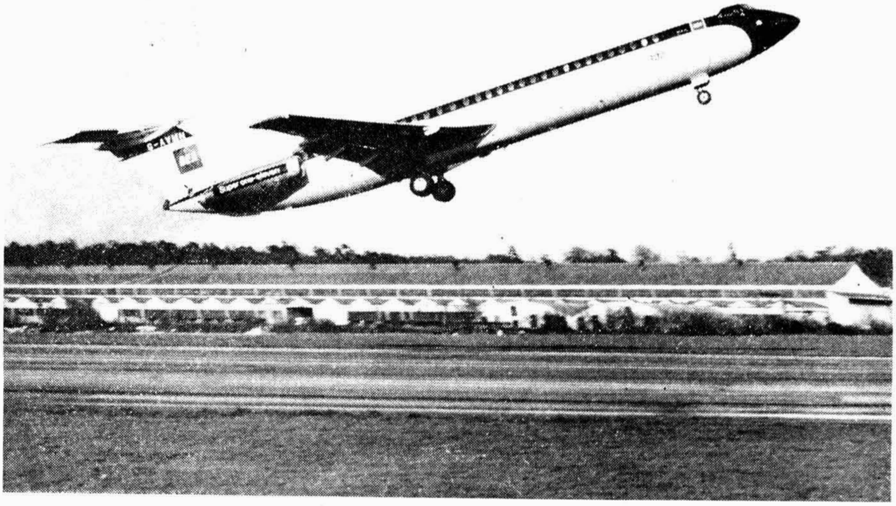

Fig. 1. BAC 1-11 airliner

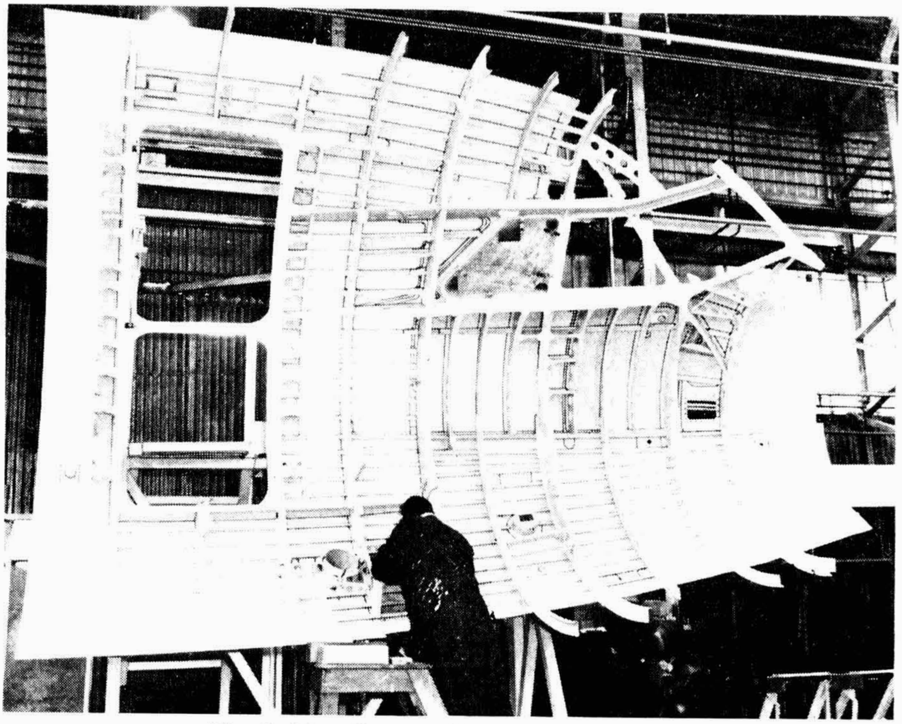

Fig. 2. Manufacture of BAC 1-11 fuselage

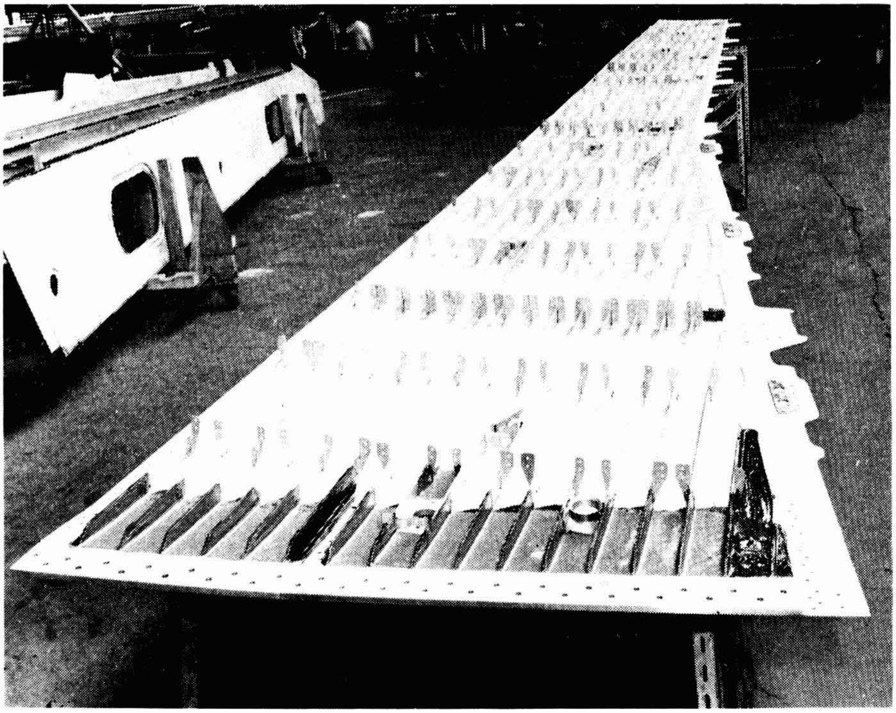

Fig. 3. BAC 1-11 wing structure

Environmental conditions

In order to appreciate the problems of aircraft protection, it is necessary to study the environmental conditions to which the modern jet airliner is subjected. First, considering the aircraft as a vehicle, some interesting comparisons can be made with the motor car. The car has a life of some 80,000 to 100,000 miles which, at an average speed of, say, 30mph, is equal to about 3,000 hours running. The modern jet is designed for 3,000 to 4,000 flying hours per year, throughout a first-line service life of 10 years, with a similar period in second-line operation. This means, for short-haul jets with average flight times of under 1 hour, some 100,000 flights in 20 years. For each flight, in taxiing out to the runway, taking off, landing, and taxiing back to the terminal, the aircraft will travel some 3 to 6 miles on the ground. Hence, in its life this type of aircraft will travel between quarter and half million miles on the ground, a good deal more than most cars, and at speeds of up to 150mph.

In one flight, an aircraft may move from, say, a temperate region up to an altitude of 6 to 8 miles where the outside air temperature is about −50°F, and a pressure differential of 6 to 7.5psi is acting on the pressure cabin. Descent may be through a thick cloud layer, to a tropical airfield where the ambient temperature is above 100°F. Thus the entire operating temperature envelope for the aircraft may be covered in the course of a few hours, and repeated many times a week. On descent, the cold structure is in contact with warm, moist air, and condensation, to the extent of gallons per flight, takes place. This is

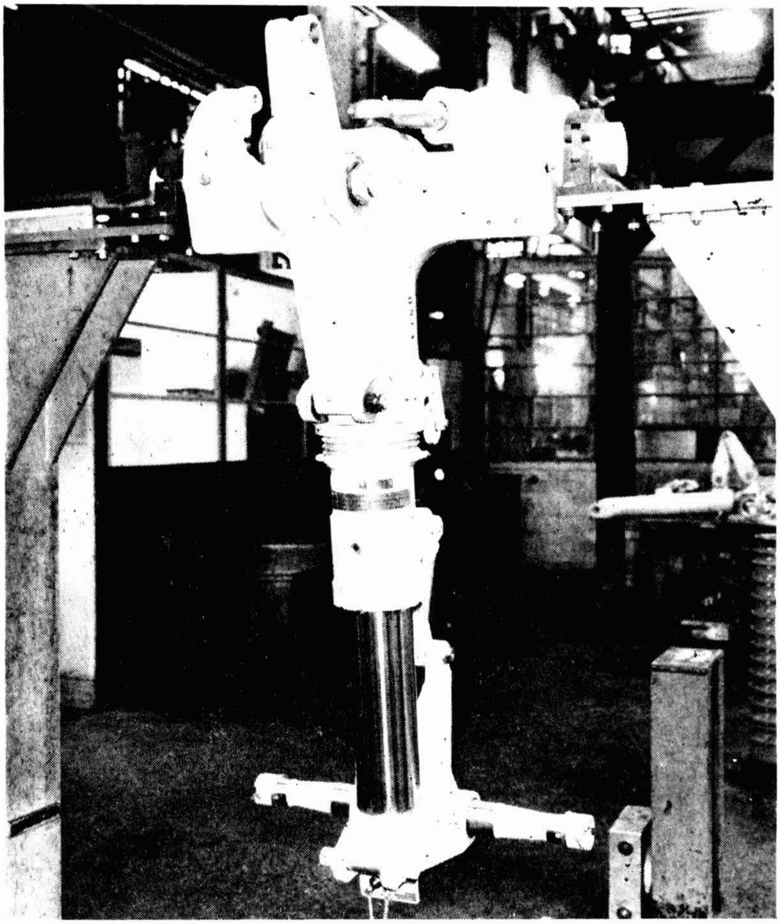

Fig. 4. Undercarriage leg for BAC 1-11

very important, because not only is the water corrosive in itself, but it also acts as a carrier for other contaminants, whether soluble or not. These other contaminants vary from operating fluids to freight, and it is a good working rule that anything which is carried will sooner or later be spilt. Operating fluids include hydraulic and lubricating oils, fuel, chlorinated water, de-icing liquids etc. Many of these are damaging to paint systems, whilst others are corrosive to exposed metal. Almost anything might be carried as freight in modern aircraft with pressurised freight holds, and the dangers involved in some materials, either singly or in combinations, may be imagined. There are also those contaminants which arise from misfortune, as for instance when an aircraft over-runs the runway and becomes partially immersed in sea water, or when residues are left from extinguishers used in the event of a fire.

Corrosion prevention

Such are the conditions which have to be met and mastered; their control is obviously of vital importance in aircraft, and the job is made more difficult by the high utilisation rate leaving little time for maintenance. Consequently, corrosion prevention commences in design, and is important at all stages in the production and subsequent maintenance of the aircraft.

First one chooses the best materials for the job, aiming at maximum corrosion resistance combined with high strength and low weight. Components are designed to avoid water traps, to allow protective coatings to be applied efficiently, and to allow those coatings to remain effective in service. Thus, drainage holes are provided where necessary, undrainable areas are filled with lightweight materials, and sharp corners and re-entrant angles are avoided. There may be a need to use stainless steels or titanium alloys in areas where elevated temperatures are expected, the corrosion risk is high, or it is otherwise difficult to protect the part properly.

Next, protective films are applied, which may be broadly classified as conversion, electroplated, or organic coatings. The first two classes include anodising or chromate conversion coatings for aluminium alloys, and phosphating or cadmium plating for steel. In many industries these finishes provide adequate protection alone, but in aircraft, where long lives must be achieved under arduous conditions, they are not enough and organic coatings are relied on mainly as the first line protection. The conversion and plated coatings (with the exception of chromium) are therefore used primarily to act as a key for the paint and to form a second line of defence in case of damage.

Paint for structural protection

At BAC, Weybridge, the entire philosophy of structural painting was changed with the Vanguard turbo-prop airliner, built about nine years ago. Previously, etch primers had been used, extensively supplemented in critical areas by alkyd, or, later, epoxy, finishes applied after assembly. Before finalising the Vanguard design, the history of protection breakdowns was studied and it was found that where paint failed it was generally because it was attacked by contaminants or because it was not sufficiently flexible to withstand the constant movement of the airframe.

It was therefore decided that paint had to be chemically resistant, and flexible enough to remain effective during the life of the aircraft. Many materials were examined, and the polyamide-cured epoxies were found to offer the best compromise between the conflicting requirements of chemical resistance, water resistance and flexibility. A strontium chromated primer is used to give good corrosion inhibition, with a glossy light grey finish in those areas subject to contamination and/or damage. The colour of the finish was chosen carefully, replacing a previous grey-green, to give good light reflection, combined with durability and aesthetic appeal.

These epoxy materials, it was found, could only be satisfactorily applied over positive film-forming pre-treatments: degreasing or pickling was not sufficient to meet the high standard required. Having applied pretreatment, there was no point in allowing it to get dirty before painting, as the part could never again be made as clean as when it came fresh from the pre-treatment cycle. Therefore primer, and where necessary, finish, is applied to each individual part, before any assembly. This means:

(a) good adhesion
(b) protection through assembly stages
(c) full protection at the vulnerable joint area
and
(d) finishes can be stoved to give maximum chemical resistance before leaving the process shop.

Previously, special finishes were needed in battery bays, freight areas etc., but the current system meets all normal structural protection requirements. The same paints are used on aluminium alloys and steels, but the use of phosphating as a pre-treatment deserves special mention. A heavy fine-grained phosphate coating is used, as good lubrication is often required on some areas of components. In the remaining areas where paint protection is necessary, it was found that only partial impregnation of the crystal structure was achieved with pigmented coatings of high solids content. Phosphated components are therefore sprayed with a low-viscosity high-bake epoxy lacquer as a first. impregnating, coat, followed by the normal scheme of primer and finish.

This protection system has worked well, and a Vanguard aircraft recently inspected after approximately eight years service was found to be completely free from any significant corrosion. After repair of local damage around freight doors, the aircraft was considered to be satisfactory for further service, without any additional maintenance to the original structural protection.

External decor painting

The exterior of the aircraft presents a different case where, although corrosion protection is still important, the paint is also required to serve a decorative function. Application problems are not as great, as one is presented with a smooth, uncomplicated surface which lends itself to cleaning, chemical treatment and painting. Primer is still applied at the detail stage, in order to ensure the all-important bond between paint and metal, but, as appearance is of major significance, finish paint is applied over a thin second primer coat after assembly is complete.

The choice of finish paint will depend to some extent on the type of aircraft, the main paints in current use being based on alkyd, acrylic, epoxy and polyurethane. Alkyd paints give an initially good appearance, but relatively poor durability and chemical resistance. Air-drying acrylics tend to lack gloss as applied, and exhibit poor chemical resistance and a tendency to pick up dirt unless maintained in a polished condition. Their main merit lies in good colour stability at elevated temperatures, making them an attractive proposition for supersonic aircraft, when kinetic heating results in skin temperatures in excess of 100°C. Epoxy paints came into use when chemical resistance properties were required, but their readiness to chalk is accentuated on high flying aircraft subject to high levels of ultraviolet light. An even higher degree of chemical resistance is available with polyurethane paints, which also provide excellent colour and gloss retention. These materials are coming into widespread use as external decor finishes, their main drawbacks being in application when surface cleanliness is critical. Decor schemes generally follow similar patterns, using white for fuselage upper surfaces, to reduce cabin temperatures in hot climates, and light grey on lower surfaces to simulate the appearance of aluminium. Individual airline motifs can be applied in paint or self-adhesive plastic labels, the latter allowing rapid changes for short-term leases.

Interior decor painting

In the cockpit, the emphasis is on non-reflective finishes and this results in a neutral, functional appearance. The cabin decor is normally designed by consultants, and uses mainly soft colours in matt or eggshell finishes because of the high light intensity above the clouds. Many furnishings are self-coloured, in pvc or laminates, often with integral designs. Where paints are used, cellulose and stoving enamels have been largely replaced by epoxies, which may be textured, or acrylics. The latter materials have an advantage in ease of application or repair, and good colour retention.

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New concepts in polymer architecture*

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Summary

The development of polymer science is briefly considered and it is suggested that there are lessons to be learned from the past. Some recent developments are discussed in relation to their potential value in the coating industry. Among these may be mentioned specific grafting techniques, ladder and semi-ladder polymers, sheet structures, ionomers, co-ordination polymers and methods for the control of polymer structure.

Key words

Binders—resins, etc.
block polymer
graft polymer
polymer

Processes primarily associated with manufacturing or synthesis
polymerisation

Nouveaux concepts dans le domaine de l'architecture polymère

Résumé

On considère brièvement le développement de la science polymère, et l'on suggère la possibilité d'en profiter des expériences du passé. On discute quelques récentes développements à l'égard de leur importance potentielle à l'industrie de peintures. Parmi ceux-ci, on peut mentionner: certaines techniques de greffage; polmères-échelles ou mi-échelles; structures sous forme de plaque, ionomères, polymères co-ordinés; et des méthodes pour contrôler la structure polymère.

Neue Vorstellungen von der Architektur der Polymere

Zusammenfassung

Die Entwicklung der Polymerwissenschaft wird kurz betrachtet, und es wird vorgeschlagen, aus der Vergangenheit eine Lehre zu ziehen.

Einige Neuentwicklungen werden hinsichtlich ihrer möglichen Auswertung in der Lackindustrie besprochen. Dazu gehören spezifische Pfropftechniken, Leiter- und Halbleiter-Polymere, Blattstrukturen, Ionomere, Koordinations- polymere, sowie Methoden zur Kontrolle der Polymerstruktur.

Новые идеи в структуре полимеров

Резюме

Кратко рассматривается развитие полимерной науки и высказывается мнение что можно кое чему научиться из прошлого. Обсуждаются некоторые современные развития техники и их потенциальное значение в производстве покрытий. Среди этих можно упомянуть специфические технические приемы прививки, лестничные и полулестничные полимеры, пластовые структуры, иономеры, координационные полимеры и методы контроля полимерных структур.

Introduction

The outstanding achievements in polymer science during the post-war years have undoubtedly been the development of stereospecific polymerisation and the elucidation of some major biological polymer structures, notably the DNA helix. These, and the parallel strides which have been taken in the understanding of polymer conformation, have so conditioned present-day thinking about polymer architecture that it will be difficult in this presentation to avoid

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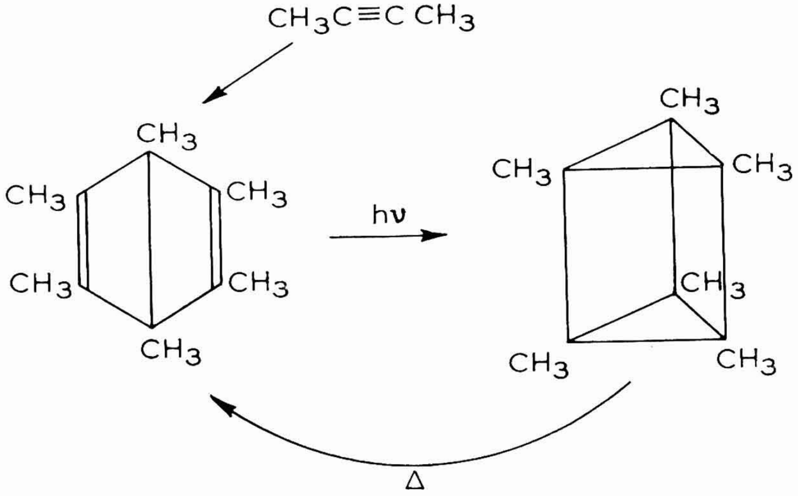
*Presented to the London Section on 18 September 1968.

reference to them, despite the plurality of excellent reviews which have been published elsewhere. An attempt will be made, however, to avoid bias towards them, because it is felt that many other developments have taken place in recent years which warrant serious consideration by all whose job it is to shape the polymer technology of the future.

In this sense, polymer architecture cannot usefully be considered in isolation from other polymer studies. Architecture can be studied from the individual standpoints of design, structure or aesthetics, but it is more profitable to relate it to materials, building methods, the function of the building and the lay of the surrounding country. All these are in dynamic relationship with architecture; they influence it and are influenced by it. So it is with polymer structures. One can think of new structures and try to build them on the one hand, and one can adapt new synthetic methods to create novel structures on the other; and all the time it is necessary to be concerned with the functions the new molecules may have to perform and with the way they will interact with their environment.

In an understandable determination to look ahead, it is easily forgotten that one can often profitably look back and see what lessons the past may hold. The recent isolation and characterisation of hexamethyl-Dewar-benzene and hexamethyl-prismane no doubt caused many chemists, brought up to think that resonance and molecular orbital theories had finally disposed of the independent existence of Dewar, Ladenburg and Kekulé benzenes, to reflect on the ever-changing bases of science.



Whilst the picture of the covalent macromolecule is little more than 30 years old, there is already a need to extend this concept, and to recognise the existence of other kinds of polymers. See Figs. 1 and 5. It is not unreasonable to suggest that the rather facile interpretation of polymer properties in terms of linear, branched and cross-linked covalent structures can have a retarding influence on original thinking, as can the tendency to interpret the reactions of polymers

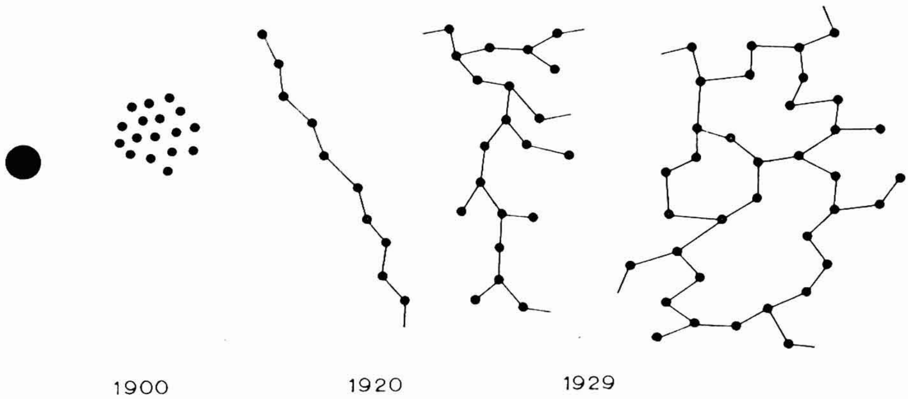


Fig. 1. Early development of the macromolecular concept

in terms of the behaviour of their monomeric analogues. There is today a growing recognition of the concerted reactions of functional groups present in polymers and their differences from the reactions of isolated, otherwise similar, groups in simple compounds, And it is sobering to recall that some of the polymer models of the transitional years, between the colloidal micelle and covalent macromolecule concepts, are now being realised as distinct entities after all. The development of viscosity theory from the Einstein spherical model, through the solvated sphere and the rigid rod, to the random coil, provides but one example. See Fig. 2. The rigid rod may well be considered an

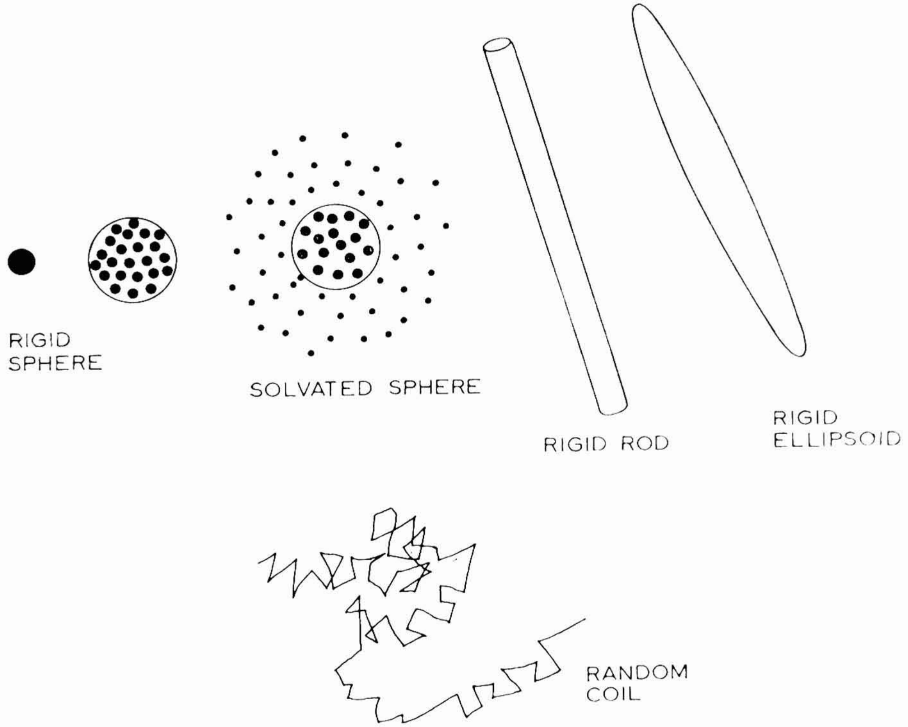


Fig. 2. Early development of viscosity theory

inadequate concept in this context, but it is nevertheless a type of structure which is now realisable in practice (*q.v.*).

Of course, it was necessary to proceed through the intermediate stages of what may presently be called incomplete understanding, but it is fatal to believe that complete understanding has yet been achieved. Looking back, it may be perceived that many ways of putting together organic macromolecules have been discovered, using, more often than not, the reactions of classical organic chemistry. Eventually, the various polymer species, so obtained, have been hybridised to yield copolymers and cocondensates of divers compositions and properties; sometimes profitably, sometimes not. None would deny that this sort of exercise was technologically desirable but, having carried it out for 30-odd years, one may perhaps be forgiven for wondering if it is now sufficient to go on proliferating alkyds, phenolics, acrylics, silicone-modified this and styrenated that. A breakaway is surely overdue; and some pointers to the way in which this may occur constitute the main theme of this paper.

Graft and block copolymers

A block copolymer was devised as a synthetic rubber in Germany during the war years, but otherwise the first breakaway from random copolymers was probably the styrenated alkyd, peculiar to the coatings field. A more recent example is the thixotropic alkyd of the polyamide-modified type. Otherwise, the potentialities of non-random copolymers seem to have been left to the rubber and plastics technologists, and even they have been slow to develop them.

The problem in making block and graft copolymers has always been that of getting a good yield of the block or graft structure, to the exclusion of random structures or homopolymer mixtures, by methods that are at once practicable on the large scale and economically realistic. Techniques are now emerging which promise to change this situation.

One of the most significant appears to be an adaptation of a reaction discovered by Weiss & Porret in 1937. It involves a redox system of a transition metal, Ce, V, or Mn, in its higher valency state, with a reducing agent such as an alcohol, aldehyde or amine. The system most studied is that comprising Ce^{4+} and an alcohol, which reacts as follows:

$$Ce^{4+} + R.CH_2OH \rightarrow \text{Complex}$$

$$\text{Complex} \longrightarrow Ce^{3+} + H^{+} + R\dot{C}HOH$$

$$\text{or } RCHO\cdot$$

The point to note here is that the radical is formed on the reducing agent, so, if the reducing group is built into a polymer, that polymer carries the radical. It is thus capable of initiating polymerisation, and, if a suitable monomer is present, that monomer must be grafted to it and homopolymer cannot be formed unless chain transfer intervenes. It is only in the last few years that this reaction has been exploited for this purpose, notably by Mino & Kaizermann of American Cyanamid and by several workers at the University of Tokyo[1-3].

Most of this work has been on the modification of cellulose fibres, but the technique is of wide applicability, as seen in Figs. 3 and 4.

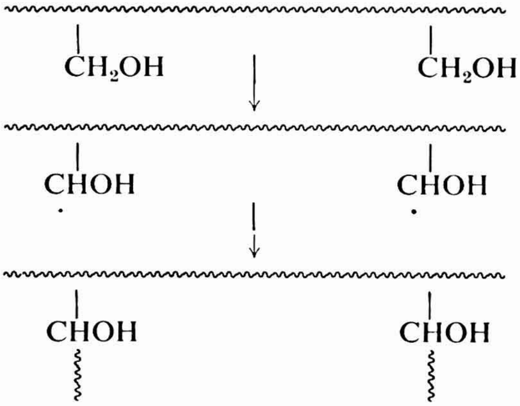


Fig. 3. Grafting on cellulose or other hydroxylic polymer

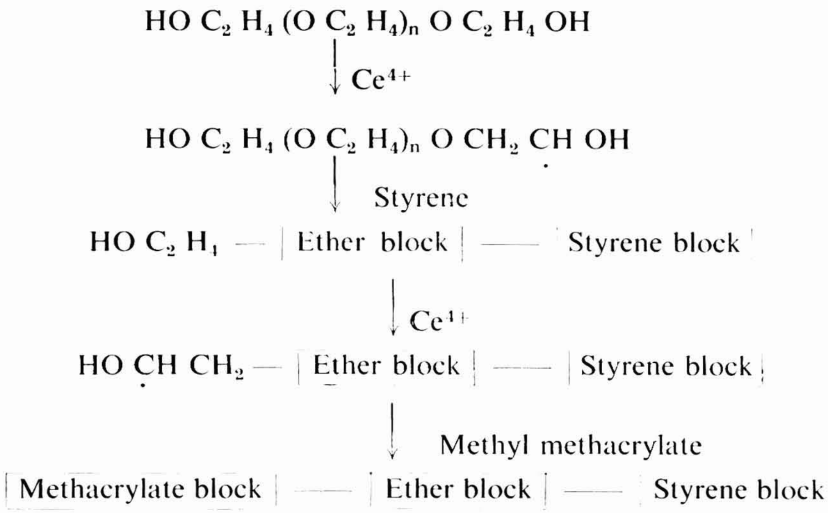


Fig. 4. Formation of block copolymer sandwich

A second reaction, applicable to similar ends, was discovered much more recently by Bamford *et al*[4,5]. This comprises the generation of free radicals by the interaction of certain metal carbonyls and organic halides in presence of a polymerisable monomer as follows:

$$Mo(CO)_6 + M \longrightarrow M \text{------} Mo(CO)_5 + CO$$

$$M \text{------} Mo(CO)_5 + CCl_4 \longrightarrow \text{Intermediate} + CO$$

$$\text{Intermediate} \longrightarrow CCl_3\text{—}M\cdot$$

(M is a monomer molecule)

If the halocarbon moiety is attached to a polymer, as when $—CCl_3$ or $—CCl_2—$ groups are present, the initiating radical is generated on the polymer, and grafting must ensue, again, unless chain transfer occurs.

In a closely related system, acetylacetonates of cobalt or copper are employed[4]:

$$Co^{2+}(acac)_2 \quad \text{or } Cu^{2+}(acac)_2$$

with

$$CCl_4 \quad \text{or } CBr_4 \quad \text{or } CCl_3COONH_4$$

$$Cu^{2+} + CCl_3COO \longrightarrow CCl_3COO\cdot + Cu^{+}$$

$$CCl_3COO\cdot \longrightarrow \cdot CCl_3 + CO_2$$

The copper-ammonium trichloracetate system is one of the most efficient of these combinations but none is as effective as the carbonyl systems[6].

Now these reactions are of obvious value in grafting but, at first view, there is little to suggest that, in simple polymerisations, they will accomplish anything more than a conventional free-radical source like a peroxide or AZDN. It has however been shown that,

(a) the carbonyl system yields free radicals very quickly at room temperature; initiation by cobalt carbonyl and CCl_4 is some 10,000 times as fast as initiation by AZDN at 25°C,

(b) the carbonyl systems can affect the fine structure of the polymers they produce; poly(methyl methacrylate) produced from nickel carbonyl has a higher isotactic content than the product of conventional free radical polymerisation.

Thus, there are differences in speed of polymerisation and nature of polymer produced which could conceivably be exploited. Such an observation, of course, is not exclusive to this system. It is well established that a heterogeneous catalyst of the Ziegler type, with a specific surface or oriented adsorption effect, is not a prerequisite of stereoregular propagation, though admittedly the most striking effects have been achieved with catalysts of this type. As examples, there may be mentioned the formation of,

(a) syndiotactic poly (vinyl formate) initiated by AZDN under UV irradiation[7]

(b) isotactic poly (2-vinyl pyridine) initiated by phenyl magnesium bromide in toluene[8]

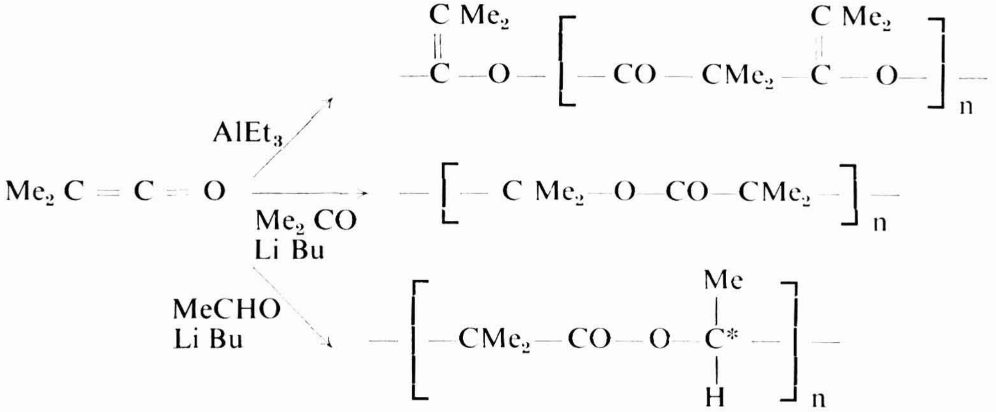
(c) optically active isotactic poly (propylene oxide) initiated by diethyl zinc in presence of D-borneol[9].

This last is of interest because it exemplifies the influence of solvent environment, in direct analogy with the classical technique of asymmetric synthesis.

Structural regulation in polycondensates

It has been widely held that polycondensates, such as polyesters, cannot be stereoregulated because of the random nature of the polycondensation process. This postulate may of itself be questioned but, be that as it may, one is not obliged to make a polyester by polycondensation. To think so is to confess to a mental conditioning by an obsolescent classification system.

Homopolymerisation of ketenes under the influence of aluminium triethyl, and the copolymerisation of ketenes with ketones by butyl lithium, both yield polyesters *via* an addition mechanism. The latter can be extended from ketones to aldehydes[10]. Use of an aldehyde or an unsymmetrical ketone yields a polyester, each repeat unit of which contains an asymmetric carbon atom (starred).



The possibility is thus afforded of preparing stereoregular polyesters by this route if by no other. An optically active polyester has in fact been prepared by the polyaddition of inactive R-propylene oxide and 3-phenyl —Δ^1— tetrahydrophthalic anhydride dissolved in toluene in presence of D-borneol and zinc diethyl.

Control of molecular weight homogeneity by techniques such as precipitation polycondensation[11] is another prospect which must be borne in mind.

Branched structures

It has become customary to think of branching in polymers as a random rather than a directed process, and to envisage branched molecules as possessing an indefinite number of branch points. But, cruciform polymers, made by a simple condensation process, and having some unusual solution properties, were reported years ago. If an ω-hydroxy acid is condensed in presence of a small amount of pentaerythritol, it can be shown statistically that the polymer tends to the pure cruciform structure as the degree of reaction approaches unity[11]. Obviously, by utilising the ceric ion redox system mentioned earlier, pure cruciform grafts of vinylic monomers on pentaerythritol should be obtainable. Applying similar ideas to dipentaerythritol, one should obtain double cruciform structures. There is no obvious limit to progress along these lines; the production of indeterminate mixtures of shapes is not inevitable after all. One can begin to think, for example, of making polymers having a regular comb-like structure with all the teeth of the comb equal in length and regularly spaced, rather than the random combs which have been produced hitherto.

Ladders, semi-ladders and sheets

Conceptually, it is not a very great stride from the comb to the ladder and semi-ladder polymers. These structures have been the target of many workers who have sought great stability in mechanically tractable polymers. Generally,

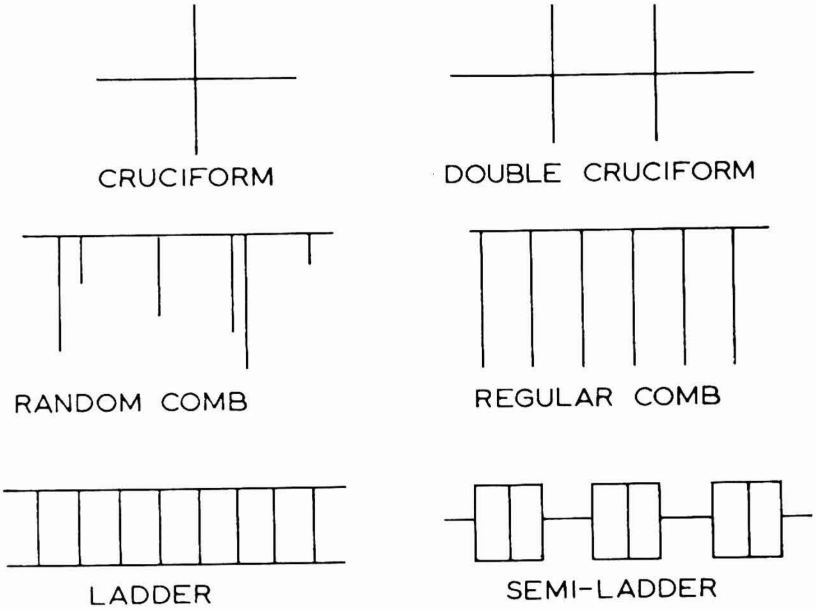
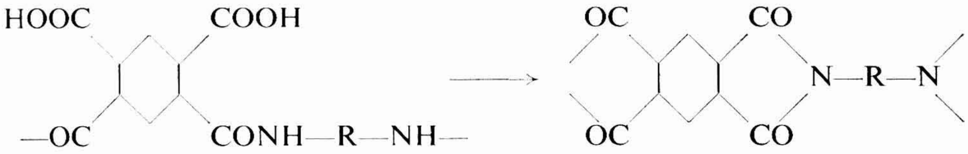


Fig. 5. Some model polymer structures

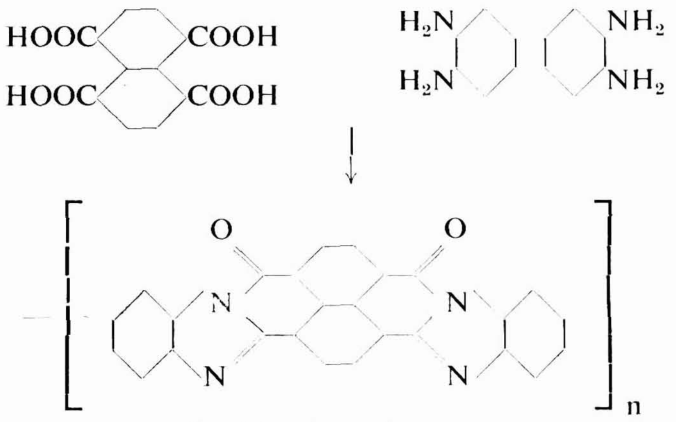
the aim has been great thermal stability, but hydrolytic stability could equally be considered, and often has been. The idea is that, in a linear polymer of the usual kind, only one bond per molecule need be broken to halve the number average molecular weight. The extent of the degradation reaction therefore does not have to be very great to cause a sharp deterioration in molecular weight and the properties which depend on it. Now, to degrade a ladder polymer, each fission requires two bonds to be broken, and these must be the bonds separating the same pair of rungs. It is easy to see that the probability that such a pair will be broken in preference to any other pair is low, and that the probability of fragmentation of a ladder polymer is much lower than that of a single strand.

The semi-ladders are generally easier to prepare than the ladders. They are also more tractable; but each single link represents a source of weakness and, other things being equal, they are not so stable.

One of the better known types is the polyimide derived from pyromellitic dianhydride, which is formed in two stages. The first product is an amidic acid which undergoes ring closure on heating to yield the semi-ladder imide[12].

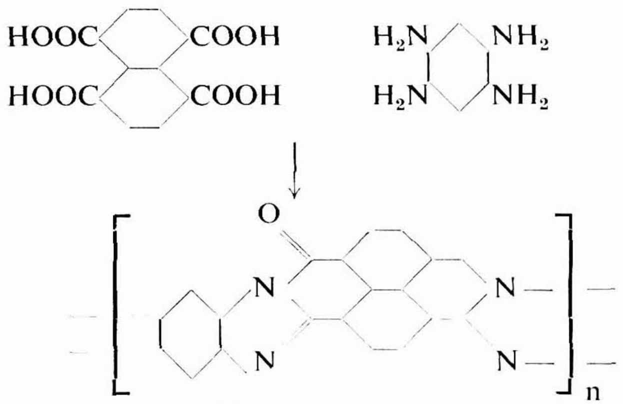


There is an extensive literature on ladders and semi-ladders, and several reviews have been published recently[13]. Although many of these products, like some of the polybenzimidazoles, have high thermal stability, their interest for the formulator of solution coatings is limited by their low solubility. There are indications, however, that such structures may find application even in coatings technology as it is currently known. For example, Van Deusen *et al.*[14] have reported the formulation of benzimidazobenzophenanthrolines by the condensation of 1, 4, 5, 8-naphthalene tetracarboxylic acid with 3,3′-diaminobenzidine in presence of polyphosphoric acid. The product was a black *soluble* polymer, the solubility being dependent on the degree of ring closure and hence on the severity of the reaction conditions.



Semi-ladder polymer

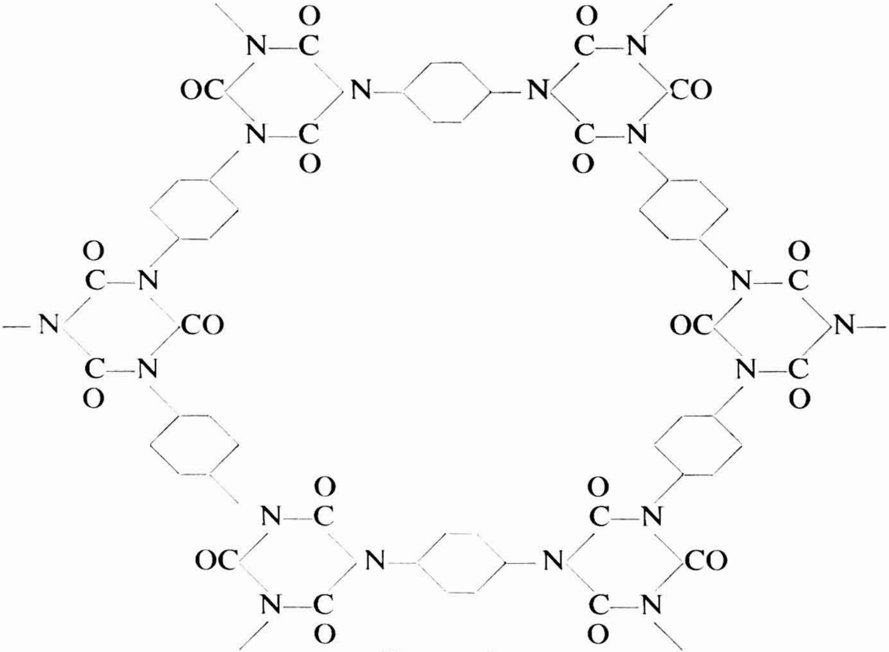
The corresponding true ladder was obtained from the same acid and 1, 2, 4, 5-tetraaminobenzene. It was more stable both to heat and hydrolysis, but was also less soluble.



Ladder polymer

One step further in the direction of complication from the ladder polymer, is the sheet polymer, or the two-dimensional network resembling chicken wire. This is well known in inorganic chemistry in such materials as graphite, mica, and certain clays, but the tetrahedral quadrivalency of carbon, not surprisingly, tends to militate against its appearance among organic polymer species. Sheet polymer formation, albeit as an irregular, flexible structure, was nevertheless postulated by Hill in 1961 when suitable condensation reactions were conducted in an adsorbed monolayer at a liquid interface[15].

Recent work seems to be opening up this area of polymer architecture. Thus, Huggins and co-workers at Stanford claim to have made a polymer composed of a series of stacked sheets by the polymerisation of *p*-phenylene diisocyanate[16].



Sheet polymer

Other examples are to be found among the polymeric metal chelates (*q.v.*).

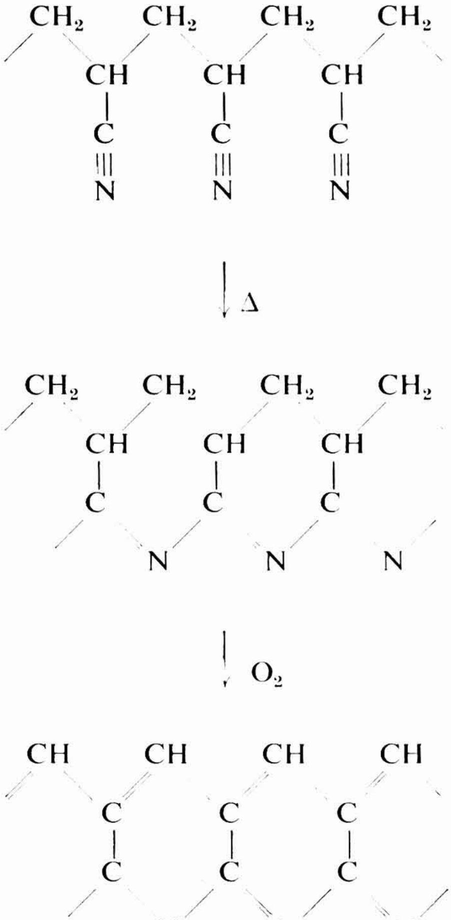
Research by objectives

The ladder polymers have been highly developed as a result of a specific target—thermal stability—for which a great deal of money has been made available through various national space and missile research programmes.

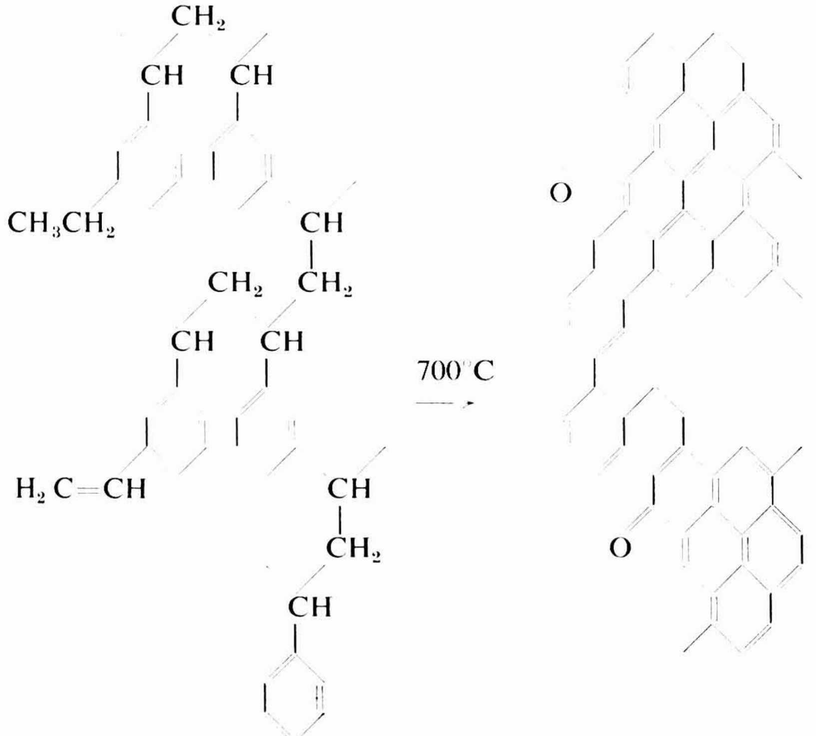
A second example of a specific objective which has generated new thoughts about polymer architecture is the semi-conducting polymer. Recognition of the semi-conducting properties of various inorganic materials has brought about an explosive development of solid-state devices, of which the silicon diode and the transistor were just the beginning. Semi-conduction is related to photo-conductivity and, hence, to lightfastness in pigments. A whole new area of coatings technology has been opened up with the development of electrographic printing processes. On the one hand, almost the whole of electrotechnology depends on the dielectric properties of the materials used as insulators, and on the other, there is an increasing recognition of the role of electrical effects in life processes.

Detailed consideration of these matters in relation to polymer structure is beyond the scope of this paper, but the work which has been, and is being, carried out in these areas provides further evidence of the existence of, and the continuing need for, new thinking, some of which seems likely to contribute to future coatings technology.

It is not difficult to envisage structures intermediate between the insulator polystyrene and the conductor graphite. Polymers composed of multiple aromatic rings or other polyconjugates are obvious candidates if one is seeking semi-conducting properties which necessitate electron mobility along the polymer chains. One of the first to be discovered was the so-called "Black Orlon," a partially pyrolysed polyacrylonitrile, which is clearly a ladder polymer.



Much more recent is a partially graphitised copolymer of divinylbenzene and ethylstyrene which is clearly seen to approach graphite in structure: see the review by Baker[17].



C 93%
H 3%
O 4%

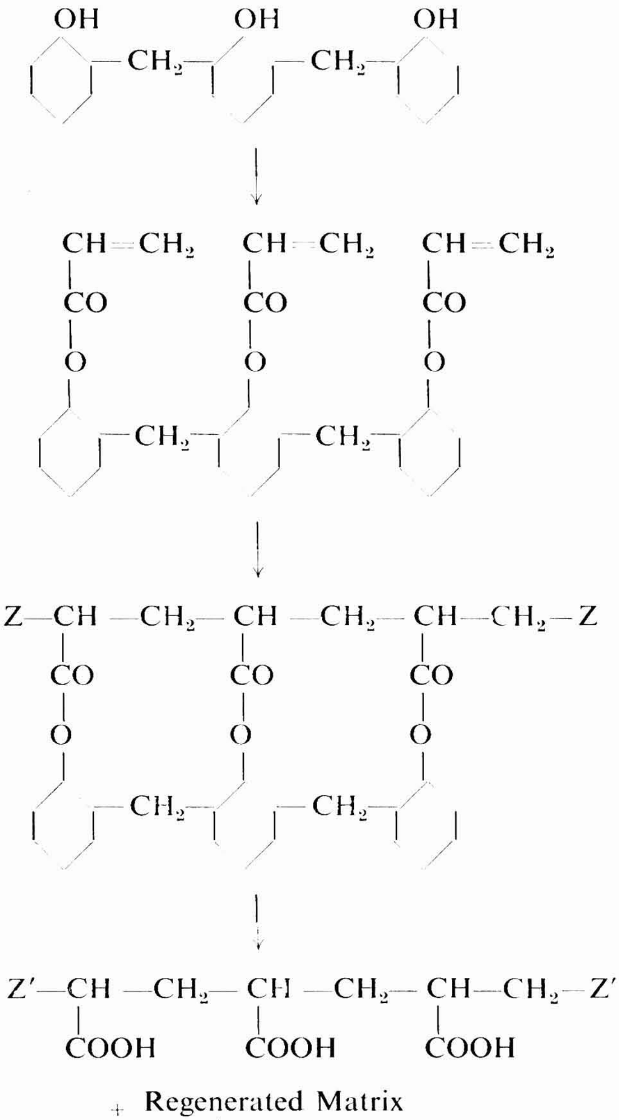
Before leaving this topic, it is worth noting that suggestions have even been made for a polymer which will be *super*-conducting at temperatures economically attainable in power lines and, in contrast, that the role of semi-conduction in the polyene chains of carotene and like materials is of importance in photosynthesis.

The purpose of this digression has been merely to show that here is just one of the areas of scientific progress which, though superficially remote from the interests of the coatings technologist, will yet contribute to concepts of polymer architecture for which he may one day find fruitful outlets.

Returning to the subject of thermal stability, Wright and Lee of RAE Farnborough have suggested with considerable weight of authority, that not enough work is being done on the correlation of behaviour with structure[18]. Without this, the vast effort being devoted to synthesis lacks adequate guidelines. It seems obvious that most ordinary chemical bonds would be strong enough to resist fragmentation if the only possible destructive mechanism required bond cleavage alone and was not followed by a chain reaction or the elimination of simple fragments. Moreover, like mechanical strength, thermal stability is greatly reduced by the occurrence of irregularities in the polymer structure. A major objective must therefore be the development of methods which yield polymers of uniform and precisely defined structures.

Control of polymer structure

Some indication of directed structure formation has already been given with reference to the role of oriented adsorption and the influence of environment during polymerisation. An extreme example of forcing monomer molecules into a local arrangement which compels them to react in a particular way is provided by a recently reported template synthesis of pure, homomolecular, oligomers of methacrylic acid[19,20].



The pure oligomeric methylene phenol is readily prepared and well characterised. Polymerisation of the acylated derivative in dilute solution (to prevent intermolecular reaction) using AZDN as initiator, yields the intramolecular polymer. When the template molecule is removed by hydrolysis, an oligomer of unequivocal composition is produced. A particularly elegant feature of this synthesis is the use of AZDN as initiator, yielding terminal groups (Z) which convert to methacrylic unit structures (Z′) on hydrolysis. It is not suggested, of course, that this "sledge-hammer" approach is likely to be commercially viable.

Rather more subtle, is the polymerisation of monomers stacked in the helical canals of urea and thiourea clathrates[21]. Extraction of the urea or thiourea after polymerisation yields highly oriented polymer in the form of needle-like aggregates. Pure crystalline poly (trans-1, 4-butadiene) and syndiotactic poly (vinyl chloride) have been made in this way. Quite precise data are available on the molecular dimensions and geometry of both the monomers and the canals, so it is possible to match monomer to clathrate by calculation, and to deduce the topography of the resultant polymer. The practical difficulty is that of finding a realisable clathrate system which fulfils the calculated spacial requirements.

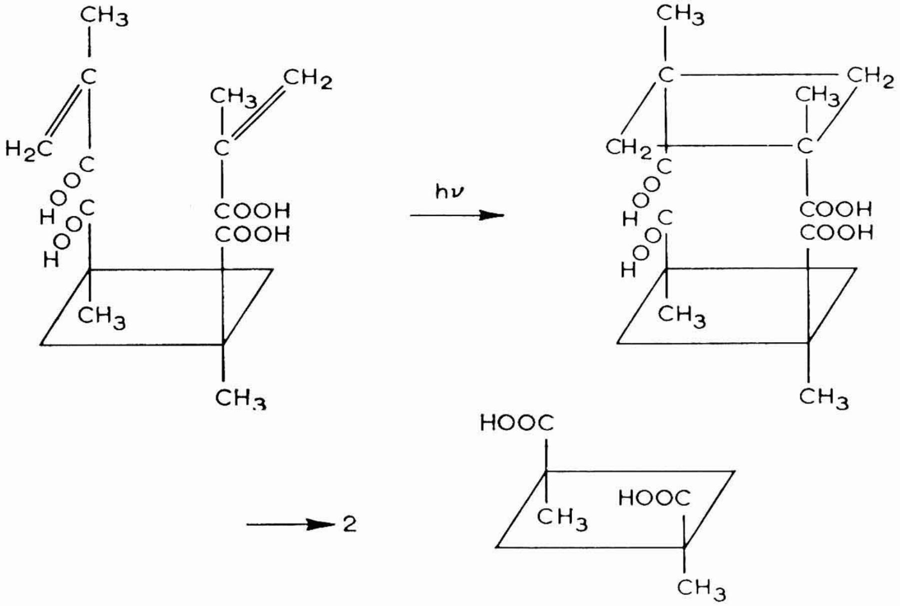
Intercalation complexes of monomers with layer silicates have been similarly used[22]. For example, copolymerisation of methyl methacrylate with glycol dimethacrylate by γ -radiation was shown by Blumstein and Billmeyer to yield a chicken-wire sheet polymer whereas similar treatment of acrylonitrile yielded a linear isotactic polymer. The spacial arrangement of the monomer in the complex is not always favourable, as shown by the failure of styrene to polymerise in the complex with nickel cyanide.

Related to this method, is polymerisation in the crystalline state[23,24]. Here, the idea is to utilise the ordered arrangement of monomer molecules in the crystal lattice to promote polymer growth in a preferred direction. This is the so-called topotactic polymerisation. Thus, crystalline trioxane yields a polyoxymethylene of high crystallinity and the same hexagonal structure as the crystalline monomer. The fatty chains of vinyl stearate crystallise readily, holding the vinyl groups in a definite configuration to yield a regulated polymer structure. Strong hydrogen bonding, on the other hand, is the orienting force in *p*-benzamidostyrene which polymerises in the crystalline state to a regular crystalline polymer. Liquid crystals provide a fascinating study: the sodium salt of *p*-styrylundecanoic acid in water yields mesomorphic phases of sheets or hexagonally stacked cylinders which are preserved or "fossilised" on polymerisation.

Surface effects, many of which are well known, are too numerous to catalogue. They are generally thought of as occurring on the micro-scale, as in the finely divided Ziegler catalyst systems. Orientation at grosser surfaces has been observed, however, leading to the so-called epitactic polymerisation. Pyrolysis of *p*-xylene yields the biradical which, when brought into contact with a cool surface, polymerises to poly (*p*-xylylene). The deposited film is found to be highly anisotropic, showing that growth occurs preferentially, either parallel or perpendicular to the surface. Polyacrylonitrile, formed on the surface of an oriented Nylon-6 fibre, has also been shown to pick up the orientation of the substrate in template fashion.

Perhaps the extreme of subtlety in template synthesis, outside the biological field, occurs in homogeneous systems. It is not confined to the influence of an optically active environment on the polymerisation of asymmetric monomers. *Cis-trans* isomerism can be similarly controlled.

When methacrylic acid is dimerised in a solvent comprising the *cis*-dimer, oriented association of solvent with monomer causes preferential formation of more *cis*-dimer[25]. In the absence of this solvent, the product is the more energetically favoured *trans*-isomer.



Electrovalent bonding in polymers

There is no intention here to enter into semantic arguments, but it will be useful now to examine the crystal lattice of sodium chloride (Fig. 6). No distinguishable *molecule* is present; instead one perceives an indefinitely large structure, the size of which is limited only by the physical dimensions of the crystal. The bonding is infinite in extent in the sense that one would use the term in a gelled polymer. The essential difference is that the bonds are ionic and may be broken on solution.

The polymeric structure of vitreous silica is, perhaps, closer to the conventional picture of a covalent macromolecule and, proceeding a stage further, to the structure of a soda-lime glass, the usual representation is seen as a hybrid, with covalent structures additionally linked by electrovalent forces. Much the same sort of thing is seen in the clays.

In the past few years a "new" class of polymers has been heralded in which ionic bonds are deliberately introduced to modify the properties of a predominantly covalent structure. Just how new is this concept may be open to discussion: whilst coatings technologists may be chary of claiming to have originated ionically bonded polymers, their zinc and calcium resinates, dating from the last century, must surely be recognised as the precursors of the ionomers.

The concept of the ionomer is essentially a simple one (Fig. 7). Attachment of a few carboxyl groups to a covalent chain molecule like polyethylene permits it to be cross-linked by ionic bonds with a polyvalent metal such as zinc. In an essentially non-polar environment, the electrovalent bond is strong, and is less localised than a covalent bond. From this derives the increase in mechanical strength and hardness which has been claimed for these materials.

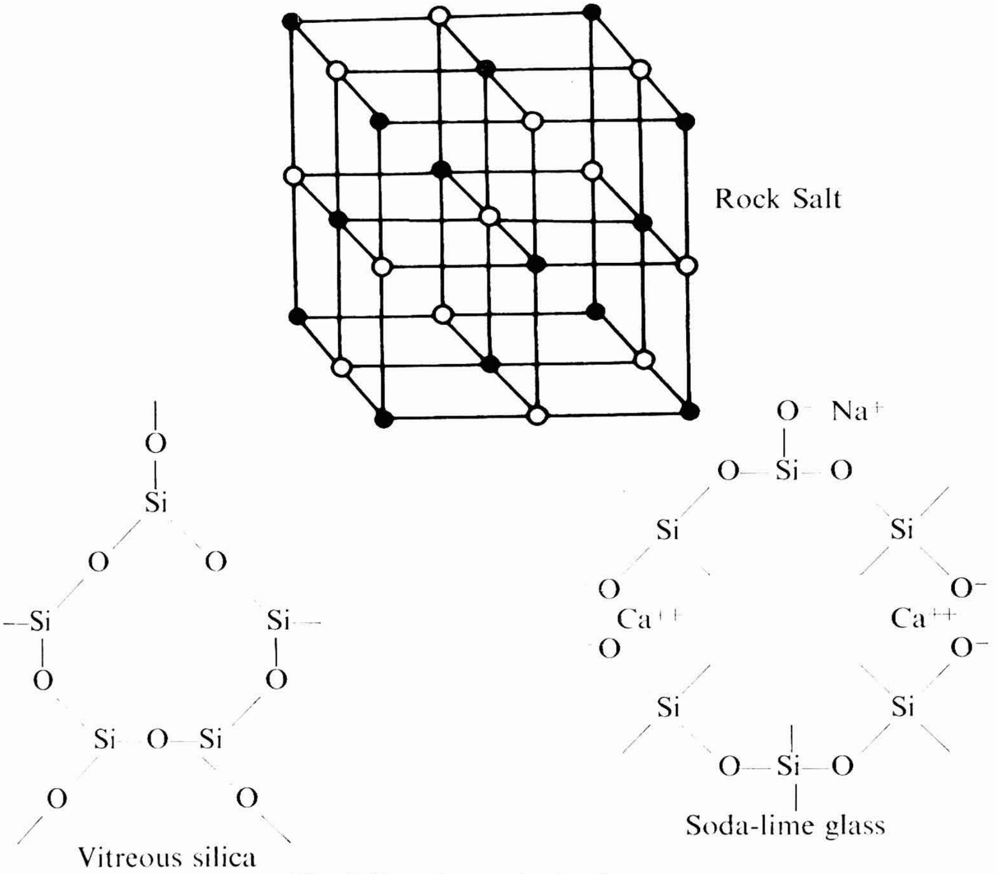


Fig. 6. Some inorganic structures

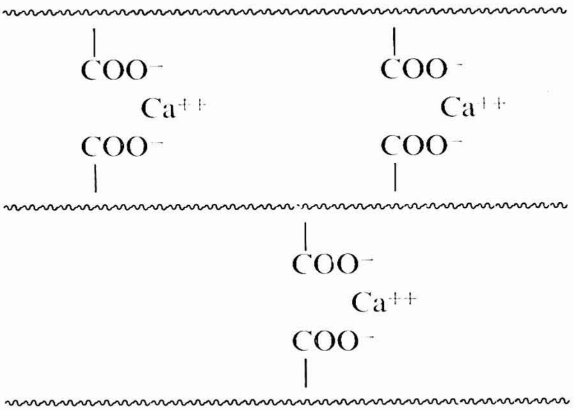


Fig. 7. A simple ionomer structure

The most recent development along these lines is the use of high levels of ionic cross-linking in polymers of the acrylic series to yield products of extreme, rock-like, hardness. The technique, which was reported in 1968 by Nielsen, resembles metallurgical powder technology[26]. A copolymer rich in acrylic acid moieties is mixed in powder form with zinc oxide, barium oxide or lead oxide and heated in moulds at 300°C and 10^4 psi. The product is a solid polyelectrolyte having a modulus several times greater than ordinary plastics due to the strong inter-chain electrostatic forces.

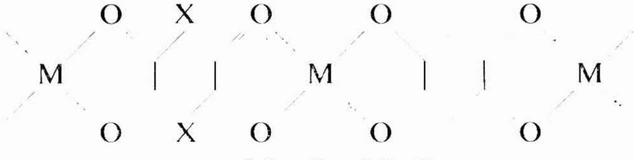
The co-ordinate bond

Co-ordination polymers are being actively studied, but again the idea is not as new as it may appear. It has been known or suspected for many years that certain highly insoluble inorganic compounds are polymers of high molecular weight. Thus, silver cyanide, nickel cyanide and Prussian blue are now known to be linear, planar and three-dimensional polymers respectively.

As long ago as 1945, Elliott prepared highly cross-linked transition-metal complexes with, *inter alia*, bis-α-amino acids in the hope that they would be highly coloured and useful as pigments. Semi-organic polymers as a whole constitute too large a topic to be generally discussed here. Suffice it to say that recent results with co-ordination polymers have been encouraging and it is clear that here is another building element for which a future can safely be predicted in polymer architecture.

Interest has again been stimulated very largely by the search for great thermal stability, and the well known fact that organic compounds can often be stabilised by co-ordination with metals. Unfortunately, of the many co-ordination polymers which have been made, few possess outstanding thermal stability combined with useful mechanical properties, and fewer still seem to be applicable in conventional coatings technology because of the extreme insolubility which seems to be characteristic of the class. This is attributable to the partially ionic nature of the covalent bond. The metal atoms retain some positive charge, leaving a corresponding negative charge on the donor atoms of the organic ligand. The resultant intermolecular binding causes a loss of plasticity, flexibility, and solubility. The search, therefore, has to be concentrated on co-ordinate bonds which are as nearly as possible covalent in character, whilst retaining just enough polarity to promote desirable properties. Two only of the more interesting recent advances will be mentioned.

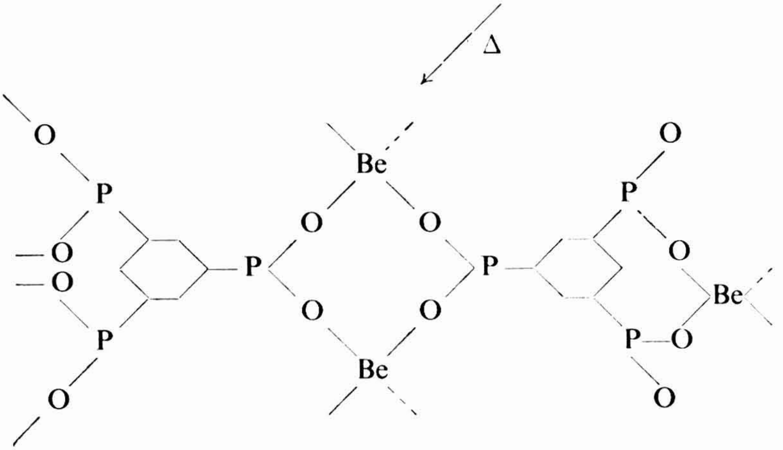
The first is the work of Kanda and Saito[27] which is of considerable philosophical interest because it recalls one of the early, rejected, models of the polymer molecule. They prepared salts of divalent 4-co-ordinate metals with 2,5-dihydroxyquinone and showed the molecules to have the form of rigid rods.



M = Cu, Ni, Zn
X = H, Cl, Br

Secondly, there are the beryllium phosphinate complexes reported by Slota *et al*[28].

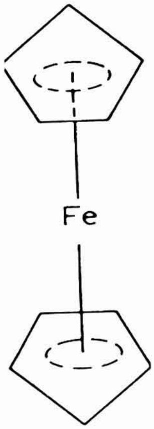
$$\text{Be acac}_2 + 2\ \varphi_2\ \text{P(O)OH} \rightarrow [\text{Be (OP}\varphi_2\text{O)}_2]_n + 2\ \text{acac}$$



The intermediate is soluble in organic solvents and, on heating, yields a cross-linked product of high thermal stability. Its mechanical behaviour has yet to be reported in useful detail.

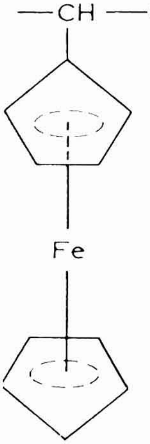
Metallocene polymers

The metallocenes are symmetrically π-bonded transition metal complexes. The first of these was ferrocene, discovered by Kealy and Pauson in 1951[29].



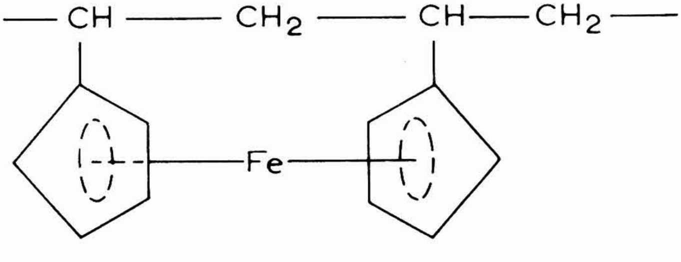
The rings are aromatic in character and subject to facile electrophilic substitution. Derivatives are thus readily accessible since the metal-organic bond is very strong. Ferrocene itself is stable almost indefinitely at 400°C. The metal atom can participate in redox and protonation processes, but cannot transmit electronic effects from one ring to another. It may be noted that the raw materials, iron and cyclopentadiene, are both cheap. The polymer chemistry of the metallocenes has been comprehensively reviewed by Neuse[38].

Perhaps the simplest type of metallocene polymer is poly(vinyl ferrocene) which was prepared by Arimoto and Haven in 1955[30].



It is just another substituted polyethylene and is unremarkable in its behaviour. Of some interest is its reduction by lithium to poly(vinyl cyclopentadiene), a material not otherwise readily accessible.

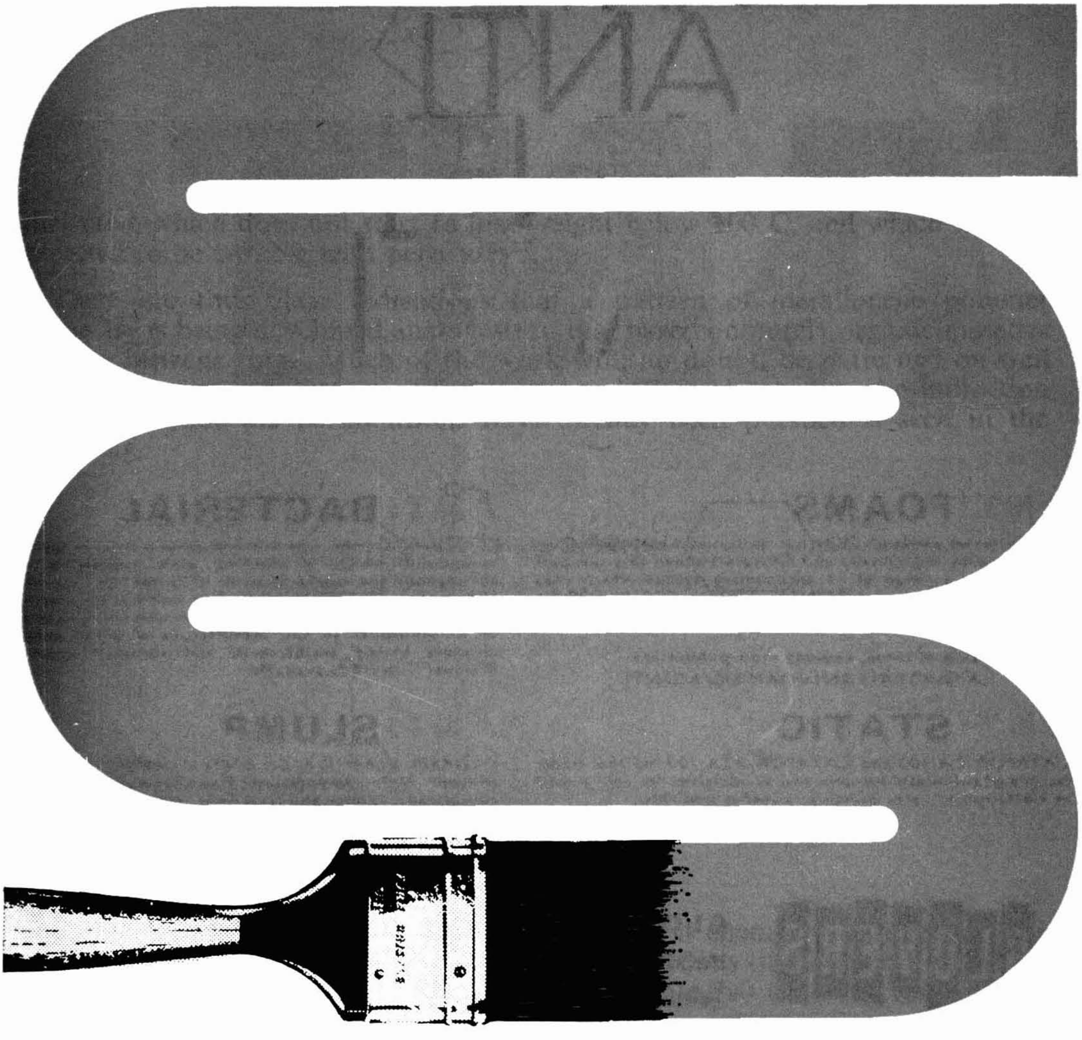
The semi-ladder type of polymer shown below is thought to be formed when methylfulvene is treated with sodamide followed by ferrous chloride[31].



This product is believed to contain a proportion of the ladder structure (see opposite).

Several variants of these have been made. An interesting example is that in which the carbon-carbon backbone is replaced by a doubly-bonded carbon-nitrogen structure, which has been found to have semi-conductor properties[32].

It is reasonable to speculate that the greatest departures from conventional, covalently bonded organic polymers should be found when the metallocene linkage occurs in the main chain, rather than as a pendant group. Introduction of functional groups into both cyclopentadiene rings has permitted the preparation of polyesters and polyamides of this type[33,34,35], whilst direct condensation of ferrocene with formaldehyde has been shown to yield a novolak type of polymer[36]. Similar condensation with *p*-hydroxy benzaldehyde gives a resin which is curable by reaction with epoxides[37]. Cinnamaldehyde gives a styryl



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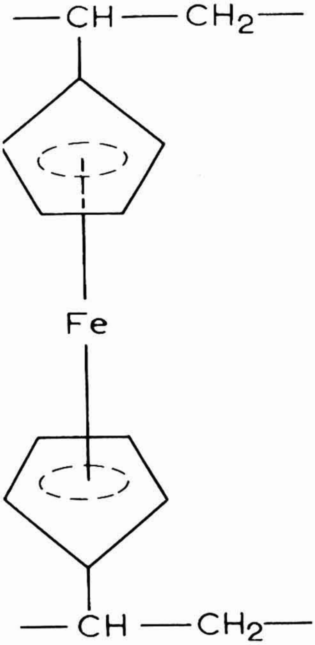
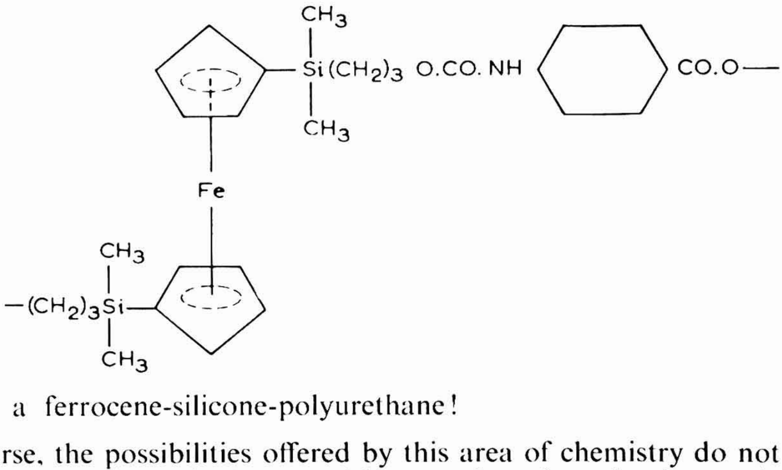


ladder structure
(see opposite)

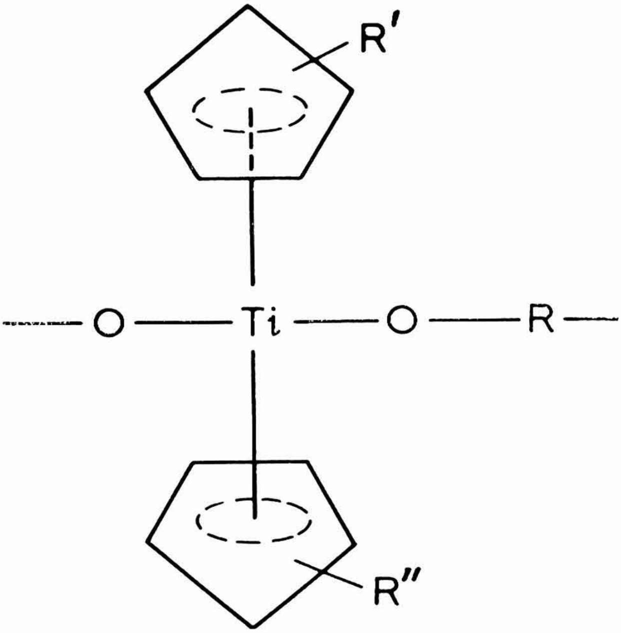
derivative which does not start to lose weight below 300°C, and which may be expected to be curable with peroxides[37].

There are thus clear indications that a pattern of metallocene polymer chemistry is being developed analogous to that based on purely organic moieties like the benzene ring. Much of the work will, no doubt, be patterned on well known polymer architecture and may lead to little real progress. An indication of just how far the permutations have already been pursued is seen in the following,



which is a ferrocene-silicone-polyurethane!

Of course, the possibilities offered by this area of chemistry do not end with ferrocene. Derivatives of other transition metals such as titanium and vanadium are already being investigated. It is interesting to note that titanium, for example, is capable of yielding another class of compound because of the additional bonding possible on the metal atom.



All this seems very exciting but, despite the efforts already made, relatively few of the products have been found to show striking properties. This may be due to deficiencies in preparative methods, to lack of understanding of possible differences between ferrocene and benzene chemistries, or just to too rigid an adherence in experimental and theoretical approach to what has gone before.

The present position of ferrocene polyamides shows a remarkable resemblance to that of von Braun's Nylon 6 in 1907. The products of Knobloch and Okawara were low in molecular weight, poor in solubility and lacking in film- and fibre-forming properties; it would seem that work on these materials has languished for this reason. None would presume to criticise these workers, who have shown commendable imagination in entering the field at all, but it is tempting to recall what happened to von Braun's polymer when Carothers brought a fresh approach to bear on polyamide chemistry. Is it not possible that something of the kind is needed here?

Catenanes and hooplanes

This roving and somewhat speculative review of some interesting new areas of polymer architecture has proceeded from a consideration of covalently bonded structures and the forms they may take, through electrovalent bonding and co-ordination, to the π-bonded metallocenes. In conclusion, there may be mentioned a recently discovered group of materials in which the component units cannot be separated without the rupture of primary bonds but between which no direct primary bonds exist. These are the catenanes and hooplanes illustrated diagrammatically in Fig. 8.

Such materials have hitherto been prepared only by laborious procedures and are so far limited to combinations of two rings or one rod and one ring[39,40], see Fig. 9. It is interesting to speculate on the properties of polymers comprising a long series of interlocked rings. One can envisage their being formed, albeit in

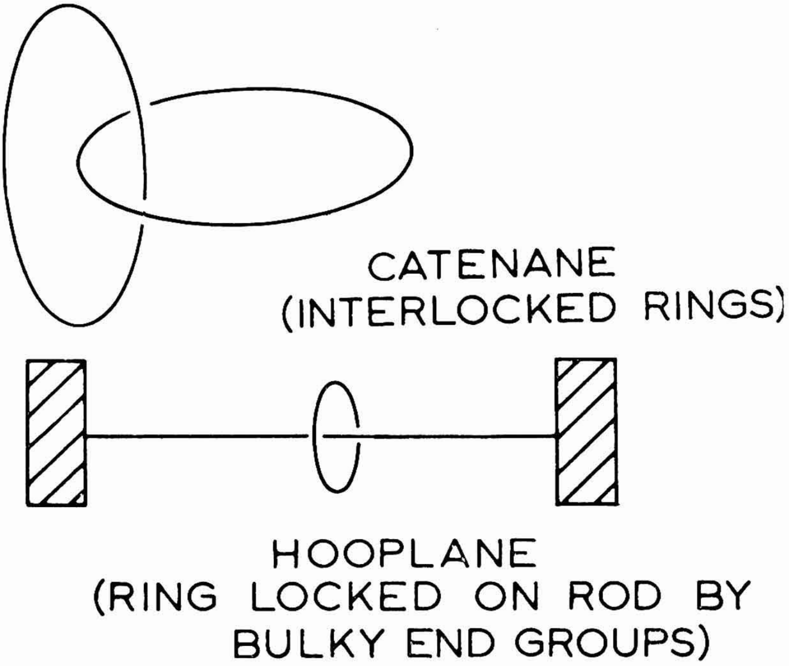


Fig. 8

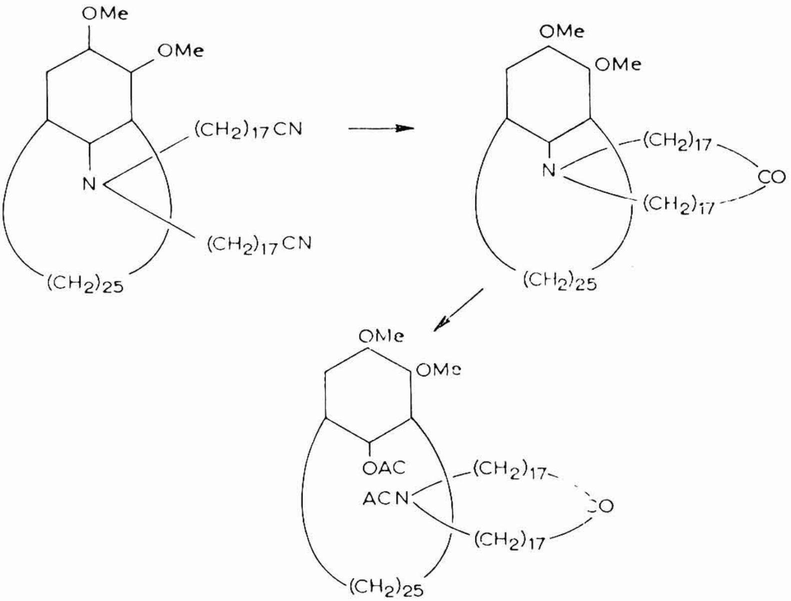


Fig. 9. Typical synthesis of catenane

vanishingly small proportions, in some presently known poly-condensations, and there seems to be no *a priori* reason why means should not be found for their synthesis in high yield.

[*Received 2 January 1969*

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J. Oil Col. Chem. Assoc. 1969, 52, 623-627

Analysis of vegetable oil mixtures by gas chromatography

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Summary

Ten samples of commercial vegetable oils were investigated. The transesterification of fatty acids into their methyl esters was performed. The relative retention times for methyl esters of fatty acids on a column of 10 per cent LAC 446 with programmed temperature 150-200°C were determined. The relative content of chosen components was determined as the values of A_x according to the expression:

$$A_x = \frac{\text{relative content of methyl ester of acid } x}{\Sigma \text{ relative contents of all methyl esters}}$$

The reproducibility of the results was satisfactory for practical purposes, the relative error σ_r being about 10 per cent for the main constituents.

Key words

Binders-oils
vegetable oils

Raw materials used in manufacture or synthesis of ingredients for coatings
fatty acids

Methods primarily associated with analysis measurement and testing
gas chromatography

L'analyse des mélanges d'huiles végétales par chromatographie en phase gazeuse

Résumé

On a examiné dix échantillons d'huiles végétales de commerce après leur transesterification aux esters méthyliques. On a déterminé les relatives durées de retention d'esters méthyliques des acides gras sur une colonne de LAC 446 à dix pour cent et à travers une gamme prédéterminée de température de 150 à 200 C. La teneur relative des constituants sélectionnés (A_x) a été calculée selon l'expression:

$$A_x = \frac{\text{teneur relative d'ester méthylique de l'acide } x}{\Sigma \text{ teneurs relatives de tous les esters méthyliques}}$$

Au point de vue pratique, la reproductibilité se trouvait satisfaisante, l'erreur relative σ_r pour les constituants principaux étant dix pour cent environs.

Die Analyse von Pflanzenölemischung bei Gas-Chromatographie

Zusammenfassung

Zehn Proben handelsüblicher Pflanzenöle wurden untersucht. Nach Überführung der Fettsäuren in ihre Methylester wurden in einer Kolonne mit 10% LAC 446 bei programmgesteuerter Temperatur (150-200 C) deren relative Retentionszeiten ermittelt. Der relative Inhalt einzelner Komponenten wurde in Form von A_x-Werten durch die Beziehung

$$A_x = \frac{\text{relativer Inhalt des Methylesters der Säure } x}{\Sigma \text{ relative Inhalte aller Methylester}}$$

ausgedrückt. Die Reproduzierbarheit dieser Werte ist für praktische Zwecke befriedigend mit einem relativen Fehler σ_r von ungefähr 10% für die wichtigsten Bestandteile.

Анализ смесей растительных масел при помощи газовой хроматографии

Резюме

Изучалось десять образцов коммерческих растительных масел. Проводилась трансэтерификация жирных кислот на их метиловые эфиры. Определялось относительное время удерживания метиловых эфиров жирных кислот на колонне 10-ти процентового лака 446 при програмной температуре в 150-200° С. Относительное содержание избранных компонентов определялось как значение A_x согласно выражению :

$$A_x = \frac{\text{относительное содержание метилового эфира кислоты x}}{\Sigma\,\text{относительного содержания всех метиловых эфиров}}$$

Найдено что воспроизводимость результатов является удовлетворительной для практических целей, с относительной погрешностью σ_r в 10 процентов для главных составных элементов.

Introduction

The commercial value of natural fats and oils is mainly dependent on the composition of their constituent fatty acids.

As shown by several authors[1–9], the identification of fatty acids by gas chromatography of their methyl esters is much simpler than by classical methods. Besides determining relative retention data some correction factors for the quantitative determination of fatty acids in mixtures have also been calculated [10–13]. It was found that for this purpose calibrations should be made.

In this paper, calibration data for some oil mixtures of commercial interest are reported.

Experimental

Ten samples of commercial vegetable oils were investigated separately or in mixtures as shown below. The transesterification of fatty acids into their methyl esters was performed according to literature[14].

Experimental gas chromatographic conditions:

Apparatus	Perkin-Elmer, Model 800
Column	10 % LAC 446, length = 183cm, diameter = 0.32cm
Column temperature	150-200°, 3.3°C/min
Injection port temperature	170°C
Carrier gas	Argon, 25ml/min
Detector	Flame ionisation

Results

The retention data for methyl esters of fatty acids and for unidentified compounds, obtained by gas chromatographic analysis of individual oils, are given in Table 1. The relative retention times were calculated with reference to the methyl ester of stearic acid (elution time 15.8 min.).

Table 1

Relative retention times of fatty acid methyl esters

Acid	TR	Acid	TR
isononanic	0.09	linolenic	1.30
pelargonic	0.16	x_2	1.40
lauric	0.29	x_3	1.48
myristic	0.48	x_4	1.55
x_1	0.68	x_5	2.02
palmitic	0.73	erucic, eleostearic	2.12
stearic	1.00	x_6	2.31
oleic	1.04	x_7	2.80
linoleic	1.13	ricinoleic	3.67

The relative content of each component was determined by multiplication of the peak height by the half-height peak width. Table 2 shows the values of A_x according to the expression:

$$A_x = \frac{\text{relative content of methyl ester of acid } x}{\Sigma \text{ relative contents of all methyl esters}}$$

for individual vegetable oils. For all components the detector response was taken as unity.

In Table 4 are given the values of A_x for several oil mixtures whose preparation is explained in Table 3.

Table 2

A_x values for individual vegetable oils

Oil Acid	corn	linseed	castor	dehydrated castor	tung	rapeseed
palmitic	0.109	0.060	0.030	0.022	0.039	0.043
stearic	0.054	0.062	0.038	0.033	0.052	0.028
oleic	0.312	0.193	0.082	0.070	0.100	0.174
linoleic	0.525	0.183	0.093	0.441	0.117	0.186
linolenic		0.502	0.021	0.187	0.026	0.120
erucic eleostearic }					0.666	0.449
ricinoleic			0.735	0.248		

Table 2 (continued)

Oil Acid	sunflower	arachidic	coconut	soyabean
pelargonic			0.064	
lauric			0.401	
myristic			0.168	
palmitic	0.074	0.121	0.098	0.114
stearic	0.056	0.046	0.045	0.056
oleic	0.200	0.425	0.089	0.259
linoleic	0.670	0.386	0.044	0.479
linolenic		0.022		0.092

Table 3
Composition of oil mixtures

Combination		Weight ratio
soyabean-linseed:	A	1—25:75
tung-linseed:	B	
dehydrated castor-castor:	C	2—50:50
dehydrated castor-soyabean:	D	
dehydrated castor-coconut:	E	3—75:25
coconut-soyabean:	F	

Conclusion

The reported data enable the construction of calibration diagrams from which the composition of some commercial vegetable oil mixtures can be determined. Additional experiments showed that the reproducibility of the results was satisfactory for practical purposes, the relative error σ_r being about 10 per cent for the main constituents.

Acknowledgment

The financial support of the paint and varnish factory "Color" (Medvode, Yugoslavia) is gratefully acknowledged.

Good mixers

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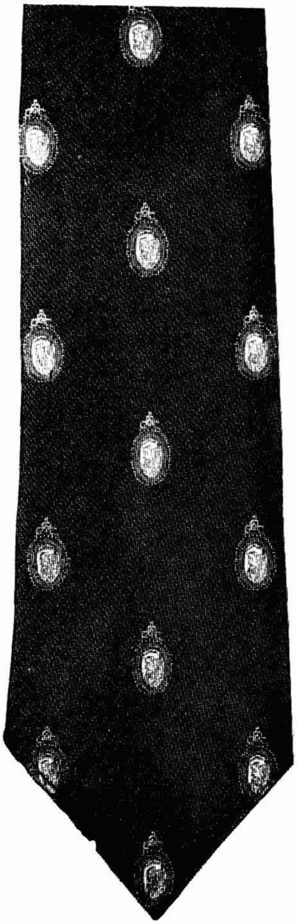

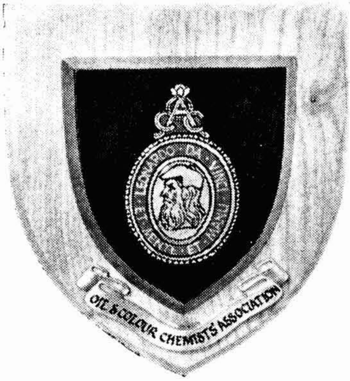

The tie is blue terylene, with the Association's insignia woven in red and gold silk.

The blazer badge has the insignia embroidered in silver and gold wire on a red and blue ground.

The plaque has the insignia hand-painted in red and gold on a blue ground.

The car badge has the insignia embossed in red and gold on a blue ground, the whole being covered in transparent polypropylene, with a thick chrome surround. Bar and grille fittings are available.

In order to commemorate the Fiftieth Anniversary of OCCA, Council has authorised the production of a tie, blazer badge, wall plaque and car badge bearing the Association's insignia. These items are available only from :—

THRESHER & GLENNY

Lancaster Place, Strand,
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As a member of the Association, please accept my order for the following:

......OCCA tie @ 20/–	....	Name ....
......OCCA blazer badge @ 63/–	....	
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(All prices include postage and packing)		....
If tie is required airmail add 6s. 6d.		....
Total Remitted		....

The ties will be supplied from stock; all other items are made to order. Only the tie can be supplied by airmail at an extra cost of 6s. 6d.

Table 4

A_x values for oil mixtures

Acid	Composition								
	A_1	A_2	A_3	B_1	B_2	B_3	C_1	C_2	C_3
palmitic ..	0.075	0.095	0.101	0.067	0.062	0.060	0.028	0.031	0.028
stearic ..	0.047	0.056	0.056	0.055	0.056	0.046	0.033	0.032	0.025
oleic	0.214	0.236	0.256	0.186	0.161	0.146	0.075	0.078	0.087
linoleic ..	0.263	0.337	0.404	0.173	0.161	0.149	0.157	0.247	0.354
linolenic ..	0.401	0.276	0.183	0.435	0.362	0.208	0.040	0.094	0.145
erucic				0.084	0.198	0.389			
eleostearic									
ricinoleic ..							0.668	0.518	0.360

Acid	Composition								
	D_1	D_2	D_3	E_1	E_2	E_3	F_1	F_2	F_3
pelargonic ..				0.062	0.059	0.036	0.025	0.045	0.064
lauric ..				0.356	0.275	0.181	0.108	0.212	0.313
myristic ..				0.137	0.109	0.069	0.045	0.086	0.119
palmitic ..	0.115	0.082	0.065	0.092	0.062	0.052	0.097	0.088	0.089
stearic ..	0.046	0.048	0.036	0.029	0.027	0.028	0.040	0.039	0.031
oleic	0.236	0.218	0.162	0.083	0.066	0.077	0.197	0.157	0.117
linoleic ..	0.484	0.499	0.459	0.088	0.162	0.244	0.362	0.248	0.152
linolenic ..	0.089	0.077	0.129	0.034	0.065	0.105	0.077	0.046	0.028
ricinoleic ..	0.030	0.075	0.148	0.024	0.062	0.153			

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J. Oil Col. Chem. Assoc. 1969, **52**, 628-634

Formulation of fungus-resistant paints: V. Addition of salicylanilide

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Summary

Salicylanilide (SA) has been assessed for its effectiveness as a fungicide in gloss and flat enamel paints. Panels coated with these paints were exposed at Lae, New Guinea, and houses in Melbourne were painted indoors with a flat enamel. The mould growth in each case was compared with that on the same paint free of fungicide.

Salicylanilide was found to be of little use as a fungicide for outdoor application, but has a tendency to increase the fungus resistance of paints used indoors. Analytical results show that SA is quickly lost from the paint film outdoors, especially under humid tropical conditions.

Key words

Types of coating	*Biologically active agents*	*Methods primarily associated with analysis and testing*
alkyd coating	fungicide	exposure testing

La mise au point des formules de peintures résistant à végétation mycélienne. Cinquième partie: L'addition de salicylanilide

Résumé

On a apprécié l'éfficacité de salicylanilide (SA) en tant que fongicide en peintures brillantes et mates. Panneaux-épprouvettes revêtus de ces peintures ont été exposés à Lae, Nouvelle Guinée, et d'ailleurs quelques bâtiments à Melbourne ont été peints à l'intérieur avec une peinture mate. La croissance de moisissure en chaque instance était comparée auprès de celle sur la même peinture exempte de fongicide.

On a trouvé que salicylanilide ne possède pas beaucoup de valeur en tant que fongicide pour l'usage à l'extérieur, bien qu'elle ait une tendance pour augmenter la résistance à végétation mycélienne des peintures à l'interieur. Résultats analytiques démontrent que SA se perd très rapidement à partir du feuil de peinture exposé à l'extérieur, notammant sous des conditions humides du tropique.

Die Rezeptur Pilzbeständiger Aestrichmittel: 5. Zusatz von Salizylanilid

Zusammenfassung

Die Wirksamkeit von Salizylanilid (SA) als Pilzverhütungsmittel in glänzenderen und matteren Emaillelacken wurde bewertet. Mit solchen Lacken gestrichene Tafeln wurden in Lae, Neu Guinea exponiert, und in Melbourne wurden Häuser innen mit matten Emaillelacken gestrichen. Das Pilzwachstum wurde in beiden Fällen mit der gleichen, kein Fungizid enthaltenden, Farbe verglichen.

Es stellte sich heraus, dass Salizylanilid für Aussenanwendung von geringem Nutzen war, aber, dass es dazu neigt, die Pilzbeständigkeit innen zu verbessern. Analytische Resultate erweisen, dass SA aussen schnell aus dem Lackfilm verloren geht, vor allem unter feuchten Tropenverhältnissen.

Формуляция красок дающих защиту против плесени: 5. Добавление салициланилида

Резюме

Оценивается эффективность салициланилида как фунгисида в глянцевых и матовых эмалевых красках. Панели покрытые этими красками подвергались выветриванию в Лае, в Новой Гинее, и дома в Мельбурне окрашивались внутри матовой краской. Прирост плесени в каждом случае сравнивался с приростом на той же краске без фунгисида.

Найдено что салициланилид мало пригоден в качестве фунгисида для применения на открытом воздухе, но повышает сопротивление против плесени в красках применяемых внутри помещений. Аналитические результаты показывают что салициланилид быстро утеривается из красочной пленки на открытом воздухе, в особенности во влажных тропических условиях.

Introduction

Salicylanilide is being used as an addition to paint to render it fungus resistant, but there does not seem to be much information available as to its effectiveness. The mould resistance of paints containing SA was investigated in Lae, New Guinea, and in Melbourne, and in accordance with the method used in this Division[1] the stability of SA in a paint film under different conditions of exposure was determined.

Experimental

Analytical work

Flat and gloss alkyd enamel paints containing SA, and the corresponding blanks, were brushed out on sheets (12in × 6in) of polyethylene terephthalate polyester film, which were then attached to hardboard panels and exposed under the following conditions:

1. outdoors, Lae, New Guinea (upper side),
2. outdoors, Lae, New Guinea (under side),
3. outdoors, Highett, Victoria,
4. fog room,
5. constant temperature room at 20°C (68°F), 65 per cent RH,
6. hot room at 38°C (100°F), 25 per cent RH.

At intervals of approximately six months, a portion of each film was removed and analysed to determine the loss of SA. The analysis was carried out by the spectrophotometric method described earlier[2].

Evaluation indoors

Evaluation of the paint indoors was carried out in 31 dwellings in Melbourne in which a comparatively high degree of mould growth had made repainting desirable. Of these, 19 houses were decorated with a flat alkyd enamel paint containing 2 per cent SA, and 12 houses were decorated with the same flat alkyd enamel without fungicide. All walls were washed down with hypochlorite solution before painting. The houses were inspected after each winter season, when mould growth is strongest, and the growth was then washed off with a hypochlorite solution. The results are summarised in Table 1.

Table 1

Incidence of mould growth in houses painted with a flat alkyd enamel paint containing 2 per cent SA

Inspection*	Control		2% SA		Significant at P
	Number inspected	% affected	Number inspected	% affected	
1	12	50	19	5	0.01
2	11	27	18	11	0.32

*Inspection made annually after each winter season.

Table 2

Assessment of mould growth on paint films exposed outdoors at Lae: upper side of panels

Paint	Replicate	Exposure													
		4 months		8 months		10 months		14 months		17 months		21 months		24 months	
		I	C	I	C	I	C	I	C	I	C	I	C	I	C
G	1	1	100	2	70	3	100	4	Tr	1	100				
	2	1	100	2	70	3	100	4	Tr	2	100				
	3	1	100	2	70	3	100	4	Tr	2	100				
GSA	1	0	100	0	100	2	Tr	1-2	100	2	100	2-3	100	2-3	100
	2	0	100	0	100	2	Tr	1-2	100	2	100	2-3	100	2-3	100
	3	0	100	0	100	2	Tr	1-2	100	2	100	2-3	100	2-3	100
F	1	3	100	2	100	0	100	9	30	9	30				
	2	2	100	2	100	0	100	1	100	1	100				
	3	3	100	2	100	0	100	9	30	9	30				
FSA	1	0	100	2-3	5	3	5	1-2	100	2-3	100	2-3	100	2-3	100
	2	0	100	2-3	5	3	10	1-2	100	2-3	100	2-3	100	2-3	100
	3	0	100	1-2	5	3	5	1-2	100	2-3	100	2-3	100	2-3	100

G, Gloss enamel paint without SA; GSA, Gloss paint with SA; F, flat enamel paint without SA; FSA, flat enamel with SA.
C = Percentage area covered by colour intensity I.
I = Intensity of colour according to scale 9 (black) → 0 (white).
I = 0 and C = 100 means that the panel is free of mould.
Tr — Trace.

Table 3

Assessment of mould growth on paint films exposed outdoors at Lae: under side of panels

Paint	Replicate	Exposure													
		4 months		8 months		10 months		14 months		17 months		21 months		24 months	
		I	C	I	C	I	C	I	C	I	C	I	C	I	C
G	1	3	1	3	100	2-3	90	4	60	4	50				
	2	3	1	3	100	2-3	60	4	60	4	50				
	3	3	1	3	100	3	70	4	60	4	50				
GSA	1	0	100	0	100	4	Tr	2	100	2-3	100	2-3	100	2-3	100
	2	0	100	0	100	4	Tr	2	100	2-3	100	2-3	100	2-3	100
	3	0	100	0	100	4	Tr	2	100	2-3	100	2-3	100	2-3	100
F	1	5	100	4	100	5	100	3-5	100	3-9	100				
	2	5	100	3-4	100	5	100	3-5	100	2	50				
	3	5	100	3-4	100	5	100	3-5	100	2-8	100				
FSA	1	0	100	0	100	2	Tr	2	5	2	100	2	100	2-3	100
	2	0	100	0	100	2	Tr	2	5	2	100	2	100	2-3	100
	3	0	100	0	100	2	Tr	2	5	2	100	2	100	2-3	100

G, Gloss enamel paint without SA; GSA, Gloss enamel paint with SA; F, flat enamel paint without SA; FSA, flat enamel paint with SA.
C = Percentage area covered by colour intensity I.
I = Intensity of colour according to scale 9 (black) → 0 (white).
I = O and C = 100 means that panel is free of mould.
Tr = Trace.

Evaluation indoors

Exposure at Lae, New Guinea

A separate set of hardboard panels painted with gloss and flat enamel paints, and the corresponding blanks, were exposed at Lae, New Guinea. The intensity and extent of mould growth was assessed at intervals of about three months, and the results are summarised in Tables 2 and 3.

Discussion and conclusions

The samples were analysed for SA, and the losses from the gloss paint films are graphed in Fig. 1 and those from the flat enamel paint films in Fig. 2. At Lae, all the SA was lost from the upper side of all panels within eight months (curve 1). The paint films containing SA appeared to be more fungus-resistant than the blanks for about 10 months.

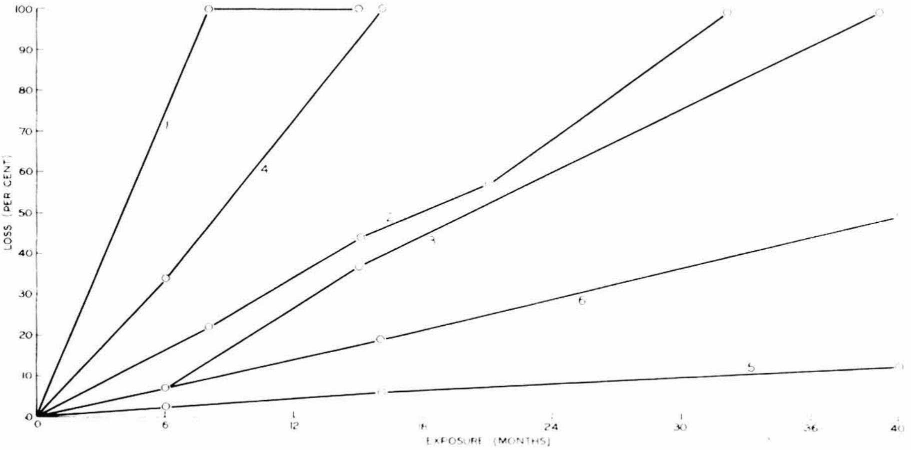

Fig. 1. Loss of salicylanilide from gloss alkyd enamel paint

1. Outdoors at Lae, New Guinea; upper side of panels.
2. Outdoors at Lae, New Guinea; under side of panels.
3. Outdoors at Highett, Victoria.
4. Fog room at 20°C (68°F).
5. Constant temperature room at 20°C (68°F), 65 per cent RH.
6. Hot room at 38°C (100°F), 25 per cent RH.

Original content of SA in paint film—2.3 per cent at Lae, 3.2 per cent at Highett.

The loss of SA from the under side of the panels was slower (curve 2), being 100 per cent in 32 months from the gloss enamel film and 93 per cent in 32 months from the flat enamel film. The mould growth was retarded for 10 months with the gloss enamel and for 14 months with the flat enamel. It would appear that the fungus can adapt to the presence of SA, or that the fungicide is lost mainly from the top layer and is not replaced quickly enough from the lower layers.

The loss in the fog room (curve 4) is fairly rapid, indicating that salicylanilide should not be used in places where heavy condensation is likely.

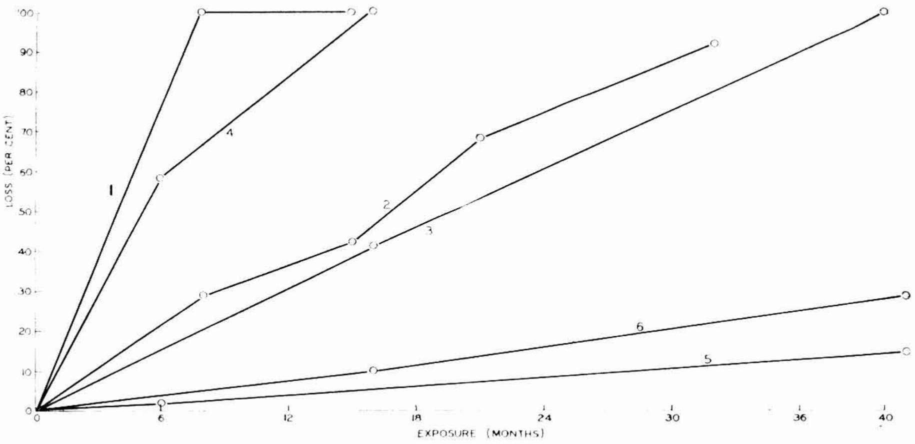

Fig. 2. Loss of salicylanilide from flat enamel paint

1. Outdoors at Lae, New Guinea; upper side of panels.
2. Outdoors at Lae, New Guinea; under side of panels.
3. Outdoors at Highett, Victoria.
4. Fog room at 20°C (68°F).
5. Constant temperature room at 20°C (68°F), 65 per cent RH.
6. Hot room at 38°C (100°F), 25 per cent RH.

Original content of SA in paint film—2.8 per cent at Lae, 4.1 per cent at Highett.

The loss at Highett (curve 3) is slower than from the under side of the panels at Lae (curve 2), and this difference is probably due to the higher humidities and temperatures prevailing in Lae.

At 20°C (68°F) (curve 5) the loss is low (13 per cent in 40 months), but at 38°C (100°F) it is appreciably higher at 50 per cent in 40 months in the gloss enamel paint. Salicylanilide can be expected to remain effective for about four years indoors, provided that no excessive condensation occurs.

The kind of control which can be achieved with this fungicide is illustrated in Table 1. In the first season the results are statistically significant to P = 0.01, but in the second season the results cannot be shown to be significant because of the comparatively small number of control houses which were available. The percentage of treated houses affected in the second season is still lower than that of untreated houses, and if it is taken into account that the SA disappears only slowly at 20°C, it is reasonable to assume that the increase in mould resistance is real.

Salicylanilide can also be used effectively in fungicidal washes[3].

Acknowledgment

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Next month's issue

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

"The surface area and porosity of titanium dioxide pigments," *by D. Urwin.*

"Detection of etch primer in paint flakes by pyrolysis chromatography," *by D. E. Hillman and H. Wells.*

"Cathodic reduction of cuprous oxide in vinyl antifouling paints," *by W. A. Anderton.*

"The influence of some selected surface active agents on the tendency of titanium dioxide and chrome yellow pigments to agglomerate during dry storage," *by L. Chromy and J. Kukla.*

"The penetration of sulphur dioxide into alkyd resin films," *by M. Svoboda, H. Kičlova and B. Knápek.*

Correspondence

The closest possible random packing fraction of pigments and some observations on the S/Y ratio as a measure of pigment dispersibility.

SIR,—The calculation of the theoretical viscosity of a suspension of non-attractive particles can be made using a modification of the formula due to Roscoe[1]:

$$\eta = \eta_0 (1 - F^{-1}c)^{-2.5}$$

where η_0 is the viscosity of the continuous (liquid) phase, c the volume fraction of the solid, and F the solid volume fraction of the solid in its closest packed condition. The accurate determination of F presents difficulties, but for dispersed pigments the critical pigment volume concentration (CPVC), as determined by the method of Asbeck and Van Loo[2], gives a reasonably close approximation. The effect on the value of F of any adsorbed resin on the pigment surface is difficult to assess, so that the use of a medium of low, uniform molecular weight, such as linseed oil, is helpful. This suggests that the pigment volume concentration in the BS oil absorption test paste might provide a possible alternative means of determining F. For this purpose, the composition of an oil absorption paste is assumed to consist of the pigment in its closest possible random packing, but with each particle surrounded by a monolayer of oil, together with just enough oil to fill the residual voids.

In considering this theoretical paste, some facts have been noted that cast doubt on the validity of Carr's[3] hypothesis that complete dispersion is indicated by a value of unity for the ratio S/Y, where S is the BET surface area in square metres per gram of the pigment, and Y the weight of oil in grams required by 100g of pigment to form the absorption paste.

Carr derives a relationship: $S/Y = 6.84\,\alpha$, where α is that fraction of the total "absorbed" oil that is required to form a monolayer on 100g of pigment, that is, αY is the weight of oil forming the adsorbed layer. Using data given in Carr's paper, the weight of oil in the monolayer can be calculated as:

$$\frac{100 \times S \times 10^{20} \times 877}{100 \times 6.02 \times 10^{23}} = 0.146\ S \quad \text{g}$$

Since $0.146\ S = \alpha\ Y$, then

$$S/Y = \frac{\alpha}{0.146} = 6.85\ \alpha$$

a relationship not significantly different to that derived by Carr.

Taking the specific gravity of linseed oil as 0.933 gives the volume of oil in the monolayer as $0.156\ S$ ml. From the definition of the oil absorption test paste given above, the theoretical total weight of oil can then be expressed as:

$$Y = 0.146\ S + 0.933 \left(\frac{100}{\rho_p} + 0.156\ S\right)\left(\frac{1}{F} - 1\right)$$

where ρ_p is the pigment density and F the solid volume fraction of the particles in their closest possible random packing. (The arrangement is assumed to be identical in the dry state and in the oil absorption paste, except for the extra centre-to-centre separations necessary to accommodate the adsorbed oil layer.)

The calculated thickness of the adsorbed monomolecular oil layer is about 15.5 Å, and the pigment surface area, S, is related to the mean equivalent sphere diameter, d_3, in microns, by the formula $S = (6/\rho_p d_3)$. This enables the formula for Y to be transposed to:

$$Y = \frac{0.876}{\rho_p\, d_3} + \frac{93.3}{\rho_p}\left(\frac{d_3 + 0.0031}{d_3}\right)^3 \left(\frac{1}{F} - 1\right)$$

In this form, the dependence of the theoretical oil absorption on pigment density, surface area and packing fraction is clearly shown. Also, the dependence of the value of $\alpha Y, \left(= \frac{0.876}{\rho_p\, d_3} = 0.146\ S\right)$, on pigment density and surface area is obvious, whilst the value of the second term $\{= (1—\alpha) Y\}$ will be greatly affected by the value assigned to F.

It follows that, for any given value of S (or d_3), the value of α will be reduced as the value of F increases. The problem is the assignment of a value to F. For a pigment consisting of uniform spheres, a value of 0.63 would be appropriate, but since the particle diameters in a sample of commercial pigment may vary by a factor of about 20, a somewhat greater value, say $F = 0.66$, would be possible. On the other hand, on examination of the nominal pigment volume concentrations in oil absorption pastes, it is found that a value of $F = 0.55$ would not be unreasonable. In the following table, the values of Y and α, calculated from the above formula for various values of S, one value of ρ_p ($= 1.6$), and three values of F are given.

S	$F = 0.66$		$F = 0.6$		$F = 0.55$	
	Y	α	Y	α	Y	α
120	56.3	0.31	69.2	0.25	81.1	0.216
80	47.0	0.25	58.7	0.2	69.4	0.17
60	42.6	0.21	53.9	0.16	64.2	0.14
50	40.1	0.18	51.0	0.14	61.0	0.12
40	37.6	0.155	48.2	0.138	57.9	0.10
10	31.26	0.047	41.0	0.036	50.2	0.029

These values show clearly that the assignment of a single value to α is not justifiable, since the value of α varies both with the particle surface area (particle diameter) and with the packing fraction of the solid. Also for any given value of S, there can be a packing fraction such that $\alpha \simeq 0.15$ and for each packing fraction, there will be a surface area such that $\alpha \simeq 0.15$. In either case $S/Y \simeq 1$, but particles of different size or packing fraction, although equally well dispersed, will *not* give an S/Y ratio of unity.

This conclusion is in agreement with observations made, during the discussion of Carr's paper, by Sunderland[4] and Crowl[5]. Also, the conclusion that the criterion $S/Y = 1$ cannot be taken as indicating "complete dispersion" in the oil absorption test paste means that an accurate value for F cannot be calculated from oil absorption test results. The writer will be pleased to receive any suggestions for the measurement or estimation of this value.

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Yours faithfully,
H. D. JEFFERIES

4 Tintern Avenue,
Billingham, Teesside.

The FATIPEC Congress Books

SIR,—Some of the most valuable fundamental work in connection with the manufacture and application of surface coatings and their raw materials is contained in the papers presented at the various FATIPEC Congresses. Unfortunately this work is very inaccessible, unless one has actually been present as a delegate at these symposia, and received the preprints of the meetings.

Would it not be possible for OCCA to arrange in co-operation with our European colleagues for the Congress books to be made available more generally, either through the normal book trade, or possibly through our own organisation in much the same way as the SCI Monographs are available?

At present the only locations of these volumes, as far as I know, are the National Library of Invention in London, and the Paint Research Station Library. They should be available in the libraries of most organisations connected with the resin and surface coating industries, and I see no reason why the technical libraries in our larger cities should not include them on their shelves. This should also be the case for university and technical colleges which deal with applied surface chemistry and with polymers.

Yours faithfully,
H. WARSON, BSc, PhD, FRIC.

284 Warwick Road,
Solihull, Warwickshire.

Editor's Note: The book of the 1970 FATIPEC Congress will be available direct from the printer, at a price not yet known, but expected to be in the region of £5. However, if members require a copy, they should apply to the Association's offices, and, if numbers are sufficient, FATIPEC have agreed to allow a reduced price.

Reviews

DISPERSIONEN SYNTHETISCHER HOCHPOLYMERER TEIL II, ANWENDUNG

By HANS REINHARD. Berlin-Heidelberg—New York: Springer Verlag, 1969, Pp. VIII+272, price: £6 2s 6d.

This book is a little masterpiece. Its pages are jam-packed with pertinent information on the properties and industrial uses of aqueous polymer dispersions. The lucid and concise presentation of the text reveals the author's mastery of his complex subject. Workers in this field will be greatly indebted to Herr Reinhard for sharing with them his practical experience, his painstaking study and critical appraisal of the literature and implicitly also the vast fund of knowledge accumulated in the BASF Kunststofflaboratorium.

The value of the book is considerably enhanced by a very comprehensive subject index, itself a model of its kind. Twenty-four pages of literature and patent references help to make this work almost into a mini-encyclopaedia of polymer emulsion technology. Many of the sources quoted are not as well known in this country as they might deserve. This provides additional spice and whets the appetite for more publications of this type.

Readers of this journal will find the sections dealing with emulsion paints, protective coatings and the principles of adhesion as well as the introductory exposé on the basic properties (rheology, stability, film formation etc.) of polymer dispersions particularly stimulating. The use of emulsion paints on various substrates, such as concrete, plaster, bricks, wood and metals is discussed in detail and the behaviour of different polymer types is compared. Outdoor performance, at present of greater importance in Germany than in the UK, is dealt with in some depth.

The excellent chapters on adhesives, paper coatings, textile applications, leather dressing, building materials and miscellaneous subjects will also well repay a thorough study. Much sound advice and important information may be found on almost every page.

This well produced book, showing all the signs of meticulous proof reading, may be highly recommended to those able to read technical German with ease. Others may find it a little difficult to extract the maximum benefit from this highly concentrated text, written with a great economy of words.

C. BONDY

OUTLINES OF PAINT TECHNOLOGY

By W. M. MORGANS, London: Charles Griffin: 1969. Pp. V+414, price £4 4s.

To bring up-to-date Noel Heaton's 'classical' "Outlines of Paint Technology" was no easy task and it is evident by the result that it was not undertaken lightly. Although retaining the title and general format of the earlier work, the present volume is virtually a new work embracing practically everything that is important in the world of paint technology.

Although it only claims to present the outlines, many subjects are treated quite thoroughly, and so the book will be well thumbed not only by students but by all directly or indirectly concerned with paint. The choice of subjects dealt with in greater detail must obviously be a very personal one. In this book the section on synthetic resins could have been expanded even at the expense of the section on natural resins. This would have been realistic, but in fairness to the author the retention of natural products was quite deliberate in order to satisfy readers from many overseas countries.

The book is divided into three parts. Part 1 on pigments is very praiseworthy, while Parts 2 and 3 on solvents, media and pigmented coatings have such a wealth of information that it would seem almost impossible to be contained within the given confines. This will ensure that the book will run to several editions, in which case there will be the opportunity to correct the minor errors and possibly make some additions.

The section on particle size mentions the Coulter Counter. A reference to the Joyce Loebl centrifugal method would be a suitable addition. It would also be desirable to clear up the mystery surrounding calcium naphthenate. Although it is not referred to under driers, it has a brief mention in the alkyd section and quite a few words under crystalline bloom, but is unfortunately omitted from the index.

The otherwise excellent section on dispersion is marred by the suggestion that pre-mixers should produce coarse dispersions. To the uninitiated this could mean any rough mixture. It would be advisable to emphasise that all pre-mixing is very important, and entails making the best possible dispersion with the means available. The work to be done by the machine for which the pre-mix is made, e.g. a sand mill, would then be minimal. Moreover, as the sand mill does not readily permit reduction while milling, the pre-mix should contain enough non-volatile medium for reasonable stability, because complete reduction after milling risks flocculation. Therefore, a pre-mixed base, not a slurry, would be most suitable for the mill.

When dealing with ball mills, an emphatic statement that the balls should be single-sized for the greatest efficiency, would be preferable to the statement that a mixed-size charge is only as efficient as a single-sized charge of the same mean diameter.

Minor errors such as "ore absorption" for "oil absorption" and "double bonns" for "double bonds" are insignificant but the reference to "totally blind people" instead of "totally colour blind people" seems somewhat bizarre.

It must be pointed out that the fact that the above few shortcomings stand out only emphasises the general excellence of the work, which includes adequate references and a good bibliography. It is well worth the four guineas.

I. BERG.

Student Review

The theory of functionality: Part V

By A. R. H. Tawn

Cray Valley Products Ltd., St. Mary Cray, Kent, and
The Borough Polytechnic, London SE1

The alkyd constant

T. C. Patton has suggested that alkyd formulation can be "simplified" by operating with an "alkyd constant" instead of functionality, and this approach has gained some popularity in recent years. He argues from the following premises, which are identical with those put forward in Part 4.

1. Alkyds are known to perform best when p approaches 1 and when they have the highest attainable molecular weight short of gelation.
2. The gel point can be *approximated* by the statement $p_{gel} = 2/f$.
3. Conventional alkyds are formulated with an excess of hydroxyl. Carboxyl is therefore the minority function and functionality is given by $f = 2e_A/m$ where e_A = no. of carboxyl equivalents and m = total no. of moles.

From these, it follows that $p_{gel} = 2/(2e_A/m) = m/e_A$ and when p_{gel} approaches 1, m/e_A approaches 1. The quotient m/e_A is called the alkyd constant, K, and it is said that a properly formulated alkyd will have $K=1$ or just over 1. This is tantamount to saying, as we did in part 4, that f will be equal to 2 or just under 2.

It is the present writer's view that all this amounts to nothing more than mathematical jiggery-pokery. It is no easier to compute $m/e_A = K$ than $2e_A/m = f$. Moreover, the concept of the alkyd constant adds nothing to the simple and straightforward functionality treatment. On the contrary, it diverts attention from the concept of *functionality* which is fundamental to polymer formation and which does so much to unify one's thoughts over the whole range of polymer types. In order to apply the alkyd constant to alkyds with excess carboxyl (*e.g.* water soluble types) or to other types of resin, it is necessary to indulge in mental gymnastics which are quite unnecessary when one uses the simple functionality theory. The use of the alkyd constant is not recommended.

The branching coefficient

Provided that all functions may be considered equally reactive and that no ring formation occurs (*i.e.* reaction is purely random and intermolecular), the statistical approach of P. J. Flory gives accurate predictions of gel points. He defines a "branching coefficient," α, as the probability that, in the system under consideration, a given functional group of a multifunctional (branching) unit will be attached, directly or indirectly, to another such unit. α clearly depends on the reacting species present at any given p, *i.e.* on p and on the nature and number of each monomer species initially present. The value of α which must be attained before infinite branching (identified with gelation) will occur depends on the functionality of the branch unit, and is given by $\alpha_{crit} = 1/(f'\text{-}1)$ where f' is the functionality *of the branch unit* (*not* the average functionality of the system). Thus for glycerol $f' = 3$, $\alpha = 1/2$, for pentaerythritol $f' = 4$, $\alpha = 1/3$. The problem then is to derive a relationship between p and α so that one can plot the approach of α to α_{crit} as the reaction progresses. This is not difficult, but it does require a grasp of mathematics which, whilst essential in a specialist polymer scientist, is seldom possessed by the average undergraduate student of paint technology.

The relationship between p and α is, unfortunately, not a general one; it must be deduced for each type of system to which one wants to apply the theory.

For the typical alkyd system of trifunctional alcohol, dibasic acid, and monobasic acid, it can be shown that

$$\alpha_{crit} = 0.5 \qquad \alpha = p^2\,\varphi/r$$

$$p_{gel} = \sqrt{1/\varphi(f-1)}$$

where p = degree of reaction of carboxyl groups

r = ratio of hydroxyl to carboxyl groups in original formulation

φ = fraction of total carboxyl groups present as dibasic acid.

For alcohols with functionalities greater than 3, the expressions for α and p are unchanged but the value of α_{crit} must be adjusted to $1/(f'-1)$. These expressions can thus be applied to a fair proportion of conventional alkyd formulations, but the situation becomes more complex and new expressions have to be derived from first principles when difunctional alcohols, or acids of higher functionality than two are present.

Since the basic principle adopted in this approach is the calculation of the probability that a given function has reacted in a particular way, it is not difficult to extend the calculations to systems in which functions of unequal reactivity are present. It is only necessary to introduce a factor expressing the lower reactivity of one group compared with another, which can be identified with its lower probability of reaction. Although simple in principle, this takes us one step further away from *mathematical* simplicity and hence from ease of practical application.

Even with these corrections, the branching coefficient method does not give accurate predictions of the gel point in real systems because it neglects a certain loss of functions which always occurs due to ring formation. Experiment always shows gelation to occur at a higher degree of reaction than that predicted by this theory, and the more dilute the system the greater this disagreement becomes. The difference between theory and practice is in the opposite sense to that observed in the Carothers treatment, where gelation is found to occur at a lower-than-theoretical degree of reaction, but the magnitude of the error tends to be about the same. Hence, notwithstanding the conceptual significance of the branching coefficient and its importance to the theoretical polymer scientist, we would suggest that, to the practical formulator of coatings, the additional mathematical labour is barely repaid. He may as well correct the Carothers prediction in one direction as the Flory prediction in the other.

Allowing for ring formation

It is a well known principle of chemical synthesis that inter-molecular reaction is less and less favoured as the concentration of the reacting system decreases. Rate of intra-molecular reaction is independent of concentration, so low concentrations tend to favour formation of rings at the expense of chain polymers.

In 1950, Jacobson & Stockmayer expounded a theory based on the idea that the extent of ring formation in a polymerising system depends on the probability that the reactive end groups of a given molecule occupy adjacent positions in space compared with the probability that one of them is adjacent to a complementary functional group on another molecule. Provided the chain length exceeds 12-15 bonds, such considerations lead to an expression which permits calculation of the fraction of cyclic species present in a polymer in terms of concentration, number of chain atoms per repeat unit, effective bond lengths and degree of reaction. From this it is a simple step to correct the Flory prediction of gel point for the effect of ring formation—if one happens to be a competent mathematician.

This idea was developed further by Harris in 1955 and by Kilb in 1958. The latter treatment in particular is applicable to alkyds and other polycondensates of similar "functionality pattern," and is to be found in *J. Phys. Chem.* 1958, **62,** 969. What emerges from Kilb's theory is a "volume dependency constant," containing some complicated mathematical functions dependent on the nature of the reaction and the reacting species, but which can be treated empirically. Knowing the value of this constant one can account for ring formation at any concentration *of a given system.* The expression for the gel point of a conventional alkyd takes the form

$$p_{\mathrm{gel}} = r/(g_{\mathrm{e}}-1)\,(1-L/C)$$

where r = ratio of total hydroxyl to total carboxyl equivalents

g_{e} is the "equivalent-weighted average" functionality of the polyol which is simply the functionality of the polyol when only one is present, and is given by $\Sigma\, g_{\mathrm{j}}\,{}^2B_{\mathrm{j}} / \Sigma\, g_{\mathrm{j}}\, B_{\mathrm{j}}$ when more than one is present, g_{j} and B_{j} being respectively the functionality and no. o moles if the jth polyol.

L = volume dependency constant

C = concentration of dibasic acid in moles per litre of reaction mixture.

All the quantities in this expression are known except L. One can thus perform a series of experiments to determine p_{gel} for different systems and hence evaluate L for those systems. It then becomes possible to predict the behaviour of similar systems in future work.

Kilb's theory has been tested by several workers, notably Blackinton who worked with alkyds (*J. Paint. Tech.* 1967, **39,** 606) and Price, Gibbs & Zimm who worked with branched polyesters (*J. Phys. Chem.* 1968, **62,** 972). The original papers should be consulted by the student seeking to embrace this subject in depth. Suffice it here to say that, whilst the Kilb approach has much to commend it, the purely theoretical treatment involves the use of complex mathematics. The semi-empirical adaptation is much simpler mathematically, but requires experimental evaluation of the volume dependency constant. Even then, some of the systems examined by Blackinton showed poor agreement with the theory.

Conclusion

The Carothers theory cannot in principle predict gelation accurately because the degree of polymerisation values which it gives are number averages. When applied in this way it provides at best an approximation. The branching coefficient treatment of Flory provides a more realistic picture of the cross-linking process but, in its original form, refers to idealised systems with all functions equally reactive and intermolecular reaction as the only process occurring. It can be corrected for unequal reactivity and for volume effects and *should* then accord with experiment. Unfortunately it does not always show such close accord with experiment as to justify the extra paper work involved compared with the approximation furnished by the Carothers theory. Further work is clearly needed before a wholly satisfactory theoretical approach to resin formulation can be recommended.

Answers to Exercises in Part 4

1. 1.959 2. 169lb. 3. 1.522.

Hull Section

Emulsion paints

The second student evening of the session was held at the Queen's Hotel, Hull, on 17 March.

The evening was again organised by Mr D. J. Robinson, the Hon. Research and Development Officer, who began by considering the results of a more detailed statistical examination of the tests made at the first meeting. In general, these largely supported the conclusions reached during that meeting.

The main topic for the evening was the "Why and what of emulsion paints." Mr Robinson started from a mixture of pigment, medium and water and considered what parts each had to play, and then examined in more detail the requirements of pigment, extender, polymer type of the emulsion. Then the various additives, coalescing agents, defoamers, fungicides and structuring agents were considered and the reasons for their presence discussed. Finally, the advantages of emulsion systems from the points of view of the manufacturer and the user were discussed.

After a break for refreshments, questions were asked of a panel of three more experienced members; amongst topics raised were the importance of emulsion particle size and the mechanism of coalescence.

Fourteen visitors and seven members were present.

S.R.F.

Manchester Section

Methods available for surface coating applications

A Student lecture "Methods available for surface coating application" was read by Mr D. Stewart to 61 members and visitors at the Manchester Literary and Philosophical Society on 15 January, under the chairmanship of the Honorary Student Activities Officer, Mr J. Mitchell.

Mr Stewart covered the complete range of application methods from brushing to fluidised beds and achieved this without undue reference to resin or polymer chemistry. He concluded by presenting in nomogram form a comparison of some dozen application techniques, giving relative costs, subdivided into those portions due to labour, capital and arising from product wastage. To the beginner in the field, this presentation was an invaluable one.

The vote of thanks was proposed by Mr A. B. Abel and carried enthusiastically.

D.A.P.

Information Received

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

Badische Anilin- and Soda-Fabrik AG has recently introduced four new pigments in its established ranges. *Fanal Red 6BM*, an addition to the *Fanal M* range, is said to be of particular interest to printing ink manufacturers because of its outstanding brilliance and colour strength. *Lithol Rubine 6RNS* is an improved form of *Lithol Rubine 6RN*, claimed to have similar colour properties, but better flow and rheological properties. *Paliogen Maroon GL* is a new grade derived from *Paliogen Maroon G*, with more transparency and a purer, more yellow, shade. *Paliogen Maroon 2BL Powder* is a new colour based on perylene, with a bluer and more transparent shade than *Paliogen Maroon G*.

Because of an increasing demand for their printing inks, **A. Gilby and Son Ltd.** have recently added new machinery to the Reliance Works at Colliers Wood. Sales of *Gilby* inks are said to be running currently at a record level.

The Research Association for the Paper and Board, Printing and Packaging Industries (PIRA) has recently published a 150 page programmed self-instruction book on the metric system. The book is intended for those in the printing industry who will first come into contact with the metric system when the changeover occurs in 1971; buyers, sales staff, estimators, production control and other clerical staff. However it is also suitable for almost anyone in the industry.

Copies are available from PIRA, Randalls Road, Leatherhead, Surrey, at 7s 6d per copy.

A new method of application of liquid epoxy coatings, the *Thermech* system, developed by **Ceilcote UK Ltd.**, is said to be a major advance in the technique of corrosion proofing.

The system overcomes the problems involved in the application of liquid epoxy systems for the protection of floors, walls and tanks of steel and concrete.

The *Thermomech* equipment automatically heats, mixes, and sprays continuously, thus ensuring the correct properties and application temperature of the mix. This apparatus is said to give quicker application, more uniform coating in depth and formulation, and greater economy.

Sissons Brothers Ltd. has recently introduced the *Sissons Spray Bureau*, a nationwide network of decorating contractors pledged to maintain the highest standards in general decoration and modern spray application of paints of all types.

It is said that all *Bureau* members have been carefully vetted before admission to the scheme, and that many of their employees have attended the Sissons spray courses in Hull.

As a result, Sissons, in co-operation with *Bureau* members, will guarantee successful results, including both materials and workmanship. The guarantee, which is underwritten by insurance, is issued with every project, and covers five years for gloss paints, three years for emulsions, and ten years in the case of *Kenitex* waterproof textured coating.

In particular, Sissons are interested in promoting the use of airless spray techniques for decorative coatings.

Constat, a liquid additive for screen inks, designed to overcome electrostatic attraction of stocks for the screen during printing, is the latest addition to the range of **Sericol Group Limited.** *Constat* is claimed to suppress stock flutter and ink feathering, even on nylon and polyester screens, and to be non-toxic, non-hazardous and easy to use, being merely stirred into the ink before thinning.

BP Plastics has recently issued three "Technigrams," "S200," "S201" and "S202," giving advice on various aspects of use of BP polystyrene. Among techniques covered are bonding and machining, chemical resistance, and the production of coloured mouldings.

The availability of the *Mark II Lovibond Flexible Optic Tintometer* has recently been announced by **The Tintometer Ltd.** The *Mark II* instrument is said to have an improved optical system, leading to greater accuracy in use. This system allows the use of smaller diameter optical glass fibre in the flexible viewing head (1mm instead of 4mm) or gives improved light transmission with the larger diameters.

Other features of the new instrument are geared control wheels for more sensitive adjustment, better electrical insulation, and a redesigned case.

A new plant for the production of *Antisettle CVP*, a superfine powdered organo-acidic material used in the paint and varnish industries to impart false body and reduce settlement, has recently been commissioned by **Cray Valley Products Limited,** and has resulted in reduced price and improved quality of product.

The plant is fully automated, and is said to be capable of producing extremely fine particle size material with a very small distribution of particles around the mean. The plant operates on a continuous basis, and can be controlled by one man.

The 1969 edition of "Adhesives Directory" has recently been published, in a completely revised form. A new classification of adhesives, by types of basic materials, and physical and general properties and methods of application, has been adopted, to make the selection of adhesives easier.

A new section, dealing with the design of adhesive joints, has also been added, and the other features of the last edition are again included.

The 1969 edition of this useful handbook is 20 per cent bigger than the 1968 edition, and can be obtained from the publishers, **A. S. O'Connor and Co. Ltd.,** 30 Paradise Road, Richmond, Surrey, at a cost of £1.

Norwegian Talc (UK) Ltd. has recently announced that its address is now: 251 Derby House, Exchange Buildings, Liverpool L2 3QG, telephone 051-236 6435-7.

The availability of a tropical exposure testing service for paint panels has been announced by **The Analytical Laboratories Ltd.,** of Singapore. Conditions at the company's laboratories, which are situated on Singapore island, combine sea breezes and some industrial pollution with the normal equatorial conditions of strong sunlight, constant high temperature and humidity, and are said to be ideal for stringent tropical exposure tests.

Standard reports on paint panels include sections for loss of gloss, colour change, chalking, checking, cracking, flaking, blistering, rusting and dirt adhesion, but can readily be tailored to individual requirements. The investigation of fungal attack and effects of exposure on plastics, metals and other materials are all within the scope of the laboratories, which are said to be staffed with well qualified people, and to have a wide range of equipment.

The organisation is completely independent, and is the largest in SE Asia. All enquiries will be welcomed.

It has recently been announced that **Hoechst-Vlissingen NV,** a wholly-owned Dutch subsidiary of **Farbwerke Hoechst AG,** is to build plant for the manufacture of dimethyl terephthalate (DMT) and polycondensate, primary products for *Trevira* polyester fibre.

The plant, at Flushing, Holland, should go on stream in 1971 with a capacity of 84,000 metric tons per year of DMT, and of polycondensate.

Inmont Corporation is the name now adopted by Interchemical Corporation. The new name, which follows internal reorganisation in the company, is said to symbolise its new, forward looking identity, being formed from its policy of INternational Marketing Of New Technologies.

The range of *Keroset* printing ink distillates manufactured by the Petroleum Refining Division of **Butler Chemicals Limited** has recently been revised, and increased by the addition of a new grade. Production capacity has also been increased to accommodate the demand for these products, which are close cut aliphatic high-boiling petroleum distillates.

Technical data sheets covering the ten grades now available are obtainable on request from Butler.

British Titan Products Company Limited has recently issued three new technical booklets, and revised two others, at the same time issuing an up-to-date list of current publications.

The new booklets are: "BTP/152—*Tioxide R-HD2*," "BTP/154—New durability scales for *Tioxide* pigments," and "BTP/155—*Tioxide R-TC6*." The new editions are of "BTP/153—*Tioxide* pigments: a guide to selection," and "BTP/135 Part Two Revised—*Tioxide* pigments in industrial finishes," and the publications list is numbered "BTP/156."

Expansion of facilities for the production of vinyl acetate monomer and acetaldehyde has recently been announced by **C. S. R. Chemicals Pty. Ltd.** The new plants, which will be at the company's Rhode, NSW, complex, are scheduled for completion in 1970, and will have an initial capacity of 12,000 tons per year of vinyl acetate, with opportunity for easy expansion, and 15,000 tons per year of acetaldehyde. These capacities are said to be sufficient to meet all Australian needs in the foreseeable future.

The vinyl acetate plant will use the process developed by **Farbenfabriken Bayer AG,** and the acetaldehyde plant a process based on technology developed by **Aldehyd GmbH,** both processes being new to Australia, and being based on ethylene supplied from the **ICIANZ** Matraville plant.

A new range of colours, said to be inspired by the colour film taken by the Apollo 9 astronauts on their orbit of the moon, has recently been launched by **A. Sanderson and Co. Ltd.**

The *Solar Glow* range of plastic emulsion paints comprises nine colours, which are said to be intermixable, and easily applicable with even colour dispersion by brush or roller.

An agreement has recently been concluded between **Federated Paints Ltd.** and **Nippon Yushi** of Tokyo for the manufacture, under licence, of the Glasgow firm's special purpose etching primer, *PA-10*, for the pre-treatment of steel.

This follows a year's field trials on the primer by the Japanese firm, and is the third manufacturing agreement made by Federated Paints, the others being in Australia and Norway.

Blythe Colours Limited has recently announced the introduction of a range of hot-printing enamels for glass, based on their new medium, *64/20*.

These enamels are claimed to have superior printing properties, to be easier to control in use than previous enamels of this type, and also to be usable over a wide range of screen temperatures, giving sharp, clear prints in mass and in fine detail work. A hard, smooth, firmly adherent film, which accepts overprints without pinholing, is also claimed, and as the enamels have built-in moisture tolerance, they can be applied to dry or damp glassware, and misprints are easily removed. Full technical details and samples are available from Blythe Colours.

It has recently been announced that **Chemische Werke Munchen Otto Barlocher GMBH,** of Munich, has appointed **Bush Beach and Segner Bayley Limited** as its UK agents. The Barlocher range of products includes PVC stabilisers, lubricants and paint additives.

Neofas 670, developed by the Nobel Division of **ICI Ltd.** as a high-viscosity cellulosic thickener for low-cost emulsion paints, is now on general sale, announce ICI.

The product, which has undergone a comprehensive evaluation programme, is a blend of selected grades of *Cellofas B* (purified sodium carboxymethyl cellulose) and *Methofas P* (hydroxypropyl methyl cellulose) in proportions claimed to give an excellent thickening effect at low concentrations.

It is claimed that *Neofas 670* possesses the desirable features of both ionic and non-ionic cellulose ethers, having good flow and levelling properties, good scrub and wash resistance, thickening power, resistance to biological attack and storage stability.

Also from ICI is a new, low-cost, process for the production of moulded articles in rigid polypropylene foam. Mouldings made by the process, which is based on sinter moulding techniques using relatively inexpensive moulds, are said to be of a density similar to that of red pine or deal, and to be almost three times as stiff as parts made from solid polypropylene, on a weight for weight basis.

Applied Chemicals Ltd. have recently introduced *Applied 5-73*, a new carbonised oil and light rust remover for internal combustion engines. Claimed to be an entirely new chemical approach to the problem of build-up of carbonised oil and decomposed leaded fuel deposits, *Applied 5-73* is a blend of alkaline salts and powerful sequestering agents, and field tests are said to have shown its superiority to other products when used at 1.5lb per gallon of water. It is sold in powder form, and Applied Chemicals are prepared to supply sufficient compound for 40 gallons of solution under a "Fair Trial Offer," on the understanding that if the product does not perform more effectively than the previous compound used, no charge will be made.

Welwyn Hall Research Association has recently formed a division specifically concerned with powder technology. This was initially based at Loughborough University of Technology, but it was decided that Welwyn Hall was a better situation, and this move should be completed by the end of July. New buildings will be available towards the end of the year to house the large amount of personnel and equipment required to meet the increasing demand for work on this subject.

Auckland

The composition, evaluation, and uses of printing inks

The first monthly general meeting of the Auckland Section was held on 19 March 1969 at Shell House where the subject presented was "The composition, evaluation and uses of printing inks" by Mr R. McCapra, of Coates Brothers Ltd.

Mr McCapra called on his long experience with the ink industry to give an interesting and informative talk on a subject closely allied with the paint industry but with its own particular materials and problems.

The talk took the form of a discussion of raw materials, finished products, test methods, manufacturing techniques and specific problems associated with substrates and customer requirements.

A very large range of pigments was used, with the main criteria being tone, end use and cost. Unless inks had to be used in outside exposure work, *e.g.* posters and signs, lightfastness and durability were not usually prime requirements. Certain pigments used extensively in printing ink manufacture were virtually never used in the paint industry; ultramarine blue, which was used in considerable quantities for toning black inks, was an example. One interesting point made by Mr McCapra was that although channel blacks made up the majority of black pigment used, furnace blacks were rapidly overtaking them and it appeared that they would make up the bulk of black pigment usage in the future.

Resins fell distinctly into two groups: oxidising and non-oxidising types. The most important members of the oxidising type were maleic, phenolic and fumaric resins which were solubilised with drying oils, and formed the basis of the majority of "oil based" inks. Of the oxidising oils used, linseed oil was by far the most important, and represented about 90 per cent of the total usage. Dehydrated castor and soya bean oils were used when non-yellowing properties were required. Nitrocellulose and similar resins were important members of the non-oxidising type, and it was within this group that resin chips, consisting of finely dispersed pigment in solid resin, were available. This class of resin was used in solvent based systems for gravure and flexographic printing. Hydrocarbon solvents as a group had a good boiling range for use in oil based inks, whereas alcohols, esters and glycols were the main solvents for non-oxidising systems.

Conventional paint driers such as cobalt, manganese and lead napthenates were used in most oil based systems, and amongst the various additives required were polyethylene and silicone waxes for slip control, and silicone antifoams.

Two types of inks and the method of their manufacture were described. Paste inks, such as those used in offset lithography, were premixed in heavy duty mixers before final dispersion through a triple-roll mill—the classic technique of ink manufacture. Liquid inks, which, as their name implied, were of low viscosity and might be manufactured in similar manner to paint in either single-roll or ball mills. Sand grinders and other modern equipment were suitable for this type of ink production.

In a section on ink testing and quality control, Mr McCapra stressed the extremely large technical personnel requirements in the ink industry and said that up to 25 per cent of company employees were essentially technical, involved in technical management, technical service or quality control. Generally, the majority of tests on printing inks were similar to those used in the paint industry, although some of the exceptions were most important. Ink which affected paper during printing, the problem of odour when inks based on oxidising resins were used in printing packs used for food packaging, and chemical resistance to the product contained within the package were amongst the most important of the exceptions.

Variations in type and quality of substrate were mentioned by Mr McCapra as being the greatest problem encountered by the ink technologist. Five classes of substrate were listed: paper, board, flexible packaging, rigid plastics and miscellaneous substrates such as glass, wood, metal, textiles, rubber, leather, meat and oranges. It was not unusual to find standard colours being formulated on many different bases due to the effect on colour that different substrates had, *e.g.* coated papers and boards, foil *etc*. Examples of the various substrates, both printed and unprinted, were displayed and the particular problems of some substrates were discussed.

The five basic printing processes, letterpress, offset litho, flexographic, gravure and silk screen, were explained in detail. Letterpress was a direct process with the paper printing directly from a relief, and was the oldest technique known. Offset litho was capable of printing a far greater range of substrates and printed from a plate to a blanket to the paper. One of the advantages of offset was that printing was done from a resilient blanket, which meant that rougher papers and boards could be used than with letterpress. A classic example of the use of offset was tin printing. The flexographic process, as the name implied, was used in the printing of flexible film from a raised relief. Gravure, printed from a relief engraved into ink-carrying cells, was extremely fast and was capable of producing excellent quality. Some experimentation with electrostatic forces for ink transference was being undertaken at present, and even faster production could be expected. Silk screen processing was ideal for short runs or substrates of varying dimensions, *e.g.* plastic bottles. It was also used in the production of printed circuits.

Mr McCapra concluded his talk with a discussion of some of the particular problems encountered by ink technologists. These he listed as small orders, specialised orders, correlation of lab-press results, and the lack of access to non-company technical information.

A lively discussion period followed, with Messrs Giles, Knights and Juster participating. The use of water based systems for the printing of cheap board of high absorption was explained. High acid value maleics and shellac in ammoniacal solutions were generally used as binders. Some research into the use of emulsions had been carried out but a problem of instability caused by the high pigment loading was found. Two-pack systems had been successfully used where difficult adhesion had been encountered. Generally, two-pack inks exhibited extremely high heat and chemical resistance.

The speaker then showed a film prepared by his company which effectively demonstrated the points he had made throughout his discussion.

Mr G. Juster, the Section Chairman, led the members present in proposing a vote of thanks to Mr McCapra for his extremely interesting and informative presentation of a subject which was almost a complete mystery to most of those present.

J.W.A.H.

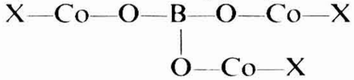
Hull

Recent developments in driers

The sixth ordinary meeting of the session was held at the College of Technology, Hull, on 3 March. Mr N. Lythgoe introduced Messrs W. K. H. Lakin and J. W. H. Turner of Hardman and Holden Ltd., who gave a most interesting lecture on "Recent developments in driers."

Mr Lakin, who presented the paper, stated that driers should: (1) exert a positive influence on the drying rate, (2) contain a high proportion of the active constituent and (3) exert no deleterious effects on the film.

The metal content of a metal soap could be increased by using an acid of as low a molecular weight as possible, but solubility in the normal paint media and solvents limited this in practice to the C_8—C_{13} range. 2-ethyl hexoic acid was generally satisfactory, and other suitable synthetic acids were produced by the Kopp and OXO processes. In general, synthetic acids were superior to naphthenic acid with respect to stability, low odour, gloss and colour retention and drying rates.

Another way to increase the metal proportion in the drier was to use a higher proportion of metal to acid than in the normal, X—M—X, salt. This could be done by using the the basic salt, X—M—OH, but the solubility of these was not usually satisfactory. Condensation of the basic salt to X_1—M_1—O—M_2—X_1 could provide a product which was often quite soluble. The linking element was not necessarily limited to oxygen, for instance boron could be used to give a very stable product  $\mathrm{X{-}Co{-}O{-}\underset{\substack{|\\ O{-}Co{-}X}}{B}{-}O{-}Co{-}X}$ which was soluble in hydrocarbons and had a high metal content. As, Sb, Si, and P could be used instead of boron and were all atoms which were not so heavy as to decrease the active metal content seriously.

Mr Lakin described the normal drying processes due to peroxide formation and considered the products that could be formed by peroxide breakdown, which were mainly electron donating substances, and this led to the co-ordination mechanism of drying. The oxidation process depended on the rate of penetration of oxygen into the film, the rate of peroxide formation and breakdown. The co-ordination mechanism depended on the mobility of the metal soap, the mobility of the polar groups present in the drying medium and the ability of the complex to breakdown. The temperature dependence of these processes might be different and thus lead to different drying rates under adverse conditions.

These considerations led to an investigation of Co and Zr and with other elements having a greater synergistic effect with Co. Mr Lakin exhibited slides showing the effects on the drying rate of various metal combinations. It is hoped that it will be possible to publish this paper in full in due course.

Messrs Read, Lythgoe, Finn, Downs, Gilroy, Fillingham, Wenham and Gibson took part in the discussion that followed the lecture. A vote of thanks was proposed by Mr S. J. Read. Thirty-one members and three visitors were present.

S.R.F.

North of England Golf Competition, 1969

The winner of the North of England Golf Trophy, Mr W. Huddart (2nd left) being presented with the cup by Mrs L. Watkinson. On the left, Mr D. Brown (runner up) and on the right Dr L. Watkinson (Chairman, West Riding)

Pannal Golf Club, Harrogate, was the host club for the first competition for the North of England OCCA Golf Trophy, held on Friday 9 May. Twenty-six members supported this event by playing in the match, which took the form of a Stableford competition, and the organisers in the West Riding Section wish to thank all those who took part, particularly those who represented other sections as far afield as Scotland, London, Manchester, Midlands and Hull.

The afternoon's golf was certainly enjoyed by all, and although conditions were wet underfoot this picturesque championship course was in good condition and a test for any man's skill.

We would congratulate Bill Huddart, of the West Riding Section, on his fine win. He deserves praise not only for his being the first name on the Trophy but from the West Riding point of view for ensuring that the Trophy is defended in that area in 1970.

D. Brown was a very worthy runner-up and only just failed to take the Trophy west of the Pennines.

During the course of this match, the West Riding Chairman's Trophy was also played for, and Bill Huddart once again deserved his win, thus going home with two for the price of one.

Prizes were presented by Mrs L. Watkinson, after an address of welcome by the West Riding Chairman, Dr L. Watkinson.

Thanks were extended to Mr L. Silver, the immediate past West Riding Chairman, whose idea it was to organise a North of England Trophy for which Members of all Sections may compete, and who has generously presented the handsome cup.

It is now hoped that this will become an annual national OCCA golfing event and it is proposed that the venue should be in the area of the current holder. Hence we can confidently announce Yorkshire as being host again next year when we trust members from all sections will take part.

Report of Council

The last meeting of Council for the session 1968-69 was held on Wednesday 30 April 1969 at Wax Chandler's Hall, Gresham Street, London, EC2, when 21 members were present under the Chairmanship of Mr F. Sowerbutts (President).

A welcome was extended to the newly-elected Section Representatives, who were attending a Council Meeting for the first time, and in particular to Mrs K. Driver of the West Riding Section, the first lady to serve on Council.

Members were sorry to learn of the death of Mr W. E. Wornum, President of the Association 1940-44, and an Honorary Member. Council stood in silence for a few moments as a mark of respect. An obituary notice appears in this issue of the *Journal.*

Reports were given on the final arrangements for the Conference at Eastbourne in June. A report was also received on the Exhibition held in March, a full report of which appeared in the May issue of the *Journal.*

Council was informed that the Exhibition Committee was to meet the following day to make arrangements for the 22nd Technical Exhibition to be held in 1970.

Council had decided at a previous meeting that badges should be presented to Past Chairmen of Sections, where desired, and a design of the new badge was shown to those present and approved.

It was reported that the completed manuscript for Volume VII ("Works Practice") of the Paint Technology Manuals was now in process of final preparation and that the authors for the 1969 edition of the Resins, Drying Oils, Paints and Varnishes Report had again agreed to undertake the work. The 1968 Report will be circulated to members towards the end of this year.

Council appointed Dr F. M. Smith to represent the Association on the newly-formed "Review of coloration progress" sub-committee of the Society of Dyers and Colourists. This committee has been constituted to produce an annual review to replace the "Review of textile progress," which will cease publication.

Recommendations were also made for speakers to present papers at the FATIPEC Symposium in Montreux, and the Joint IRI/PI/SCI/SDC/OCCA Symposium to take place in London from 29 September to 1 October 1970 under the title "Chemistry of liquid polymers and thermoplastic co-polymers."

It was reported that Dr J. E. O. Mayne, of the London Section, had been asked to convey greetings from the Association to the meeting of Gesellschaft Deutscher Chemiker Fachgruppe Antrichstoffe und Pigmente on 8-9 May at Bad Ems.

The Federal Committee of OCCA Australia had requested that any member likely to be visiting Australia in June 1970 and willing to present a paper at their Convention at Victor Harbour, should inform the Director and Secretary, who would forward details.

The Working Party on Education, Training and Qualifications was still in the process of preparing a comprehensive document to present to Council during the next session. In the meantime Section Committees were being asked for as much information as possible for the Working Party to consider.

The Jordan Award Committee had met on 17 April and Council were informed that the Committee had decided on this occasion to divide the prize of £100 equally between Mr R. J. King (for a dissertation) and Mr M. J. B. Franklin (for his paper published in the June 1968 issue of the *Journal*). Certificates were being prepared for presentation (with the cheques) to the winners at the Annual General Meeting at Eastbourne on 20 June.

Reports were received on the activities of the Sections since the last meeting of Council.

As this was the last meeting of Council during Mr Sowerbutts' term of office as President, a vote of thanks was passed with acclamation by the members, drawing particular attention to the way in which Mr Sowerbutts had put himself wholeheartedly into his duties as President, with visits to the Sections in the UK, New Zealand and South Africa, and the newly independent OCCA Australia.

In his reply, the President stated that he had been particularly happy to have had the honour of being President during the Jubilee Year and had thoroughly enjoyed his term of office. It had been more arduous than he had anticipated and it was only because he was now retired from business that he had been able to devote so much time to Association affairs.

London Section

Annual General Meeting

The 31st Annual General Meeting was held on 24 April 1969 at the Criterion in Piccadilly, London W1. The Committee's Annual Report was adopted unanimously: in presenting it Mr R. H. E. Munn commented on the highly successful Ladies Night. Mr J. T. Tooke-Kirby, the Chairman of Southern Branch, said that they were having a reasonable attendance at their meetings, and would always welcome members from London Section. Mr J. Pooley gave some details of the response to the membership survey, which showed that 25 per cent of members were in the paint industry, and 10 per cent in printing ink. Attendance at meetings was varied, only 18 per cent claimed to attend more than three meetings a session and 4 per cent most meetings. There was a strong preference for meetings to be held in Central London rather than in the suburbs. Eighty-three per cent of members were satisfied with the present balance of the programme contents. Dr H. R. Hamburg presented the Financial Report, which was carried unanimously.

The Officers for the coming session were elected as follows. Hon. Secretary, Mr R. H. E. Munn, Hon. Treasurer, Dr H. R. Hamburg, Hon. Publications Officer, Dr V. T. Crowl, Hon. Programmes Officer, Mr D. E. Eddowes, Hon. Auditor, Mr A. H. Soane. In proposing the election of Mr J. E. Pooley as Chairman, Mr Wheeler referred to his long period of service on London Section Committee and his past chairmanship of Mitcham Paint Club.

Mr D. E. Eddowes proposed a vote of thanks to Mr Wheeler for his faithful and conscientious service to the section and to OCCA. Mr Pooley thanked the retiring members of the Committee, Mr F. Davies, Mr V. Jenkins and Mr R. M. W. Wilson.

As a result of a ballot, the three new members of the committee elected were Mr J. C. Martin, Dr W. M. Morgans, and Mr P. Whiteley.

After the dinner, Mr D. Roe gave a talk entitled "From paint to television—or out of the frying pan into the fire." This proved to be a fascinating story of entering a completely new field and building up a highly successful company, Television Recordings Ltd., by taking advantage of a market requirement. Television broadcasting companies suffered from the problem of peak loading and under-utilisation of their very expensive equipment. Consequently the companies were prepared to pay for assistance with their peak load problems. The company now had its own studios, and colour and black and white equipment. Mr Roe had brought along some of the equipment and used it to illustrate some of the techniques used in recording, showing typical sequences in making up a TV commercial. There was also a considerable demand for closed circuit transmissions, and an example of a recording used by a firm in the paint industry in launching a new product was shown. After an interesting discussion, a vote of thanks for an extremely entertaining talk was proposed by Mr J. Hawkey.

Southern Branch

Seen on Ryde pier (left to right) Mr W. H. Morris (Hon. Secretary, Southern Branch, who organised the outing), the President, Mr F. Sowerbutts, Mrs Sowerbutts, and Mr J. T. Tooke-Kirby (Chairman, Southern Branch)

Southern Branch Outing

Although the main function of an OCCA section or branch is to provide regular technical meetings, it is invariably the annual social event that imposes the greatest strain upon the committee. Will a dinner dance attract sufficient support when membership is spread over a wide area? Will a stag dinner be even less of a success? To what extent can the event be subsidised if numbers are low? To the Southern Branch Committee with only a small membership the event would obviously need to be unusual if it was to attract the interest of London Section members, and it was eventually decided to organise a summer evening hovercraft trip across Spithead followed by dinner in Ryde on the Isle of Wight. Having announced the event for Friday 16 May the Committee were rather alarmed to discover that the Queen had decided to review the NATO fleet at Spithead on the same date. After much discussion it was decided that the event should not be postponed, despite the complications in transport that were bound to arise.

For those members of the London Section who can avoid work on a Friday afternoon, Southern Branch hospitality commenced with a tour of the Victory, dressed overall in honour of the Royal visit. Shortly before six o'clock members began to assemble at Portsmouth Harbour, just as the Queen was due to arrive to board her train to London. After struggling through the crowds lining the approaches the poor members were hurried by the police through a side entrance to the station, presumably because they appeared to be too disreputable to meet the Queen! At this stage a certain amount of difficulty arose as the police would not allow members to wait outside the entrance yet they were not allowed in until the Hon. Secretary appeared with the group ticket. After a circuitous tour of the station also designed to keep the Queen and OCCA apart, the party eventually assembled at the Seaspeed terminal only to learn that hovercraft operations had been delayed through restrictions on entering and leaving the harbour during the review manoeuvres. At this point it began to rain.

Actually the situation was not as bad as it sounds for the party all found shelter and about 20 members were offered seats on a delayed service hovercraft that was about to leave for Ryde. This hovercraft, a Hovermarine solid-sidewall type, left for Ryde almost immediately, pausing briefly at Clarence Pier, Southsea, on the way but then passing through the lines of ships drawn up in Spithead. The remainder of the party were less fortunate in the sense that they had to wait about an hour for their chartered hovercraft to arrive but they were rewarded for their patience by a complete tour through the sixty-odd warships with a continuous commentary.

To the local branch members the arrival at Ryde pier was unspectacular but they were highly amused when some London section members who had never previously visited the island were amazed to see cars and a railway, although the ex-London Transport Underground trains made them feel at home, despite their blue paintwork! By this time the rain seemed to be over and the two parties eventually met again at Yelf's Hotel where dinner had been arranged. At this point the Southern Branch Chairman, Mr Tooke Kirby, presented the ladies with carnation buttonholes and everyone was presented with a coloured souvenir issue of the Portsmouth Evening News celebrating the Royal review of the NATO fleet.

All too soon the time arrived for the return to the pier to await the veteran paddle-steamer "Ryde" for the crossing to Portsmouth but the evening was not yet finished. As the sun set in the west and darkness spread across Spithead the vast armada, stretching for eight miles, was lit up with floodlights and strings of lights showing the silhouettes of the individual ships. To many the arrival at Portsmouth marked the end of the evening but to some it marked only the start of another party in the Keppel's Head Hotel where some of the visitors were staying.

Certainly the event attracted support. In fact it was later calculated that over 60 members travelled on the tickets made out for only 56! The only problem for the Committee is to arrange as popular an event for next year, although it seems unlikely that they can rely again on the co-operation of the Queen and the NATO fleet!

Scottish Section

Annual General Meeting and Smoking Concert

The Annual General Meeting of the Scottish Section was held on 11 April 1969 in the Whitehall Restaurant, Glasgow, with Mr J. Miller in the chair. After the various reports had been considered and approved, Mr Miller announced that the Vice-Chairman, Mr P. Birrell, had tendered his resignation on account of his forthcoming departure to take up an appointment in Canada, and paid tribute to the excellent service which Mr Birrell had given to the Section as a Committee member, Student Liaison Officer and Vice-Chairman, and to the Association as a whole as an elective member of Council. New office bearers and committee members for the forthcoming year were elected as follows:

Vice-Chairman: Mr D. Rowley.

Hon. Research Liaison Officer: Mr H. A. Munro.

Committee Members: Messrs A. D. C. Brown, I. R. McCallum and C. S. MacLean.

The company then adjourned to the Eglinton Arms Hotel at Eaglesham for the Section's Annual Smoking Concert. Following an excellent meal, Mr Birrell, the retiring Vice-Chairman, introduced the entertainers for the evening and emphasised that the Scottish Section were about to depart from tradition by having a female singer for the first time at one of their concerts. It was obvious that this announcement went down very well with all members and Janette Melville proceeded to convince her audience that she had lived up to their expectations. Janette's repertoire ranged from Puccini to modern musical comedy and she was ably accompanied on the piano by Glen Dale. Gary Denis proved himself more than capable of keeping his audience fully entertained with numerous stories, jokes and anecdotes, none of which can be reported here.

The evening finished with the singing of "For he's a jolly good fellow" to our departing Vice-Chairman. Mr Birrell in reply stated that the strength and success of the Scottish Section were due to the high personal calibre and integrity of each member, and that it had been a great pleasure to him to have worked with and for the members.

Fifty-nine members and their friends enjoyed the evening's entertainment.

Obituary

William Esmond Wornum
Born 27 August 1897
Deceased 8 April 1969

William Esmond Wornum

William Esmond Wornum had ideas. He thought deeply about technical problems, sometimes in unusual ways. Recently some of those who knew him, particularly on the technical side, were asked, "What comes to mind when the name Wornum is recalled?" They said "micelles"—clear evidence of the lasting impressions made by his views on varnish making expressed many years ago. He considered varnish making and film formation to be essentially the building up of colloidal complexity to desired levels with the formation of "micelles" or organic flocculates. The actual chemical nature of the molecules formed was less important. Some resin-oil reactions were considered as swelling processes rather than in terms of chemical reactions.

Such views received much support at the time—and Wornum successfully applied them to many practical varnish problems. There was then little knowledge of molecular weights and of the species involved. It is only recently, with the aid of gel permeation chromatography and infra-red spectroscopy, that detailed information on the structure and distribution of molecules in, say, an alkyd resin is being obtained, and no significant amount of work has yet been done on the relationships between detailed resin structure and paint properties. However, after a period during which some "colloidal" ideas were out of favour, some people have recently returned to thoughts of highly developed groupings of molecules (in and around clusters of pigment particles for example) to explain some aspects of the behaviour of media and paints. My feeling is that Wornum was right in many respects, at least within the field of varnishes with which he was immediately concerned.

On many aspects of our technologies he had unorthodox approaches, and when presenting his ideas and discussing their practical significance he was quietly enthusiastic, firm in exposition, and confidently serious in manner. But in more general conversation, the amusing side, wit and humour were not far away. There are treasured memories of his telling funny stories. He would start. Then the humour of what was to come, which only he knew, would well up and he would start to laugh. Then he would try again; and so on until those around would all be laughing long before the denouement. A story which when told by a straight-faced raconteur would take two minutes, took ten, but the laughter was greater. It was delightful.

This may be an unusual way to introduce an obituary appreciation, but he was an unusual man who left distinctive personal impressions on those who knew him closely, and the formal record of his technical training, his services to our industries, and his achievements is unusual as well as outstanding.

Wornum served with H.M. Forces for nearly four years in the first World War. He joined the 28th London (Artists) Rifles in 1915 and was commissioned in the Royal Artillery in the following year. He was awarded the Military Cross and promoted in the field to the rank of Captain.

He later graduated with honours in chemistry at the Royal College of Science and in 1925 he began his 30 years' service with Mander Brothers Ltd. He started as a research chemist under the late Dr R. S. Morrell, whose work on varnishes (including the "bloom" of films) became well known. A number of joint papers were published and the collaboration obviously initiated his thinking on the varnish complex. He was appointed chief chemist in 1930 when Morrell retired.

It is perhaps also significant that Morrell had been President of OCCA in 1920-22 (succeeding the founder President, Dr F. M. Perkin). Wornum followed in his footsteps, becoming a member of Council in 1933, and Hon. Research and Development Officer in 1934, a post which the records say was "created to give opportunities for the exceptional abilities which Mr Wornum possesses," and which brought him responsibility for the technical arrangements at early OCCA conferences. His subsequent election as President brought his talents to bear upon problems which, although only guessed at, were expected to be serious, namely those of maintaining a sound Association during the second world war. He was elected in 1940 and served until 1944 when the end of the war was in sight, thus becoming the longest serving President. The achievements of those years are recorded in "A Fascinating Story—the History of OCCA, 1918-68," He was elected an Honorary Member on the occasion of the June 1967 Conference in Scarborough.

He served on numerous technical committees concerned with paints, printing inks, resins and varnishes, including committees of the British Standards Institution and the Printing and Allied Trades Research Association. He was founder chairman of the Surface Coating Synthetic Resin Manufacturers Association, and founder President of the Wolverhampton Society of Applied Science. After the second war he led technical teams which investigated the German paint and ink industries.

All this was no more than had come to be expected of him, but he carried a very considerable additional responsibility during 31 years' service to the Paint Research Association. He was a member of Council 1941-63, twice a Vice-President 1945-47, 1961-63, Chairman of the General Purposes Committee 1947, and Chairman of the Technical Advisory Committee 1952-63, after many years' experience on the Subject Panels. His remarkable contributions to the work of the Research Association were recognised by the award of Honorary Membership in 1964.

His industrial service was continued after the Mander Brothers period with Smith & Walton Ltd. in Haltwhistle, where he found new opportunities to apply his vast technical knowledge and experience, and to indulge his love of nature in his garden and the countryside.

He retired in 1963 after 38 years in industry, but maintained contact with many old friends. Indeed, whilst it is essential to record services rendered and honours received, as indicating the scope of his talents and ability, I have found whilst writing this appreciation of Wornum that my mind has continually returned to incidents, conversations, debates and those many occasions when his personal characteristics were manifest, not least his kindness and concern for others. Some of us also enjoyed the hospitality of his home, where we met his charming wife. To her our sincere condolences are extended. We trust that knowledge of the gratitude of numerous people for the life and work of her husband will give her consolation.

S. H. BELL

News of Members

Mr J. P. Smith, an Ordinary Member attached to the London Section, has joined the Market Research and Product Development Group of Hercules Powder Company Limited. Mr Smith was previously with Abco Petroleum Limited.

Mr P. Birrell, an Ordinary Member attached to the Scottish Section, and Vice-Chairman of that Section, recently accepted the position of Product Manager with The Dominion Colour Corporation Ltd., of Toronto, Canada, and will take up his post in Toronto in July.

Mr Birrell, who was previously with the pigments division of Geigy (UK) Ltd., and with James Anderson & Co. (Colours) Ltd. until its incorporation into Geigy, has served the Scottish Section as Committee Member (1964), Hon. Student Group Liaison Officer (1965-68), and Vice-Chairman from 1968. He was also an elective member on Council from 1967 until his recent resignation, and is a member of the Working Party on Education, Training and Qualifications.

Conferences and Symposia

FSPT 47th Annual Meeting and 34th Paint Show

Advance registration forms for the Federation of Societies for Paint Technology 47th Annual Meeting and 34th Paint Industries Show are to be included in the July issue of the Journal of Paint Technology, and will be sent direct to all members of the FSPT in August. The Annual Meeting is to be held at the Conrad Hilton Hotel, Chicago, from 5-8 November 1969, and the registration fees will be $35.00 for men and $20.00 for ladies. Those taking advantage of the advance registration forms will be allowed reduced fees of $31.50 and $18.00 respectively.

Block bookings have been made in several Chicago hotels, and hotel reservation forms are now available from the FSPT.

It has also been announced that the Joseph J. Mattiello Memorial Lecture, given each year at the Annual Meeting, will be presented in 1969 by Mr H. Burrell, of the Interchemical Corporation, whose subject will be "Entropy: the hidden ingredient."

Emulsion polymers

The University of Manchester Institute of Science and Technology, in collaboration with the Society of Chemical Industry, is to hold a symposium on emulsion polymers on 16 and 17 September 1969, at the University's student village at Owens Park, 3½ miles south of the city centre.

Fees for the symposium, which is to contain three main lectures and 17 original papers for discussion, are £15 (£10 for members of the SCI, and £1 for full-time university staff and students).

The three main lectures are "Mechanism of emulsion polymerisation," by Dr J. L. Gardon (M & T Chemicals Inc., New Jersey), "Outstanding problems in emulsion polymerisation" by Dr E. W. Duck (The International Synthetic Rubber Co. Ltd.) and "Mechanism of film formation of latexes" by Dr J. W. Vanderhoff (Dow Chemical Co.

Michigan). The 17 original papers, which will be preprinted for discussion, will be from authors from Austria, Canada, Germany, Japan, Norway, Switzerland, the United States and Britain. Videotape recording of parallel sessions for evening playback is planned.

Copies of the prospectus, and registration forms, are available from The Registrar, UMIST, Sackville Street, Manchester M60 1QD.

Joint ACS-CIC Conference

The American Chemical Society and the Chemical Institute of Canada are to hold a joint conference in Toronto, Canada, from 24 to 29 May 1970.

The conference will comprise two symposia, on "Scanning electron microscopy" and "Behaviour of pigments in organic coatings," and papers are invited from any interested persons.

Titles of papers should be in the hands of the respective session chairman by 1 December 1969, and four copies of a 200 word abstract and a copy of the final paper by 1 January 1970.

The session chairmen are given below.

"Scanning electron microscopy": ACS Chairman—L. H. Princen, Northern Regional Research Laboratory, 1815 North University, Peoria, Illinois 61404; CIC Chairman—T. G. Perlus, Ontario Research Foundation, Sheridan Park, Ontario.

"Behaviour of pigments in organic coatings": CIC Chairman, I. H. McEwan, Canadian Industries Limited, 1330 Castlefield Avenue, Toronto 340, Ontario.

The European market of paint and varnish 1970-1975

The International Business Contact Club (i.b./c.c.) is to organise a symposium with the above title in Brussels on 22 and 23 October 1969. Among subjects discussed by international experts will be: the market for raw materials and additives for paint and varnish, the evolution of European production, the European producers and their new dimensions, the evolution of distribution, sales and employment by sectors, the evolution of prices, and foreign trade.

Further information is available from the i.b./c.c., 99 avenue Nouvelle, Brussels 4, Belgium

PRS development featured on television

On 7 May, the BBC Television programme "Tomorrow's World" featured a coating developed by the Paint Research Station which can be used as "spray-on central heating."

The PRS has for some time been studying the use of inorganic materials, such as silicates, as binders for paints, instead of the more usual organic binders. In the main silicate-based coatings have been useful for their temperature resistance and general inertness, and coatings of this type have been used on space satellites, where temperature control and corrosion protection in extreme conditions are required.

In a search for more "down-to-earth" applications, PRS workers have developed an electrically conductive coating that can be readily applied, by brush, spray or roller to existing wall surfaces, to provide a heating element in domestic buildings. Particularly low electrical resistance has been imparted to the coatings, so that a low voltage supply (no greater than 40 volts AC) may be used for heating, thus eliminating the hazard arising from electric shocks from exposed surfaces of the coating. The paint does not contain any known toxic materials, and could be considered quite harmless to children, animals, etc.

The coating is dark in colour, but can be overcoated with a decorative paint without noticeably affecting its high radiation efficiency, and small and medium scale trials over a six-month period have shown the system operates without deterioration under daily heating and cooling cycles.

The paint is said to be little more expensive to manufacture than a high-quality decorative paint, and its advantages of ease of application and use of little space, together with the facts that walls are used to some extent as storage heaters and warm-up of a room is quick owing to the large area heated, indicate that its value in use may be considerable.

A patent application has been filed.

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

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introduction to paint technology

second edition with additional chapter

The sales of this Association publication now exceed 13,000, and because of continuing high sales of the second edition, and the need for a work of reference to be constantly abreast of the latest developments in its field, the Council of the Oil and Colour Chemists' Association has authorised the addition of an eleventh chapter to the 'Introduction to Paint Technology. Entitled 'Recent Developments,' the Chapter incorporates up-to-date information on the latest advances in the technology of the paint and allied industries.

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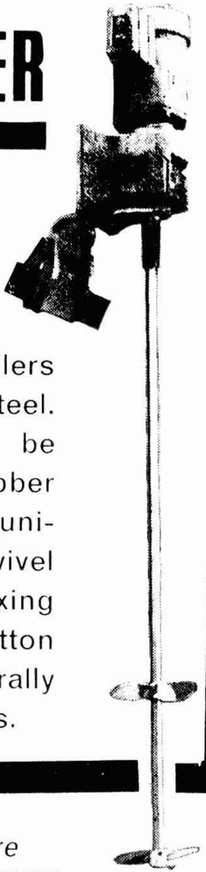

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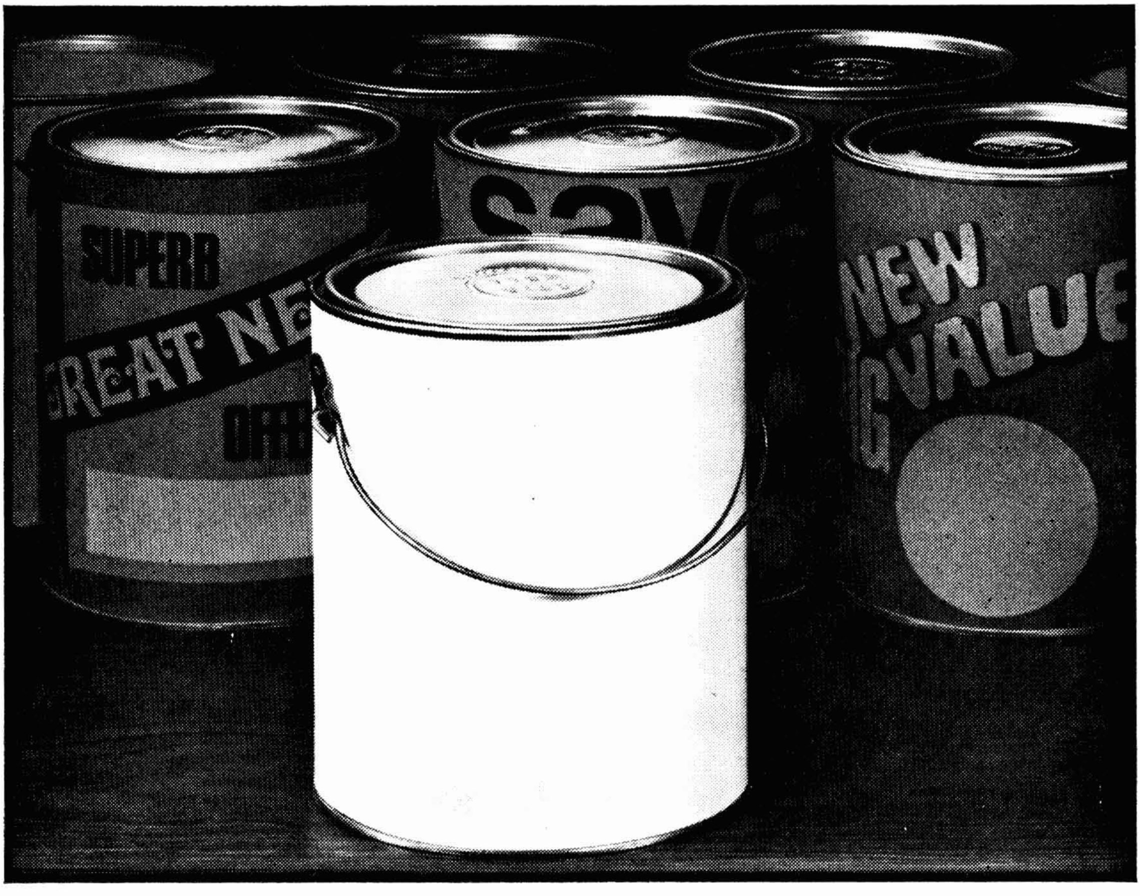
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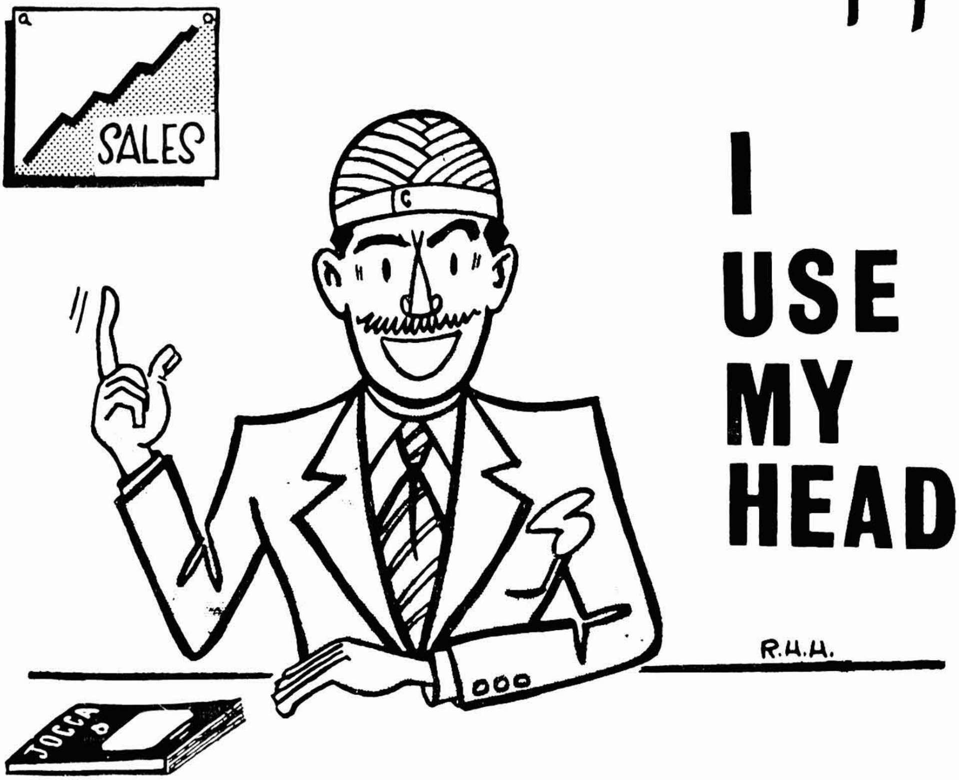

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