# JOURNAL
OF THE
# OIL AND COLOUR CHEMISTS' ASSOCIATION

**Vol. 47 No. 4** **April 1964**

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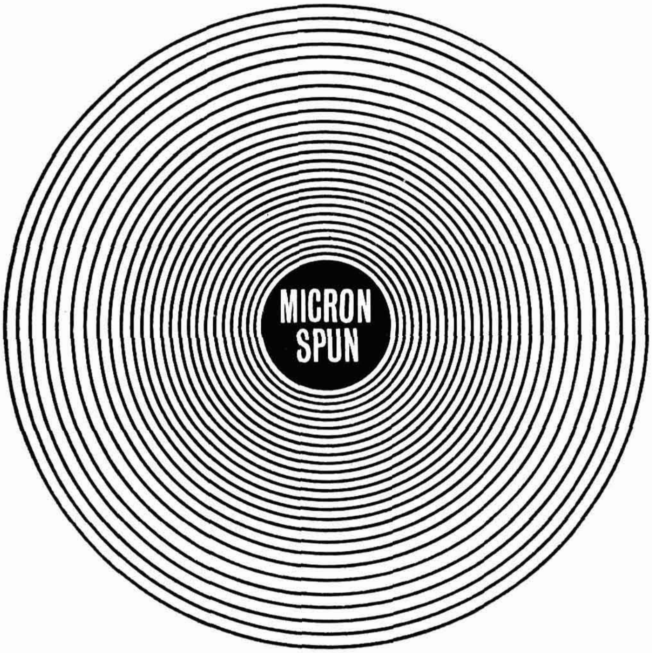
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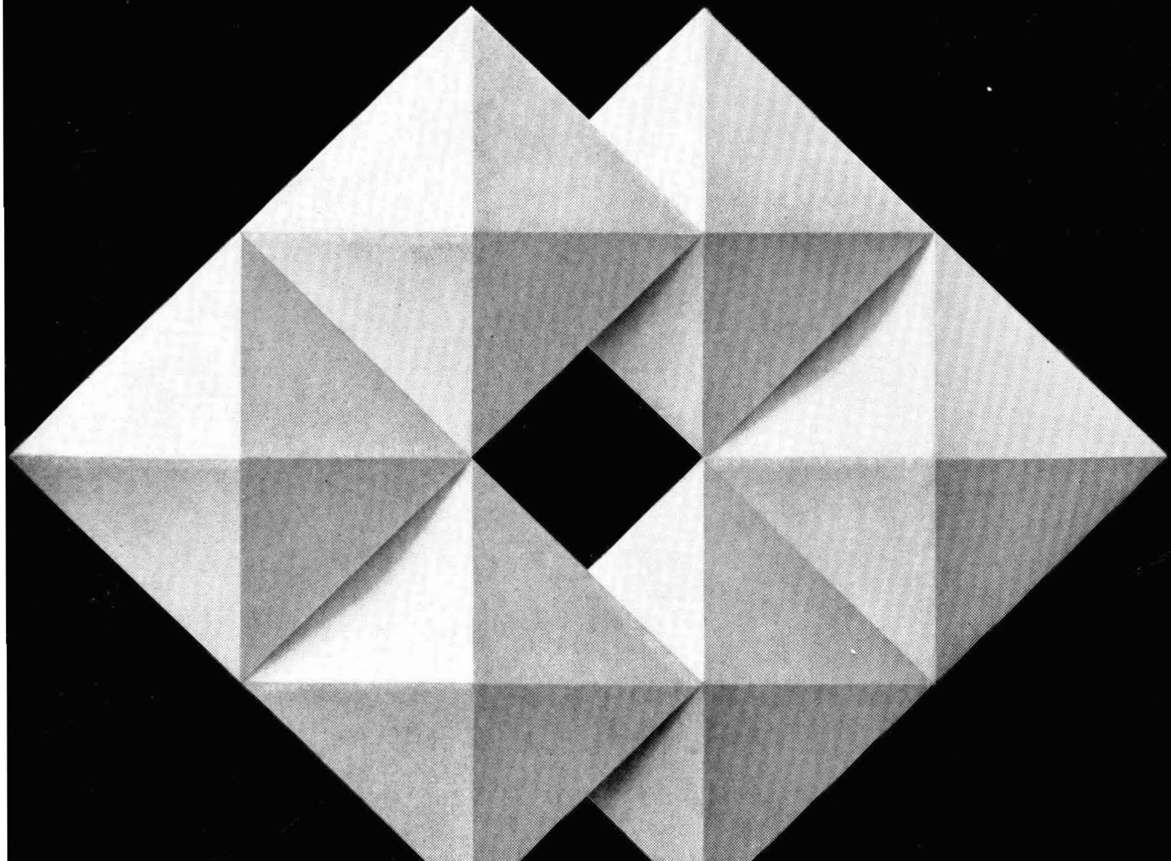

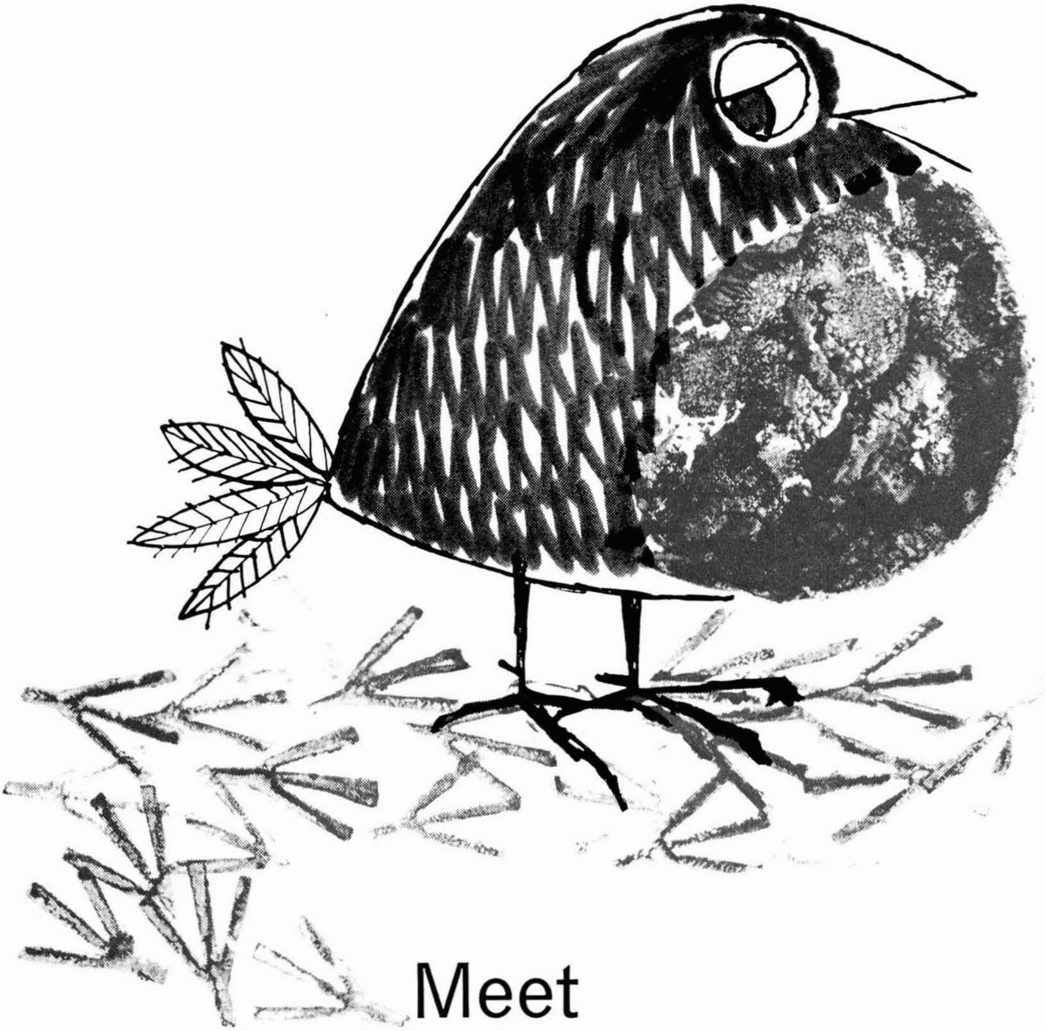

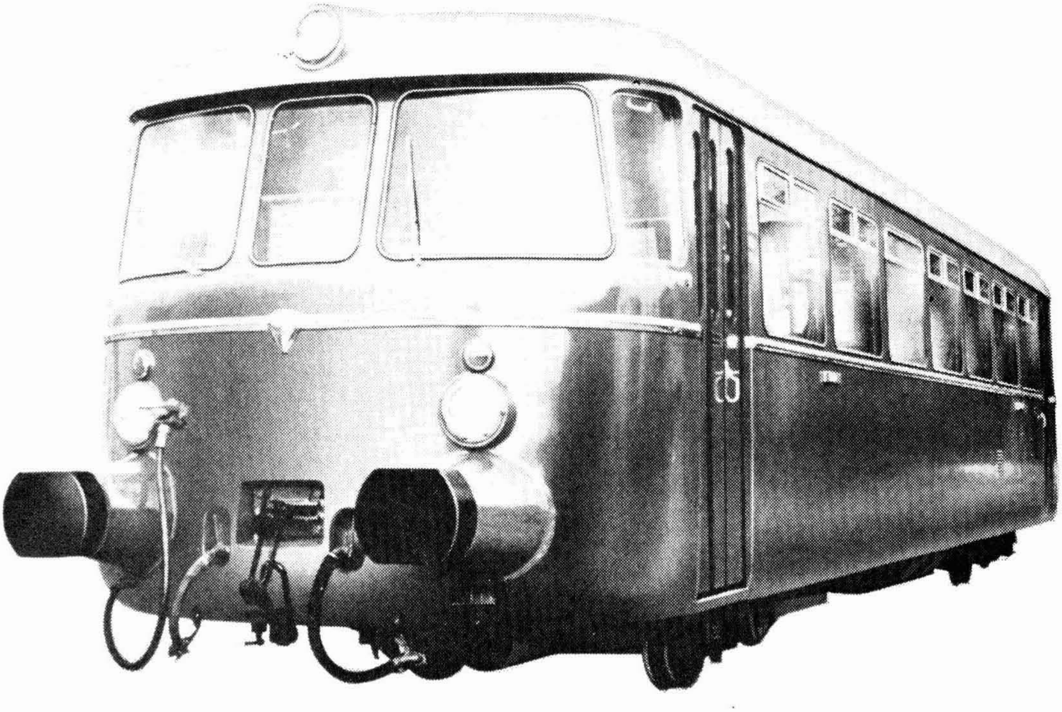

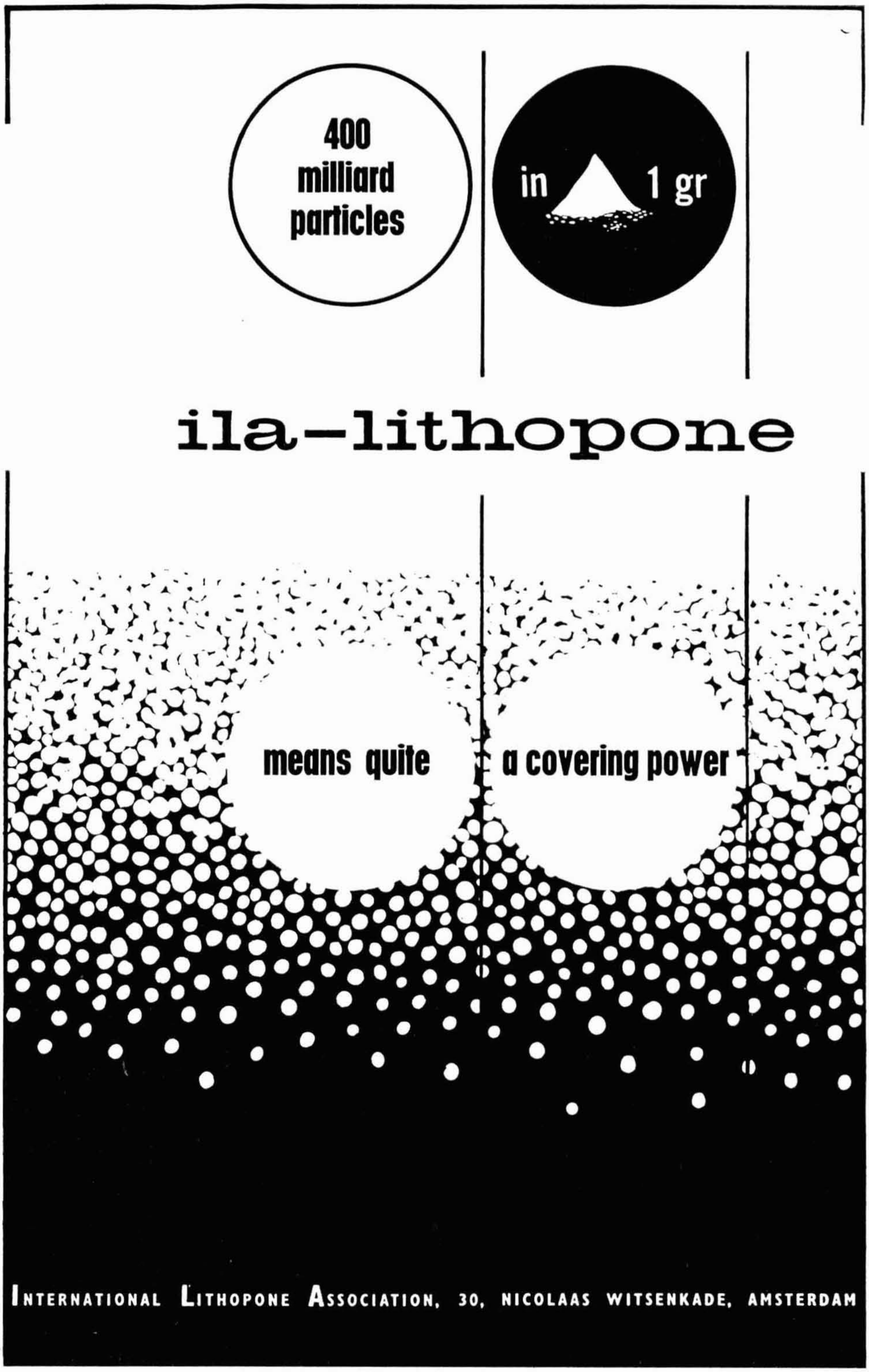
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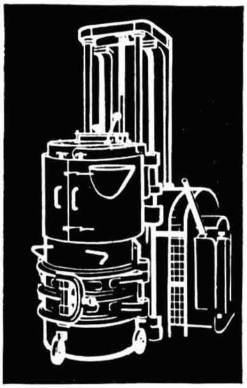

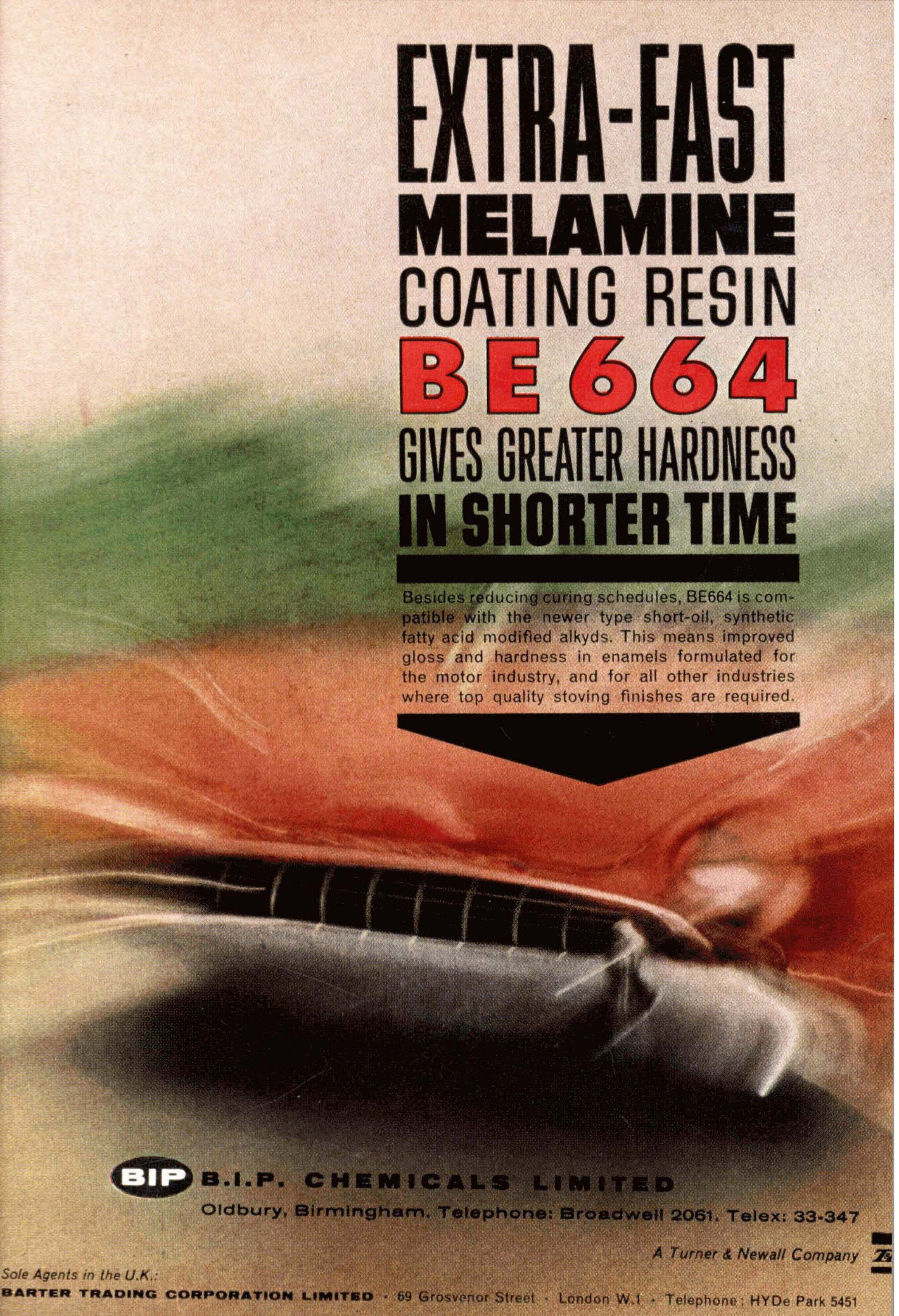

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**JOURNAL OF THE OIL & COLOUR CHEMISTS' ASSOCIATION**

**Vol. 47 No. 4 April 1964**

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# JOURNAL OF THE OIL & COLOUR CHEMISTS' ASSOCIATION

Vol. 47. APRIL 1964 No. 4

## TRANSACTIONS AND COMMUNICATIONS

# Polyamide-Epoxy Blends: A Corrosion Inhibiting Vehicle for Paints*

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*Summary*

When dimerised vegetable oil fatty acids are condensed with polyamines such as diethylene triamine, low molecular weight amino-containing polyamide resins result. Because of their amine functionality, these resins react with epoxy resins to provide hard thermosetting structures useful as castings, adhesives and films for protective purposes.

Polyamide resins, because they contain small polar amine groups and long fatty functions, are surface active agents. Because of the structural features which make them surface active, they possess not only high adhesion but are also corrosion inhibitive. When combined with epoxy resins, thermosetting compositions, such as films, result which retain both the adhesive character and the corrosion inhibiting character of the polyamide resins.

In the past the corrosion inhibiting character of paints has been achieved largely through the use of corrosion inhibiting pigments. The polyamide-epoxy combination provides a means for achieving corrosion inhibition through the vehicle. One virtue of a corrosion inhibiting vehicle is that as the continuous phase of the paint it can depolarise the entire anodic surface. A corrosion inhibiting pigment, on the other hand, which is necessarily the discontinuous phase, can depolarise the anodic surface only at those points where it comes in contact with the surface.

In this paper, data are presented to support the corrosion inhibiting character of the polyamide-epoxy vehicle and these data are reinforced by actual exposure tests. The point is made that the polyamide-epoxy vehicle can be applied to wet and lightly rusted surfaces by brushing and thus one of its virtues is tolerance in application.

The relationship between molecular weight of the polyamide resins and their properties is also discussed.

Finally, some of the important uses of the polyamide-epoxy vehicle which have developed over the past ten years are discussed.

## INTRODUCTION

The chemistry of the polyamide-epoxy vehicle is basically the relatively simple chemistry of the interaction of an amine group with an epoxy group (I).

Thus, if a primary amine group reacts with an epoxy group, a secondary amine group is generated together with a hydroxyl group. Similarly, a secondary

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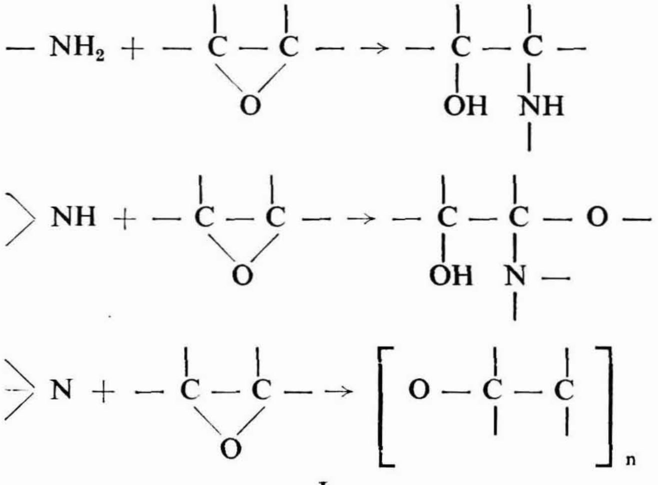
* Read before the Manchester Section on 30 May 1963.



I

amine group may react with an epoxy group to generate a tertiary amine group and a hydroxyl group. A tertiary amine group, on the other hand, in contact with an epoxy group, exerts a catalytic effect and the epoxy group undergoes self-polymerisation to form a polyether[1].

The amine groups involved in the particular reactions under discussion are present in low molecular weight polyamides which result from the condensation of dimerised vegetable oil acids with polyamines such as diethylene triamine[2, 3]. The epoxy resins with which this paper is largely concerned are the well-known bisphenol α-epichlorohydrin condensates with equivalent weights of about 500.

Although the reactions of an amine group with an epoxy group are relatively simple, the thermosetting structure which results when the amine-containing polyamide resin is allowed to interact with an epoxy resin is a highly cross-linked complex material. In the original polyamide resin, primary, secondary and tertiary amine functions are believed to be present. Their reaction, coupled with the reaction of the newly generated amine groups, provides a highly complex thermosetting film.

Three generalisations, however, are possible. First, if the reaction is carried out under prescribed conditions, there will be no epoxide groups left in the resulting film, an observation of interest when considered relative to the inhibition of embrittlement on ageing[4]. Secondly, the film will contain amine groups in much the same fashion as a cross-linked ion exchange resin might contain amine groups.

Finally, the film will have much of the character of the epoxy resin while at the same time demonstrating the " fatty character " inherent in the polyamide resins. Thus, the film will contain polar amine groups and non-polar fatty entities. Without question the most interesting characteristics of the film depend on the presence of the polar and non-polar groups ; for it is these structural features which confer upon the vehicle its corrosion inhibiting character.

## CORROSION OF METALS

The corrosion of ferrous metals is generally believed to result from the electrochemical reactions shown in II. These equations indicate that for the process of corrosion the requirements are (*i*) an anode which is the iron or steel substrate itself, (*ii*) a cathode which may be the mill scale or rust present on the iron or steel surface or it may actually be a portion of the steel whose physical characteristics differ from the steel adjacent to it, (*iii*) that a current flow must take place between the anode and the cathode, (*iv*) a salt solution must be present in order to allow for this current flow. The water for the solution is provided, in the corrosive reaction, by atmospheric moisture or by the water into which a coated structure may be immersed. The salt is provided by contaminants which are practically always present, by some of the by-products of the corrosion reaction itself, or, under certain environmental conditions, by the salt in the atmosphere or in sea water ; (*v*) that oxygen is necessary in order for the corrosion phenomenon to exert itself.

$$\begin{array}{ll} 2Fe \rightleftharpoons 2Fe^{++} + 4e & \text{(anodic reaction)} \\ 4e + O_2 + 2H_2O \rightleftharpoons 4OH^- & \text{(cathodic reaction)} \end{array}$$

II

Thus, five parameters contribute to the corrosion phenomenon, and the elimination of only one of these will inhibit corrosion. It is of interest, then, to explore to what extent the polyamide-epoxy vehicle can be of value in eliminating one or more of the conditions essential to corrosion.

## ANTI-CORROSIVE PROPERTIES OF THE POLYAMIDE-EPOXY VEHICLE

It is obvious that the vehicle bears no relationship to either the anode or the cathode, two of the parameters basic to the corrosion phenomenon. The vehicle, however, can be of value in eliminating access of water, oxygen and salts to the substrate whose protection is desired.

The water resistance of the polyamide-epoxy film, as indicated in Table I, has been measured by the Pittsburgh Society for Paint Technology[5]. It is

TABLE I

WATER PERMEABILITY

| System | Rate of transmission in Grams per day |
|---|---|
| Alkyd .. .. .. | 0.0572 |
| Urethane .. .. .. | 0.0399 |
| Phenolic .. .. .. | 0.0387 |
| Vinyl .. .. .. .. | 0.0261 |
| Epoxy Ester .. .. .. | 0.0118 |
| Epoxy-Amine.. .. .. | 0.0097 |
| Epoxy-Polyamide .. .. | 0.0089 |

WATER ABSORPTION

| | |
|---|---|
| Polyamide-Epoxy .. .. | 2.10% |
| Amine-Epoxy.. .. .. | 5.36% |

obvious that both the amine-epoxy vehicle and the polyamide-epoxy vehicle demonstrate a low degree of water transmission. On the other hand, the water absorption of the amine-epoxy film is over twice that of the polyamide-epoxy film, a consequence no doubt of the fatty character of the latter.

The behaviour of a variety of films immersed in distilled water has been studied by the Pittsburgh Society[5]. The results indicated in Table II show that only the vinyl film approached the polyamide-epoxy film in blister resistance. The water resistance of films of this sort has also been discussed by Wray and Tator[6].

TABLE II

BLISTERING OF COATED "Q" PANELS IMMERSED IN DISTILLED WATER

| Coating | Hours of immersion | |
|---|---|---|
| | 24 | 300 |
| Alkyd .. .. .. | 2 | 5 |
| Vinyl .. .. .. | 0 | 1 |
| Phenolic .. .. .. | 1 | 4 |
| Amine-epoxy .. .. | 4 | 5 |
| Polyamide-epoxy .. | 0 | 0-½ |

0 = No blistering 5 = Large blisters

Oxygen permeability, the second parameter, has also been studied by the Pittsburgh Society[5]. The data, reproduced in Table III, indicate that the oxygen permeability of the polyamide system is greater than that of the amine-cured system ; this is a consequence of the tighter cross-linking that can be expected in the latter vehicle. The fact that the polyamide system is capable of withstanding the corrosive effects of oxygen was shown by further work of the Pittsburgh Society[5] in which coated panels were immersed in water which was aerated continually. These data are indicated in Table IV.

TABLE III

OXYGEN PERMEABILITY OF RESIN FILMS

| Film | Permeability in cc at 73°F and 50° RH/100 in$^2$/24 hrs/Atm/mil |
|---|---|
| Phenolic .. .. | 302 |
| Alkyd .. .. | 74 |
| Polyamide-epoxy .. | 49 |
| Vinyl .. .. | 33 |
| Amine-epoxy .. | 8 |

TABLE IV

EFFECT OF AIR ON THE RUSTING OF COATED PANELS IMMERSED IN WATER

| Coating | Hours of immersion | |
|---|---|---|
| | 50 | 300 |
| Alkyd .. .. .. | 1 | 3.5 |
| Vinyl .. .. .. | 0 | 0 |
| Phenolic .. .. .. | 2 | 3 |
| Amine-epoxy .. .. | 3 | 5 |
| Polyamide-epoxy .. | 0 | 0 |

0 = No rusting 5 = Failure

The third parameter relates to the ability of the film to prevent the passage of electrical current ; this may be prevented in several ways. If the film prevents access of salts to the substrate then an electrical current cannot flow. If the film is highly insulating then the passage of electrical current will also be inhibited. Mayne[7, 8, 9] has placed important emphasis on the relationship of the corrosion-inhibiting character of the vehicle and the ability of that vehicle to prevent the passage of electrical current or to restrict the passage of charged ions. Indeed, Mayne, as well as MacDonald[10], believes that the ability of the film to prevent passage of electrical current is a determining factor in corrosion-inhibition. These workers emphasise the contribution of this property over and above the contribution of water and oxygen impermeability. Even so, it seems reasonable to believe that a high level of water and oxygen permeability may contribute to film performance particularly from the point of view of long life.

Maitland and Mayne[8] have pointed out that paint films tend to assume a negative charge when immersed in water or in solutions of electrolytes. Accordingly, they restrict the passage of negatively charged ions. Presumably the negative charge arises from the ionisation of free carboxyl groups present in most oil-based films. It follows from this work that most films will not resist positively charged ions. It can be expected, however, that the polyamide-epoxy film will assume a positive charge when immersed in water or solutions of electrolytes because of the ionisation of the amine groups. What is perhaps unexpected is a recent indication[8] that the polyamide-epoxy film tends to act as a zwitter ion when immersed in aqueous solutions, assuming either a positive or a negative charge depending on factors such as formulation and pH. The behaviour in which the polyamide-epoxy film is positively charged in solutions of low pH and negatively charged in solutions of high pH has been confirmed by measurement of diffusion potentials[8]. It follows then that a film that can resist both positively and negatively charged ions can be expected to make an important contribution to corrosion inhibition.

As indicated above, the electrical insulating properties of a paint film can provide indirect evidence of corrosion inhibition, for a good insulating film will obviously prevent passage of electrical current. Electrical properties of the polyamide-epoxy film are summarised in Table V. It is of interest to point out that the volume resistivity of the film is of the same order of magnitude as that of mica and an order of magnitude higher than can be obtained with amine-cured systems.

TABLE V
ELECTRICAL INSULATION (ASTM STANDARD PROCEDURES)

| Property | Results |
|---|---|
| Dielectric constant .. | 3.32 at 1 megacycle<br>3.02 at 1 kilocycle |
| Dissipation factor .. | 0.039 at 1 megacycle<br>0.013 at 1 kilocycle |
| Dielectric strength .. | >740 volts/mil for 0.112 in thickness |
| Arc Resistance .. .. | 72 seconds |
| Volume Resistivity .. | 1.1 x $10^{15}$ohms/cm |

Of particular interest is the electrical resistance of a pigmented polyamide-epoxy film[11] which was found to be greater than $10^9$ ohms. Mayne[9] has made the point that an unpigmented film should have an electrical resistance of $10^8$ ohms for good corrosion inhibiting properties. Pigmentation can be expected to decrease electrical resistance. Even so, the pigmented polyamide-epoxy film has an electrical resistance an order of magnitude higher than the level set by Mayne for good corrosion resistance.

At least two other factors relate to the overall corrosion inhibiting character of a film. One of these is adhesion and the other is the basic corrosion inhibiting character of the vehicle itself. If the adhesion of a film to a substrate is great, then the adhesive phenomenon of its own accord will prevent the access of corroding materials to the substrate. Finally, if all of the factors discussed are involved, it should be possible to demonstrate by laboratory tests that the vehicle is itself corrosion inhibiting.

Fundamental to the phenomenon of adhesion are the structural features previously mentioned which characterise surface active agents, namely small polar "heads" and long fatty "tails." These same structural features characterise chemical compounds which are corrosion inhibitors of the type used to prevent the dissolution of metals in acid or in other corroding media. Such compounds are invariably surface active and lower interfacial tension. The ability of the polyamide resins to lower interfacial tension is demonstrated by the data in Table VI. Here it is shown that concentrations of polyamide resins as low as 0.1 per cent lower the interfacial tension between water and a solution of the polyamide resin in a mixture of xylene and Cellosolve sixfold. The same ability to lower interfacial tension is possessed to a much lesser degree by an epoxy resin and practically not at all, as would be expected from structural considerations, by ethylenediamine.

TABLE VI

INTERFACIAL TENSION DATA AT 25°C

| Product | Concentration percentage in cellosolve-xylene (1:9) | Interfacial tension vs. distilled water |
|---|---|---|
| Control (cellosolve-xylene, 1:9) .. | | 18.1 |
| Polyamide 100 .. .. .. | 1.0 | 3.8 |
| | 0.1 | 2.9 |
| Polyamide 115 .. .. .. | 1.0 | 4.8 |
| | 0.1 | 3.6 |
| Polyamide 125 .. .. .. | 1.0 | 5.6 |
| | 0.1 | 2.8 |
| Polyamide 140 .. .. .. | 1.0 | 2.8 |
| | 0.1 | 3.0 |
| Polyamide 2000 .. .. .. | 1.0 | 4.0 |
| | 0.1 | 3.7 |
| Epoxy Resin .. .. .. | 1.0 | 10.2 |
| | 0.1 | 11.1 |
| Ethylenediamine .. .. .. | 1.0 | 12.9 |
| | 0.1 | 17.6 |

The reflection of these surface active properties on adhesive character is demonstrated by the data in Table VII. It is obvious that these are far greater adhesive strengths than one normally finds, or indeed normally requires, in a coating vehicle.

TABLE VII

TYPICAL STRENGTH PROPERTIES OF CURED POLYAMIDE-EPOXY COMBINATIONS*

| | |
|---|---|
| Tensile strength (ultimate) .. .. .. | 7,000 to 8,000 psi |
| Tensile modulus .. .. .. .. | 30,000 to 40,000 psi |
| Flexural modulus .. .. .. .. | 10,000 to 20,000 psi |
| Compressive strength (ultimate) .. .. | 7,000 to 12,000 psi |
| Compressive strength (ultimate) with filler | 20,000 psi |

*Tested by methods presented in ASTM procedures D-1002-52T and US Military Specification MIL-A-5090-B. Tests conducted on 24ST aluminium, 0.064 in thick. Bonds were 1 in wide with ½ in overlap. Aluminium surface was lightly sanded prior to bonding.

Equally as important as the high adhesive strength achievable with the polyamide-epoxy system is its broad range of adhesion to numerous substrates. For example, its adhesion to aluminium, magnesium and a variety of related light alloys makes it suitable for use in the aircraft industry. Its adhesion to brass and copper makes it useful in the electronics industry, whereas the marine industry makes use of the adhesion of the system to wood, steel, glass and reinforced polyester. Adhesion is possible to cellulosic substrates as well as to foamed structures. The system adheres to cured and uncured masonry as well as to the difficult surfaces presented by inorganic zinc rich primers and by cured phenolics.

TABLE VIII

MINERAL ACID INHIBITION

| Product | Conc. (p.p.m.) | Conditions | Corrosive Agents | Results |
|---|---|---|---|---|
| Polyamide 115 .. .. | 250 | Static, 70°C* | 5% $HCl$ | 95% protection |
| Polyamide 125 .. .. | 250 | Static, 70°C | 5% $HCl$ | 97% protection |
| Polyamide 2000 .. .. | 250 | Static, 88°C† | 15% $HCl$ | 0.4 lb/ft$^2$/day |
| Control .. .. .. | 250 | Static, 88°C | 15% $HCl$ | 1.1 lb/ft$^2$/day |
| An accepted inhibitor .. | 250 | Static, 88°C | 15% $HCl$ | 0.3 lb/ft$^2$/day |
| | NACE[12] CORROSION TEST | | | |
| Polyamide 115 .. .. | 10 | Static, ambient | $H_2S$, $NaCl$ | 65% protection |
| Polyamide 140 .. .. | 10 | Static, ambient | $H_2S$, $NaCl$ | 64% protection |
| Polyamide 2000 .. .. | 10 | Static, ambient | $H_2S$, $NaCl$ | 88% protection |
| An accepted commercial inhibitor .. .. | 10 | Static, ambient | $H_2S$, $NaCl$ | 93% protection |
| | DYNAMIC CORROSION TEST‡ | | | |
| Polyamide 140 .. .. | 50 | Dynamic, 140°F | $H_2S$, $NaCl$ | 71% protection |
| Polyamide 2000 .. .. | 50 | Dynamic, 140°F | $H_2S$, $NaCl$ | 57% protection |
| A good commercial inhibitor | 50 | Dynamic, 140°F | $H_2S$, $NaCl$ | 88% protection |

*1 in × 1 in × 16 gauge precleaned and weighed 1020 cold rolled steel coupons are suspended in 200 ml of 5 per cent HCl at 70°C (unstirred) for six hours. The coupons are weighed and weight loss data calculated as compared to a control (no inhibitor).

†1 in × ½ in × ⅛ in precleaned and weighed 1020 cold rolled steel coupons are suspended in 200 ml of 15 per cent HCl (unstirred) at 190°F for 18 hours ; coupons are reweighed and data presented as weight loss in pounds per square foot surface per day.

‡½ in × 5 in × 16 gauge 1020 cold rolled steel coupons are immersed in 900 ml of test fluid (one part clay treated kerosene, 7.5 parts 5 per cent NaCl in distilled water containing 500 ppm $H_2S$) at 140°F for 24 hours rotating at two revolutions per minute. Data presented, as compared to a control (no inhibitor), are calculated from weight loss.

Finally, it is of interest to test the corrosion inhibiting properties of the polyamide resins alone. A number of applicable tests is available, most of which have been devised to test the effectiveness of corrosion inhibitors utilised for the protection of oil-well casings and similar metal structures during the production of petroleum. The results of three such tests[12] are indicated in Table VIII. It may be seen from a study of these data that the polyamide resins are in themselves corrosion inhibitors against such corrosive agents as hydrochloric acid, hydrogen sulphide and sodium chloride when utilised at very low concentrations of ten to 250 ppm at both room temperature and at slightly elevated temperatures.

## EXPOSURE TESTS

The results of extensive studies on exposures of various polyamide-epoxy primers and topcoats in the Florida Tidewater area have been published by Glaser and Floyd[13]. Relative to the corrosion-inhibiting character of the polyamide-epoxy vehicle, it is of interest to review studies on primers after two years of exposure. For this work, angle irons measuring 3 in × $3\frac{1}{8}$ in × 7 in long were utilised. These had a surface composed of a tight oxide scale and some loose rust. All angle irons were cut from the same piece of steel to minimise differences in steel composition.

The panels were degreased with xylene and were wire-brushed to remove loose rust before coating. Tightly bound scale and rust were left on the panels. Also, one side of each of the panels was wetted with water. It was felt that the wet, rusted surfaces would simulate the conditions found in many maintenance situations.

The primers were applied by brushing in alternate directions utilising three or four coats to achieve thicknesses of approximately four mils.

The above procedure was utilised in every instance except with a vinyl resin, where it was necessary to apply five coats over a wash primer on a carefully prepared surface.

The panels were allowed to dry for one to two days, after which they were checked for pinholes with a spark tester. When pinholes were found, they were " touched-up." Thereafter, the panels were allowed to stand for seven days at room temperature prior to installation on the tidewater racks near Miami, Florida. The panels were in salt water part of each day and in salt-laden air for the remainder of the time. They were also subjected to the strong sunlight typical of the area. All of the panels were mounted on 45° south exposure racks avoiding metallic contact of any sort. The coatings tested are listed below :

(*a*) *Polyamide* 115—*Epoxy resin* 525* (35 : 65) zinc yellow, 32 per cent Pigment Volume Concentration (PVC).

(*b*) *Polyamide* 100—*Epoxy resin* 525 (50 : 50) zinc yellow, 40 per cent PVC.

(*c*) *Polyamide* 100—*Epoxy resin* 525 (50 : 50) zinc yellow, 32 per cent PVC.

(*d*) *Polyamide* 115—*Epoxy resin* 525 (35 : 65) red lead, 34 per cent PVC.

(*e*) *Phenolic resin, red lead* (TTP86-IV), 41 per cent PVC.

(*f*) *Polyamide* 100—*commercial primer*, zinc yellow.

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* Condensation product of bisphenol A and epichlorhydrin ; mp about 70-75°C, epoxide equivalent about 525.

(*g*) *Linseed oil, red lead* (TTP86-I), 36 per cent PVC.
(*h*) *Alkyd—zinc yellow* (JAN-P-735), 40 per cent PVC.
(*i*) *Alkyd—zinc yellow* (TTP-636), 47.5 per cent PVC.
(*j*) *Vinyl—zinc yellow* (MIL-P-15930A), 36.5 per cent PVC.
(*k*) *Experimental solventless Polyamide-Epoxy Coating*, red lead, 10 per cent PVC.
(*l*) *Polyamide* 100—*Epoxy resin* 525 (50 : 50) red lead, 35 per cent PVC.
(*m*) *Red Oxide commercial metal primer*, alkyd, fish oil.
(*n*) *Epoxy resin* 525, *diethylene triamine*, red lead, 35 per cent PVC.
(*o*) *Epoxy resin* 525, *diethylene triamine*, strontium chromate, 32 per cent PVC.
(*p*) *Polyamide* 115—*Epoxy resin* 525 (35 : 65) chrome green enamel, 10 per cent PVC.
(*q*) *Polyamide* 115—*Epoxy resin* 525 (35 : 65) lead silico-chromate, 36 per cent PVC.

The panels were examined at six-month intervals and the tests were stopped after two years. In each examination, the panels were rated in terms of uncorroded areas remaining after exposure. In this rating system, 10 is perfect and 0 indicates corrosion of the entire surface of the metal.

As might be expected, corrosion began at the sharp edges of the angle irons, probably because of the stresses concentrated there. Also, the films were probably thinner at these points, despite efforts to produce uniform film thickness. Corrosion was usually accompanied by blistering and, in some instances, by flaking of the film. The results are indicated in Table IX, where the primers are identified according to the letters in the above tabulation.

TABLE IX
ANGLE IRON EXPOSURE TESTS—TIDEWATER LOCATION
CORROSION RESISTANCE RATINGS

| Primer Type | 6 months | | 12 months | | | |
|---|---|---|---|---|---|---|
| | Dry side | Wet side | Dry side | Wet side | 18 months | 24 months |
| *a* | 10 | 10 | 9.5 | 9.5 | 9 | 7 |
| *b* | 10 | 10 | 9.5 | 9 | 9 | 7 |
| *c* | 10 | 10 | 9 | 9 | 9 | 8 |
| *d* | 10 | 10 | 9 | 9.5 | 9 | 6 |
| *e* | 8 | 8 | 2.5 | 4 | 0 | 0 |
| *f* | 10 | 10 | 9.5 | 9.5 | 9 | 7 |
| *g* | 9 | 9 | 6 | 5 | 3 | 0 |
| *h* | 9.5 | 9.5 | 8 | 8 | 6 | 0 |
| *i* | 9 | 9 | 6 | 7 | 6 | 0 |
| *j* | 10 | 9.5 | 9.5 | 8 | 8 | 5 |
| *k* | 9.5 | 9.5 | 7 | 9 | 7 | — |
| *l* | 9.5 | 9.5 | 8.5 | 9 | 9 | 7 |
| *m* | 9 | 8 | 3.5 | 4 | 2 | 0 |
| *n* | 9.5 | 9.5 | 7 | 8 | 7 | — |
| *o* | 8 | 8 | 1 | 2 | 0 | 0 |
| *p* | 10 | 10 | 9 | 9 | 8 | 6 |
| *q* | 10 | 10 | 9.5 | 9.5 | 9 | 8 |

From these data, certain conclusions may be drawn.

1. Vehicles containing ester linkages (*g*, *h*, *i*, *m*) performed very poorly. This was true also of the phenolic system (*e*).
2. The amine-cured epoxy system pigmented with strontium chromate (*o*) behaved poorly. Red lead pigmentation (*n*) provided somewhat better results.
3. All of the polyamide systems held up well with zinc yellow and lead silicochromate providing particularly good protection.
4. The vinyl system which was applied to a carefully prepared surface provided good protection, but was not as effective as the polyamide systems.
5. The most important result was obtained with panel *p*, a polyamide-epoxy system pigmented with chrome green, a pigment not normally considered corrosion inhibiting. Despite the absence of the corrosion-inhibiting pigment, the results were nearly as good for this system as for polyamide systems containing highly corrosion-inhibiting pigments (*c*, *q*). This indicates that the polyamide vehicle is at least as important as the inhibitive pigment in primer systems, because of the inherent corrosion-inhibiting character of this vehicle.

Indeed, the corrosion-inhibiting character of the vehicle, coupled with its surface activity, makes possible the application of polyamide-epoxy paints, by brushing, to wet surfaces which have been prepared only by wirebrushing.

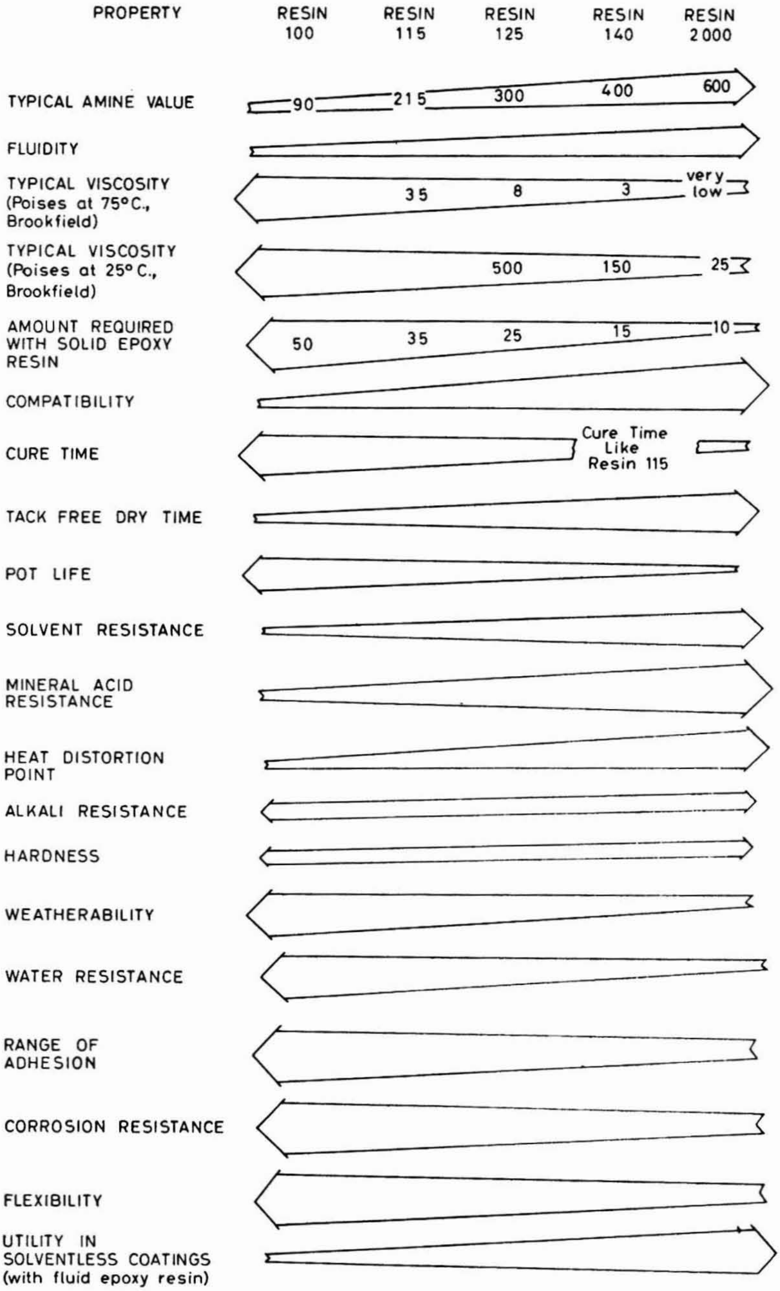
## THE RELATIONSHIP OF THE POLYAMIDE RESIN TO FILM PROPERTIES

A variety of polyamide resins are available for reaction with epoxy resins. These polyamide resins differ primarily in viscosity which is a function of both molecular weight and structure. To compare the properties contributed to a film by the various polyamide resins the valid assumption may be made that the more fluid the polyamide resin, the lower its molecular weight. Also the more fluid the polyamide resin, with one important exception, the more reactive the material is and accordingly the faster it will cure. In the reaction of these polyamide resins with an epoxy resin with an equivalent weight of approximately 500, the more fluid the polyamide resin and the higher its reactivity, the less will be required in the formulation. Thus the least reactive, most viscous resin will comprise 50 per cent of the vehicle, whereas the most fluid or the lowest molecular weight resin will comprise 10-15 per cent of the vehicle.

Table X demonstrates the change in properties which may be expected when one combines polyamide resins of varying viscosity with an epoxy resin of an equivalent weight of about 500. Reference to the table indicates, as already stated, that the amount of polyamide resin required in the formulation decreases as the viscosity or the molecular weight decreases. Compatibility increases whereas cure time, with the exception noted, decreases. Pot life, as might be expected, decreases as cure time decreases.

The three properties of solvent resistance, mineral acid resistance and heat distortion point, improve as the molecular weight of the resin decreases. This is a function of the increasing amount of epoxy resin in the formulation, since the epoxy resin contributes to these properties. Alkali resistance, on the other

TABLE X



PROPERTY TRENDS OF POLYAMIDES FOR USE IN SOLVENT BASED COATINGS

hand, is constant since both resins contribute to this property. Hardness also remains constant since this is a function of the curing phenomenon rather than the ratio of the two materials which co-react. On the other hand, the properties of water resistance, weathering, flexibility, range of adhesion and, of course, corrosion resistance all decrease as the molecular weight of the polyamide resins decrease, because these properties are contributed to the vehicle by the polyamide resin. Accordingly, they are a function of the concentration of the polyamide resin present in the final cured film.

## APPLICATIONS OF THE POLYAMIDE-EPOXY VEHICLE

The most important area of application for the polyamide-epoxy vehicle is general maintenance painting, particularly where difficult climatic conditions make surface preparation difficult. The system is widely used in coastal areas where salt problems are frequently encountered, on offshore oil-well riggings, and on other types of offshore installations where maintenance painting is a problem. The petroleum industry makes good use of the system on refinery equipment and on plant which processes very acid crude oils. Chemical plants, dairies where lactic acid resistance is required, bakeries, hospitals and industrial areas of all types are coated with the polyamide-epoxy paint. Pipelines such as the Trans-Canada Pipeline are coated on the inside with this system since its smooth, glossy surface facilitates the flow of gas or liquid through the pipeline while providing adequate product resistance and high flexibility.

The system is, of course, widely used as a primer both for the polyamide-epoxy topcoat and for other systems with relatively poor adhesion such as vinyls, polyurethanes and polyesters. Zinc rich primers may be formulated from the polyamide-epoxy system, and one of the important new applications for such primers is the shopcoating of steel as soon as it has been manufactured in the rolling mill. The shopcoated steel may subsequently be fabricated into tankers and ships ; here, the zinc rich polyamide-epoxy primer will resist the strain of the bending required in the fabrication of the ships and will also allow for welding from the back of the steel panel.

The coating of the inside of railway wagons in which abrasive particulate matter such as flour, salt, sugar, phosphate ore and finely divided plastics are to be shipped is an interesting application.

The system is widely used in the aircraft industry where room temperature curing coatings are required which adhere to aluminium and magnesium. Marine coatings also provide an important area of application.

The coating of masonry surfaces such as swimming pools and the masonry blocks used in building also provides an important outlet.

Metal decorating where mild stoving is utilised is an excellent application because of the decorative qualities of the film and because it provides a finish which allows further fabrication, bending and working of the coated metal. The electronics industry provides specialty uses for the polyamide-epoxy film ; and the combination of the very fluid polyamide resins with fluid epoxy resins has provided the basis for solventless coatings. In this latter use sand-filled coatings which may be used for the repair of concrete or in place of concrete, where greater strength and resistance properties are required, is important. Solventless coatings pigmented in normal fashion are also making progress in the maintenance area. One of the most interesting solventless coatings which has been formulated based on an excess of the polyamide resin with a fluid epoxy resin is intended for application to offshore structures. The mastic-like material actually adheres and cures under water and in the presence of water spray and salt spray.

## ACKNOWLEDGEMENT

The author wishes to acknowledge the important contribution of Dr. D. E. Floyd and Mr. D. W. Glaser, whose many years of research in the area of polyamide-epoxy coatings have helped to make this paper possible.

## REFERENCES

1. Shechter, L., Wynstra, J., and Kurkjy, R., *Ind. Eng. Chem.*, 1956, **48**, 94.
2. Cowan, J. C., Falkenberg, L. B., Teeter, H. M., and Skell, P. S., US Patent 2,450,940, 12 October 1948.
3. Peerman, D. E., Tolberg, W., and Wittcoff, H., *J. Am. Chem. Soc.*, 1954, **76**, 6085.
4. Peerman, D. E., Tolberg, W., and Floyd, D. E., *Ind. Eng. Chem.*, 1957, **49**, 1091.
5. Wettach, W., *Off. Dig.*, 1960, **32**, 1463 ; 1961, **33**, 1427.
6. Wray, R. I., and Tator, K., *Materials Protection*, 1963, **2**, 30.
7. Mayne, J. E. O., " Corrosion " in : *The Science of Surface Coatings*, ed. by Chatfield (H. W., D. Van Nostrand Co., Inc., New York, 1962), p. 423.
8. Maitland, C. C., and Mayne J. E. O., *Off. Dig.*, 1962, **34**, 972.
9. Mayne, J. E. O., *Off. Dig.*, 1952, **24**, 127.
10. MacDonald, D. M., *Off. Dig.*, 1961, **33**, 7.
11. Floyd, D. E., and Glaser, D. W., *Off. Dig.* 1963, **35**, 38.
12. NACE Technical Committee Report, *Corrosion*, 1955, **11**, 143t.
13. Glaser, D., and Floyd, D. E., *Off. Dig.*, 1960, **32**, 108.

[*Received* 10 *September* 1963

## DISCUSSION

DR. C. G. BELL asked if, in view of the wide field in which polyamide-epoxy coatings might be used, the speaker would kindly say something of the ease or difficulty of various application methods.

DR. H. WITTCOFF replied that he did not believe there were any particular difficulties that people encountered in application. The first difficulty that had to be overcome, of course, was that this was a two-component system of limited pot-life ; it demanded a great deal of work in order to convince the paint industry that such a system would be practical, but this had now finally been done. To achieve the properties described, namely to allow people to put this system over a rusty or wet surface, it was necessary to brush, but any sort of brush could be used.

As regards spraying, all the common spraying devices could be used for this system, for example, normal type spray guns. He thought that some of these materials were even being used with airless spraying.

Dr. Wittcoff added that he felt there was a problem with dip coating because of the pot-life, but it had been found in the past few years that people had to a great extent overcome this. The way that it could be done was to mix the batch in the normal fashion, but at the end of the day to add what was left to the next day's supply of polyamide resin. This diluted the small amount of unused resin and prevented gelation.

MR. J. J. ZONSVELD asked if Dr. Wittcoff had referred to inorganic zinc silicate paint surfaces when he had mentioned that good adhesion was achieved to inorganic zinc surfaces. If so, had he been referring to work done in the API Tanker Corrosion Project to apply topcoats to inorganic zinc silicate. He also inquired whether it would be possible—vice versa—to overcoat epoxy-polyamide/zinc shopcoated primers with inorganic zinc silicate coatings.

DR. WITTCOFF explained that actually the reference that he had made was to the inorganic zinc silicate top coatings. At least one publication of work outside his own laboratory had pointed out that one could apply this material to the inorganic zinc coating, and the virtue of this was that it gave protective properties, and particularly it allowed the curing of the organic coating to continue in moist atmospheres, which was frequently a problem with these types of material. As regards the idea of overcoating primers which Dr. Zonsveld proposed, he had no information on this, but it certainly seemed a very good, interesting idea.

MR. P. G. WONG commented that polyamide-epoxy primers were stated to have a pot-life of several days. He asked what effects there were on the physical properties of the cured film by varying the ageing period prior to application.

DR. WITTCOFF considered this a very good question. He replied that the ageing time or induction period, if properly utilised, was a very useful thing. It allowed one to lay down a partially-reacted material rather than a film of unreacted molecules. If the painter was going to paint in highly moist atmospheres, where humidity was, say, 95 per cent, then he would be well advised to allow for an induction period of up to a day before he started painting. Thus, he could avoid the blushing that high humidity causes. However, if one let the paint stand for too long, then very poor flow-out resulted as judged by viscosity. So, in general, in formulating the most common coating, which is a 50/50 mixture of one of the polyamides and one of solid epoxy resins in solvent at a solids concentration of about 30 per cent, it was advisable to use an induction period of about 40 minutes. The higher the ambient temperature, the shorter the induction period could be.

DR. WITTCOFF confessed, in reply to a question about rates of reaction of amine groups, that he wished he could answer that question in detail, because if he could it would mean that a great deal more would be known about this field. He believed that the rate of reaction of the primary and secondary amine groups is practically the same. There were probably several other factors which controlled the rate, but he thought that if one had unhindered primary and secondary amine groups, the difference in rate of reaction would be small. As far as the tertiary amine group was concerned, whether or not this was effective at room temperature was very hard to say, but the only evidence available related to the fact that the tertiary group was a cure-accelerator. Tertiary amine groups were present in many cure-accelerators such as a proprietary material called DMP-30.

A further question related to the fact that a secondary or a tertiary amine group and a hydroxyl group were generated when a polyamide resin reacted with an epoxy resin. Did the hydroxyl group accelerate cure and why did it not contribute to poor water resistance? He felt that there was a strong possibility that the hydroxyl group accelerated cure although there was no direct evidence on this score. There was good practical evidence that the hydroxyl groups did not detract from water resistance. This was probably because the fatty chains in the polyamide resins shielded the hydroxyl groups in the same way as they shielded the amide linkages. It was pointed out that polyamides, like nylon, were highly water-susceptible. Fatty polyamides, on the other hand, were impervious to water. The difference was attributed to the shielding effect of the fatty groups so that the polar groups or linkages were not readily available for attack by water.

DR. H. A. HAMPTON posed the question as to how it was that, if the fatty chain protected the hydroxyl groups from being moisture-attracting, the adjacent amine groups were not hindered from reacting.

DR. WITTCOFF replied that there was little doubt that the amine groups, too, were shielded by the fatty chains. However, it was obvious that sufficient of the amine groups were available to effect the desired curing reaction. In part, this was because the reactive amine groups were, to a large extent, terminal groups. Also, one needed to bear in mind that, in order to achieve cross-linking, only a small percentage of the amine groups present was necessary.

**MR. R. S. JOHNSON** requested further comment on acid resistance of the systems.

**DR. WITTCOFF** stated that acid resistance improved with the lower molecular weight polyamide resins. Thus, using the lowest molecular weight resins, it was possible to obtain very good resistance to mineral acids and even to oxidising acids like nitric acid. Even so, one would not use these coatings on the inside of tanks for acid storage simply because long-term acid resistance was not satisfactory.

On the other hand, resistance to acid contamination, to acid atmosphere, to the acid crude oils encountered in the petroleum industry, to lactic acid in a dairy, or to the acids encountered in chemical plants was sufficiently good to make the polyamide-epoxy system a preferred maintenance paint for these situations.

**MR. C. I. ATHERTON** asked whether Dr. Wittcoff would comment on the effect of water on the rate of cure of polyamide-epoxy systems, and secondly on the effect of the presence of imidazolines in the polyamide.

**DR. WITTCOFF** confessed that he felt more intelligent on the second question than on the first, so he would answer the first question first.

There was no doubt that water accelerated cure. A small amount of water could be such a powerful accelerator that, with certain materials, foaming actually resulted because of the heat generated. Thus, one did not need to worry about water in the solvents because their effect was usually salutary. The accelerating effect of water was perhaps related in some way to the accelerating effect of hydroxyl groups. On the other hand, it must not be forgotten that high humidities tended to inhibit reaction for which reason the induction period discussed earlier which caused the reaction to start prior to the time that the film was laid down, was of extreme importance.

Relative to the second point of imidazoline groups, Dr. Wittcoff stressed the fact that the imidazoline linkage reduced rate of cure and, correspondingly, the degree of exotherm. On the other hand, it provided films with improved solvent resistance, better acid resistance and higher heat resistance. The tertiary amine in the imidazoline ring no doubt altered the course of reaction so that these differences in end properties resulted.

**DR. J. B. HALEY** said that Dr. Wittcoff had stated that the variations in properties of the epoxy-polyamide system using solid epoxies did not apply with liquid epoxies and asked him to enlarge on this point.

**DR. WITTCOFF** replied that the liquid epoxy resins had a lower molecular weight than solid epoxy resins. In general, properties of films were adversely affected by the lower molecular weight epoxy resins. This was not the situation with the lower molecular weight polyamide resins which appeared to contribute very similar properties to a film as did the higher molecular weight resins. Because they were of lower molecular weight, however, lesser amounts were used and thus the salutary effects of the polyamides were achieved to a lesser degree with lower molecular weight resins. Conversely, with the lower molecular weight polyamide resins, the film took more of the properties of the epoxy resins which were present to a greater extent.

One of the important properties which was impaired by the use of low molecular weight epoxy resins was flexibility. Resistance to solvents and acids was also decreased.

**DR. HALEY** went on to ask whether, with liquid epoxies, Dr. Wittcoff was saying that little difference existed as to whether they were cured with polyamides or amines.

**DR. WITTCOFF** stated that the virtue of using an amine with liquid epoxy was that a tightly linked film resulted. This tight cross-linking contributed to such properties as solvent resistance and acid resistance. On the other hand, an amine-liquid epoxy system emphasised lack of flexibility and lack of adhesion. Accordingly, in liquid epoxy systems where one desired flexibility and adhesion, and, of course, corrosion resistance, he would use a polyamide resin. In liquid epoxy systems where solvent resistance was the major consideration, one would use an amine.

MR. J. J. ZONSVELD commented that induction of curing could be overcome by using an excess of polyamide curing agent, which would be preferentially adsorbed at the interface steel coating. The adsorbed portion would not be available any more for the curing reaction, and an excess was therefore required.

DR. WITTCOFF said he was pleased to have this information.

MR. F. W. KENNA commented that the figures for water sensitivity given were worst in the case of the urethane used and asked if the lecturer could indicate the type, whether one-component or two-component.

DR. WITTCOFF said he had the actual information with him and would be glad to check it afterwards.

MR. KENNA also asked whether any work had been done on the use of lead titanate (cured with silica) in the improvement of chalk resistance. He stated that work in the USA had already indicated much improvement in this respect.

DR. WITTCOFF replied that he was not familiar with this work at all.

# Vinyl and Acrylic Modified Alkyds: Part III[1, 2.]

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## *Summary*

The preparation and evaluation of vehicles suitable for use in polishable thermosetting acrylic coatings is described. Formulation changes have been studied and a range of resins described which enable the balance of properties of the final coating to be varied to suit individual customer requirements.

## INTRODUCTION

In the automotive industry, two main types of topcoats are used. First there is the lacquer or thermoplastic system which dries by solvent evaporation, the majority of which use a polymer derived from acrylic or methacrylic esters and have a molecular weight above 55,000[3]. The second type of product is the enamel or thermosetting system and until recently this has used an alkyd/alcohol-modified melamine/formaldehyde condensate as a resin blend.

Both systems have advantages. Thus, whereas the lacquer is usually expensive and applied at low (20-30 per cent) solids content, the ease of repair facilitates production. Conversely, the enamels or thermosetting systems are relatively cheap, give higher application solids content (45-55 per cent) and hence require fewer coats, but are difficult to repair.

The difference in the ease of repair is clearly shown if the surface coating has dirt or other minor imperfections in the film. Whereas the lacquer can be polished to remove these defects, the enamel invariably loses gloss and the polished area shows up as a dull patch compared to the unpolished surface. There is thus a major need for enamel formulations which on polishing return to their original gloss and, therefore, simplify and cheapen production.

One approach to this problem has been to replace the alkyd resin in the enamels referred to above by an acrylic polymer of molecular weight approximately 30,000 and having the necessary functional groups to undergo thermosetting reactions on heating. Such polymers possess the desirable polishing properties required but unfortunately, suffer from other defects which detract from the advantages of such systems. First, they tend to be expensive and to lose the advantages previously held over lacquer and thermoplastic systems in this connection. Secondly, the desirable properties of the alkyd, especially ease of pigment dispersion, surface wetting and flow properties, are lost. It is, therefore, desirable to combine the general resistance, hardness and polishing properties of the acrylic with the flow, surface wetting and pigment dispersion properties of the alkyd.

It is possible simply to blend acrylic copolymers with an alkyd/melamine-formaldehyde condensate formulation and arrive at a desirable balance of properties in the surface coating. However, this approach is limited since in many cases the alkyd and acrylic tend to be incompatible. To overcome this problem, it is preferred to combine chemically the alkyd and vinyl polymers.

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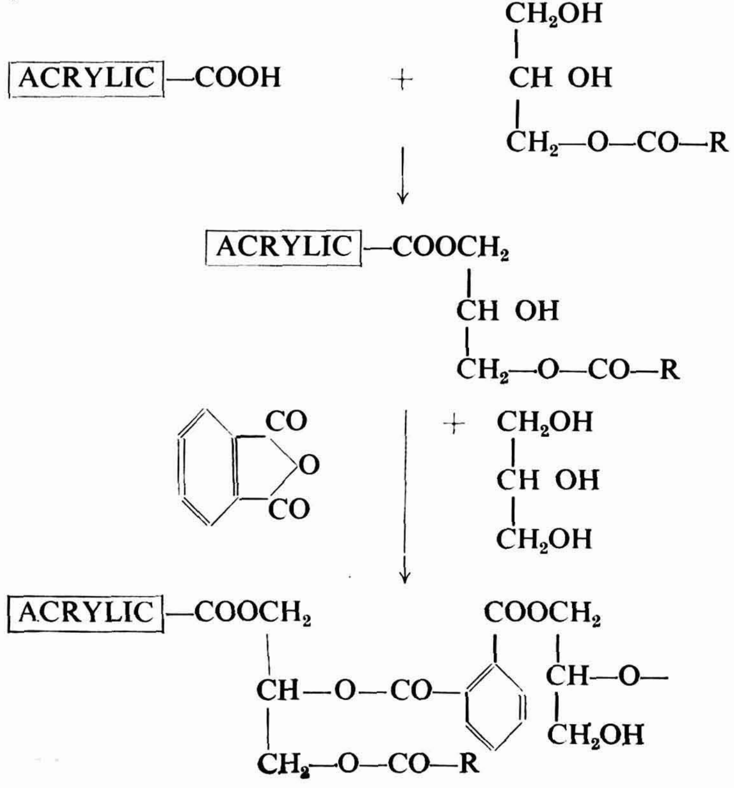
Previously, vinyl and acrylic modified alkyds have been prepared by using the unsaturation present in the drying oil as a means of chemically joining the vinyl and alkyd polymers. However, this procedure is now known to give a heterogeneous product consisting of alkyd, the vinyl homopolymer and the vinylated alkyd. The presence of the vinyl homopolymer is particularly undesirable and can lead to incompatibility and poor durability of the final film since the polymer does not contain functional groups and hence does not enter into the final three-dimensional film structure.

Another limitation of the above procedure arises from current market requirements which are for maximum durability and minimum discoloration of pastel shades when subjected to excessive stoving. It is well established that the more saturated vegetable oils are superior to the unsaturated oils in both of these properties.

A procedure has previously been reported for overcoming the above disadvantages and for synthesising vinyl and acrylic modified alkyds based on non-drying oils. Briefly, this involves preforming an addition polymer containing acid functional groups, esterifying the acid groups with a " monoglyceride " of a saturated fatty acid and then further condensing this product with a dibasic acid and additional " monoglyceride or polyol." These reactions are represented in the following equations and to distinguish this procedure from those reported previously, we have called it the " monoglyceride process ".



The present paper describes the development of vinyl and acrylic modified alkyds by the above process ; these are suitable for polishable automotive topcoats.

## EXPERIMENTAL

### General

The acrylic monomers used were commercially available. Immediately before use, the monomers were tested for the presence of polymer by the standard dilution tests. Benzoyl peroxide powder was 99.7 per cent pure when analysed by potassium iodide/thiosulphate titration. The phthalic anhydride, glycerol and solvents (and the test methods used) were similar to those used previously[2].

### Addition Copolymers

*Prepolymers*

The monomer mixture containing the dissolved benzoyl peroxide (2 per cent by weight of monomer) was added at a constant rate over three hours to an equal weight of refluxing xylene. The mixture was refluxed for a further one hour. The composition of the copolymers is given in Table I.

TABLE I

COMPOSITION OF COPOLYMERS

| Polymer Number | Mole % Methyl Meth-acrylate | Mole % Metha-acrylic Acid | Mole % Butyl Meth-acrylate | Mole % Ethyl Acrylate | Solids % | Viscosity (Gardner Holt) |
|---|---|---|---|---|---|---|
| A | 96 | 4 | — | — | 49.2 | V |
| B | 48 | 4 | 48 | — | 49.6 | G |
| C | 89 | 4 | 7 | — | 48.9 | W |
| D | 50 | 4 | 43 | 3 | 49.2 | G |

*Blending copolymer*

A mixture of methyl methacrylate (13.96 pts. by weight), butyl methacrylate (13.96 pts.), acrylamide (2.72 pts.), thioglycollic acid (0.25 pts.), n-butyl alcohol (8.17 pts.) and xylene (19.02 pts.) was heated under reflux. To this solution was added, at a constant rate over a period of two hours, a mixture of methyl methacrylate (6.78 pts.), butyl methacrylate (6.78 pts.), ditertiary butyl peroxide (0.94 pts.), benzoyl peroxide (0.60 pts.), thioglycollic acid (0.13 pts.) and xylene (26.69 pts.). The mixture was refluxed for a further one hour. Solids content was 43 per cent and the Gardner-Holt viscosity U.

*Vinyl and acrylic modified alkyds*

The following example illustrates the procedure for preparing the modified alkyds.

Hydrogenated castor oil and 67 per cent of the total glycerol were heated to 150°C and lead naphthenate solution (0.1 per cent lead based on the oil) added. The temperature was raised to 200°C and maintained at this temperature

## TABLE II

### EFFECT OF PROCESSING CONDITIONS ON POLYMER AND ENAMEL PROPERTIES OF 30 PER CENT METHACRYLATED HYDROGENATED CASTOR OIL ALKYD

| | Polymer properties* | | | | Enamel properties† | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Processing conditions | $AV_I$ | $AV_{II}$ | Viscosity | Solids | 60° gloss | Hardness Knoops | Conical mandrel | Impact 28 in/lb | Overbake gloss ½ hour at 150°C | Overbake hardness Knoops | Enamel-enamel adhesion | Polish-ability |
| The procedure described above was followed.‡ | 3 | 24 | V | 61 | 91.0 | 7.8 | Pass | Crack but adhesion good | 89.0 | 11.0 | Excellent | Satis-factory |
| As above, but temperature kept at 150°C for 1 hour after phthalic anhydride addition. | 3 | 24 | V | 60 | 90.0 | — | Fail | — | 85.0 | — | — | — |
| Oil, glycerol and prepolymer reacted simultaneously, i.e. no " monoglyceride " stage. | 3 | 24 | V | 60 | 89.5 | — | Fail | — | 84.0 | — | — | — |

*The formulation consisted of Polymer A 30 pts., glycerol 11 pts., hydrogenated castor oil 36 pts., and phthalic anhydride 23 pts.
†Methacrylated alkyd : melamine resin = 73 : 27.
‡This resin and process were used in subsequent evaluations.

for one hour. The mixture was cooled (approximately 180°C), the acrylic prepolymer added and the temperature raised to 220°C by removal of solvent. This temperature was maintained and water removed by a Dean and Stark separator until the acid value was less than 3 (acid value I or $AV_I$). The mixture was cooled (approximately 180°C), phthalic anhydride and the remaining glycerol added and the condensation continued at 220°C to the required acid value (acid value II or $AV_{II}$) and viscosity. The resin was thinned with xylene.

## Evaluation

The resins were made up into automotive topcoat formulations by pigmenting with rutile titanium dioxide such that the final pigment : binder ratio was 50 : 100. A butyl alcohol modified melamine formaldehyde condensate, and where applicable, the acrylamide blending polymer, were added and the enamels sprayed over an epoxy ester undercoat and baked half-hour at 127°C. The test methods used to evaluate the enamels were those described previously[2]. Polishing tests were carried out using a high speed buff (2000 rpm) and a mildly abrasive polish. Results are recorded in the following tables.

TABLE III

EFFECT OF HYDROXYL AND ACID VALUES ON RATE AND DEGREE OF CURE OF 30 PER CENT METHACRYLATED ALKYD

| Formulation | $AV_{II}$ | Viscosity (Gardner Holt) | Solids | Set-up time of enamel (mins) | Hardness (degree of cure) |
|---|---|---|---|---|---|
| Standard formula from Table II | 24 | V | 61 | 4 | 7.8 |
| Lower acid value by increasing the excess glycerol in standard formula | 14 | Z | 59.5 | 6 | 4.5 |
| Lower hydroxyl value by increasing amount of oil and reducing glycerol | 18 | Y | 57.2 | 5 | 5.0 |

TABLE IV

DURABILITY ON EXTERIOR EXPOSURE OF ENAMELS

| Polymer Composition | Initial Gloss | Gloss after 14 months |
|---|---|---|
| 30 per cent methacrylated alkyd : melamine resin = 73 : 27 | 91 | 84 |
| 30 per cent methacrylated alkyd : melamine resin : acrylamide copolymer = 63 : 10 : 27* | 92 | 70 |

*Other properties of this enamel were comparable to the 30 per cent methacrylated alkyd.

### TABLE V
### PROPERTIES OF 40 PER CENT ACRYLATED ALKYDS AND CORRESPONDING ENAMELS*

| Polymer properties† | | | | | Enamel properties | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acid copolymer used | $AV_I$ | $AV_{II}$ | Viscosity (Gardner Holt) | Solids | 60° gloss | Hardness Knoop | Impact 28 in/lb | Overbake gloss $\frac{1}{2}$ hour at 150°C | Overbake hardness Knoop | Enamel—enamel adhesion | Polish-ability‡ | Gloss after six months |
| A (refer Table I) | 3 | 24 | X | 60 | 89 | — | Cracks, poor adhesion | — | — | — | — | 89 |
| B | 3 | 24 | W | 59 | 90.5 | 7.7 | Cracks, but adhesion good | 89 | 9.2 | Very good | Satisfactory | 90.5 |
| C | 3 | 24 | U | 59 | 86.5 | 10.0 | Cracks, but adhesion good | 85 | 13.2 | Excellent | Satisfactory | 86.5 |
| D | 3 | 24 | Q | 61 | 90.0 | 5.6 | Cracks, but adhesion good | 88.5 | 8.2 | Very good | Satisfactory | 90.0 |

*Enamels had a polymer composition of acrylated alkyd : melamine resin = 73 : 27.

†The acrylated alkyd was prepared from acid copolymer 40 pts., glycerol 9.5 pts., hydrogenated castor oil 31 pts., and phthalic anhydride 19.5 pts.

‡Under the conditions used for the polishing test a 33 per cent coconut oil alkyd/melamine-formaldehyde (80/20) enamel in commercial use gave a gloss drop of 12 units.

## DISCUSSION

A copolymer of methyl methacrylate-methacrylic acid (96-4) was taken as the initial acrylic component because of the known durability and polishability of polymethyl methacrylate in thermoplastic systems[3]. The acid content was based on previous experience where it was shown that higher concentrations gave a system which was too functional, difficult to control and expensive while lower concentrations of acid groups reduced the reaction rate considerably[1]. Modification of this copolymer with a hydrogenated castor oil " monoglyceride " followed by further condensation with additional glycerol and phthalic anhydride, yielded methacrylated alkyds with up to 30 per cent by weight of acrylic component. A small amount of monomer was liberated during the reaction, presumably due to thermal depolymerisation. This aspect will be discussed in a later communication.

Pigmented enamels based on the above polymer and using as the crosslinking agent a butyl alcohol modified melamine formaldehyde condensate gave films, after baking for half-hour at 127°C, which were satisfactory for gloss, hardness, flexibility, adhesion and overbake gloss retention and which could be polished with a high speed buff.

Hydrogenated castor oil was used in the above formulation as it contains no carbon unsaturation and would, therefore, give a minimum amount of discoloration on overbake and because the additional hydroxyl group in the fatty acid chain should contribute to reaction and compatibility with the melamine resin. It is well established that in making simple alkyds from hydrogenated castor oil it is not necessary to first form a " monoglyceride," as is done with non-hydroxylated oils, in order to get compatibility when the dibasic acid or anhydride is added. However, when the above methacrylated alkyd was prepared by simultaneously reacting the acrylic copolymer, hydrogenated castor oil and glycerol, i.e., no "monoglyceride" stage, and subsequently adding the phthalic anhydride, the resin gave an enamel which was not satisfactory for the bend test and showed excessive loss of gloss on overbake.

It would be expected that by analogy with simple alkyds, formation of a " monoglyceride " before reaction with the copolymer would give a more homogeneous methacrylated alkyd in terms of molecular weight and composition distribution. Similarly, processing conditions which are related to molecular weight distribution in alkyds[4], are important in the present system but because of the complex nature of the polymers involved, this aspect has not been fully investigated.

For commercial reasons, it is necessary to have a range of enamels available to meet specific customer requirements. Among the more important properties which need to be controlled and varied in automotive enamels are the rate and degree of cure. In the methacrylated alkyds, this can be achieved by varying the amounts of the formula components other than the acrylic such that the number of hydroxyl and carboxyl groups which are involved in the reaction with the melamine resin, are altered.

The results recorded in Table III indicate that reduction in either hydroxyl or acid value increases the set-up time and gives softer films and that with this formulation, acid value has a larger effect on these properties than the hydroxyl number.

In some specific cases, polymers with a balance of properties more towards those of a straight thermosetting acrylic system are required and the possibility of incorporating more acrylic polymer into the above methacrylated alkyd was, therefore, investigated. However, using a methyl methacrylate-acid copolymer, the incorporation of more than 30 per cent of the acrylic component into the alkyd gives enamels which are brittle and lack flexibility. Therefore, it seemed necessary to supplement the plasticising action of the fatty acid chains by the introduction of higher methacrylate esters or the simple acrylates. Initially, this was done by blending into the 30 per cent methacrylated alkyd a plasticising polymer of methyl methacrylate-butyl methacrylate-acrylamide (45.6 : 45.6 : 8.8). The amide groups were included to give sufficient polymer-polymer interaction for compatibility[5] and because of the possibility of this group reacting during the baking with the melamine resin.

Whilst this blending procedure gave acceptable initial film properties and polished readily, the durability on exterior exposure was unsatisfactory and not comparable with the 30 per cent methacrylated alkyd. This was possibly caused by the failure of the acrylamide copolymer to react appreciably with the other polymer systems under the conditions used, half-hour at 127°C, since other workers have reported that the amide/urea formaldehyde reaction requires external acid catalyst and slightly higher temperatures than used here[6].

The second method used to increase the acrylic content was to incorporate the plasticising monomer into the original acid copolymer and thereby ensure that all the acrylic component would enter the final three-dimensional network. Polymers were prepared by this technique with up to 40 per cent acrylic content and gave the required properties (Table V).

The process described, therefore, offers a means of producing a range of polishable thermosetting acrylic modified alkyds and the possibility of varying the balance of properties of the enamel to meet specific requirements by composition changes in the polymer.

[*Received* 19 *December* 1963

## REFERENCES

1. Solomon, D. H., *JOCCA*, 1962, **45,** 88.
2. Fletcher, J. R., Kelly, D. P., and Solomon, D. H., *JOCCA*, 1963, **46,** 127.
3. Crissey, L. W., and Lowell, J. H., Aust. Patent 203067, 1954.
4. Fletcher, J. R., Polgar, L., and Solomon, D. H., *J. Applied Polymer Science*, in press.
5. Flory, P. J., *Principles of Polymer Chemistry*, p. 555 (New York, Cornell University Press, 1953).
6. Allenby, Owen C. W., Canadian Patent 567,165 (1958).

# Short Oil Pentaerythritol Alkyds Achieved by Lactic Acid Modification

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## *Summary*

Modification of conventional alkyd formulations by lactic acid produces resins of low viscosity. This property has been used to prepare linseed/pentaerythritol alkyds of short oil length, the range of oil lengths examined being from 55 per cent to 40 per cent. The resins exhibited good drying properties giving rapidly hardening films of good flexibility. They also possessed good white spirit tolerance. Films stoved for 30 minutes at 120°C developed exceptional hardness.

## INTRODUCTION

It has been demonstrated previously[1] that alkyd resins can be satisfactorily made by incorporating lactic acid as a reactant. The lactic acid is thought to act by modifying the polymer chain to give a more flexible structure and in particular to space out the phthalic and polyol residues in the chain. Since it contains one hydroxyl and one carboxyl group, it can obviously take part in the esterification reaction in such a way that one hydroxyl of the polyol or one carboxyl of the acid is extended from the molecule by one lactic acid residue.

These conclusions have been demonstrated by the previous work in which resins of low viscosity and slow bodying rates were obtained. Nevertheless, the resins gave films of at least comparable performance to similar but unmodified resins. It seemed, therefore, probable that these properties could be used to produce alkyd resins in which the polyol is pentaerythritol and of short oil length, where to date difficulty is normally experienced either in incorporating all the fairly large proportion of pentaerythritol to achieve a homogeneous product or in controlling the reaction to obtain a reasonably low acid value without the risk of excessively high viscosity or gelation. The present work was undertaken as a preliminary examination of this possibility.

## EXPERIMENTAL

Four resins were prepared, commencing with an oil length of 55 per cent and reducing the oil length in steps of 5 per cent to the fourth resin at 40 per cent. The formulations are given in Table I.

The method of cooking was as follows :—

*T79* and *T80* : Alcoholysis was carried out at 250°C using 0.1 per cent sodium hydroxide as catalyst. On reaching maximum methanol tolerance, the charge was cooled to 150°C, the phthalic anhydride added, followed by the lactic acid. Esterification was carried out at 225-230°C.

TABLE I

| | *T79* | *T80* | *T99* | *T171* |
|---|---|---|---|---|
| Alkali Refined Linseed Oil | 51.5 | 46.7 | 42.5 | 37.3 |
| Pentaerythritol | 11.9 | 13.5 | 16.3 | 17.7 |
| Phthalic Anhydride | 23.1 | 24.8 | 25.7 | 28.0 |
| RR Lactic Acid | 13.5 | 15.0 | 15.5 | 17.0 |
| | 100.0 | 100.0 | 100.0 | 100.0 |
| Theoretical Water | 5.5 | 5.9 | 6.2 | 6.8 |
| Oil Length (per cent) | 55 | 50 | 45 | 40 |
| Excess Hydroxyl* (per cent) | 6.5 | 10.0 | 20.0 | 20.0 |

*Calculated on total hydroxyl content.

*T99* and *T171* : Alcoholysis was carried out at 250°C using 0.1 per cent sodium hydroxide as catalyst, but only the theoretical amount of pentaerythritol was used, namely an oil/pentaerythritol ratio of 3.5:1. On reaching maximum methanol tolerance, the charge was cooled to 150°C, the balance of the pentaerythritol was added and the temperature raised to 200°C. On cooling to 170°C, the phthalic anhydride and lactic acid were added, and esterification carried out at 220°C. This technique was found to be the most successful, but it was also necessary to increase the excess hydroxyl content over that employed previously in lactic modified resins (Table I).

The characteristics of the resins are given in Table II.

TABLE II

| | *T79* | *T80* | *T99* | *T171* |
|---|---|---|---|---|
| Colour PRS scale (60 per cent in xylol) | 4-4½ | 3½-4 | 4½-5 | 2½-3 |
| Viscosity (60 per cent in xylol) | 1.5p | 1.5p | 30p | 58p |
| Viscosity (50 per cent in xylol) | 0.5p | 1.2p | 7p | 3.5p |
| Acid Value (base resin) | 17.0 | 18.1 | 19.3 | 22.7 |
| White Spirit Tolerance (60 per cent in xylol) | Infinite | Infinite | Infinite | 5 |
| Esterification Time (min) | 375 | 400 | 220 | 220 |

The resins were evaluated by dissolving them in xylol to give 60 per cent non-volatile content and adding driers to give 0.05 per cent cobalt on base resin. They were applied to glass, mild steel and tin plate panels by a doctor blade with a gap set at 0.002 in. Rocker hardness and pencil hardness were determined after 24 hours, 48 hours and 168 hours air drying. Adhesion was examined by making a series of cuts through the film in such a way that a grid of squares of 2 mm sides was formed. Over this a piece of adhesive cellulose tape was firmly applied, this was then removed with a sharp pull. The percentage of squares remaining attached to the substrate was calculated and recorded, and observations are given in Table III.

The bloom was typical of pentaerythritol alkyds and was readily removable in the case of T79 and T80 but was slightly more adherent at the shorter oil lengths.

TABLE III

| | | *T79* | *T80* | *T99* | *T171* |
|---|---|---|---|---|---|
| Touch Dry Time (hr) | | $1\frac{1}{2}$ | $1\frac{3}{4}$ | $1\frac{3}{4}$ | $1\frac{1}{4}$ |
| Hard Dry Time (hr) | | $2\frac{3}{4}$ | $3\frac{1}{4}$ | $5\frac{1}{4}$ | $2\frac{1}{4}$ |
| Rocker Hardness | 24 hr | 51% | 53% | 43% | 62% |
| | 48 hr | 45% | 53% | 45% | 60% |
| | 168 hr | 53% | 56% | 46% | 58% |
| Pencil Hardness | 24 hr | 7H | 5H | 7H | 7H |
| | 48 hr | 7H | 6H | 7H | 7H |
| | 168 hr | 8H | 9H | 7H | 7H |
| $\frac{1}{8}''$ Bend Test | 168 hr | Passed | Passed | Passed | Passed |
| Adhesion to Glass | 48 hr | Nil | Nil | Nil | Nil |
| | 168 hr | 40% | 100% | 100% | 100% |
| Adhesion to Mild Steel | 48 hr | 100% | 100% | 100% | 100% |
| | 168 hr | 100% | 100% | 100% | 100% |
| Adhesion to Tin Plate | 48 hr | 100% | 100% | 100% | 100% |
| | 168 hr | 100% | 100% | 100% | 100% |
| Wrinkling | | Nil | Nil | Nil | Nil |
| Blooming | | Severe | Severe | Severe | Severe |

All four clear finishes developed an elastic skin on storing in partly filled but closed containers for 7 days at room temperature.

The water resistance of the resins was examined by applying to glass panels as above, drying for 48 hours and immersing in water for 48 hours. The four resins behaved similarly, showing no whitening and a large number of small blisters coupled with slight film embrittlement. On drying out, all the films recovered their initial hardness, but water spotting was evident under ×10 magnification at the sites of the blisters.

Films were also applied to glass panels as above and stoved for 30 minutes at 120°C. On cooling a brief examination of the films gave the results in Table IV.

TABLE IV

| | *T79* | *T80* | *T99* | *T171* |
|---|---|---|---|---|
| Rocker Hardness (per cent) | 66 | 78 | 71 | 75 |
| Pencil Hardness | 9H | 9H | 9H | 9H |
| Wrinkling | Nil | Nil | Nil | Nil* |

*T171 tended to wrinkle in thick films.

## DISCUSSION

Short oil modified lactic pentaerythritol alkyds present certain points of interest, in particular, the rapid drying and rate of hardening of the films. Maximum hardness of a high order appeared to be developed in 24 hours' drying, after which very little further hardening took place. The films showed no tendency to wrinkle and had good adhesion to mild steel and tin plate. Adhesion to glass was initially poor but improved on ageing.

The resins showed a definite tendency to skin. Water resistance was good inasmuch as the mechanical properties were little impaired and recovery was excellent, but they did blister on immersion. The hardness of stoved films, even at comparatively short stoving times, was noteworthy.

One interesting fact was the general similarity in drying, hardness and other properties irrespective of oil length over the range studied. It should also be noted that xylol solutions of the resins possessed very good tolerance for aliphatic solvents.

## CONCLUSIONS

It has been shown that short oil pentaerythritol alkyds can be prepared readily by incorporating lactic acid. Such resins are of interest mainly because of their rate of drying and particularly the rapid development of hard films on both air drying and stoving.

The work described was only designed to explore the possibilities of cooking such short oil resins with pentaerythritol. There are obviously a number of aspects which will demand further study but this should prove to be worthwhile in view of the probability of extending the range of alkyd resins and performance.

[*Received* 25 *October* 1963

## REFERENCE

1. Touchin, H. R., *JOCCA*, 1963, **46,** 118. *Paint Technology* 1964, **28,** 30.

## PAPERS ACCEPTED FOR PUBLICATION

The Honorary Editor has approved the following papers for publication in the *Journal.*

*Solomon, D. H.* et al. Vinyl and Acrylic Modified Alkyds, Part IV.

*Hoffmann, E.* Sulphide Staining caused by Phenylmercury Compounds In Paint.

*Marsh, J. S.,* and *Plant, D. A.* Colour Match Prediction using Organic Pigments.

*Monk, C. J. H.* A Pressure Cup for the Determination of the Weight per Gallon of Aerated Products.

*Obiakor, E. K.,* and *Whitmore, R. L.* The Effect of Stepwise Flocculation on the Rheology of a Kaolin Clay Suspension.

*Greaves, J. H.* Use of Gas-Liquid Chromatography in the Field of Drying Oils and Oleoresinous Media.

*Sheppard, I. R.* A Comprehensive Study of Optimum Milling Conditions in Conventional and Planetary Ball Milling.

A Machine Dependent Method of Calculating Optimum Milling Conditions for Ball Milling.

*Cope, G.,* and *Boulton, A.* Some Rheological Phenomena In Mill Bases.

*Haken, H. J.* et al. The Gas Chromatographic Analysis of Residual Oil on Tinplate.

*Sjollema, F.* et al. The Influence of Raw Materials on Electrostatic Spray Painting.

*Marson, F.* An Accelerated Leaching Rate Technique for Cuprous Oxide Based Antifouling Paints.

Four Papers from the Manchester Symposium on Plastic Coatings.

*Rybicka, S. M.* Versatility of Chromatographic Techniques in their Application to Paint Research.

*Haken, H. J.,* and *Mackay, T.* The Gas Chromatography of Solvent Mixtures Using Sequential Applications of Solubility and Functional Group Tests.

# The Determination of the Light Fastness of Coloured Materials Faster than Standard 8

REPORT OF SDC/OCCA JOINT LIGHT FASTNESS EXTENSION COMMITTEE

## INTRODUCTION

The official method for determining light fastness (BS 1006 : 1961) was originally devised for textiles, but it has been widely and successfully adopted in other industries. This method does not permit quantitative differentiation between coloured materials that are more resistant to exposure than Standard 8, which defines the highest light fastness on this scale. However, such differentiation is now required by other industries and a special committee was created to devise a suitable method, the committee consisting of members of the Light Fastness Committees of the Society of Dyers and Colourists and of that of the Oil and Colour Chemists' Association, augmented by other interested persons[1]. The committee has studied the problem and is now in a position to make a recommendation.

## BASIC PRINCIPLE OF PROPOSED METHOD

The method proposed consists of exposing the specimen together with a piece of Light Fastness Standard No. 7 until the latter has faded to an extent visually equal to Grey Scale Grade 4 contrast. At this stage the piece of Standard 7 is replaced by a fresh piece and the exposure continued until it in turn has faded to a Grey Scale Grade 4 contrast. This procedure is repeated until the specimen under test has faded to a Grey Scale Grade 4 contrast. When this has occurred the light fastness is calculated from the number of Standard 7s which have been exposed, preserving the geometric progression of the existing scale : thus 2 × Standard 7, Light Fastness = 8 ; 4 × Standard 7, Light Fastness = 9, etc.

## DISCUSSION

This repeated exposure technique is by no means new : it was used by the British Association as long ago as 1891. It was independently suggested for its present purpose by McLaren in a letter to the BSI Anodised Aluminium Committee in August 1961[2], and by Carr and Fishpool in a letter published in *JOCCA* and *JSDC*[3]. The chief objection to the method was the belief that the inevitable subjective errors are cumulative and, therefore, greater than those occurring when the normal method is used. This belief is, however, entirely erroneous and a detailed proof of this is given in an appendix.

The other objections to the repeated exposure technique are so trivial in comparison with the considerable difficulties which were expected in the establishment of physical standards 9, 10, 11, etc., that the committee felt that further work on these lines was not warranted.

## CHOICE OF UNIT STANDARD

The obvious standard to be used in the repeated exposure method would appear to be Standard 8, but this was rejected by the committee because the exposure necessary to produce a Grey Scale Grade 4 contrast often causes physical degradation of the wool substrate which makes accurate assessment of the amount of fading impossible ; Standard 7 is, therefore, proposed instead.

## OTHER POSSIBILITIES

The committee considered the possibility of using instrumental methods both as an adjunct to the normal method of using physical standards (i.e. for colour measurement) and also as a replacement for the standards (i.e. for measuring radiation), but concluded that there was no immediate possibility of success in either case. The committee awaits with interest the results of work being carried out in many different places on both these themes and will consider using them if and when they offer a sound basis for an alternative method of determining light fastness.

Harris[4] had suggested extending the effectiveness of the existing scale by exposing one of the standards for a known proportion of the time required for fading the specimen with precautions to ensure reproducibility. The committee considered this proposal to be most ingenious but somewhat limited. In daylight testing in the United Kingdom the scale could not be safely extended by more than one unit as to do so would mean exposing a specimen of the chosen standard for only one week in four, eight, 16, etc., and the week chosen could not be expected to be typical of the whole period. In lamp testing this restriction would not apply : however, the known decrease in light output from the preferred source, the xenon arc, would make it essential to spread the exposure of each specimen of the chosen standard over the whole exposure period and this would be much more complicated than the method proposed.

## STATUS OF PROPOSED METHOD

The method is published as a tentative test and it is hoped that it will be widely used. The committee will welcome any comments or criticisms and in the light of these a decision will be taken concerning the official establishment of the method.

[*Received* 3 *February* 1964

## REFERENCES

1. *JSDC*, 1963, **79,** 67 ; *JOCCA*, 1963, **46,** 151.
2. McLaren, K., *JSDC*, 1962, **78,** 503 ; *JOCCA*, 1962, **45,** 726.
3. Carr, W., and Fishpool, J. K., *JOCCA*, 1962, **45,** 666 ; *JSDC*, 1962, **78,** 502.
4. Harris, J., *JOCCA*, 1962, **45,** 839.

The membership of the joint committee was as follows :

(*a*) Representing Society of Dyers and Colourists :

Mr. A. E. Bratt
Dr. F. W. Lindley (*Chairman, Light Fastness Sub-Committee*)
Mr. K. McLaren (*Chairman, Fastness Tests Co-ordinating Committee*)
Miss O. Rawland (*Secretary, Light Fastness Sub-Committee*)

(*b*) Representing Oil and Colour Chemists' Association :

Mr. G. A. Campbell (*Chairman, Light Fastness Committee*)
Dr. J. G. Gillan
Mr. A. T. S. Rudram (*Hon. Research and Development Officer*)
Dr. V. G. Jolly

(*c*) Other representatives :

Dr. S. H. Bell (Paint Research Station)
Dr. W. Carr (Geigy Co. Ltd.)
Mr. W. E. Green (Associated Lead Manufacturers Ltd.)
Mr. C. Musgrave (Geigy Co. Ltd.)

(*d*) By invitation :

Mr. J. S. Mudd (Nene Finishes Ltd.)

## APPENDIX

Let us imagine an ideal set of Standards 6-12 which would require the following exposure to a standard source to produce a Grey Scale Grade 4 (GS4) contrast :

| *Standard* | *No. of Hours* |
|---|---|
| 6 | 40 |
| 7 | 80 |
| 8 | 160 |
| 9 | 320 |
| 10 | 640 |
| 11 | 1,280 |
| 12 | 2,560 |

and a specimen which requires 1,280 hours' exposure to GS4 contrast, i.e. its true light fastness is 11.

Let us now consider the errors made by an extreme deviant who correctly judges a GS4 contrast on the specimen, but who assesses a GS4-5 contrast on each standard as a GS4 contrast.

### Normal Methods

He will expose the specimen and standards for 1,280 hours and will say that Standard 12 shows the same contrast as the specimen, i.e. he will assess the light fastness as 12, one grade too high.

### Repeated Exposure Method

He will again expose the specimen for 1,280 hours and will remove a Standard 7 after every 40 hours, i.e. 1,280/40=32 Standard 7s. However, $2\times7\equiv8$, $4\times7\equiv9$, $8\times7\equiv10$, $16\times7\equiv11$ and $32\times7\equiv12$, so he will assess the light fastness as 12, *the same as by the normal method.*

The same reasoning applies to observers who deviate from the mean in other ways ; their errors by the repeated exposure method are exactly the same as by the normal method.

## PROPOSED APPENDIX C TO BS 1006

### DETERMINATION OF LIGHT FASTNESS OF COLOURED MATERIALS FASTER THAN STANDARD 8

The maximum exposure which is recommended in BS 1006 is that necessary to produce a contrast on Standard 7 visually equal to Grade 4 on the Grey Scale. If at this stage a specimen has not faded, the only numerical assessment of its light fastness which can be given is "at least 8." If this is inadequate, the following method should be used for obtaining a numerical rating :

Remove the exposed standards and replace the card AB in Fig. 3 and the cards AB, CD and EF in Fig. 4 in exactly the same position over the unfaded specimen.

Partially cover a fresh portion of Standard 7 so that the exposed/unexposed areas will be similar in size and orientation to those defining contrast Grade 4 on the Grey Scale.

Continue the exposure of the specimen and the fresh portion of Standard 7 until one or other shows a Grey Scale Grade 4 contrast. If Standard 7 shows the contrast first, replace it by another portion of Standard 7 covered in the same manner and repeat the procedure until the specimen shows a Grey Scale Grade 4 contrast. Report the rating of the specimen according to the total number of Standard 7s exposed, viz. :

| *No. of Standard 7s Exposed* | *Light Fastness of Specimen* |
|---|---|
| 2 | 8 |
| 3 | 8-9 |
| 4 | 9 |
| 6 | 9-10 |
| 8 | 10 |
| 12 | 10-11 |
| 16 | 11 |
| 24 | 11-12 |
| 32 | 12 |

*Notes*

1. If it is expected that the specimen is faster than Standard 8, the initial exposure against Standard 1-8 can, of course, be omitted, the first exposure period being against a portion of Standard 7 alone.

2. It will be observed that light fastness 8 is now defined in two different ways according to whether the original or new method is used. It is theoretically possible that they would give different results in some cases, but the extent of the difference is not considered to be of any practical importance.

3. It is advisable to mask the exposed specimens and portions of Standard 7 with black card and to place them against the Grey Scale so that there is no gap between the exposed areas and the pair of chips illustrating Grade 4. It is advisable to assess each exposed Standard 7 against the Grey Scale and not against one of the Standard 7s already exposed as by this procedure the inevitable subjective errors will tend to cancel out.

4. The standard method, BS 1006, is based primarily on the use of natural daylight, but the use of fading lamps is recognised and recommendations concerning their use are made in Appendix A. The need for fading lamps for determining light fastness ratings higher than 8 is much greater and it is anticipated that in the United Kingdom the proposed method will chiefly be used with fading lamps rather than with natural daylight.

# Information Received

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

PLASTANOL LTD. announce the introduction of a styrenated alkyd resin *Plastyrol S-77X*. This resin was developed to give very rapid drying and good flexibility without resort to resin or resin derivative. The properties reported by PLASTANOL LTD. are:—set-up in five minutes, surface dry in 10 minutes; these are allied to good flexibility, adhesion, colour retention, through hardening, mechanical properties and stability. It is also claimed that recoating properties are good for a resin of this composition.

Two new solvent soluble dyes for use in flexographic and rotogravure printing inks for packaging materials are being marketed by the GEIGY CO. LTD. *Grasol Fast Pink 5LB* is a blue shade red, soluble in alcohols and glycol ethers. It is reported to show good fastness to water, soap and fats, it is also claimed to have good fastness to light even in nitrocellulose inks. *Grasol Fast Rubine 2BL* is yellower in shade than *Grasol Fast Pink 5BL*, it is claimed to have outstanding tinctorial strength and good solubility in alcohols, glycol ethers and methyl ethyl ketone. It is reported to have good fastness to water, soap and fats, allied to good light fastness.

Because of the increased demand for printing inks in the Midlands area, AULT & WIBORG LTD. have moved their Birmingham factory to the following address, Ault & Wiborg Ltd., Jameson Road, Birmingham 6.

LAPORTE INDUSTRIES LTD. report that their sulphuric acid plants at Stallingborough have produced more than a million tons of acid since they came on stream 11 years ago. It is noted, however, that hardly any of the acid produced was sold, as nearly all was consumed in the manufacture of titanium dioxide.

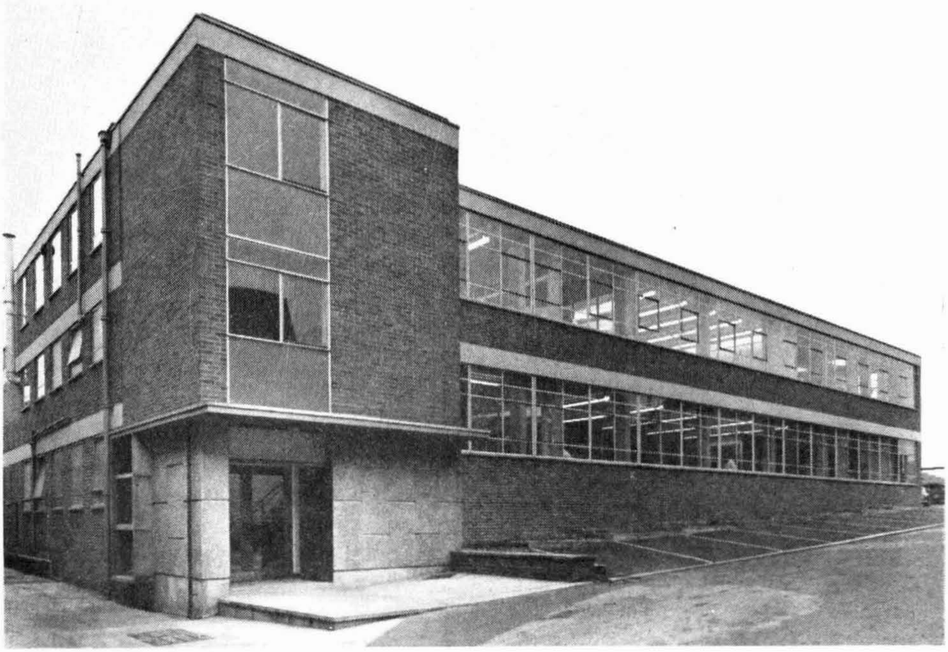
The first industrial process to utilise the phenomenon of electrophoresis to deposit paint is being used at the Cowley works of the PRESSED STEEL CO. LTD. The process employed, known as *Electrocoat*, is the result of two years' joint research between ICI LTD. (Paints Division) and the PRESSED STEEL CO. LTD. It is being used to coat, both internally and externally, petrol tanks produced by the Pressed Steel Co.

JOSEPH CROSFIELD & SONS LTD. announce the possibility of producing high ratio lithium silicate in a soluble form. Experimental work is reported to indicate a ratio of 16:1, $Li_2O$:$SiO_2$ and above. The advantages of this material have been demonstrated in zinc-rich coating formulations where superior coatings were reported compared with conventional silicates.

A new fungicide called *Omadine* is being produced by the OLIN MATHIESON CHEMICAL CORPORATION of the United States. Available in two forms *Zinc Omadine* and *Sodium Omadine* it is claimed to act as a preservative in water-based paints.

We have received from RALPH N. EMANUEL LTD. a catalogue describing organic research chemicals that can be obtained from the ALDRICH CHEMICAL COMPANY INC. The catalogue is divided into sections giving the compounds in alphabetical order, by structure and by chemical class; there is also a section on inorganic chemicals. The catalogue can be kept up to date by means of a monthly issue of index cards.

Sir Harold Roxbee-Cox, Chairman of the Research Council of Scientific and Industrial Research opened, in Birmingham, a new research and testing block for ARTHUR HOLDEN & SONS LTD. (see photograph). The building which cost £100,000 has a floor area of 13,760 sq ft contains laboratories equipped to simulate every type of condition and hazard to which paint and lacquers are subjected during their working life. Also the laboratories can reproduce the applicational processes used by the Company's clients.



A VIEW OF THE NEW ARTHUR HOLDEN LABORATORIES REFERRED TO ABOVE

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The *Journal* was represented at the press preview of three films sponsored by a group of companies who are members of the Paintmakers Association. These films will be shown on commercial television in the Midland area from March to October. The object is to stimulate the sales of paint and it is the first attempt to use co-operative advertising for the paint industry as a whole. Retailers in the area have been supplied with " streamers " bearing the slogan :—

***Paint can change the world you live in***

Also being sent to the retailers are explanatory cards giving details of the campaign.

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The PFIZER GROUP have started production of organotin compounds ; the company states that when incorporated into paints the organotin compounds give resistance to fungi and bacteria. They will be marketed under the trade name of *Stan-Guard.*

# Bristol Section

### THE PIGMENT PARTICLE AND THE PIGMENTED FILM

Thirty-three members and visitors were present at the sixth ordinary meeting of this session, held at the Royal Hotel, College Green, Bristol, on Friday 31 January. The Chairman, Mr. L. Brooke, welcomed the speakers, Mr. R. J. Cole and Dr. V. T. Crowl, of the Paint Research Station, whose subject was " The Pigment Particle and the Pigmented Film."

The paper is likely to be published later in full, so this report will be brief. Dr. Crowl opened and discussed the pigment particle, reviewing the types of particle likely, methods of particle size analysis, and finally the use of particle size data in interpreting differences in colour and strength of samples of benzidine yellows.

Mr. Cole continued, discussing the problems of dispersion, maintaining uniform dispersion, and the effects of absorption. Finally, Mr. Cole considered methods of determining CPVC and the effect of PVC on various film properties.

After an interesting discussion, contributed to by Mr. Newton, Mr. Brooke, Mr. Woodbridge and Mr. Lock, the meeting closed with a vote of thanks to the lecturers, proposed by Mr. Woodbridge and supported by all present.

R. J. W.

## IRISH BRANCH

### SOLVENTS FOR MODERN FINISHES

On Friday 31 January 1964 the Irish Branch of the Bristol Section held its first meeting for 1964 in Jury's Hotel, Dublin. The lecturer on this occasion was Mr. D. Cook, who read a paper on " Solvents for Modern Finishes."

Mr. Cook gave a lucid explanation of the steps involved in the choice of solvents for the surface coating industry. The topics which were covered included aerosol packed lacquers, electrostatic spray systems, solvents for air drying, stoving and cold curing, synthetic resin based coatings and water thinnable coatings. His paper caused some considerable comment from the 14 members and 18 visitors present. Those taking part in the discussion included Mr. A. Grainger, Mr. R. C. Sommerville, Mr. M. O'Callaghan, Mr. J. Quick, Dr. F. Smyth and Mr. W. J. Barrett.

A vote of thanks was proposed by Mr. K. Waite and seconded by Mr. F. D. Sharp. The meeting closed at 9.35 p.m., when refreshments were served.

F. D. H. S.

## STUDENT GROUP

### PUTTING THINGS TOGETHER

The last of the series of junior lectures was given on Friday 13 December, Mr. D. Newton presenting a paper entitled " Putting Things Together."

Under this heading, he considered what happens within a pigmented surface coating during and after manufacture, and how this may affect the behaviour of the paint film.

It was pointed out that it was physically impossible in normal practice to obtain a uniform mixture of pigments, uniform distribution of pigments throughout the medium, uniform dispersion during manufacture, or maintain attained dispersion on storage. Similarly, during application and drying, conditions of shear, flow, solvent evaporation, stress during drying, pigment settlement or flotation within the film, pigment packing variations and changes after the film has apparently set, all contributed to further lack of uniformity. When one considered all these effects it was a wonder that one was able to produce any satisfactory coatings!

Mr. Newton said it was the lack of uniformity within the film that was responsible for film breakdown. One could postulate that in an ideal film, with absolute uniformity, there would be no warning of breakdown, which would occur suddenly at the end of the film's life.

Finally, Mr. Newton considered paint testing, particularly the subjective nature of many tests, and also the particular properties which were measured in an accepted test—often far more complex than one realised. Mr. Newton concluded by exhorting the young chemists to be far more objective in their approach—to ask " why " as often as possible.

R. J. W.

# London Section

## THE DIFFUSION OF WATER AND RADIOACTIVE MATERIAL INTO ALKYD PAINTS

The seventh meeting of the session was held at Manson House, on 19 February 1964, with Mr. A. T. S. Rudram in the chair, when Mr. R. B. Wilson, of the Admiralty Research Laboratory presented a paper on " The Diffusion of Water and Radioactive Material into Alkyd Paints."

Mr. Wilson said that his work was concerned with the problems arising in decontamination of naval vessels following nuclear attack, so that all kinds of surfaces were involved, and amongst them he had studied the particular long oil alkyd paint in general use, which was not a material specifically developed for ease of decontamination. Decontamination of a surface appeared to take place in two stages: a rapid initial removal of the bulk of the contamination, followed by a very gradual removal of the remainder, and it was this latter tenaciously held material which was of main interest. This material could be either on the surface, or it could have penetrated into the film. Ships were now fitted with a pre-wetting system by means of which all surfaces were covered with an envelope of water, and this removed some 85 per cent of the contamination immediately.

In the laboratory, films had been prepared by spinning on a PTFE surface, and permeability, adsorption properties, density changes, and oxygen uptake had been studied. It was found that water vapour permeability fell rapidly in the first 10-15 days and was then constant. The permeability of the unpigmented film was higher than that of the pigmented film. A weathered paint film showed only a slight increase over the laboratory sample. There was very little change in permeability with humidity. If a film was built up by successive applications, with several days' interval between each coat, the permeability was considerably lower than if the same film thickness was built up by more rapid application of successive coats. The adsorption of water vapour was studied by a silica spring technique, and up to about 80 per cent Relative Humidity, Henry's law was obeyed. With weathered paints, however, there was a great increase in adsorption at high humidities. The adsorption of liquid water showed a rapid decrease within a few days, and a similar though less marked effect was shown by the unpigmented film. It was concluded that most of the adsorption took place in the thin clear layer on the surface of the paint film, and that there was an activated diffusion process involved.

In experiments with radioactive materials, $Cs^{137}$, $Sr^{89}$, $Ce^{144}$, and $I^{131}$, a microtome technique was used to measure the degree of penetration into the surface, and it was found that some materials giving a low adsorption in the surface appeared to penetrate more deeply ; this was particularly so with $I^{131}$. The penetration rates were in the order $Cs > Sr > Ce$, the monovalent ions having the greatest penetration. Experiments conducted in sea water (pH 8) showed the penetration was less than with distilled water (pH 5.4). The conclusions that arose from the work were that penetration was generally limited to the layers near to the surface, and decontamination could be effected by removal of the top 5-10 microns of the film. The layer of encrusted salt normally found on ships would aid such a removal of surface contamination.

In the discussion which followed, Mr. T. R. Bullett, Dr. J. E. O. Mayne, Mr. H. E. Ashton and Mr. R. N. Wheeler took part. In proposing a vote of thanks, Mr. W. J. Arnot, Chairman of the Thames Valley Branch, said that Mr. Wilson had presented a very interesting paper, and it had been pleasant to have an outlook on paint presented by someone from outside the paint industry.

V. T. C.

## SOUTHERN BRANCH

### WRITING INKS

The sixth technical meeting of the current session was held in Portsmouth at the Queen's Hotel on 10 February, when Mr. J. Bell gave a talk entitled " Writing Inks."

Mr. Bell began by tracing the history of writing inks from about 3000 B.C. to the present day. The earliest known inks were believed to be chemically similar to the modern products in that they contained metal salts, organic acids and dyestuffs, but this knowledge seems to have been lost because in the Roman era writing fluids were basically charcoal black containing liquids and it was not until after A.D. 1066 that inks were chemically constituted from formulae that were handed down from generation to generation. It was not until the middle of the 19th century that the first patents on writing ink were issued and from about that time the science of ink making started leading to the type of products available today.

The speaker continued by describing the manufacture of a typical blue-black permanent ink and discussed the reasons for the various ingredients. Basically the ink was a colourless fluid which on drying and oxidising gave a black trace of iron salts in the paper ; the ink was coloured blue to show where one had written. It was the deposition of iron salts which gave the permanent character to the ink, permanency being defined as being legible for at least 25 years. In the testing of inks many problems familiar to the paint technologist existed. Difficulties associated with colour stability, flow rate and drying characteristics were discussed and mention was made of the research work carried out in this field.

Mr. Bell also talked of his other experiences within the ink world, including work on secret or invisible inks and the part he and his colleagues played in helping to solve writings in invisible inks during the war.

During the discussion which followed many questions were put to Mr. Bell, who, when answering them, included a number of humorous experiences connected with his work. Dr. Bell, in proposing the vote of thanks, expressed the thoughts of all those present when he thanked Mr. Bell for a most enjoyable evening.

A. F. R.

## THAMES VALLEY BRANCH

### NEW DEVELOPMENTS IN SURFACE COATINGS

The second meeting of the Branch was held at the Royal White Hart Hotel, Beaconsfield, on Thursday 23 January 1964, when Mr. F. Armitage spoke on " New Developments in Surface Coatings."

Mr. Armitage said that he would be reviewing some of the more important developments in the paint field and how they fitted in with the general economic development of the industry. Of the British patents in the surface coatings field, 41 per cent were by American, 36 per cent by European and 23 per cent by British companies. The pre-war figure for British companies was 48 per cent. Research was being blocked by master patents held by organisations outside the United Kingdom and British companies were competing for the privilege of buying foreign knowledge. The present trend was likely to continue because of the 8 : 1 ratio of non-British to British big companies. Serious rethinking was needed by the 600 paint companies in the United Kingdom although the industry was at least taking advantage of overseas developments.

Mr. Armitage then outlined the developments in major markets. In the decorative paint market, 80 million gallons of emulsion paints were used yearly in the United States, almost as much as the whole of the output of the British paint industry. 45 per cent of these paints were based on styrene/butadiene latices, the remainder on vinyl acetate and acrylics. It had been forecast that in four to five years' time acrylics would lead the field. Because of the use of aluminium house sidings the linseed oil industry had lost business, and was sponsoring research on the use of linseed oil based water paints. Paints based on *Linapol* (an emulsion prepared frcm a very highly bodied oil) had been tested over the last 3½ years. They gave a quicker dry (recoatable in one to two hours) and better colour retention than linseed oil/zinc oxide paints. Compared with established emulsion paints, they could be used for coating chalking surfaces and zinc oxide could be incorporated to inhibit fungus growth. In Europe new paints were being developed from vinyl acetate/vinyl caprate and vinyl versatate copolymers. Thixotropic emulsion paints had been developed ; these paints were not proving to be as acceptable in the United States as they were not suitable for use in the colour mixing machines that were very popular there.

The use of colour measuring instruments and computers was increasing in the United States in producing paint, the pioneers in this work being the *Pittsburgh Plate Glass Company* and *Sherwin Williams*. Small companies could be put at a serious disadvantage. Users of strip coating plants were demanding readings on colour measuring instruments and automobile manufacturers were following suit.

Zinc rich primers were becoming very important because of unitised body construction and many companies in this country were working on co-operative programmes with the *National Smelting Co.* The most striking advance in car painting was the use of waterborne primers. The trend started with a *Glidden Company* styrene/butadiene primer at the *Ford Company*, later *Chrysler* used a modified maleinised oil primer by the *Pittsburgh Plate Glass Company* and in Europe, *Volkswagen*, *Fiat*, *Volvo*, *Rolls-Royce* and *Rover* were using primers based on *Vianova P411* resin. Maleinised oils were known 20 years before the primer was developed ; the first *P411* patents were taken out in 1949. The success of water based materials led to work on electrodeposition, which had practical advantages ccmpared with dipping. The *Glidden* patents gave a wealth of information on the principles of electrodeposition and of formulations. They introduced the feature of adding solvent in order to control the viscosity of the bath (high viscosity gives runs and tears and poor heat conductivity) and they also mention the principle of osmosis, separating the cathode and anode with a semi-permeable membrane to remove the ammoniacal ions and avoid the build up of pH, giving greater tank stability. Guy and Burden suggested that it was advantageous to use a mixture of emulsion and solution resins, the mixture being very good for coating welded parts, possibly eliminating the need for a zinc-rich primer. Thermoplastic acrylics were probably the most important finishing development ; *DuPont*, *Rinshed-Mason* and the *Pittsburgh Plate Glass Company* were in the field. *General Motors* changed over from nitrocellulose to get a better performance ; car manufacturers using baking enamels saw no reason to change, but in view of the success of the thermoplastic acrylics were now interested in thermosetting qualities.

Strip coating, particularly of aluminium, was a very important development in the United States ; 75 per cent of the aluminium coil was precoated and the tonnage was expected to be doubled over the next five years. There were only two lines in this country ; 50 per cent of strip in the United States was used for siding on houses ; the market in this country was restricted. An alkyd melamine coating, over a primer, could be expected to last outdoors for 15 years. Twelve years' durability data were available for solutions of vinyl coatings, which had very good forming properties. Thermoplastic acrylics were coming up fast, although they have somewhat inferior forming properties and their long term durability has not been proved. Laminated strips have been developed by BISRA e.g. *Stelvatite* (laminated with pvc sheet). An interesting development also by BISRA was the use of a pvc powder dispersed on the heated strip by a vibrating sieve, after which the strip was passed through *Teflon* coated rollers. The powder flows through the rollers like paint and is evenly distributed. Mention was made of other developments in powder coating, e.g. the fluidised bed, *Stafluid*, and electrostatic techniques.

Mr. Armitage's talk was followed by a lively discussion in which Mr. Rankin, Mr. Peacock, Mr. Walters, Mr. Howarth, Mr. Williams, Mr. Walker, Mr. Holt and Mr. Whigmore took part.

In conclusion, Dr. Long thanked Mr. Armitage for a most lucid talk, remarking that the attendance (68) was an indication of the interest in the subject and the speaker.

W. S.

# Newcastle Section

## SOME IMPLICATIONS OF SOLVENT INTERACTION

A lecture under the title of " Some Implications of Solvent Interaction " was given on Thursday 6 February by Mr. C. W. Andrews and Mr. E. Chadwick. The Chairman, Mr. J. G. N. Smith, presided.

Mr. Chadwick dealt with the theory of evaporation from ideal mixtures, and with examples of non-ideal mixtures showing both positive and negative deviations from Raoult's Law. Constant-evaporating mixtures had been compared with constant-boiling mixtures obtained by boiling at 25°C, under reduced pressure. Differences between them were attributed to the effect of moisture in the air on water-soluble solvents, and if dry air were used for the evaporation experiments the compositions of the two mixtures became fairly close.

Questions were asked by Dr. Neville, Mr. Jenkins, Mr. Dowling and Mr. Smith; a vote of thanks was proposed by Mr. H. D. Jefferies.

D. M. J.

# Scottish Section

## PETROLEUM CHEMICALS IN SCOTLAND

On Thursday 13 February 1964 at More's Hotel, Glasgow, the Scottish Section held their fifth meeting of the session under the chairmanship of Mr. A. S. Fraser. The lecturer on this occasion was Mr. J. Habeshaw who spoke on "Petroleum Chemicals in Scotland."

Mr. Habeshaw stated that his lecture would deal with industries in Scotland and how his own company's interests were concerned with them.

He referred first of all to the Scottish shale industry, which originally was engaged in making lamp oil, and to the work of J. Young who carried out the first basic cracking operation in Scotland in an attempt to increase production of lamp oil. In time, Mr. Habeshaw said, the internal combustion engine increased the demand for light petroleum products and later—50 years after Young's experiments—the higher boiling components were cracked to increase the lower boiling fractions. Cracking was developed then as the demand for petroleum products increased.

Mr. Habeshaw described the first industrial cracking processes and gave some detail of those set up between the wars.

The second world war increased demands for toluene and for synthetic rubber, the latter necessitating greater quantities of butadiene and styrene. At this stage specialised cracking processes were evolved, these the origins of many of the products used in industry today.

To illustrate and provide additional detail of the various aspects of his subject the lecturer showed a number of slides dealing with :

(*a*) The production of organic chemicals in the United Kingdom ; (*b*) Old and modern types of cracking plants ; (*c*) Some uses of ethylene derivatives in plastics, insecticides, anti-freeze liquids, lacquers, emulsions for paint, detergents, rayon and *Terylene* ; (*d*) The United States ethylene consumption in 1960, 1962 and (forecast) 1967 ; (*e*) Some uses of propylene derivatives in solvents, phenolic resins, detergents, fibres, explosives, copolymer rubbers ; (*f*) The United States' consumption of propylene in 1959, 1961 and (forecast) 1965 ; (*g*) Some uses of butadiene and $C_4$ olefins in butyl and other rubbers, transformer oil, caulking compounds and *Nylon 66* ; (*h*) Some uses of aromatics in phenolic resins, plastics, *Nylon 66*, *Nylon 6*, styrenated oils and plasticisers ; (*i*) Some uses of the lower paraffins in paint resins, explosives, fertilisers, synthetic fibres, rubbers and dry-cleaning solvents.

In conclusion Mr. Habeshaw summed up by stating that as the petroleum industry developed, its technology also developed in many directions. There was in it, he pointed out, an inter-related complexity.

Following the lecture Mr. W. W. Horsburgh warmly thanked Mr. Habeshaw for presenting such a lucid and interesting paper.

T. B. H.

## West Riding Section

### The Dispersion of Titanium Dioxide By Modern Methods

A meeting of the Section was held on Tuesday 14 January at the Great Northern Hotel, when Mr. G. Willison gave a lecture entitled "The Dispersion of Titanium Dioxide by Modern Methods."

In introducing the subject, Mr. Willison said that the discussion would be limited to titanium dioxide dispersions in air-drying alkyds and stoving enamels. Of the pigment itself this, he said, could be classified into three main groups, untreated rutile, after-treated rutile which has been treated with other oxides to improve the photochemical stability and ultra-refined rutile.

After the manufacturing processes the finely divided powder tends to flocculate and absorb approximately 0.75 per cent of water and it is therefore the function of the paint making process to convert this flocculent system in air to a disperse system in an approximate paint medium.

Mr. Willison continued by summarising the work of Jefferies (*JOCCA* 1962, **10**, 681) who described the mechanism of dispersion as :

(*a*) Wetting whereby the air from between the flocculates was displaced by medium.

(*b*) Disruption whereby the flocculates, cemented or sintered aggregates were mechanically separated.

(*c*) Dispersion whereby the separated particles were stabilised so that they remain deflocculated.

It was generally conceded, he said, that the more efficient the milling process, the greater was the extent of resin adsorption on the pigment surface, and hence the greater was the stability of the dispersion.

Turning to the machinery for making these dispersions, Mr. Willison said he had no hesitation in including the ball mill for this purpose. If the correct pebble charge, millbase charge and milling speed were used then this was a very efficient method. For optimum results a flowpoint determination described by Daniel (Circular 744 National Paint, Varnish and Lacquer Assoc., October 1950) should be used to find the best millbase formulation. The lecturer then, by means of slides, showed how these results could be transferred to the triangular graph to produce a curve of limiting compositions.

In general, he said, the pigment concentration of a millbase should be as high as possible consistent with good milling efficiency.

The next machine to be discussed was the Attritor, which could be best described as a ball mill stood on end having the grinding charge rotating round a vertical axis. As the charge was able to be driven at a higher speed than the conventional ball mill, a considerable increase in speed of dispersion was achieved. The design of this machine, he said, made it possible to modify it so that it could operate in a continuous fashion.

Its most useful feature, was that this mill could disperse organic pigments which gave highly structured millbases at low solid content.

The lecturer next considered the Sand Mill as this too, was a development of the conventional ball mill. Since, he said, it had been agreed that dispersion in the ball mill was achieved by the action of the shearing forces generated as adjacent balls move past one another at different speeds on the thin layer of millbase between them, it was to be expected that an increase in the number of such contacts per unit volume, by using sand as the grinding medium would increase the rate of dispersion. The difficulty was the removal of the sand from the millbase in a conventional mill, but the special design of the sand mill overcomes this, and also allows production as a continuous process. It had been found by Brownlie (*JOCCA*, 1960, **43**, 737) that the formulation of suitable formulations was dependent on the pigment and resin to be used. It was desirable, he said, that the millbases should be approximately Newtonian as a reduction in production occurred with thixotropic systems. Also it had been found that to achieve more stable dispersions prior to the let-down stage millbases containing a higher resin concentration than the optimum for maximum output in terms of pounds of pigment/hour should be used.

When working with the machine, he said, it was best to find the optimum formulation to give the maximum volume output by two series of experiments. The first was to determine the optimum resin concentration and the second to determine the optimum pigment concentration. The results required were the output in volume per unit time and weight of pigment milled in unit time.

The lecturer next considered the High Speed Impeller Mill. These, he said, depended largely for their successful functioning on two prime essentials which were the use of a suitable pigment and a suitable medium. As an example he said that most medium and long oil alkyds gave a suitable flow pattern with treated and ultra refined grades of titanium dioxide. The grade of pigment used was very important as inorganic pigments which have not been subjected to micronisation or some similar process, cannot be satisfactorily processed in mills of this type. Even so, Mr. Willison said, many products such as primers and undercoats can be satisfactorily made where very fine dispersions are not called for.

The millbase for this type of mill should possess sufficient viscosity and " tack " to develop shear forces between adjacent layers of millbase moving at different velocities.

At the same time, he said, it was also necessary for the millbase to be fluid enough to develop a satisfactory flow pattern so that " dead spots " did not occur in the milling vessel.

The last mill Mr. Willison considered was the Kinetic Dispersion Mill. This was one of the first mills to take advantage of the improvements made in the ease of dispersion of pigments. Although great interest was aroused when they were first introduced, he said, their popularity had not increased because of certain limitations. The main one was that a large quantity of solvent was needed in the millbase which necessitated the use of high viscosity resins to produce paints of acceptable viscosity.

Finally Mr. Willison discussed the stabilisation of pigment dispersions. This, he said, was an essential stage in the process of pigment dispersion. Most millbases contained large percentages of pigment and only a small amount of resin. This factor led to difficulties at the let-down stage as in some cases the millbase was unstable on storage or even when the dispersing forces had been withdrawn.

The speaker said that the main rules to overcome the difficulties of flocculation and seeding were as follows :

(*a*) When adding resin to a dispersion or *vice versa*, never allow an interface to form. (*b*) If possible, do not use a resin concentration below 20 per cent in the milling medium. (*c*) After milling, reduce the consistency with resin solution which is the same as or lower than the concentration of that used in the milling medium. (*d*) Add higher solids solution in portions with a short milling cycle between additions. (*e*) If the formulation permits, use a weaker solvent in the millbase and a stronger one in the let down solution.

L. J. W.

# ASSOCIATION CONFERENCE, 1965

As already announced in the *Journal* the Association's Conference will take place at Torquay from 25 to 29 May 1965, with the headquarters at the Palace Hotel.

Council has now approved the provisional title for the Conference as " Recent Progress in Coatings Technology." The papers will be arranged by the Honorary Research and Development Officer, Mr. A. T. S. Rudram, to take place on the mornings of the 26, 27, 28 May. Summaries of these papers will be appearing in a later issue of the *Journal*.

Full details will be sent to members early in 1965 and non-members wishing to receive details should write to the General Secretary, Mr. R. H. Hamblin, at the address shown on the front cover.

# OCCA FELLOWSHIP

DR. K. E. LEWIS DR. G. D. PARFITT

Council has had under consideration for some time the suggestion that the Association should institute a post-doctoral Fellowship on a research project of fundamental interest to the industries.

In 1963, therefore, Council set up a sub-committee under the Chairmanship of the President, Dr. J. E. Arnold, to consider the choice of subject and to explore where such work could be carried out. The other members of the committee were :

Mr. A. T. S. Rudram
(Hon. Research and Development Officer)
Mr. M. H. M. Arnold
Dr. C. Bondy
Dr. F. M. Smith
Dr. L. Valentine

The recommendation of the committee was that an approach should be made to the University of Nottingham, where

Dr. G. D. Parfitt (now an Ordinary Member attached to the Midlands Section) was carrying out research of a similar nature. Subsequently, the President and the Hon. Research and Development Officer discussed this project with Dr. Parfitt, who expressed a keen desire to co-operate with the Association. Early in 1964 he was able to report to the President that he had found a suitable research worker (Dr. K. E. Lewis), whom he could recommend for the Fellowship. It was agreed that the work would be under the general title of "The Relation between Adsorption on Pigment Surfaces and Stability of Dispersion with particular emphasis on Flotation and Related Phenomena," and would commence on 1 March 1964 for an initial period of three years.

It was agreed that reports of the progress of the project should appear from time to time in the *Journal*, and further it is possible that either Dr. Parfitt or Dr. Lewis may present a paper to a forthcoming Association Conference, possibly in 1967.

### News of Members

Mr. A. N. Pirie, an Associate Member attached to the Bristol Section, has been appointed Midlands Area Sales Manager for Laporte Industries Ltd. He will be based at A. W. Brook Ltd. the Group's Midland selling organisation.

Mr. C. E. Rowe, an Ordinary Member attached to the London Section, has been appointed Technical Manager of Carson-Paripan Ltd.

Mr. G. Wiseman, also an Ordinary Member attached to the London Section, has been appointed Chief Chemist of the Battersea Works of the same Company.

Mr. M. J. Heavers, an Ordinary Member attached to the Manchester Section, has been appointed Marketing Manager of Styrene Co-Polymers Ltd. Mr. D. Stewart, also an Ordinary Member attached to the Manchester Section, takes over Mr. Heavers' former position of Technical Service Manager.

In the February *Journal* (page 182) it was stated that Mr. D. C. Wall had been appointed Technical Director of Smith & Walton Ltd. This was in fact incorrect as Mr. Wall's position is that of Technical Manager. Any inconvenience caused by this error is very much regretted.

## Obituary

It is noted with regret that Mr. J. Milligan a Past Chairman of the Scottish Section has died. A full appreciation will appear in the May issue of the *Journal*.

### British Standards

*Optical Microscope Method*

As a result of a conference on powders held in 1952 the British Standards Institution is issuing a series of standards dealing with *Methods for the Determination of Particle size of Powders*. Part 4 of the series has just been issued, this is BS 3406 Pt. 4 1963 *Optical Microscope Method.*

The method is used to determine the size distribution of particles in those fractions of powders which pass through a BS 75 micron test sieve. It involves viewing a representative sample through a microscope and comparing the areas of their magnified images with those of reference circles inscribed on a graticule. By determining the numbers of particles in each of a series of sizes it is possible to find the size distribution by number and express it as a percentage.

As a special graticule is needed for this method, the Institution has issued a separate Standard giving the design and construction of suitable eyepieces. The standard is BS 3625:1963 *Eyepiece and Screen Graticules.*

Both the above standards can be obtained from the BSI Sales Branch, 2 Park Street, London, W.1, at the following prices :

| | |
|---|---|
| BS 3406 Part 4 | 20s. each |
| BS 3625 | 3s. each |

*Calcium Plumbate Standards*

The British Standards Institution has issued two specifications covering the use of Calcium Plumbate in paints. The standards are BS 3698:1964 *Calcium Plumbate Priming Paints* and BS 3699:1964 *Calcium Plumbate for Paints.*

The Association was represented on the committee that helped prepare the above standards.

Copies of the above standards can be obtained from the BSI Sales Branch, 2 Park Street, London, W.1, at a cost of 4s. 6d. each.

### Sixth Annual Symposium on New Coatings and New Coating Raw Materials

The Sixth Annual Symposium on New Coatings and New Coating Raw Materials will be held at the North Dakota State University, Fargo, North Dakota, USA from 1-4 June 1964. A total of 19 papers will be given covering various aspects of the above title.

Further details can be obtained from Professor A. E. Rheineck, North Dakota State University, Fargo, North Dakota, USA.

# Register of Members

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

### Ordinary Members

EDMONDS, LESLIE, 25 Merchant Avenue, Spondon, Derby. (*Midlands*)

GUEST, DAVID WADSWORTH, B.SC., 27 Lower Church Street, Ashby-de-la-Zouch, Leics. (*Midlands*)

HARE, ERIC, Via Gellia Colour Co. Ltd., Matlock, Derby. (*Midlands*)

HEATHCOTE, BARRIE, 13 Needham Street, Codnor, Derbys. (*Midlands*)

JEFFERY, ERNEST RICHARD, 12 Green Avenue, Chellaston, Derby. (*Midlands*)

MCCARTIE, NORMAN WILLIAM, 93 Leeds Road, Mt. Waverley, Victoria, Australia. (*Victorian*)

MELLOR, DOREEN, 48 Nottingham Road, Belper, Derby. (*Midlands*)

PERYER, BRYAN MILTON, M.SC., 13 Westerfield Drive, North Clayton, Victoria, Australia. (*Victorian*)

SMITH, KENNETH, B.SC., 48 Westway, High Heath, Pelsall, nr. Walsall, Staffs. (*Midlands*)

SPIVEY, ARTHUR MARSHALL, B.SC., PH.D., Tan-y-Foel, Trevor, Wrexham, Denbighshire. (*Midlands*)

TOMLINSON, JOSEPH RANDALL, " Woodbine Cottage," Rear 260, Abbey Street, Derby. (*Midlands*)

WARD, JOHN CLIFFORD, 48 Jackson Street, Derby. (*Midlands*)

WHITMORE, DONALD EDWARD KAYE, B.SC., Bostik Ltd., Ulverscroft Road, Leicester. (*Midlands*)

### Associate Members

CLAPPIS, PIO, 289 East Boundary Road, East Bentleigh, Victoria, Australia. (*Victorian*)

MEGGITT, DAVID LLOYD, P.O. Box 116, Footscray, W.11, Victoria, Australia. (*Victorian*)

### Junior Members

| | |
|---|---|
| BUXTON, JOHN FRANK, 31 Bridge Street, Belper, Derby. | *(Midlands)* |
| FANCUTT, BRIAN CHARLES, 2 Westcroft Avenue, Littleover, Derby. | *(Midlands)* |
| FLINT, ALAN ARTHUR, 27 Claramount Road, Langley, Heanor, Derby. | *(Midlands)* |
| HILL, JOHN RICHARD, 3 Wilmot Street, New Sawley, Long Eaton, Notts. | *(Midlands)* |
| SMITH, KEITH ALAN, 71 Parliament Street, Derby. | *(Midlands)* |

# Forthcoming Events

*(Note: Details are given of meetings arranged in the UK up to the 15th of the month following publication, and in South Africa and the Commonwealth up to the 15th of the second month after publication.)*

**Friday 3 April**

*Newcastle Section.* Ladies' Night at the Royal Hotel, Hexham.

*Newcastle Section—Junior Group.* " Durability Testing," at Rutherford College of Technology, Northumberland Road, Newcastle upon Tyne, at 3 p.m.

*Scottish Section.* Annual General Meeting at 6 p.m. at St. Enochs Hotel, Glasgow.

Smoking Concert at 7.30 p.m. at the Eglinton Arms, Eaglesham.

**Monday 6 April**

*Midlands Section—Trent Valley Branch.* Annual General Meeting.

**Tuesday 7 April**

*London Section—Thames Valley Branch.* Annual General Meeting at the White Hart, Beaconsfield, at 7 p.m. followed at 7.45 p.m. by films (including " A Light in Nature ").

**Wednesday 8 April**

*Scottish Section—Eastern Branch.* " Phthalocyanine Pigments—Relation between Physical Form and Performance," by Dr. F. M. Smith and Dr. J. D. Easton, at 7.30 p.m., at the North British Hotel, Princes Street, Edinburgh.

**Thursday 9 April**

*Newcastle Section.* Annual General Meeting.

**Friday 10 April**

**OCCA Dinner-Dance at the Savoy Hotel, London, WC2.**

**Monday 13 April**

*London Section—Southern Branch.* 4th Annual General Meeting at the Queens Hotel, Portsmouth.

**Tuesday 14 April**

*West Riding Section.* Annual General Meeting.

**Wednesday 15 April**

*West Riding Section.* Works Visit to the Metal Box Company. Follow up to the paper given on 11 February.

**Friday 17 April**

*Manchester Section.* Annual General Meeting.

**Wednesday 22 April**

OCCA Council Meeting 2 p.m.

**Thursday 23 April**

*London Section.* Annual General Meeting at the Criterion, Piccadilly, London, W.1.

**Friday 24 April**

*Bristol Section.* Annual General Meeting at the Royal Hotel, College Green, Bristol 1, at 7.15 p.m. followed by a film show.

*Midlands Section.* Annual General Meeting at George Hotel, Solihull at 7 p.m.

**ASSOCIATION ANNUAL GENERAL MEETING**

**17 June 1964, at the Painter Stainers Hall at 6.30 p.m.**

*The 12th Edition of the Gardner-Sward*

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For many years this manual has been the authority on paint testing. The 12th Edition has been completely rewritten and brought up to date. It is now more compact and is printed in three columns. It contains 554 pages $8\frac{1}{2} \times 11$ in size. It contains over 700 figures including 300 new illustrations. New methods of test and analytical procedures. Nearly 400,000 words and 2,000 entries of subject index. Heavy "*Fabrikoid*" binding with 22 carat gold stamping.

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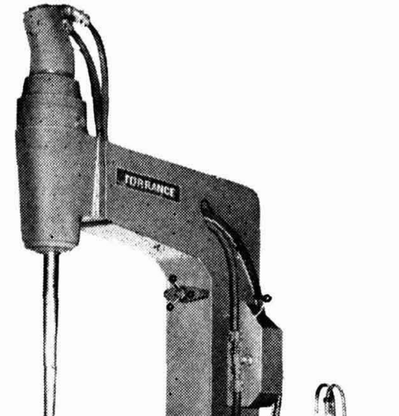

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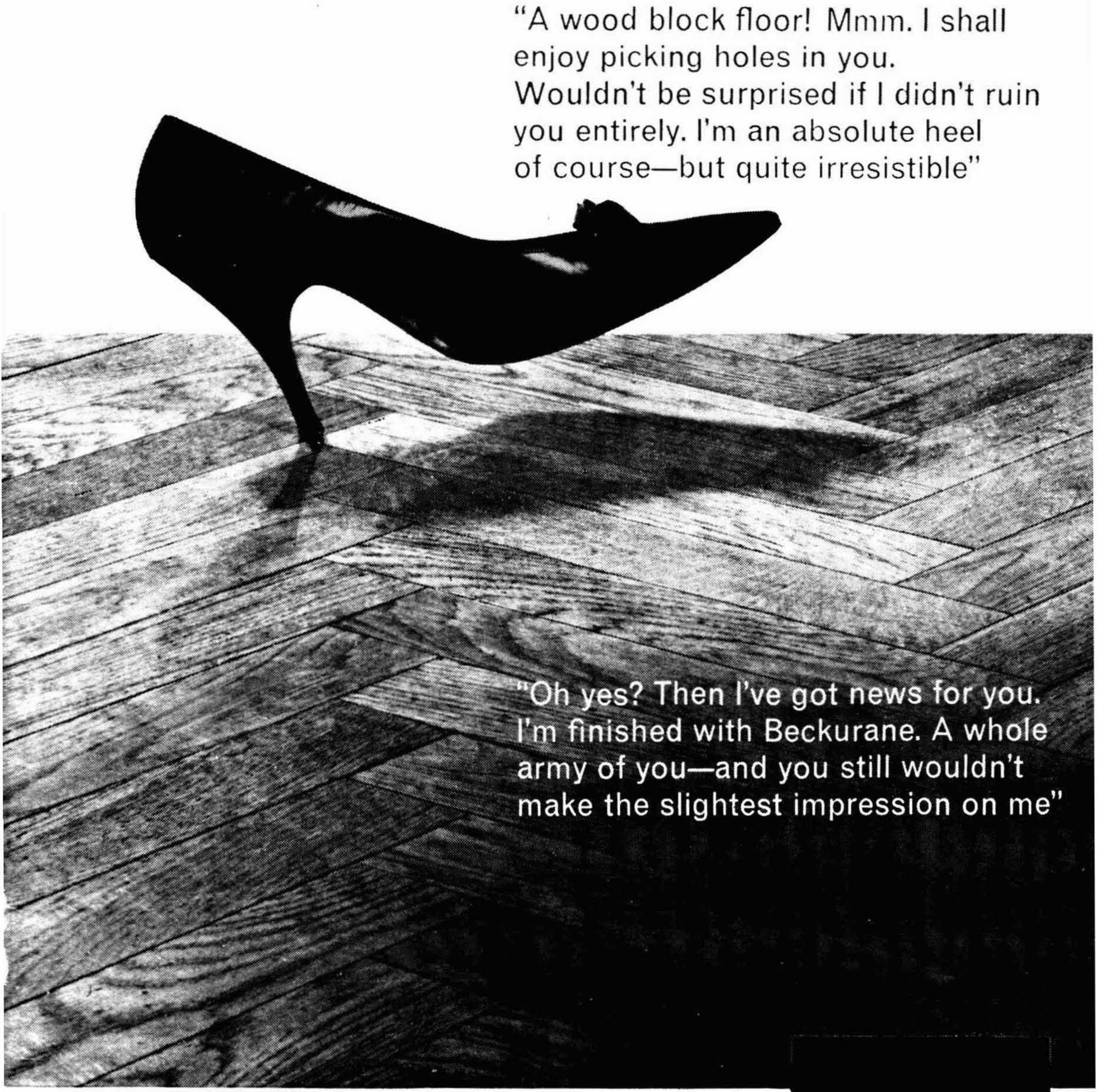
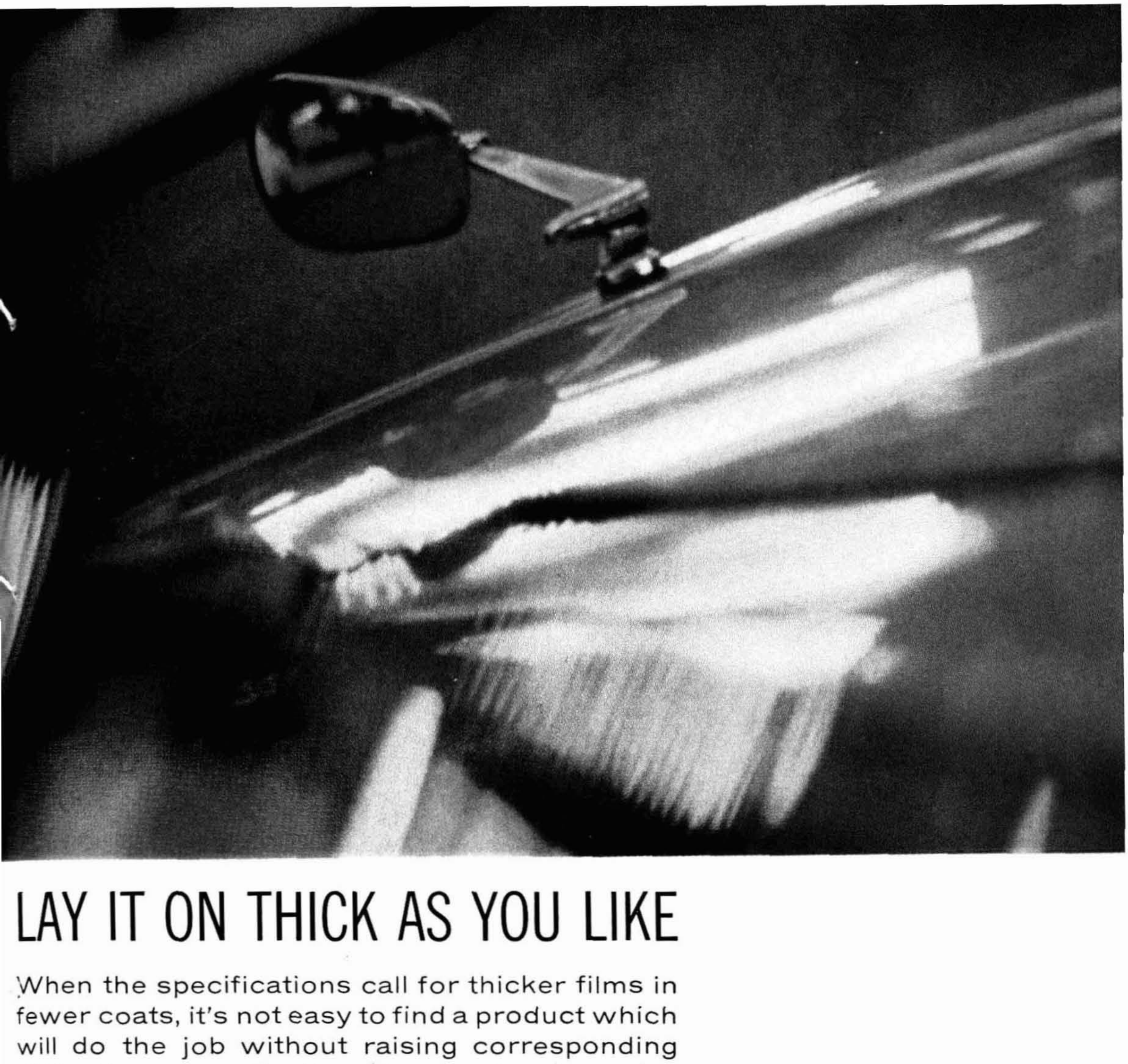
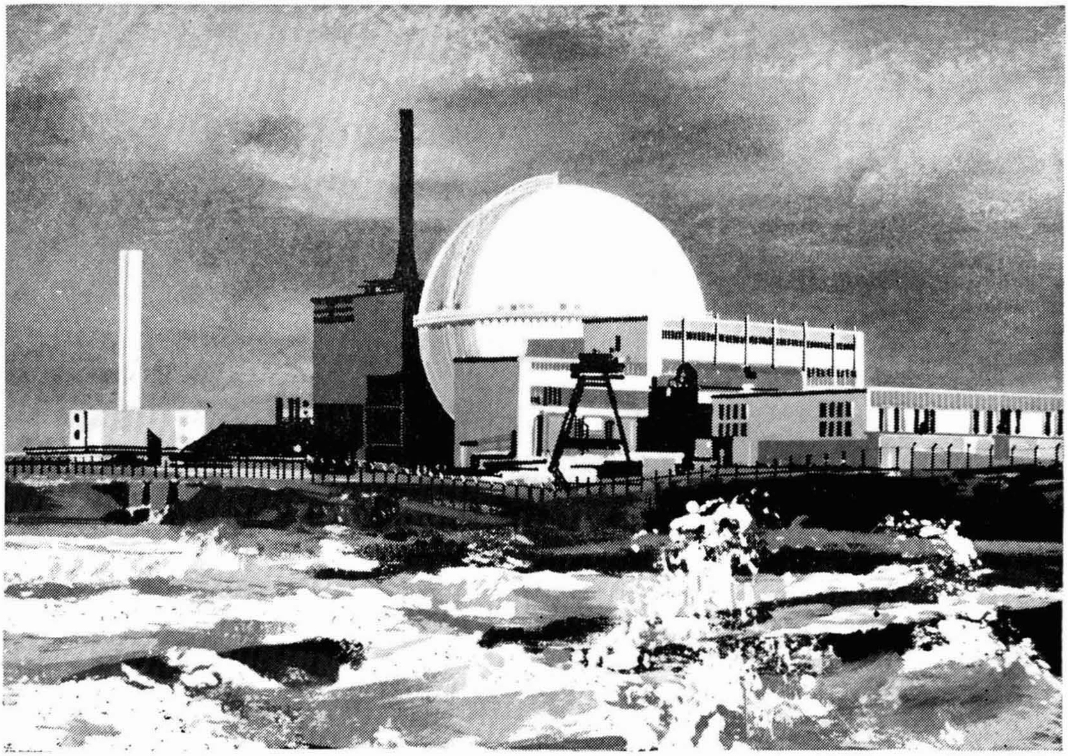

"A wood block floor! Mmm. I shall enjoy picking holes in you. Wouldn't be surprised if I didn't ruin you entirely. I'm an absolute heel of course—but quite irresistible"
"Oh yes? Then I've got news for you. I'm finished with Beckurane. A whole army of you—and you still wouldn't make the slightest impression on me"



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To join and help supervise a group working on slags and refractories mainly, but not entirely, on the laboratory scale and is aimed at improving existing materials and techniques and devising new ones. The work involves studies of chemical reactions at high temperatures, of mineral and glassy phases by optical and X-ray diffraction methods and of the physical and chemical properties of new products. Ref. No. CHEM/REF/5.

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Applications giving details of age, qualifications and experience and quoting relevant reference number should be sent to :—

*The Personnel Officer,*
**BRITISH IRON AND STEEL RESEARCH ASSOCIATION**
**24 Buckingham Gate, London, S.W.1.**

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Staff Manager,
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