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The surface treatment of pigments J. A. Moilliet and D. A. Plant

Papers from the South African Convention

Acrylic resins for industrial chemical coatings *H. L. Wampner*

Exterior durability of coatings

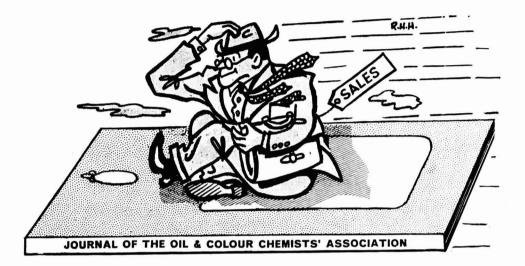
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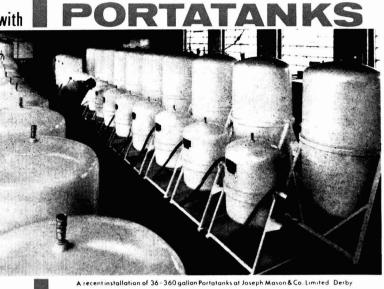
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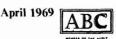
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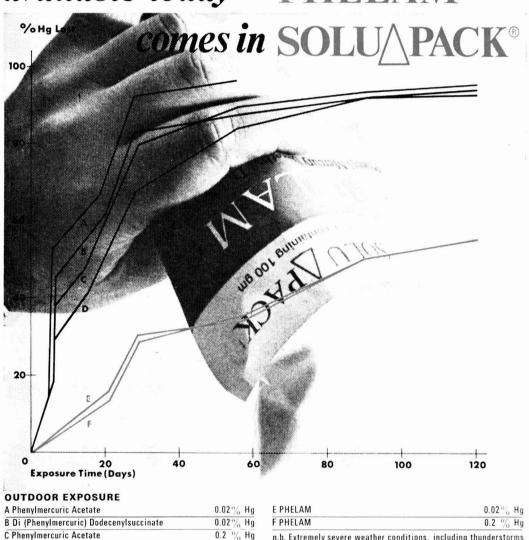
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Transactions and Communications

The surface treatment of pigments*

By J. Moilliet and D. A. Plant

ICI Ltd., Hexagon House, Blackley, Manchester

Summary

Methods used in the past for pigment surface treatment are summarised, particularly those designed to improve pigment dispersion properties and stability of pigment dispersions. The mechanism of surface treatments which reduce hydrophillic aggregation and enhance wettability are discussed.

Specific treatments are presented which are designed to produce spontaneously dispersible pigments for publication gravure inks, flocculation resistant phthalocyanine blues for many applications and structured pigments of a wide variety of types for easy dispersion in paint and printing ink vehicles.

For each of the three special cases presented, the effects achieved by the treatments are described by drawing examples from the appropriate branch of paint or ink technology; particular reference is made to the improved simpler and cheaper production methods which are made available.

Key words

Properties associated with materials in general dispersibility wettability Prime pigments benzidine yellow toner phthalocyanine pigment

Le traitement de surface des pigments

Résumé

On fait un résumé des méthodes utilisées au préalable pour le traitement des surfaces de pigments, notamment ces traitements destinés à l'amélioration des caractéristiques pigmentaires de dispersion et de la stabilité des dispersions de pigments. On discute le mécanisme des traitements de surface qui réduisent l'agrégation hydrophillique ou qui ameliorent la mouill-abilité.

On présente des traitements spécifiques destinés à rendre des pigments spontanément dispersibles dans les liants pour encres d'imprimerie à gravure, des bleus de phtalocyanine, résistant à floculation, convenables à plusieurs applications et une variété étendue de pigments de telles structures pour assurer leur facilité de dispersion dans les liants des industries de peintures et d'encres d'imprimerie.

Pour chacun des trois cas particuliers mentionnés dans cet exposé, on décrit les effets que produisent les traitements, au moyens des exemples tirés du secteur juste de la technologie de peintures ou d'encres d'imprimerie; on mentionne en particulier les méthodes perfectionnées, plus faciles et également moins coûteuses, que permettent ces traitements.

Die Vorbehandlung von Pigmentoberflächen

Zusammenfassung

Die bisher für die Oberflächenbehandlung von Pigmenten eingesetzten Methoden, besonders solche, die Verbesserung der Dispersionseigenschaften von Pigmenten und der Stabilität von Pigmentdispersionen bezweckten, werden zusammengefasst. Der Mechanismus von Oberflächenbehandlungen, welche die hydrophile Aggregation reduzieren und die Benetzungsfähigkeit verbessern, werden besprochen.

*Presented to the Manchester Section on 9 February 1968 and to the West Riding Section on 12 March 1968.

Spezifische Verfagren, die dafür bestimmt sind, von selbst dispergierbarer Pigmente für Tiefdruckfarben für Druckschriften, nicht ausflockende Phthalozyaninblaus für zahlreiche Anwendungszwecke und strukturierte Pigmente grosser Verschiedenheit im Verhalten bezüglich leichter Dispergierbarkeit in Bindemitteln für Lack- und Druckfarben zu erzeugen, werden vorgetragen.

Die dank der Behandlung erzielten Resultate werden für jeden der drei vorgeführten Spezialfälle beschrieben, indem Beispiele aus den entsprechenden Gebieten der Anstrich- oder Druckfarbentechnologie gebracht werden; auf die berbesserten, vereinfachten und verbilligten möglich werdenden Produktionsmethoden wird besonders hingewiesen.

Поверхностная обработка пигментов

Резюме

Рассматриваются применявшиеся в прошлом методы поверхностной обработки пигментов, в частности методы расчитанные на улучшение свойств и устойчивости пигментных дисперсий. Обсуждается механизм поверхностных обработок, снижающих гидрофильное скопление и повышающих способность увлажнения.

Иллюстрируются специфические обработки расчитанные на получение самопроизвольно дисперсирующихся пигментов для гравюрных печатных чернил, фталоцианиновых синей различного применения, устойчивых против флоккуляции и структурных пигментов широкого ряда разнообразных типов, для свободной дисперсии в красочных и печатно-чернильных растворителях.

Для каждого из трех приведенных специальных случаев, эффекты вызванные обработкой описываются примерами взятыми из соответствующей отрасли красочной или чернильной технологии; делается специальная ссылка на усовершенствованные, упрощенные и более дешевые методы производства, имеющиеся в распоряжении.

Introduction

The surface treatment of pigments for use in paints, printing inks and other non-aqueous media, is the subject of a very large patent and technical literature, which goes back to the last century. Broadly speaking, these surface treatments have one or both of two aims: to improve the ease of dispersion of pigments in non-aqueous media, and to control (usually to decrease) their degree of flocculation in the final dispersion.

The first of these objectives arises from the fact that most pigments are isolated from water and dried as aqueous press cakes. No matter how carefully it is carried out, drying by conventional methods causes some "hydrophilic aggregation," i.e., as the water is removed, the particles are subjected to virtual compressive forces which cause aggregation. These compressive forces are due to the positive work of adhesion between all solids and liquids, aggravated by the high work of cohesion of water. The aggregates have to be broken down— and then usually only incompletely—by milling the pigment into the non-aqueous dispersion medium. If, however, the individual pigment particles are coated, *before* the pigment paste is dried, with a layer of a *hydrophobic* substance which is soluble in the non-aqueous medium, hydrophilic aggregation may be reduced in several ways. In the first place, such a layer will reduce the work of adhesion of water to the pigment particles during the drying operation if it makes them less water-wetted, i.e., if it increases the contact angle θ in the well-known expression:

 $W_{a} = \gamma_{w} (1 + \cos \theta),$

where W_a is the work of adhesion and γ_w is the surface tension of the aqueous phase (both against air). Secondly, surface layers may act mechanically, if they

1969 (4) THE SURFACE TREATMENT OF PIGMENTS

are thick enough and robust enough, by forming barriers which diminish the number of direct pigment-pigment contacts. And finally, surface treatments which render the pigment particles water-repellent will usually cause flocculation in the aqueous press cakes, loose structures being set up which resist shrinkage of the press cake during drying.

At the risk of over-simplification, these surface treatments for improved ease of dispersion can be grouped under three or four headings. The oldest and best-known technique is to use a double decomposition reaction, in which an aqueous solution of a surface-active agent is added to the pigment "strike" or to the press cake, followed by a precipitant which forms the hydrophobic laver in situ. Well-known combinations are sodium soaps or resinates, followed by acid, calcium or barium salts, or by salts of amines such as octadecylamine or diphenylguanidine. Another general technique is to add a water-soluble surfaceactive material which is adsorbed by the particular pigment with "reversed orientation," i.e., with the polar groups attached to the pigment and the hydrophobic groups turned outwards. Examples of this type of treatment are the addition of soaps to white lead or lead chromate pigments, or of cationic surface-active agents to Prussian blues and many organic pigments. It is also appropriate to consider the well-known co-flocculation treatments, in which an aqueous pigment paste is mixed with an emulsified or dispersed oil, wax, resin, or polymer, or with an emulsion polymer, and the mixed dispersion flocculated (usually by insolubilising the dispersing and emulsifying agents present) before being isolated and dried.

Pigment preparations made by these methods may contain anything from less than 1 per cent of total additives on the weight of actual pigment up to an equal weight or more, i.e., they vary from compositions in which the additive barely forms a monomolecular layer, to others which are essentially pigment "master-batches." Although, in the authors' opinion, the main function of these additives is to reduce hydrophilic aggregation during drying, they also sometimes improve *wettability*, i.e., they promote the displacement of air by an "oil" medium (or of water by an "oil" in flushing processes). This wetting effect can sometimes be usefully interpreted in terms of surface thermodynamics, the function of the treating agent being to reduce the pigment-oil interfacial tension, and hence the (advancing) contact angle of the oil phase. A recent investigation of the flushing process in these laboratories¹ suggests, however, that at least some of the double decomposition treatments which improve pigment "wettability" do not act in this way at all, but may even make the surface thermodynamics less favourable to (equilibrium) wetting. The function of these treatments is rather to promote wetting by a sort of *irreversible* "osmotic surge" of free energy, which comes from the process of solution of the oil-soluble layer in the oil medium. See Fig. 1. (To give a homely analogy, the water-wettability of cocoa powder can be improved by grinding it intimately with sugar, which is not a wetting agent). This mechanism is important in considering the behaviour of the Easily Dispersible pigments which will be described later.

So far care has been taken to refer to *reductions* in the extent of hydrophilic aggregation, rather than to its *elimination*. This is because, to the best of the authors' knowledge, it has never been possible in practice to avoid aggregation

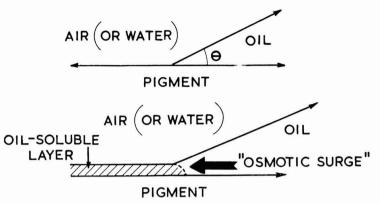


Fig. 1. Promotion of wetting by "osmotic surge"

completely, except by adding so much diluent that the products are effectively master-batches. At more modest dilutions (say 5 per cent to 30 per cent, depending on the specific surface area of the pigment) it is the authors' experience that surface treatments alone will not eliminate hydrophilic aggregation completely, and that some grinding is still necessary, even with powerfully deflocculating non-aqueous media. However, a new type of treatment will later be described which, thanks to the formation of a sufficiently strong "lattice" structure of hydrophobed pigment particles, achieves this target of complete elimination of hydrophilic aggregation.

It is well known that improvements in the ease of dispersion of pigments in non-aqueous media are often not accompanied by any changes in the degree of deflocculation in the final pigment suspension. In fact, most of the agents which are used to improve initial dispersibility have very little true surface activity in non-aqueous liquids, and we usually rely for deflocculation and protective colloid action on ingredients of the medium, such as alkyd resins, linseed oil polymers, etc., which are present in fairly large amounts. There are, of course, surface-active agents, such as lecithin and the paraffin-chain amines, which have an effect in paints, but they tend to be specific—far more specific than deflocculating agents for aqueous media. This is due to the absence of a simple, clear-cut mechanism of non-specific amphipathic adsorption in nonaqueous media. In water we have a wide range of surface-active agents which contain hydrophilic groups, suitably separated from hydrophobic structures, and these hydrophobic structures are not only expelled by the medium, but are capable of forming interfacial layers (e.g. against a pigment) of lower surface free energy than can be formed by the aqueous medium itself. It is this last condition which is difficult to satisfy in non-aqueous media: there are many chemical structures which are expelled by non-aqueous pigment dispersion media, but very few of them are capable of fairly generally lowering the already low surface free energies which are exhibited by these media. Low surface free energy groups such as polysiloxanes and perfluoroalkyls may eventually fill this need, but at present we largely depend on specific interactions to achieve adsorption. However, two recent developments will be described in which progress has been made in finding more powerful "anchoring" mechanisms, which may prove to be less specific than most of those now in use.

1969 (4) THE SURFACE TREATMENT OF PIGMENTS

Pigment deflocculation treatments

Although electrokinetic potentials play a part in deflocculating some very dilute pigment/oil systems, it seems clear that, with the particle sizes and concentrations with which one is concerned in paints and printing inks, their role is secondary to that of steric barriers. (Albers and Overbeek² have pointed out that, in a medium such as benzene, the thickness of the "ionic atmosphere" corresponding to an electrokinetic potential of 100mV will be several microns. It can readily be shown that this is greater than the average distance between particles in typical paints and printing inks; under such conditions of interlocking ionic atmospheres the electrical repulsive forces are unable to act effectively.) The requirements for an effective steric barrier are well known: it must adhere strongly to the surface of the pigment and must be of the "condensed" type (i.e. it must be robust); it must be thick enough to ensure that, at the closest approach of individual particles, the van der Waals forces of attraction (which decrease with the sixth/seventh power of the distance) are still too small to cause mutual adhesion; it must be externally solvated by the solvent. This last requirement suggests, among others, two types of structure which would be expected to have a high "affinity" for typical hydrocarbon media: long alkyl chains, and oil-soluble macromolecules. The new deflocculating treatments which will be described illustrate the use of both these types.

Spontaneously dispersible pigments

It is well known that long-chain alkyl amines will deflocculate some pigments in non-aqueous media^{3, 4, 5, 6}. This is attributable to a specific adsorption of the agent with the amino groups orientated towards the pigment, the outwardly orientated alkyl chains forming the steric barrier. It has recently been discovered⁷ that the strength of attachment of this steric barrier can be increased, in the case of azo acylacetarylamide pigments, if the treatment is carried out in such a way that the amine reacts chemically with the pigment. If, for example, 73 parts of dry Monolite Yellow GT (CI Pigment Yellow 12) are kneaded at 140°C with 27 parts of molten Duomeen T (technical quality 3-octadecylaminopropylamine, marketed by Armour Hess), a reddish-brown plastic mass is obtained, which can be pulverised when it cools. The powder spontaneously disperses (without milling) in aromatic hydrocarbons, and in gravure inks, to give highly deflocculated dispersions in which many of the particles are sub-microscopic, and the visible ones (less than 0.5μ in diameter) are in strong Brownian motion. Other long-chain amines also give this effect, as do other methods of incorporation which enable an intimate mixture to be heated.

As the result of a study of the above reaction, and of model experiments with simpler (and purer) ingredients, Dr A. Topham (private communication) has concluded that the reaction shown in Fig. 2 occurs in the preparation described above.

The formulae of CI Pigment Yellow 12 and of the Schiff's base (I) can, of course, be written in other tautomeric forms, the latter being the aminocrotonanilide (see Fig. 3, II).

The evidence for this type of structure, rather than for an amidine resulting from a reaction at the amide group, is largely chemical: compounds identical with those of types (I) or (II) were obtained by coupling tetrazotised 3,3'-dichlorobenzidine with substituted aminocrotonanilides such as III of Fig. 3.

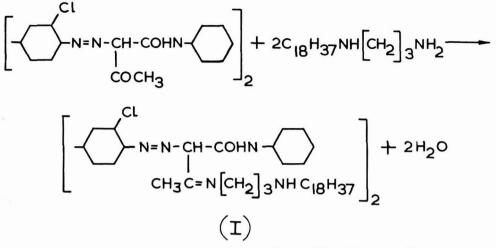


Fig. 2. Reaction between Monolite Yellow GT and Duomeen T

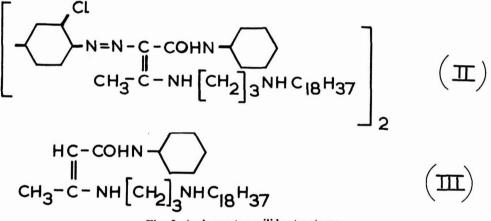


Fig. 3. Aminocrotonanilide structures

In the example given above, it is postulated that a layer of (I) or (II) is formed in situ on the pigment particles, with the octadecyl groups orientated outwards. Alternatively, (I) or (II) can be made in bulk and then coated on the pigment particles, though the degree of spontaneous dispersibility is then not so good. The superiority of the *in situ* treatment is almost certainly due to the more intimate incorporation of the (I) or (II) which is formed, and perhaps also to the fact that it takes advantage of any desorption hysteresis. Deflocculation is *not* due to the achievement of a completely irreversible chemical anchoring of the long alkyl chains to the crystal lattice of the pigment, but to the fact that (I) and (II) are more strongly adsorbed than is the 3-octadecylaminopropylamine itself, and it is known that the agent is held by physical adsorption because the coloured agent can be separated by thin layer chromatography from the finely divided pigment. 1969 (4) THE SURFACE TREATMENT OF PIGMENTS

Flocculation-resistant copper phthalocyanines

The use of condensation products of copper tris (chloromethyl) phthalocyanine with aliphatic amines for reducing the degree of flocculation of copper phthalocyanines in paint media (though not for obtaining spontaneous dispersibility) is described elsewhere^{8, 9, 10}. These condensates vary from relatively simple "monomers" of type (IV), which are soluble in hydrocarbons, to "dimers" (V) and still more complex molecules, some of which are completely insoluble (See Fig. 4).

V) $CPC(CH_2NHR)_3$ $(\operatorname{R}\operatorname{NHCH}_2)_2\operatorname{CPC}\operatorname{CH}_2\operatorname{NCH}_2\operatorname{CPC}\left(\operatorname{CH}_2\operatorname{NHR}\right)_2(\Sigma)$ R

Fig. 4. Condensation products of copper tris (chloromethyl) phthalocyanine

where R is an aliphatic radical and CPC represents a copper phthalocyanine residue.

Both these types can be very conveniently applied to the pigment from largely aqueous media as soluble salts (e.g. acetates or formates), which are then precipitated by adding alkali. The mechanism of their deflocculating action in paint media has been investigated by Black, Hesselink, and Topham¹¹. Coating copper phthalocyanine with (IV R = isopropyl) markedly increased the adsorption of stearic acid and of 2-ethylhexyl hydrogen phthalate; from this, and from the fact that these basic phthalocyanine agents are all completely ineffective in the absence of acid polymers, it is concluded that they act as "mordants" for dissolved alkyd resins, holding them by hydrogen bonds between the basic nitrogen atoms in the agent and COOH groups in the resin. In this way a steric barrier of adherent macromolecules is formed, which reduces the degree of flocculation. (Dr V. T. Crowl (private communication) has found that treatment of the solvent-stable, slightly chlorinated copper phthalocyanine (Monastral Fast Blue LBX) with an agent of type (IV) has no significant effect on its electrokinetic mobility in a typical alkyd resin (Paralac 9HW) in xylene, or in a butylated melamine resin (Beetle BE 615) in 50:50 xylene/butanol. This confirms the picture of the negligible role of electrokinetic potentials in the action of this type of agent. (See also V. T. Crowl¹².)

It is worth noting that the adsorption of basic phthalocyanines such as $CPC(CH_2NEt_2)_3$ from hydrocarbon solvents is not attributable to an attraction of "like-for-like" between the agent and the phthalocyanine pigment, since the agents are adsorbed on a variety of substrates (including TiO₂, carbon black, azo pigments, and lead chromes). This powerful, non-specific adsorbability may be due to the presence of large flat phthalocyanine nuclei and their tendency to be more associated in non-aqueous media near an interface. (As pointed out by Barron et al.⁹, this type of agent can also be based on other coloured structures such as isodibenzanthrone). Their only specificity appears (unfortunately) to reside in the fact that they are coloured.

Easily dispersible pigments: The "ED structure"

Reference was made in the introduction to the fact that hydrophilic aggregation can be diminished—though not eliminated—by coating pigment particles with thin oil-soluble layers before they are dried. This lack of complete success is presumably due to the fact that the particles are not held sufficiently far apart (unless the preparations are diluted to "master-batch" strengths) in order for the net van der Waals attractive forces between particles to remain negligible. More recently, however, Ambler and Tomlinson¹³ have found that hydrophilic aggregation can be virtually eliminated if the particles are held apart by being embedded in a stable, open structure, in which the "cement" is an oil-soluble resin or polymer of adequate mechanical strength. This structure, shown in Fig. 5, is formed by depositing the resin on the particles in aqueous suspension

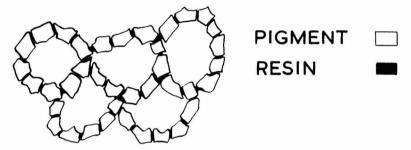


Fig. 5. "ED structure" (Schematic)

(either from a solution of a "resinate" or from a very fine aqueous dispersion), softening the resin, re-hardening it, and then isolating the product and drying it below the softening temperature of the resin. The softening-hardening cycle is most simply carried out by heating and then cooling the suspension, but it can also be done by introducing a solvent for the resin (e.g. methyl ethyl ketone) and then removing or diluting it, or by a chemical reaction, such as converting a softened resin to its calcium salt at a temperature at which the latter is a solid.

A test for detecting this "ED structure" has been described by Ambler and Tomlinson¹³. A sample of the pigment is gently pulverised and subjected to a uniform pressure of 20lb in⁻²; if the structure is present, the powder resists compression sufficiently to give a volume/volume concentration below 0.18 (0.13 in the case of carbon black). A number of examples, covering a range of pigments and resinous materials (including some special emulsion polymers which are further described subsequently¹⁴), are given in the literature¹³.

The ED structure cannot be distinguished clearly by microscopical examination, but is inferred from the results of compression tests. It seems clear, however, that the improved oil-dispersibility of the ED products is due to the presence of this special structure, since the alternative explanations can be eliminated on the following grounds:

(i) A possible *deflocculating action* by the resins can be ruled out: ED products do not re-disperse in hydrocarbon solvents, but require the presence of polymeric dispersing agents such as alkyd resins, and linseed oil polymers. Moreover, the final state of deflocculation in the paint or

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printing ink is substantially the same as that given by untreated (or conventionally treated) controls which have been milled into the medium.

(ii) The ED treatment does not appear to make the pigment particles more oil-wetted and/or less water-wetted. Table I gives the results of measurements of the work of adhesion of water (against white spirit) for several treated pigments, as determined by the "apparent boundary tension" method¹⁵. In each case the work of adhesion for the ED product is compared with that for a "conventionally" treated product of identical composition which has not undergone the softening-hardening treatment: the latter appears, if anything, to make the pigments more hydrophilic.

active composition						
	Work of adhesion (erg cm ⁻²)					
Composition	Isolated without E.D. temperature cycling	Isolated with E.D. temperature cycling				
Monastral Fast Blue LBX treated with Polypale resin ¹⁷	16.0	16.6				
Monolite Yellow GT treated with Bedesol 11 ¹⁶	14.5	17.5				
Monolite Fast Yellow IOG treated with Dymerex resin	9.9	13.1				
Monolite Fast Yellow IOG treated with calcium salt of Dymerex	11.4	13.1				

Effect of E.D. structure on work of adhesion of water (v. white spirit) to treated pigments of identical composition

Table 1

(NOTE: The completely untreated pigments in the above table give lower values for the work of adhesion (5-6erg cm⁻²), which are, however, not strictly comparable. The significance of the *increased* water-wettability by agents of this type has been discussed¹; their action here is probably a combination of the reduction of hydrophilic aggregation, with an increase in effective oil wettability by virtue of their free energy of solution in the oil).

The technological effects of pigment surface treatments

Spontaneously dispersible pigments

At the present time the four-colour rotogravure printing process is used on the large scale for the production of items such as coloured newspaper supplements, magazines and catalogues, and for coloured advertisement page inserts which appear in the daily Press. A restricted pigment range is used for ink coloration—anilide benzidine yellow (CI Pigment Yellow 12), calcium 4B toner (CI Pigment Red 57), β form phthalocyanine blue (CI Pigment Blue 15) and carbon black. The inks are required to be highly dispersed, of good flow properties to transfer adequately from cylinder to paper, to give good transparency and satisfactory gloss, usually on low quality paper. The scale on which the process is operated by the leading gravure printers involves the preparation and storage of large volumes of ink, and although orthodox powder pigments can be dispersed by ball milling, a simpler, quicker means of ink manufacture brings obvious advantages both organisationally and financially.

The surface treated benzidine yellow previously described can be dispersed in high-speed cavitation mixers in a fraction of the time needed for ball milling the powder quality, see Fig. 6. This is a very large advantage arising directly

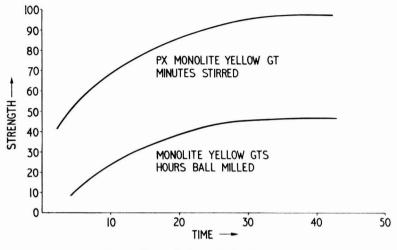


Fig. 6. Rate of strength development

from the surface treatment, but it is by no means the only one. When compared at equal pigment content the ink prepared from the treated pigment is found to be appreciably the stronger, a result arising from the finer particle size of the dispersion. This, however, is only advantageous if the pigment dispersion is de-flocculated, i.e., if there is no interference with the flow properties of the dispersion. That the surface treatment produces this effect also can be seen from an examination of the per cent discharge of mill bases at equal pigmentation levels. See Table 2.

Table 2

Flow properties of treated and untreated benzidine yellows-gravure ink zinc rosinate in SBP3

% Pigment in millbase	••	•••	25	20	15	10	6
% Discharge of millbase							
a) Monolite Yellow GT	• •		0	0	0	6	74
b) PX Monolite Yellow GT			9	50	84	90	92

The transparency and gloss of the ink is also materially improved when the surface treated pigment is used as shown in Fig. 7.

The one surface treatment therefore produces five separate beneficial results —stir-in dispersibility, and superior strength, flow, transparency and gloss compared with powder products.

Flocculation-resistant phthalocyanine blues

Phthalocyanine blue pigments possess such outstanding fastness properties that they are manufactured and used on the large scale throughout the world.

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Some 10 to 15 years ago changes in usage, vehicles, opaque whites and perhaps acceptance standards, led to an increasing incidence of flocculation resulting in unsatisfactory paint performance. For example, an enamel applied by spray and dip failed to produce the same coloured appearance, that from the dipping process being weaker. As a result, flocculation-resistant phthalocyanine blues were introduced and the paint industry's problems became less acute. At this stage, however, the treatments available were relatively unsophisticated and the tinctorial properties of the original pigment were considerably affected in the direction of weakness, greenness, and some loss of brightness.

By use of highly specific surface treatments such as those described earlier, it is possible to confer flocculation resistance without impairing tinctorial properties. In addition to this major advance, the rheology of dispersed systems is also improved. Phthalocyanine blues with their high specific surface area and fine particle size have always been prone to give thixotropic dispersions. In paint applications this has caused little difficulty in finished products because of the low concentrations at which phthalocyanine blues are used. In paint mill bases, however, the pigment concentrations at which stainers could be produced were limited by the need to maintain cascading throughout the milling time, and to avoid undue thixotropy in the stabilised mill base which would lead to difficulty in discharging the mill. The flow properties are so much improved by the surface treatment that pigment loading in mill bases can be increased while obtaining improved discharge from the mill. See Table 3.

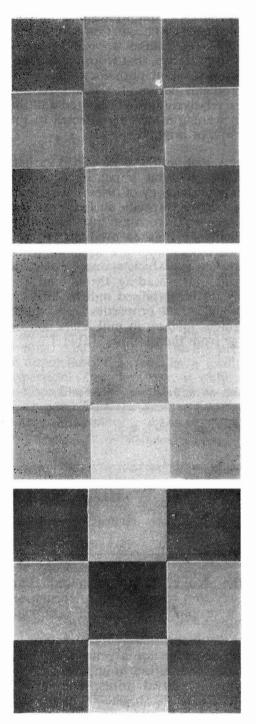
Table 3

Effect of surface treatment of phthalocyanine blues on millbase flow in paint medium

		2.5.5		% Pigment	% 20% resin solution	% Discharge of stabilised millbase
Monastral Fast Blue LBXS	••	•••	••	20	80	15
Monastral Fast Blue FBS	•••	• ••	••	20	80	90
Monastral Fast Blue FBS	•••	• •		25	75	55

In addition, the dispersion properties of the product are also enhanced. Here it is evident that the surface treatment in addition to promoting flocculation resistance is also reducing the degree of hydrophilic aggregation occurring during the pigment drying process. See Fig. 8.

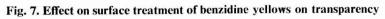
Parallel quality improvements are also observed in liquid printing inks of the gravure type. Flocculation in these systems, in addition to impairing rheology, makes its presence visible in the form of mottled prints. The surface treated product gives greatly reduced mottle, (Fig. 9), together with better dispersion properties (Fig. 10), enhanced mill loading and improved discharge (Table 4).



PX Monolite Yellow GT at equal pigmentation

Monolite Yellow GTS





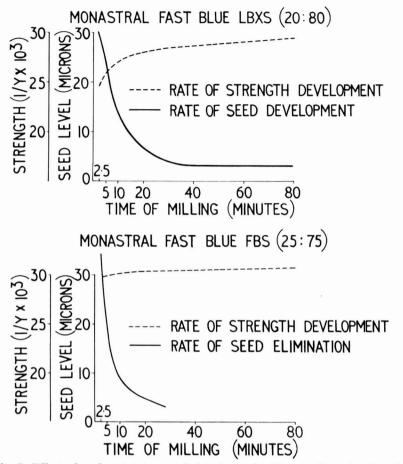
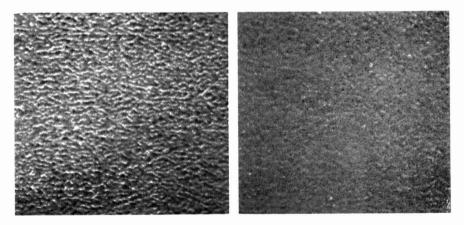


Fig. 8. Effect of surface treatment of phthalocyanine blue on dispersion in paint



Monastral Fast Blue LBXS **Monastral Fast Blue FBS** Fig. 9. Mottling in gravure prints

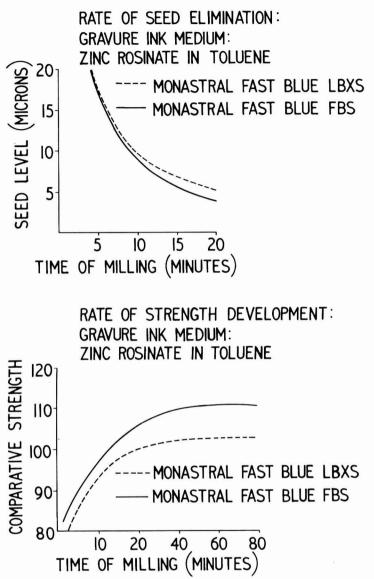


Fig. 10. Effect of surface treatment of phthalocyanine blue on dispersion in gravure ink

Easily Dispersed pigments

Reference has been made to the use of small proportions of compatible resins with pigment dispersions of controlled particle size to produce a structured pigment. Such a product possesses intrinsically excellent dispersibility because hydrophilic aggregation has been virtually eliminated. Penetration of the structure by resin solutions is rapid and complete, solution of the structuring resin component in the vehicle occurs, and normal pigment vehicle adsorption mechanisms produce a stable dispersion. Given time, dispersion can take place without mechanical aid, but this will greatly accelerate the process resulting in 1969 (4)

59 87 92 87 87 87

LBXS rosinate in SBP3 Zinc FBS 85 86 93 93 93 LBXS 0 6 51 51 in toluene rosinate Zinc FBS 555 92 888 92 LBXS 210400 Nitrocellulose ethyl acetate in toluene/ FBS Medium LBXS Polyamide in 1/1 SBP3/ n-propanol FBS 82022 LBXS 26 67 90 90 Bedesol 76 ethanol Ξ FBS 93 95 95 LBXS 004510 Alloprene toluene E FBS 92 88 88 92 92 concentration Mill base

Monastral Fast Blue FBS compared with Monastral Fast Blue LBXS

Flow comparison as percentage mill base yield

Table 4

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uniform dispersions. The proportions of the various components of mill bases is not as critical as when conventional pigments are processed.

It must be stressed that structured pigments can be prepared from all types of organic pigment and those inorganic pigments which do not undergo a final calcination process, and that although conventional forms of different pigments may differ greatly in ease of dispersion, their modification into structured forms results in a great similarity of dispersion properties, i.e. all are easily dispersed.

Because different types of pigments, vehicles and dispersion equipment are used in printing ink and paint manufacture, it is convenient to divide the subsequent discussion to cover the separate industries, but it should be remembered that in principle, i.e. ignoring such specific pigment properties as shade, strength, light fastness and solvent resistance, the structured pigments are equally applicable in both industries.

Printing ink manufacture

The process of dispersion is the key operation in printing ink manufacture during which the tinctorial properties of a coloured pigment are developed and the particle size reduced to a satisfactory level. Since the coloured pigment content and hence the viscosity of the final product are high, machines capable of handling high viscosity materials are used, e.g. dough mixers, Z-blade mixers, vertical change-can mixers, to prepare a base suitable for subsequent dispersion and refining on a three-roll mill. Recent changes in printing have resulted in lower viscosity levels for some inks, and premixing of these products on highspeed cavitation mixers has become possible.

Two procedures are employed in ink manufacture, the "concentrate" process, and the "straight through" process. The first produces high pigment content dispersions which are stored, and later blended with other concentrates and vehicles, to give finished inks at lower pigmentations. Its advantage is chiefly one of flexibility; with concentrates available, finished inks can be prepared rapidly by blending and refining, and concentrates can be manufactured to a prearranged production programme. Against this must be set the cost of storage of concentrates, losses due to skinning, transfer, and from residues, and the frequent necessity to store concentrates of a given pigment in more than one vehicle to minimise subsequent compatibility problems. See upper sequence Fig. 11.

Structured Easily Dispersed pigments can be used in the concentrate process but their dispersion properties are such that they are virtually completely dispersed during the normal premixing operation and require only a loose pass on a three-roll mill, principally to give de-aeration before storage. This is in contrast to the conventional pigments which, dependent on pigment type, will require one to three grind passes at high pressure on a three-roll mill. See lower sequence Fig. 11.

At the stage of ink preparation from concentrates, it is of course possible to blend concentrates prepared from Easily Dispersed pigments and those prepared from conventional pigments.

The straight through process is more suitable for the manufacture of large quantities of ink, particularly where this can be carried out at predetermined 1969 (4)

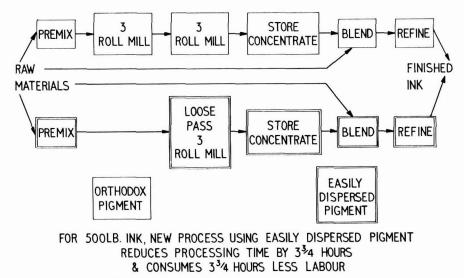


Fig. 11. Ink manufacture—"concentrate" process

intervals. A similar premix followed by three-roll mill dispersion routine is followed, but frequently pigment mixtures are employed and there is less necessity to achieve maximum pigment content. Easily Dispersed pigments are of great value in this process also, the large reduction in the amount of threeroll milling required can result in a total ink production time from basic materials very similar to that obtainable from concentrates. Where blends of easily dispersed and conventional pigments are employed, it is possible to introduce the latter in the form of concentrates by adding these to the premixer prior to the refining operation. See Fig. 12.

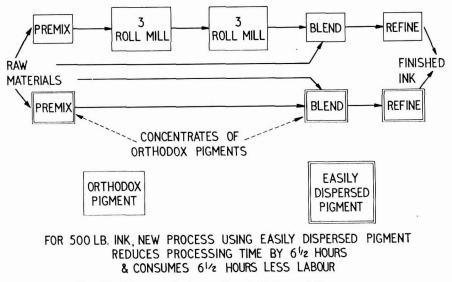


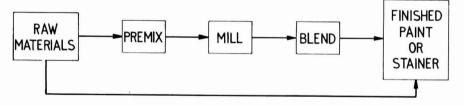
Fig. 12. Ink manufacture-"straight through" process

In considering the application of Easily Dispersed pigments in both methods of ink manufacture, it is apparent that the new products have a direct effect in reducing the cost, machine occupation and labour involved in the operation of three-roll mills, and that this factor alone can have a major effect on manufacturing processes. The fact that Easily Dispersed pigments fit naturally into present ink production methods should not, however, become restrictive. Their introduction should stimulate new thinking concerning manufacturing operations; in particular their ability in the straight through process to provide finished products in a similar time to that presently achieved from concentrates, can bring about a reorganisation of manufacture with subsequent reductions in costs.

Paint manufacture

Although an essentially similar operation to ink making, in that pigments are dispersed in vehicles, the lower viscosity and pigment content of the final paint compared with an ink makes possible the use of a much wider variety of processing methods and machines. A proportion of paint is still manufactured by premixing and three-roll milling, and although this method is declining in importance, the comments pertaining to the use of Easily Dispersed pigments in ink manufacture are directly applicable where similar processing methods are used in paint production.

The manufacture of paint may be illustrated by the flow diagram of Fig. 13.



SIMPLE MIXERS EFFICIENT MIXERS CAVITATION MIXERS PUG MIXERS Z BLADE MIXERS 3 ROLL MILLS SINGLE ROLL MILLS COLLOID MILLS PERL MILLS SAND MILLS

BALL MILLS-ATTRITORS Fig. 13. Paint manufacture

Raw materials such as pigments, resins and solvents are charged to premixers where a wetted homogeneous mixture is produced. This is then milled to give a fully dispersed product which is adjusted in composition by the addition of further resins and solvents to give the final formulation.

The use of pug and Z-blade mixers enables bases for uniroll and three-roll mills to be prepared, and cavitation machines premix the lower viscosity products for dispersion in sand or "Perl" mills; the premixing and dispersion steps are telescoped in ball mills and attritors. Combinations of various types of machines are used, according to the scale of manufacture. 1969 (4) THE SURFACE TREATMENT OF PIGMENTS

No new equipment is needed to exploit the properties of Easily Dispersed pigments in paint manufacture, it is possible to disperse them rapidly and completely in existing machinery, including those types normally only used for premixing conventional pigments. The choice exists either of operating existing processes at much higher rates of output or using non-conventional methods, in practice to disperse the new pigments in mixers.

It is now convenient to discuss in more detail the effects of Easily Dispersed pigments on several paint-making processes.

Ball milling is a widely used dispersion process where, after loading, the mill is left to run for times between 18 and 40 hours. The efficiency of the operation in terms of time required to reach a required degree of dispersion is highly dependent on the maintenance of efficient conditions measured in terms of ball loading, charge to voids ratio, pigment, resin and solvent content of the charge, and recommendations for such conditions have been published¹⁸. With Easily Dispersed pigments, milling conditions are not critical and it is possible to alter conditions considerably to achieve higher pigment loading. For example, the ball loading can be halved (from 55 per cent of mill volume to 27.5 per cent) and the quantity of mill base doubled from 22 per cent of mill volume to 44 per cent.

Under factory conditions dispersion times of 1-3 hours can be achieved with mill sizes from 25 to 100 gallons and the production of two mill loads per day, each at twice normal pigment content, is feasible. A four-fold increase in production can thus be achieved if the normal dispersion time for the orthodox product involves a 24 hour cycle; where longer cycles exist, the production increase is correspondingly higher. With a lower ball content, discharge from the mill is more complete and wear on balls, linings and bearings is reduced. Where it is inconvenient to reduce ball loading it is still possible to increase output when using Easily Dispersed pigments by overloading the mill either in terms of higher charge to voids ratio or increased pigment content of mill base or a combination of these.

For subsequent sand milling, pigments can be premixed in a cavitation or pony mixer and then pumped through the mill at a rate adjusted to give satisfactory dispersion. Some products will require two passes each with an equivalent dwell time of about eight minutes. After a very short premixing period an Easily Dispersed pigment requires only refining by being passed through the sand mill at the maximum rate. In this case, equivalent to a dwell time of about two minutes, a four-fold increase in production rate is attainable.

Three-roll milling has already been mentioned; on the mill itself rate of throughput can be increased about four times because a high output refining pass is used, and the overall factor, including the premixing stage, is two to three.

It is in the use of non-conventional processes that the most striking changes in manufacturing methods can be achieved. Here the aim is to complete the dispersion in a mixer and, if space considerations permit, complete the let down and adjustment stages in the same container so that transfer is avoided. High speed cavitation mixers such as the Torrance, Kady, and Cowles are now widely installed and Easily Dispersed pigments are rapidly processed in these machines. In addition, simpler, cheaper, but still efficient mixers such as the Greaves, Silverson or Ultramix are also capable of carrying out the process. In all these machines mill base formulations are not highly critical, the requisite being that the rolling doughnut flow pattern is produced and maintained. With arylamide yellows which can give thix otropic mill bases, it is better to use fairly high resin solids in the region of 50-60 per cent to maintain flow. With toluidine reds, 30-40 per cent resin solids will give satisfactory results.

In a similar manner it is possible to obtain satisfactory dispersion in premixers, for example, pug mixers. Resin solids here should be high and pigment loading as high as practicable so that shear is transmitted while maintaining flow in order to avoid dead spots.

The advantages arising from the use of Easily Dispersed structured pigments may be summarised as follows:

Reduced processing costs are obtained by using less labour, power and time.

Lower stocks of stainers and finished products are required because processing is faster and more flexible.

Unexpected demands can be met rapidly.

Capital required to make a given quantity of product is lower and production can be expanded without capital expenditure.

In this summarised review of the effects of surface treatment in promoting pigment dispersion, emphasis has been laid on the excellent dispersion properties achieved and the application of the products in existing equipment and processes. It should be remembered that the dispersion properties of pigments have been drastically changed and that the scope and flexibility of dispersion processes available has been enormously widened. The effect of these changes on the efficiency of ink and paint production and the productivity of the industries will be very great.

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Acrylic resins for industrial chemical coatings*

By H. L. Wampner

Reichhold Chemicals, Inc, South San Francisco, California, USA

Summary

A detailed experimental comparison is made of some thermosetting acrylic systems with alkyd-amino, epoxy-amino, polyurethane and unsaturated polyester systems, with particular reference to their utility in industrial chemical coatings. This is followed by a comparable evaluation of some commercially available materials which are also considered in terms of cost. It is not thought realistic to conclude that any one system is "the best"; on the other hand, the data are helpful in indicating the areas in which each is likely to prove most useful.

Key words

Types of coating acrylic coating alkyd coating epoxy coating thermosetting coating urethane finish

Types of surface steel

Binders (resins etc.) amino resin polyester resin

Analysis and testing

processes abrasion test immersion testing impact test mandrel test salt spray testing sward test weathering apparatus weatherometer Properties primarily associated with dried or cured films alkali resistance chemical resistance mar resistance stain resistance

Résines acryliques destinées aux revêtements pour l'industrie de chimie

Résumé

On considère, au point de vue expérimental, quelques systèmes acryliques thermodurcissables en comparaison détaillée de ceux à l'alkyde-amine, polyuréthanne, et polyesters non-saturés, à l'égard particulier de leur utilité en revêtements pour l'industrie de chimie. Ensuite on discute une pareille comparaison de quelques matériaux de commerce et l'on les considère en termes de prix de revient. On n'en juge pas réaliste de conclure si un de ces systèmes soit "le meilleur"; d'autre part, les données sont utiles en indiquant ces applications dont chaque système a la possibilité d'être le plus effectif.

Akrylatharze für Chemikalienbeständige Industrielacke

Zusammenfassung

Zwischen einigen wärmehärtbaren Akrylatharzsystemen mit Alkyd/Aminoharz-, Epoxy/ Aminoharz-, Polyurethan- und ungesättigten Polyesterharz- Systemen werden experimentelle Vergleiche gezogen unter besonderer Berücksichtigung ihrer Brauchbarkeit als chemisch beständige Industrielacke. Daren anschliessend folgt eine vergleichsweise Bewertung einiger im Handel erhältlicher Materialien, die auch vom Kostenstandpunkt aus betrachtet werden. Man ist der Meinung, es sei unrealistisch, den Schluss zu ziehen, dass irgend ein System "das beste" sei, andererseits helfen die Vergleichswerte durch Hinweis auf die Gebiete, in welchen das eine oder andere sich aller Wahrscheinlichkeit nach am zweckmässigsten erweisen dürfte.

*Presented to the Second National Convention, South African Section, Durban, 18-20 October 1968.

Акриловые смолы для промышленных химических покрытий

Резюме

Делается подробное экспериментальное сравнение некоторых термореактивных акриловых систем с алкидо-аминовыми, эпокси-аминовыми, полиуретановыми и ненасыщенными полиэфирными системами, ссылаясь в частности на их полезность для промышленных химических покрытий. За этим следует сравнительная оценка некоторых коммерчески доступных материалов, которые также рассматриваются с точки зрения стоимости. Считается нереалистичным сделать заключение что какая либо одна из этих систем является «наилучшей», но тем не менее вышеупомянутые данные весьма полезны, так как они указывают области в которых каждая из этих систем может оказаться наиболее практичной.

Introduction

It has become customary to refer not only to acrylic ester polymers as "acrylic resins" but also to include methacrylic derivatives in this terminology. Of these, methyl methacrylate is the chief constituent of many of the commercial acrylic resins, although in some cases it is present merely as a modifier for other acrylic and non-acrylic constituents. Such other non-acrylic materials can be alkyd resins, styrene, vinyl toluene and other vinyl-type polymerisable materials.

Thermoplastic acrylic lacquers find their chief use in the automotive field, where they are frequently modified with cellulosic derivatives to improve their resistance to solvents and to cut down on their thermoplasticity. There is, however, also a substantial market for such resins in miscellaneous industrial uses. They contribute exceptional durability to nitrocellulose lacquers. Some of them are used as the sole vehicle in metallised aerosol finishes and in fluorescent coatings. Resins of this type can be made which are compatible with vinyl chloride copolymers, with chlorinated rubber and with cellulose acetate butyrate. In addition, such thermoplastic resins can be used as modifiers for the thermosetting acrylics.

A substantial market, which is making headway at present, is in the seamless flooring field. Here a solution of a thermoplastic resin is used as the binder for pigmented polyvinyl acetate chips to give a decorative flooring. Its chief advantage over the moisture-curing urethanes is freedom from yellowing. The disadvantages are slower film build and somewhat poorer abrasion resistance. However, if the floor does begin to show a traffic pattern, it can be given a good scrubbing and then one or more additional coats of acrylic lacquer.

Clear finishes of thermoplastic acrylics are also being used to renew the appearance of weathered polyester-fibreglass panels. After years of exposure, the glass fibres frequently appear on the surface of such panels and, if left uncoated, serve as a point of further deterioration by wicking moisture into the panel itself. A spray or brush coat of acrylic lacquer seals the surface, restores the glossy appearance, and brings back colour by giving a continuous film.

It is possible, by selecting monomers, to make thermoplastic copolymers over a broad range of flexibility. Unfortunately, those polymers which are hard enough to have the required mar resistance are generally too brittle for use without a plasticiser and, when plasticisers are used, embrittlement on ageing frequently occurs because of plasticiser evaporation or migration.

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The acrylics which are chiefly used in the industrial field are of the thermosetting type. It is with these that this paper will be mainly concerned.

Thermosetting acrylics

The thermosetting characteristic is contributed to acrylic resins by incorporating therein functional groups which remain unreacted during initial resin formation, but which can be cross-linked with di- or polyfunctional molecules during film formation. Examples of mechanisms covered in some of the numerous patents in this field are as follows.

- 1. Carboxylic acid groups in the polymer supplied by copolymers of acrylic or methacrylic acid with other monomers are cross-linked with:
 - (a) di-epoxides (CIL and du Pont),
 - (b) amino resins (CIL and du Pont and Devoe and Raynolds),
 - (c) polyols (du Pont).
- 2. Hydroxyl groups on polymers are supplied by use of hydroxyethyl (American Cyanamid) or hydroxypropyl acrylates (Rohm & Haas) or methacrylates or allyl alcohol (Monsanto) or allyl oxyethanol (Interchemical). These are cross-linked with amino resins or polyanhydrides (Firestone).
- 3. Amide groups are supplied by methacrylamide or acrylamide copolymers with other monomers and are cross-linked with di-epoxides or reacted with formaldehyde and cross-linked through the methylol groups or with added amino resin (PPG).
- 4. Amino functional groups, supplied by use of aminoethyl acrylate or methacrylate compounds, cured with di-epoxides (Rohm & Haas).
- 5. Epoxide functional groups provided by glycidyl acrylate or methacrylate copolymerised with other monomers and cross-linked with polyamines (du Pont).
- 6. Hydroxyl groups and carboxyl groups provided by alkyd resins copolymerised with monomers and cross-linked with melamine resins (RCI). Further modified with epoxy resins in some cases.

The acrylic modified alkyd resins would parallel, in some cases, the styrenated or vinyl toluenated alkyds used in quite large quantities in industry for fast drying finishes. Their durability on exposure, however, is outstandingly superior.

While some acrylic resins of the thermosetting type are used in the automotive field, possibly their chief outlet is in the appliance and related market. Here they would fall under the broad definition of chemical coatings, which are materials designed for a specific end use and to meet certain specific resistance requirements. In this field, they are, of course, competitive with other materials vying for the same market. The industrial acrylics should therefore be considered in relationship to such other finishes.

Industrial chemical coatings

The tests which have been used for evaluating the performance of these finishes are as follows:

gloss	iodine stain
colour comparison	falling sand abrasion
Sward hardness mar resistance	acetone resistance
caustic soda—24hr Mazola-oleic acid—48hr	impact resistance—direct and reverse conical mandrel
5% acetic acid—24hr	salt spray
mustard staining—24hr	humidity
Clorox resistance—48hr	weatherometer

Fourteen systems which would be representative of the bulk of the industrial work being done in the field were selected as base vehicles for enamels. No allowances were made for possible weaknesses of a given resin type and the amine resin modification level was arbitrary but consistent with normal recommendations. These fourteen enamel systems are listed below.

- 1. Short soya alkyd with 25 per cent urea.
- 2. Short coconut alkyd with 25 per cent urea.
- 3. Short coconut alkyd with 15 per cent melamine.
- 4. Short dehydrated castor oil alkyd with 25 per cent urea.
- 5. Medium soya alkyd with 25 per cent urea.
- 6. Rosin modified soya alkyd with 10 per cent urea.
- 7. Phenol modified tall oil alkyd with 10 per cent urea.
- 8. Acrylic modified alkyd with 10 per cent melamine.
- 9. Soya epoxy ester with 25 per cent urea.
- 10. Pure epoxy with 30 per cent urea.
- 11. Solvent-soluble thermosetting acrylic.
- 12. Water-soluble thermosetting acrylic.
- 13. Two-component polyurethane.
- 14. Peroxide-cured unsaturated polyester.

The first 12 are baking finishes and were compared at three temperatures: 250°, 300°, and 350°F. All the bakes were 30 minutes and, as a consequence, they are not equivalent. Enamels No. 13 and 14 are catalysed systems and consequently were not baked. All the enamels were held as close to the same basic formula as possible in order to minimise differences introduced by changing pigmentation. As a result, enamels no. 1 to 13 had about a 16.7 pigment volume concentration, although enamel no. 12 and 13 did vary for total solids. Enamel no. 14 required a much higher vehicle content, consequently had a very low PVC which is usual with this type of material.

The basic enamel formulations are given in Table 1.

These enamels were to be applied over both bare steel and Spra-Bonderite 100 panels, but it was felt they should also be applied over primed and unprimed surfaces. As a result, a standard epoxy ester primer-surfacer was selected to be used as the primer under all systems where primer was used. Unfortunately,

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this particular primer was a little higher in PVC than it should have been, which showed up in the humidity test and Tide test. The formula for the primer used is given in Table 2.

**************************************	No. 1-11	No. 12	No. 13	No. 14
Non-chalking titanium dioxide Total resin solids Solvents and additives	 200.0 277.0 375.0	200.0 277.0 752.0	200.0 277.0 212.0	31.0 277.0 2.5
% Total non-volatile % Pigment on non-volatile % Vehicle solids % Pigment volume concentration	 56.0 42.0 42.5	39.0 42.0 27.0 16.7 Av.	69.6 42.0 56.7	100.0 15.0 100.0 3.0

Basic	enamel	formulations	

Table 2
Primer formulation

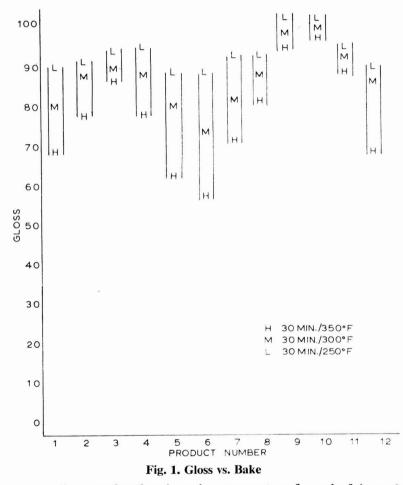
								lb/100gal
								, .
Titanium dic	oxide	•••	••	••				75.0
Barytes	• •					••	• •	361.0
Bentone 34								4.0
Ethanol								1.5
Soya epoxy	ester (5	0% N	V in x	vlol)				88.0
Lignocol					•••	•••		1.5
Xylol								41.0
VM & P nag								50.0
vin a r naj	Jinna	••	••		• •	••	••	50.0
Steel ball mi Soya epoxy	10.00		. , .					
								265.0
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Urea-formal SC-100	dehyde	resin					 .nol) 	20.0 25.0
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Urea-formal SC-100 Xylol VM & P nag 6% Cobalt r	dehyde phtha naphthe	resin 	(60%) 	NV ii 	n ethan 	iol-buta 		20.0 25.0 30.0 210.0
Urea-formal SC-100 Xylol VM & P naj	dehyde phtha naphthe	resin 	(60% 	NÝ in 	n ethan 	iol-buta 	 	20.0 25.0 30.0 210.0 1.7
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Urea-formal SC-100 Xylol VM & P naj 6% Cobalt r 24% Lead n % Non-vola % Pigment of	dehyde phtha naphthe aphthe tile on non- volume	resin enate nate -volati	(60 % 	NÝ ii 	n ethan 	iol-buta 53.5 69.9	 	20.0 25.0 30.0 210.0 1.7

The film thickness of all systems was closely controlled to hold variation to the minimum. On enamels no. 1 to no. 12 the film thickness could be held between 1.2 and 1.3 mils and, where a primer was used, the film thickness of the primer was about the same—1.2 to 1.3 mils. On enamel no. 13 the average film thickness was 1.5 mils without the primer; where the primer was used it was 1.2 to 1.3 mils. On enamel no. 14 the topcoat film thickness was about 5 mils with the normal difference of 1.2 to 1.3 mils where primer was used.

Evaluation results are summarised in Figs. 1-3 and Tables 3-5.

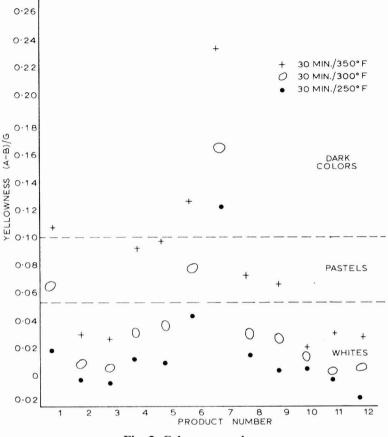
Fig. 1, showing the gloss of each enamel at low, medium and high bake, is self-explanatory. Nos. 3, 10 and 11 showed excellent gloss retention on baking. The remarkable failure of no. 12 is attributed to exudation of surfactant at the higher temperatures.

It should be noted that a difference in yellowness of ca 0.01 unit on the ordinate of Fig. 2 represents about the threshold for discernible difference by eye. Yellowness values up to 0.05 seem to be acceptable in white enamels, and up to 0.1 will not cause serious trouble in light pastel shades.



The gloss readings are plotted at the various temperatures for each of the products

The outstanding materials in this comparison were no. 11, the heat converting acrylic, and no. 3, the coconut-alkyd-melamine combination. Another interesting point is the difference between the no. 3 and the no. 2 which represents the difference between melamine and urea. Also note no. 7 which is too dark for anything but dark colours, being a phenolated alkyd. In general, the presence of drying oil is also detrimental at the higher bakes.

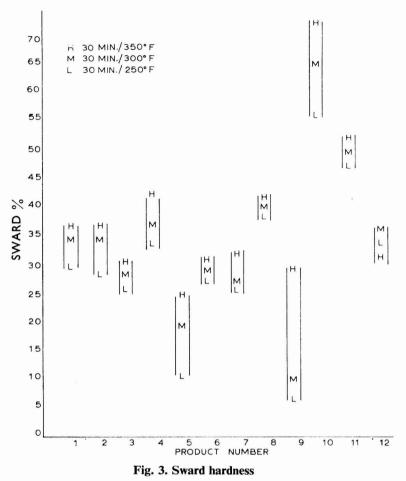




A comparison of the no. 2 enamel with the no. 3 enamel shows that the 15 per cent level of melamine was not quite as effective as the 25 per cent level of urea. A comparison of no. 5 and no. 1 shows the effect of the longer oil alkyd in no. 5. It is quite evident that the no. 9 film needed a minimum of 350° F in order to produce adequate hardness and the no. 10 film was very hard but other data indicates that the film was not cured. Here the exudation of surfactant in enamel no. 12 is quite evident by the lowest hardness reading at the highest bake.

Table 3 shows that mar resistance of all the films improved as the bake increased, except for no. 12 which again showed the effect of surfactant exudation. No. 9, the epoxy ester, is of interest because it changed from poor to very good, indicating that the 350°F bake is desirable. Also no. 10 changed from poor to good, indicating a minimum of 350°F, and no. 11 from fair to very good when the threshold of 300°F was reached. Of the alkyds, no. 7, the phenolated alkyd, was the poorest for mar resistance.

The alkali resistance chart (Table 4) shows the pure epoxy and the solvent based acrylic to be outstanding. The epoxy ester and the acrylic alkyd-melamine



combination, no. 8, look quite good. The polyurethane is very good and no. 14, the polyester, while it shows a low reading due to dulling, was not in any sense destroyed by the caustic.

For Mazola-oleic acid resistance (Table 5) all films showed a modest improvement as the bake was increased. In this test the ratio of Mazola to oleic acid was 1:1. The polyester (no. 14), the polyurethane (no. 13), the pure epoxy (no. 10), the short soya (no. 1), and the short dehydrated castor (no. 4) were excellent. Resin modified alkyds did not fair so well. In this test, the lack of cure on no. 9 and no. 11 at the lower bakes is clearly evident.

From Table 6, showing resistance to acetic acid, it is again seen that the increase in the bake improves the resistance. It will be noted that the polyester, the acrylic alkyd-melamine combination (no. 8), and the heat converting acrylic are again outstanding.

On mustard staining (Table 7), the stain tends to disappear or fade as the panel ages after it has been wiped off. The polyester and the solvent-based

1909	(4)	ACRYLIC	RESINS	FOR	INDUSTRIAL	CHEMICAL	CUA	INGS	51
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ng: 10=No effect 1=Complete failure acrylic seemed to be the best with the acrylic alkyd-melamine combination a close second.

In the Clorox spot test (Table 8) it was interesting to note that the polyurethane and everything with epoxy showed a distinct yellowing. The author has noted that as low as 5 per cent epoxy added to an acrylic system will give yellowing in this Clorox test.

For iodine staining (Table 9) the only outstanding film was no. 11, the converting acrylic solution. Again a bake of at least 300°F is indicated.

Falling sand abrasion is recorded in Table 10 as litres per mil of film. The polyurethane was outstanding, as was the polyester, and as might be expected from some of the other tests, the epoxy ester was very good. Also it is interesting to note the values tend to drop from the low bake to the high bake, indicating that as the film becomes harder it also becomes more brittle.

Table 11, detailing acetone resistance clearly shows that the pure epoxy, no. 10, was not cured at the two low bakes, and even the 30min at 350°F bake is questionable. As might be expected, the thermoplastic acrylic alkyd-melamine combination, no. 8, was moderately poor.

The Tide immersion test (Table 12) showed the phenolated alkyd to be very good. The use of the primer in this test tends to increase the resistance about 24 hours on the average. No. 2 and no. 4 are exceptions in that they improve further. The pure epoxy and the solvent based acrylic seem to be outstanding. The polyurethane was outstanding where the primer was available to provide proper adhesion.

On direct impact (Table 13) both cold rolled steel and Spra-Bonderite 100 panels were tested. The cold rolled steel panels were 24 gauge and the Bonderite panels were 20 gauge. On the cold rolled, in general, the unprimed steel were better than the primed and it will be seen that in general the bonderised panels were better than the cold rolled steel. The alkyds, the epoxy ester, and the polyurethane seemed to give the best results.

The comments made for direct impact can be made with regard to reverse impact recorded in Table 14, except that in this case the Bonderite was not superior to the cold rolled steel. In general, the unprimed were better than the primed panels and again the alkyds, the epoxy ester, and the polyurethane seemed to be the best. There is reason to question whether or not this type of bonderised surface should be used for all of the films involved.

On the conical mandrel test (Table 15), the alkyds, specifically the castor alkyd and the medium oil soya alkyd, and the epoxy ester seem to have performed the best on the unprimed bonderised surface. The same general pattern is observed on the primed surface, and here, of course, the polyurethane did extremely well.

It will be seen from Table 16 that, on the cold-rolled unprimed surface, more than a resin is needed to get good salt spray results over bare steel. In this particular instance the pigmentation is too low to be of any assistance on salt spray resistance. It is interesting to note that pure epoxy at the high bake and, to a lesser extent, the heat converting acrylic were the only two that seemed

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Table 6

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Table 9 staining. S	5	ν N N N		Table 10 Id abrasion	5	20 20 20	Table 11 resistance.	5	226	-
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	12	24 88 88	24 48 96	
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tance-	5	09 00 09 00	00 00 00	0000	0000	
ıct resis	4	888	505	0000	60 60 60 60 60 60 60 60 60 60 60 60 60 6	
Impo	3	6 44	505 50 50	0900	444 404	lb
	2	242	10 20 10	60 60 60	44 4 4 4 4	at 60, 40, 20 and 10in lb
	1	09 09 09	2420 2420	0900	40 60 40	40, 20 al
		:::	:::	:::	:::	
	Product No.	Cold rolled—unprimed 30min/250°F 30min/300°F	Cold rolled—primed 30min/250°F 30min/300°F 30min/350°F	Bonderised—unprimed 30min/250°F 30min/300°F 30min/350°F	Bonderised—primed 30min/250°F	Direct impact checked

1% Tide immersion at 165°F. Hours to failure Table 12

				Impuci	nicical	וורבוב	unpuct resistance-reverse inch pounds	cu poun	SU						
Product No.			5	3	4	5	9	7	∞	6	10	11	12	13	14
Cold rolled—unprimed														Ň	3
30min/250°F 30min/300°F 30min/350°F		2002	∧ ∧ ∧ 4 4 4	0144	010 4	500	∧ ∧ ∧ 4 4 4	\land \land \land 4 4 4	\land \land \land 4 4 4	555	$\begin{smallmatrix} \wedge & \wedge \\ 4 & 4 & 4 \end{smallmatrix}$	\land \land \land 4 4 4	∧ ∧ ∧ 4 4 4	t	+ √
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30min/250°F 30min/300°F 30min/350°F		∧ ∧ ∧ 4 4 4	∧ ∧ ∧ 4 4 4	\land \land \land 4 4 4	$\begin{pmatrix} \wedge & \wedge \\ 4 & 4 & 4 \end{pmatrix}$	10 20	\land \land \land 4 4 4	∧ ∧ ∧ 4 4 4	$\stackrel{\wedge}{}_{444}$	888	\land \land \land 4 4 4	$\begin{smallmatrix} \wedge \land \land \\ 4 4 4 \end{smallmatrix}$	\land \land \land 4 4 4	07	4
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Bonderised—primed														Ű,	1
30min/250°F 30min/300°F 30min/350°F		∧ ∧ ∧ 4 4 4	∧ ∧ ∧ 4 4 4	$\stackrel{\wedge}{4} \stackrel{\wedge}{4} \stackrel{\wedge}{4}$	$\land \land \land$ 4 4 4	444	\land \land \land 4 4 4	∧ ∧ ∧ 4 4 4	$\land \land \land$ 4 4 4	500	$\land \land \land$ 4 4 4	$\land \land \land$ 4 4 4	∧ ∧ ∧ 4 4 4	07	1 /
Reverse impact checked at 2	0, 10	20, 10 and 4in lb	n lb	-											

Impact resistance—reverse inch pounds

Table 14

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	14	-	-	-	-	-	-	+	-
	13	v	C	0	10	0	10	0	21
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lameter	7		$\infty \infty \infty$				444		L44
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	3		1001		10 8 8		10 10		10 10 9
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	Product No.	Cold rolled—unprimed	30min/250°F 30min/300°F 30min/350°F	Cold rolled—primed	30min/250°F 30min/300°F 30min/350°F	Bonderised—unprimed	30min/250°F 30min/300°F 30min/350°F	Bonderised—primed	30min/250°F 30min/300°F 30min/350°F

Table 15 Idvel 1 to 3 in 1

to hold up. On the cold-rolled surface, using a primer increased the performance by three to five times in general. No. 13 and 14, where poor adhesion was the basic reason of failure unprimed, showed an even greater improvement when primed. The low bakes on no. 9 and 10 failed by dulling at 24 hours because of lack of cure of the film. By comparison with the cold rolled surface, the bonderised unprimed gave excellent salt spray resistance and where primer was used life was extended by about the same number of hours as it was on the cold rolled steel. The percentage increase is not as large because of the better performance over-all. No. 9 at the high bake was particularly good.

On humidity resistance (Table 17) over a cold rolled steel surface, it is interesting to note that the primer improved the performance by 72 to 120 hours, about the same as on salt spray. No. 10, the pure epoxy, no. 11, the heat converting acrylic, and no. 12, the water base acrylic, had outstanding humidity resistance at the 350°F bake on the unprimed panels. On the bonderised surfaces the improvement was very much parallel to improvement shown on the salt spray test, although the time to initial failure took longer. Another interesting point on the humidity resistance is that primer was of no particular help at the higher bakes.

The weatherometer results of Table 18 show that there was a gradual reduction in gloss up to 500 hours, but enamels no. 7, 12, 13 and 14 showed a much greater loss after 250 hours of exposure.

Comparison of commercial acrylics

There were only three acrylic finishes in the foregoing series, and a question might be raised as to whether these were representative of thermosetting acrylic resins in general. Work of the same type was therefore repeated using resins of seven different manufacturers and representing several different methods of cross-linking. A descriptive list of the vehicles, which were all pigmented with 42 per cent non-chalking titanium dioxide, as in the previous test, is as follows:

а.	carboxylic activated-me	elamine ad	duct			100%
<i>b</i> .	carboxylic activated-ep	oxy-melan	nine			65:28:7
с.	alkyd acrylic-melamine		• •			94:6
d.	alkyd acrylic-melamine		• •			87.5:12.5
е.	carboxylic activated-me	elamine	••		••	100%
f.	carboxylic activated-me	elamine			••	100%
g.	carboxylic activated-me	elamine			••	100%
h.	? (carboxylic suspected))-epoxy	• •			60:40
i.	? (carboxylic suspected))-epoxy				60:40
<i>j</i> .	short oil coconut alkyd	l-melamine	e (con	trol)		70:30
k.	carboxylic activated-ep	oxy-melan	nine			72:14:14
<i>l</i> .	unknown system		•••			100%
m.	carboxylic activated-ep	oxy-melan	nine			88:10:2
n.	unknown system					100%
0.	unknown system	••		• •		100%

Product No.	1	7	ю	4	S	9	7	8	6	10	11	12	13	14
Cold rolled-unprimed													5	5
30min/250°F 30min/300°F 30min/350°F	224 244 244	244 244	244 24	24 84 84	24 24 24 24	24 24 24	244 244	224 24 44	24 84	24 168 240	55 55 57 57 57 57 57 57 57 57 57 57 57 5	244 244	t 7	+7
Cold rolled-primed													504	216
30min/250°F 30min/300°F 30min/350°F	120 120	72 77 72	525 525	222	120 120	120 120	120 120	240 120 120	168 72 120	168 120 240	120 120 240	72 120 240	100	000
Bonderised-unprimed													504	071
30min/250°F 30min/300°F 30min/350°F	504 504 504	504 504 504	240 504 504	504 504 504	504 504 504	504 504 504	504 504	504 504 504	336 504 504	336 336 504	504 504 504	168 240 240	1 00	001
Bonderised-primed													-	4
30min/250°F 30min/300°F 30min/350°F	009 009 009	00000	00000	000 009 009	000 009 009	8 9++	000000	0 0+00	$^{312}_{++32}$	00000	600 600 600	216 504 600	ŀ	F
+ = Over 600 hours	_													

Salt spray resistance. Hours to failure Table 16

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12 13 14	144			144 144		144 504 +		141 +++
=		312 504 +		408 408 408		++++		5 0+++
10		$^{1}_{44}$		216 504		441 + 441		504 + 1
6		144 312 312		144 504 408		144 504		$\frac{1}{4}$ + +-
∞		312 408 408		408 408 408		+ + +		504 504 504
2		504 504 504	•	408 504		+++		504 +
9		312 408 408		504 504 +		5 04 ++		+ 5 +
5		312 408 312		504 +		5 04		5 04 + +
4	÷	144 216 312		144 408 504		5 04 + +		504 504
3		144 144 312		504 504 504		408		504 504 504
5		144 144 216		216 504 504		$\frac{1}{4}$ ++		504 + +
		144 312 312		144 504 504		504		504 +
Product No.	Cold rolled-unprimed	30min/250°F 30min/300°F 30min/350°F	Cold rolled-primed	30min/250 ⁵ F 30min/300 ⁵ F	Bonderised-unprimed	30min/250°F	Bonderised-primed	30min/250°F
	Cold r	30min/ 30min/ 30min/	Cold ra	30min 30min/ 30min/	Bonder	30min/ 30min/ 30min/	Bonder	30min/ 30min/ 30min/

Humidity resistance. Hours to failure Table 17

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+ = 0 ver 504 hours

Table 18 Weatherometer exposure

6 7 8 9 10 11 12 13 14	16 56 16 56 66 66 66 66 66 66 66 66 66 66 66 66	56 68 83 95 100+ 88 83 55 68 81 95 100+ 88 83 60 60 75 90 86 85 69 58 17 70 86 70 82 43	58 70 90 100+ 85 71 70 90 100+ 85 49 67 84 97 82 14 59 80 84 97 82
=	93 93 86		
10	100 94 61	100+86	100+100+
6	99 96 92	95 90 86	90 84 80
8	87 85 79 72	83 81 75 70	70 59 59
7	86 86 65 16	68 60 17	58 71 14
. 9	77 75 79 73	56 55 58	37 37 49
S	85 77 68	70 66 64	52 53 53
4	93 88 84 88	80 80 79 79	70 75 75
3	89 86 77 71	83 81 75 71	75 75 69 65
7	91 90 83 76	81 81 77 73	67 69 66
-	88 85 80 80 80	80 77 77	63 66 70
	::::	::::	::::
to.	::::	::::	::::
Product No.	250°F 	300°F 	350°F
Pro	Bake 30min/250°F Gloss— Initial 100hr 250hr 500hr	Bake 30min/300°F Gloss— Initial 100hr 250hr 500hr	Bake 30min/350 [°] F Gloss— Initial 100hr 250hr 500hr

$\begin{array}{cccccccccccccccccccccccccccccccccccc$
E F F G G F F F E E F F E F E F E F E F

Table 19 norv._commercial resins In each of the foregoing vehicle combinations, the recommendations contained in the manufacturer's literature was followed with regard to the amount and type of resin used to cross-link the acrylic. An alkyd-melamine combination was included as a control. As a further cross-reference between these two series, vehicle a in this series is the same as vehicle 11 in the previous set.

While mandrel, impact, Tide immersion, salt spray and humidity tests were run on unprimed and primed cold-rolled steel and bonderised steel surfaces for many of the systems, the results reported here are only for unprimed Spra-Bonderite 100 panels. Films were sprayed to a dry film thickness of 1.0-1.2 mils. A summary only of the data is given in Table 19. In explanation, the earlier tests were run at bakes of 30 minutes at 250° F and 30 minutes at 300° F; later tests were also checked at a 30 minute at 350° F bake. For some enamels and for some tests, no appreciable change in properties was evident between the low bake and the high bake; thus only one rating is given in those instances. Where a change occurred, the rating at the lower bake is given followed by a solidus, then the rating at the higher bake.

Florida exposure

Contrary to the commonly-held belief, the mere fact that a resin contains acrylic does not ensure excellent gloss retention or even good gloss retention. It will be noted that none of these thermoset acrylic systems were as good as the control coconut alkyd-melamine system which is representative of Ford and Chrysler body enamel quality from 1959 to 1964. On 18 months 45° South Florida exposure, no failure by checking or cracking was evident. There was considerable loss of gloss, slight to moderate chalking, and, in the case of epoxy-containing systems, yellowing.

The only system that was close to the coconut alkyd-melamine system was enamel d, which was the high melamine modification of the alkyd modified acrylic. The current Ford and Chrysler specifications do not allow alkyd modification.

Conclusions on commercial acrylics

From examination of the data, it becomes evident that there is no single resin or resin system that is superior for every test condition; in fact, every system is rated poor in at least one category. Each system has a grouping of good properties that would make it suitable for a particular industrial application. The selection of the resin system for a given end use would be dependent then upon the specific resistance, flexibility, durability or other property, or combination of properties, required for the application.

Acrylics vs polyesters ("oil-free alkyds")

A new type of resin was introduced at about the time the previously reported experiments were being conducted. These were polyesters or oil-free alkyd resins. While primarily intended for use where exterior durability was a prime consideration, their potential use in the appliance field was also considered by subjecting them, in comparison to acrylics, to the same series of resistance tests. The systems examined were as follows:

а.	carboxylic activate	ed-mela	mine a	dduct	• •	 100%
	carboxylic activat	ed-epox	y-mela	mine		 65:28:7
c.	alkyd acrylic	• •	••	••	••	 100%

	alkyd acrylic-melamine	••			 85:15
е.	polyester A-melamine				 80:20
f.	polyester B-melamine		· •		 80:20
g.	polyester A-polyester B-r	nelamir	ie	•••	 40:40:20
h.	polyester A-melamine	• •			 70:30
i.	polyester B-melamine		••		 70:30

As before, the vehicles were pigmented with non-chalking titanium dioxide, and applied over the same white primer. All the enamels were baked for 30 minutes at 300° F.

The results obtained are shown in Table 20. The greater resistance of the polyester finishes to mechanical damage is apparent. Modification of the acrylic with either epoxy or alkyd resin improves resistance to mechanical damage. Acrylics and polyesters appear to rate about equally in resistance to

	-				285			EC	
Resin	a	b	с	d	е	f	g	h	i
Sward hardness % Falling sand abrasion	46	28	18	36	24	54	42	54	76
litres/mil	15	18	20	21	36	28	33	31	37
Direct in lb	30	60 + 20	60 + 20	60 +	60+	30	60 +	60 +	30
Reverse in lb Conical mandrel* $\frac{1}{8}$ in to	<10	30	30	10	60+	<10	30	10	<10
³ / ₄ in dia 5% NaOH Resistance,*	1	10	8	1	8	6	8	3	1
spot test	10	10	10	10	10	10	10	10	10
24hr 48hr	10	10 10	10 10	10 10	10 10	10 10	10 10	10 10	10 10
5% Acetic acid resist- ance,* spot test									
24hr	10	10 7	1	10	8	10	10	10	10
48hr $1%$ Tide immersion,	10	1		1	1	10	7	10	10
hours to failure at 165°F	96+	96+	48	96 +-	24	48	24	72	96
5% Salt spray, hours to	500+	500+	144	144	216	264		. –	
100% Relative humidity*	10^{-500+}	10	10	10	7	264	264 5	264 10	264 10
Iodine staining, spot test* initial	7	5	3	3	1	1	1	3	3
96hr recovery Original gloss, 60°, 30min/	9	7	3 5	5	3	3	3	5	5
300°F	94	93	94	96	97	97	97	96	97
Gloss on overbake, 60° , $4hr/450^{\circ}F$	30	62	44	33	75	79	79	75	85
Degree of yellowing Mazola-oleic acid resist-	.3408	.5812	.3310	.2875	.1003	.0889	.0736	.1031	.0901
ance,* 48hr	9	6	6	7	9	10	9	9	10
Mustard staining,* 24hr Acetone resistance,* 1hr	9 10	8 10	7 1	8	7 1	9 1	8 1	8 1	9 1

 Table 20

 Comparison of commercial acrylics with polyesters (oil-free alkyds)

*Rating 10=no effect 1=complete failure

5 per cent NaOH, 5 per cent acetic acid, fats and mustard but the results for acetone immersion indicate that melamine modification *per se* is no sure cure. The way in which the melamine is reacted into the cured film may be relevant here. The acrylics show distinct superiority in resistance to salt spray and humidity, though it may be presumed that the performance of the polyesters could be improved by the use of a more resistant primer with a lower level of pigmentation. The superior gloss and colour retention on overbake of the polyesters is clearly seen, as is the contribution of epoxies to yellowing.

Effect of pigment level on gloss retention

In the previous series the poor gloss retention of the acrylics was noted. It should be remembered that the pigment level used was that most generally found in appliance finishes where exterior durability is generally not a factor. However, to see how finishes pigmented at different levels would behave on exposure, the following three vehicle systems were each pigmented with a non-chalking titanium dioxide at levels of 30 per cent, 35 per cent, 40 per cent and 45 per cent of the total non-volatile:

а.	hydroxy activated-melamine	••			75:25
<i>b</i> .	polyester A-melamine		••		80:20
с.	short coconut alkyd-melamine		••	••	75:25

Enamels were sprayed on epoxy ester primed panels and baked 30min/300°F. Results are given in Table 21.

From the Florida exposure, it is obvious that the pigment level is a very important factor in the gloss retention of acrylic resins. It has practically no effect on the gloss retention of polyesters and only a moderate effect when a coconut oil alkyd-melamine combination is used.

It may well be that the performance of the acrylics would be improved if one of the newer chloride process titanium dioxides had been used in these studies.

Costs

Having gone through the complete series of tests, the story is incomplete without some knowledge of relative costs. The following figures are the vehicle cost at 50 per cent non-volatile to deposit a 1mil film on 1,000sq ft of surface. (This is equivalent to approximately 1.2mil of pigmented films.) July 1968 price lists, USA, West Coast, were used.

		\$
1. Short soya alkyd with 25% urea		2.42
2. Short coconut alkyd with 25% urea		2.59
3. Short coconut alkyd with 15% melamine		2.80
4. Short dehydrated castor oil alkyd with 25% urea	••	2.91
5. Medium soya alkyd with 25% urea		2.22
6. Rosin modified soya alkyd with 10% urea		2.18
7. Phenol modified tall alkyd with 10% urea		2.18
8. Acrylic modified alkyd with 10% melamine		3.05
9. Soya epoxy ester with 25% urea		3.27

Vehicle			a	a	a	а	9	9	9	9	c	0	c	c
% Pigment on non-volatile	:	:	30	35	40	45	30	35	40	45	30	35	40	45
% Sward	:	:	42	40	4	4	22	20	22	22	4	44	4	46
Original 60° gloss	:	:	92	92	90	90	96	95	100	100	96	95	94	92
18 months unwashed	:	:	51	33	27	16	88	87	85	81	46	44	36	34
18 months washed	:	:	51	35	27	16	86	95	94	96	45	45	41	33
		-		-	-			-						

 Table 21

 Effect of pigmentation level on durability

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1969 (4)	ACRYLIC RESINS FOR INDUSTRIAL CHEM	MICAI	COATI	NGS
10.	Pure epoxy with 30% urea	••		3.41
	Solvent soluble thermosetting acrylic	••		3.27
	Water soluble thermosetting acrylic	••		5.45
	Two-component polyurethane	• •		3.70
14.	Peroxide-cured unsaturated polyester			1.60
	Hydroxy activated acrylic-melamine	• •		3.54
	Polyester A-melamine			3.63
	Acrylic modified alkyd			3.06
18.	Styrenated alkyd	•••	• •	2.31

These are average figures which are reasonably accurate. One thing should be borne in mind with the low cost of No. 14, which appears the cheapest of all, is that at less than 3mil this film is inadequate. Consequently, it is not a true cost of a serviceable film.

No attempt is made to draw conclusions as to which film is best. The purpose of this paper has been to orient all of these raw materials and to attempt to show where each has its usefulness. In this, economics has a definite place and it should be recognised that it is possible to over-engineer a finish.

Acknowledgment

The author wishes to pay special tribute to the RCI Service Laboratory at Detroit where all of this evaluation work was done; especially to R. Drew Baker and P. McCurdy for allowing use of their reports, articles and slides. Also, to C. J. Meeske of Detroit for information on RCI and competitive acrylic resins.

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Exterior durability of coatings*

By J. E. Fullard

Organic Coatings Division, South African Bureau of Standards

Summary

Exposure trials have been conducted over a period of 15 years at Pretoria and Durban on a wide variety of structural steel paints, enamels, oil paints, aluminium paints, emulsion paints, zinc chromate primers, and red lead primers. Relative durabilities are assessed and the nature and degree of breakdown are discussed. There is evidence to suggest that many paints available in South Africa are not being fully utilised in terms of service life because of deficiencies in substrate preparation and application procedure.

Key words

Types of coating	Types of surface	Binders oils etc.	resins etc.
alkyd coating aluminium paint emulsion paint enamel	Douglas fir pine saligna steel	fish oil	acrylic resin phenolic varnish polyvinyl acetate
red lead primer structural steel paint zinc chromate prime		<i>Raw materials used in manufacture or s</i> _tall oil	

La durabilité à l'extérieur de revêtements

Résumé

Essais de vieillissement ont été éffectues pendant une période de 15 ans à Pretoria et à Durban sur une gamme étendue d'émaux, de peintures; à l'huile, pour charpentes en acier, à l'aluminium, émulsions; de primaires au chromate de zinc et au minium. On considère les durabilités correspondantes et l'on discute le type et le degré de la déterioration. L'evidence suggère que beaucoup de peintures en Afrique du Sud ne revèlent pas de vie utile correspondante à leurs durabilités intrinsèques, à cause des défauts au point de vue de la préparation du support et de la mode d'application.

Wetterbeständigkeit von Anstrichmitteln

Zusammenfassung

Während eines Zeitraumes von 15 Jahren wurden Bewitterungsversuche in Pretoria und Durban mit einer grossen Auswahl von Schutzfarben für Eisenkonstruktionen, Emaillelacken, Ölfarben, Aluminiumfarben, Emulsionsfarben, Zinkchromat-Primern und Bleimennige durchgeführt. Die relativen Wetterbeständigkeiten werden bewertet, und Art und Grad des Anstrichschadens besprochen. Es liegen Beweise für die Annahme vor, dass zahlreiche der in Südafrika vorhandenen Anstrichmittel, soweit deren mögliche Lebensdauer in Frage kommt, als Folge mangelhafter Vorbehandlung des Substrates und der Handhabung bei der Anwendung, nicht voll ausgenutzt werden.

Внешняя стойкость покрытий

Резюме

В течение 15-лет в Претории и в Дурбане производились испытания на выветривание широкого ряда красок для строительной стали, эмалей, масляных, алюминиевых и эмульсионных красок, хромовокисло-цинковых грунтовок и свинцово-суриковых грунтовок. Оцениваются сравнительные стойкости и обсуждаются характеристика и степень разрушения. Есть основания полагать что многие краски коммерчески доступные в Южной Африке не полностью используются с точки зрения их срока службы, из-за несовершенства приготовления субстрата и метода применения красок.

*Presented to the Second National Convention, South African Section. Durban, 18-20 October 1968.

1969 (4) EXTERIOR DURABILITY OF COATINGS

Introduction

The exterior durability of a paint or coating is its ability to withstand the combined factors which exert an influence on it during its exposure to the elements and during its life to perform the function of decoration and protection of the substrate to which it is applied. These factors include resistance to many physical forces, such as film injury or hail or other form of damage, abrasion or erosion, the influence of high and low temperatures, and solar radiation. Other factors are of a chemical nature and constitute an attack on both the substrate and the film by chemicals and water, in the form of vapour, dew, rain and snow, or through immersion.

The economic life of a coating can be defined as the period during which it affords an effective resistance to these factors in such a manner that it continues to perform its decorative function and protects the substrate. Durability, then, is synonomous with economic life, and constitutes the most important property of coatings.

Although reasonable indications of the likely performance of some coatings can be given as a result of accelerated laboratory tests, this is not the case by any means for all coatings. The forecast and predictions that can be made from such tests are limited particularly to coatings with a life of less than five years, and, where the expected life exceeds this, resort must be had to other means. It is not strange, then, that refuge is taken in panel exposure and test fence trials. It is common practice, also, to confirm test fence exposure results by means of actual service tests.

Since different climates vary considerably in their critical deterioration factors, even test fence exposures or panel tests still do not present a guarantee of all-round performance. Nevertheless, this method still presents the most valuable information on performance, and paint exposure stations with 10,000 to 50,000 panels are not unusual.

In addition to their decorative function, the protection of the substrate and prevention of corrosion are the most important functions of coatings and, consequently, a high percentage of panel exposures is confined to this purpose. In many countries, and especially on the continent of Europe (particularly Holland) other problems, like the blistering of paint on wood during winter, are most serious. It is not strange, then, that many paint manufacturers have built blister houses to study the effect of high humidity on coatings.

Some consumers are suspicious of panel exposures, and there is some justification for this viewpoint, but in general it is unnecessary to be too sceptical when all the relevant conditions of exposure are known and the tests are in the hands of experienced technologists.

The information presented in this paper is mainly confined to results obtained at the Pretoria and Durban exposure stations of the South African Bureau of Standards, and essentially refers to panel exposures.

It is the intention to present information acquired from numerous exposure tests which, in some cases, have lasted up to 15 years, while some of these are still being continued. It is hoped that this information will add to the knowledge of these materials and assist in the formulation of durable coatings. It will be necessary to select from the many tests and coatings, a number of the most important types in relation to their volume and importance as protective and decorative coatings. For this reason, only the following architectural paints have been selected, namely, structural steel paints, enamels, oil paints, aluminium paints, emulsion paints, zinc chromate and red lead primers.

The breakdown of coatings

The object of this type of work is to determine the durability or probable effective life of the coatings, and it is necessary to consider systematically both the nature of the substrate and the environment. Before results are considered, however, the causes of breakdown will be briefly reviewed. These can conveniently be condensed to a failure of

- (a) the pigment component or
- (b) the medium or vehicle of the coating, and
- (c) the causes of detachment of the protective layer from the substrate.

It is not the intention to elaborate on the failure of the pigment component in this paper, but it is nevertheless important to mention certain aspects in relation to its influence on the performance of pigmented coatings. Many of the results reported include formulations with relatively high pigment volume concentrations and the use of titanium dioxide pigment. Many of these paints show excessive chalking because of both these factors. Results of anti-corrosive primers are not discussed in relation to pigment failure.

It is, however, appropriate to mention the profound influence the type of pigment may have on the performance of the coating. The exceptionally long life obtained with red iron oxide in roof paints has been reported¹ previously, but will also be evident from the results to follow. The amazingly good performance of zinc dust—zinc oxide pigmented coatings² is now well known and their performance must primarily be ascribed to the screening effect of the metallic pigments, thereby protecting the medium from degradation. Further evidence of this type of protection will be given in relation to the performance of aluminium paints. It is interesting to note that Tomecko³ has indicated that future research may be directed also to building a pigment molecule into the vehicle molecule.

The breakdown of protective films is generally attributed to a combination of many factors, but it is an undisputed fact that the greatest degree of breakdown is caused by the combined effect of two factors, namely, solar radiation and the effect of water, whether in the form of high humidity, dew, rain, or periods of total water immersion. It is common knowledge that in countries such as South Africa, with high average daily hours of sunshine, the effect of radiation on coatings is considerable, and requires the serious attention of the formulator of all exterior coatings. Research work⁴ conducted at the Council for Scientific and Industrial Research has indicated that the proportion of ultra-violet radiation compared to visible radiation in Pretoria is appreciably higher than that reported for the northern hemisphere. This is said to be only partly attributable to Pretoria's altitude of 4,500 feet above sea level. In the same paper, information is given about the energy distribution of solar radiation, illustrating the high energy level in the short-wave and ultra-violet region. Much has been written about the damaging effect of ultraviolet radiation on coatings during 1969 (4)

weathering but recently Jettmar⁵ has shown, by means of photo-micrographs, that the damage to the pigment by radiation effects the adhesion between the pigment and medium, and influences the weather resistance of the paint coating.

It may, therefore, be inadvisable to separate the effect on the pigment and the medium. The considerable effect of solar radiation on unpigmented coatings, particularly as experienced with varnishes in South Africa, is well known. Research work done by the South African Paint Research Institute⁶ has shown what little effect even large quantities of ultra-violet absorbers have. The resistance of the medium to radiation during exposure, therefore, is of paramount importance, even in pigmented coatings, and probably constitutes the over-riding factor in the formulation of exterior coatings. For the purpose of this paper, the emphasis will be on the weatherability of various types of paint and, more particularly, in relation to the performance of the organic media and the synthetic resins used in the formulations.

Experiments with structural steel paints

In 1954 it was decided to formulate and expose a wide range of structural steel paints in order to obtain first-hand knowledge of the performance of various types of media under South African conditions. Forty of these formulations were based on grey with the same pigmentation for 29 paints based on the following:

Rutile titanium dioxide	75 parts by weight
Asbestine	12.5 parts by weight
Mica	12.5 parts by weight
Carbon black	0.5 parts by weight

Nine grey paints (Nos. 49 to 53, 58 to 60 and 70) were based on the following pigments:

Lead titanate	84.6 parts by weight
Asbestine	2.5 parts by weight
Mica	12.4 parts by weight
Carbon black	0.5 parts by weight

Grey paints Nos. 47 and 48 were based on the following pigments:

Rutile titanium dioxide	15 parts by weight
Zinc oxide	10 parts by weight
White lead	50 parts by weight
Asbestine	12.5 parts by weight
Mica	12.5 parts by weight
Carbon black	0.5 parts by weight

Paints nos. 4 to 22, 56 and 61 to 69 were all based on red oxide as follows: Natural red iron oxide Asbestine Mica Natural red iron oxide Asbestine Mica Natural red iron oxide Asbestine Mica

All oil paints were based on a pigment volume concentration of 32 per cent and all varnish and alkyd containing paints on a PVC of 25 per cent.

All 70 formulations were exposed in Pretoria and in Durban on steel and wood. One set of cold-rolled steel panels was primed with a zinc chromate primer complying with the United States Military Specification JAN-P-735,

at a wet film thickness of 0.0025in and a second set was primed with a red lead primer complying with SABS 312-1951, Type I, Grade I. One half of the 9×18 in panel received two coats of the experimental paint while the second half had only one coat. All oil base paints were applied at 0.002in while alkyd and varnish base paint were coated at 0.003in wet film thickness. These panels, and in fact all panels of which results are reported here, were exposed at 45 degrees north facing.

The tests on wood consisted of three series on South African *pinus radiata*, Douglas fir (Oregon pine) and saligna (*eucalyptus grandis*): 6×12 in is the standard size for wood panels.

The panels were exposed in October 1954, and the results, therefore, cover 14 years' exposure on wood and steel in Pretoria. The wood and steel panels in Durban were lost in the floods of April 1959.

Details of the composition of the media are given in Tables 1 and 2. Included in the tables are the original dry film thickness for the two coats on primer

No. $3x$ $2x$ 1 Penta linseed oil alkyd 20% PA 6 4.2 3.6–3.8 2.1–2.4 5.6 4.2 3.4–3.6 2.1–2.2 5.0 5.5 4.5 2.9 2.0 5.5 4.3 3.2–3.4 2.0–2			Dry film thickness (in $\times 10^3$)								
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Paint No.	Composition of medium	Original		19	58	Original		1968 (44P)		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				2x	3x	2x	3x	2x	3 x	2x	l x
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	Penta linseed oil alkyd 20% PA	6	4.2	3.6-3.8	2.1-2.4	5.6	4.2		2.1-2.3	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	50/50 Long DCO alkyd	5.5	4.5			5.5	4.3	3.2-3.4	2.0-2.3	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	Pure phenolic varnish					6.5	4.6	2.8 - 2.9	1.9 - 2.0	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4	Linseed stand oil (Z2-Z3)	5.8					4.3		Contraction Contraction	1.8
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5	4 Linseed stand:1 RLO	4.8								1.6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6	4 Linseed stand:1 tung oil							2.4		1.8
93 RLO:1 linseed stand8.05.8 $3.4-3.9$ 2.86.04.52.8104 RLO:1 DCO stand7.04.5 $3.6-4.0$ 3.06.04.3 $3.4-3.8$ 11Linseed stand oil (U-V)8.04.8 $3.1-3.5-4.0$ $2.4-2.5$ 8.04.3 $3.9-4.0$ 12Pure phenolic varnish7.04.8 $3.2-3.8$ 2.05.84.0 $1.8-1.9$ 131:2 Pure phenolic varnish7.05.0 $3.8-3.9$ $1.6-1.8$ 5.54.0 $1.3-1.5$ 141:2 Pure phenolic varnish5.0 4.2 $2.4-2.8$ $1.8-2.2$ 5.8 4.0 14Rosin modified phenolic5.0 4.2 $2.4-2.8$ $1.8-2.2$ 5.8 4.0 151:3 Rosin modified phenolic 5.0 4.2 $2.4-2.8$ $1.8-2.2$ 5.8 4.0 161:4 Rosin modified phenolic 5.0 4.2 $2.4-2.8$ $1.8-2.2$ 5.8 4.0 161:4 Rosin modified phenolic 5.0 4.2 $2.4-2.8$ $1.8-2.2$ 5.8 4.0 171:4 Rosin modified phenolic 5.0 3.2 $2.3-2.5$ 4.8 3.2 $2.1-2.3$ 2050/50 Long penta alkyd/1:2 pure 5.5 4.6 $2.8-3.4$ 2.8 5.2 3.9 $1.8-2.2$ 21 </td <td></td> <td>1.6</td>											1.6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$											1.7
11Linseed stand oil (U-V)8.04.83.1-3.5-4.02.4-2.58.04.33.9-4.0121:2 Pure phenolic varnish7.04.83.2-3.82.05.84.01.8-1.9131:2 Pure phenolic varnish7.05.03.2-3.82.05.84.01.8-1.9141:2 Pure phenolic varnish6.54.52.9-3.21.3-1.65.03.51.3-1.5151:3Rosin modified phenolic6.54.22.4-2.81.8-2.25.84.0161:4Rosin modified phenolic5.04.22.4-2.61.6-1.84.23.0161:4Rosin modified phenolic5.04.02.5-2.61.6-1.84.23.0171:4Rosin modified phenolic5.04.02.8-3.22.4-2.84.43.61.5-1.9191:6Copal ester varnish5.03.22.3-2.54.82.92.1-2.32050/50Long penta alkyd/1:2 pure phenolic varnish6.54.82.8-3.5-3.82.5-3.05.84.52.3-2.82150/50Medium alkyd/1:2 pure phenolic varnish6.54.52.8-3.42.85.23.91.8-2.2231:2Pure phenolic varnish5.54.62.8-3.42.85.23.91.8-									2.8		1.6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$											2.5
13112Pure phenolic varnish7.05.0 $3.8-3.9$ $1.6-1.8$ 5.5 4.0 $1.3-1.5$ 1412Pure phenolic varnish 6.5 4.5 $2.9-3.2$ $1.3-1.6$ 5.0 3.5 $1.3-1.5$ 151.3Rosin modified phenolic 6.5 4.5 $2.9-3.2$ $1.3-1.6$ 5.0 3.5 $1.3-1.5$ 161.4Rosin modified phenolic 5.0 4.2 $2.4-2.8$ $1.8-2.2$ 5.8 4.0 161.4Rosin modified phenolic 5.0 4.0 $2.5-2.6$ $1.6-1.8$ 4.2 3.0 171.4Rosin modified phenolic 5.0 4.0 $2.5-2.6$ $1.6-1.8$ 4.2 3.0 181.4Copal ester varnish 5.0 3.2 $2.3-2.5$ 4.8 2.9 $2.1-2.3$ 20 $50/50$ Long penta alkyd/1:2 pure phenolic 5.0 3.2 $2.3-2.8$ 6.0 4.3 $1.8-2.5$ 2112Pure phenolic varnish 5.5 4.6 $2.8-3.4$ 2.8 5.2 3.9 $1.8-2.2$ 241:2Pure phenolic varnish 5.5 4.0 $2.5-3.0$ 2.0 5.0 3.5 $1.6-1.3$ 251:2Pure phenolic varnish 5.5 4.6 $2.8-3.7$ 2.8 5.2 3.9 $1.8-2.2$ 241:2Pure phenolic varnish 5.5 4.6 $2.8-3.1$		Linseed stand oil (U-V)				2.4 - 2.5					1.8
141:2Pure phenolic varnish6.54.52.9-3.21.3-1.65.03.51.3-1.5151:3Rosin modified phenolic 5.0 4.22.4-2.8 $1.8-2.2$ 5.84.0161:4Rosin modified phenolic 5.0 4.2 $2.4-2.8$ $1.8-2.2$ 5.8 4.0 161:4Rosin modified phenolic 5.0 4.0 $2.5-2.6$ $1.6-1.8$ 4.2 3.0 171:4Rosin modified phenolic 5.0 4.0 $2.5-2.6$ $1.6-1.8$ 4.2 3.0 181:4Copal ester varnish 5.0 3.2 $2.3-2.5$ 4.8 2.9 $2.1-2.3$ 2050/50Long penta alkyd/1:2 pure phenolic varnish 5.0 3.2 $2.3-2.5$ 4.8 2.9 $2.1-2.3$ 2150/50Medium alkyd/1:2 pure phenolic varnish 6.5 4.8 $2.8-3.5-3.8$ $2.5-3.0$ 5.8 4.5 $2.3-2.8$ 211:2Pure phenolic varnish 5.6 4.6 $2.8-3.4$ 2.8 6.0 4.3 $1.8-2.2$ 231:2Pure phenolic varnish 5.6 4.5 $4.4-4.5$ 3.9 5.7 4.5 $2.2-2.6$ $1.6-1.3$ 241:2Pure phenolic varnish 5.5 4.0 $2.5-3.0$ 2.0 5.0 3.5 $1.8-2.3$ 251:3Modified phenolic 5.5 4.0 $2.5-2.8-3.0$ 2.0 5.5 4.5 $2.8-2.9$ $1.5-1.4$ 261:4		1:2 Pure phenolic varnish									1.2
151:3Rosin modified phenolic varnish5.04.22.4–2.8 $1.8-2.2$ 5.84.0161:4Rosin modified phenolic varnish5.04.13.6 $2.0-2.2$ $1.9-2.0$ 4.63.5 $1.5-1.9$ 171:4Rosin modified phenolic varnish5.04.0 $2.5-2.6$ $1.6-1.8$ 4.2 3.0 181:4Copal ester varnish5.0 3.2 $2.3-2.5$ 4.4 3.6 $1.5-1.9$ 181:4Copal ester varnish5.0 3.2 $2.3-2.5$ 4.8 2.9 $2.1-2.3$ 2050/50Long penta alkyd/1:2 pure phenolic6.5 4.8 $2.8-3.5-3.8$ $2.5-3.0$ 5.8 4.5 $2.3-2.8$ 2150/50Medium alkyd/1:2 pure phenolic varnish7.0 4.8 $3.0-3.1$ $2.1-2.2$ 5.0 3.8 $2.2-2.3$ 221:2Pute phenolic varnish 5.5 4.6 $2.8-3.4$ 2.8 5.2 3.9 $1.8-2.5$ 231:2Pure phenolic varnish 5.5 4.6 $2.8-3.4$ 2.8 5.2 3.9 $1.8-2.2$ 241:2Pure phenolic varnish 5.5 4.0 $2.5-3.0$ 2.0 5.5 4.5 $2.8-2.9$ $1.5-1.4$ 251:3Modified phenolic varnish 5.5 4.0 $2.5-2.8-3.0$ 2.0 5.0 3.8 $2.0-2.5$ $1.8-2.3$ 271:4Rosin modified phenolic varnish 5.5 4.0 $2.5-2.8-3.0$ <td></td> <td>1:2 Pure phenolic varnish</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>1.1</td>		1:2 Pure phenolic varnish									1.1
varnish5.04.22.4–2.81.8–2.25.84.0161:4Rosin modified phenolic5.04.02.5–2.61.9–2.04.63.51.5–1.9171:4Rosin modified phenolic5.04.02.5–2.61.6–1.84.23.0181:4Copal ester varnish5.03.22.3–2.54.82.92.1–2.32050/50Long penta alkyd/1:2 pure phenolic varnish6.54.82.8–3.5–3.82.5–3.05.84.52.3–2.52150/50Medium alkyd/1:2 pure phenolic varnish7.04.83.0–3.12.1–2.25.03.82.2–2.3221:2Penta rosin ester tung varnish6.04.02.3–2.86.04.31.8–2.5231:2Pure phenolic varnish5.54.62.8–3.42.85.23.91.8–2.2241:2Pure phenolic varnish5.54.62.8–3.02.05.54.52.2–2.61.6–1.1251:3Modified phenolic varnish5.54.02.5–3.02.05.54.52.8–2.91.5–1.0261:4Rosin modified phenolic5.54.02.5–3.02.05.03.82.0–2.51.8271:4Rosin modified phenolic5.54.02.5–2.8–3.01.85.54.22.5–3.02.2281:4Copal ester varnish5.55.54.02.5–2.8–3.01.		1:2 Pure phenolic varnish	6.5	4.5	2.9-3.2	1.3 - 1.6	5.0	3.5	1.3-1.5		0.7
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	15		-								
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		varnish	5.0	4.2	2.4-2.8	1.8 - 2.2	5.8	4.0			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	16			2.4	20.22	10.20		2.5	1 - 1 0		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		varnish			2.0-2.2				1.5-1.9		1.3
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		1:4 Rosin modified phenolic							1.5.1.0		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		1:4 Copal ester varnish			2.8-3.2	2.4-2.8					1.5
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		1:6 Copal ester varnish	5.0	3.2	2.3-2.5		4.8	2.9	2.1-2.3		1.3
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	20		6.5	10	202520	25.20	50	15	2220		1.0
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	21	phenolic	0.5	4.0	2.8-3.3-3.8	2.5-5.0	5.0	4.5	2.3-2.8		1.8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	21	50/50 Medium alkyd/1.2 pure	7.0	10	20.21	21.22	5.0	20	2222		1.5
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	22	1.2 Ponto rosin ester tung varnish				2.1-2.2					1.5
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	22	1.2 Penta rosin ester tung varinsi				20			1.0-2.3		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		1.2 Pure phenolic varnish							2226	16.10	1.2
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		1.2 Modified phenolic varnish							2.2-2.0		1.4
varnish $$ $$ 5.0 4.0 $2.4-2.5$ 2.0 5.0 3.5 $1.8-2.3$ 27 1.4 Rosinmodifiedphenolic 5.5 4.0 $2.4-2.5$ 2.0 5.0 3.5 $1.8-2.3$ $varnish$ $$ $$ 5.5 4.0 $2.5-2.8-3.0$ 1.8 5.5 4.2 $2.5-3.0$ 2.2 28 1.4 Copal ester varnish $$ 5.6 4.0 $2.8-3.1$ 2.1 5.0 3.8 $2.0-2.5$ 1.8 29 1.6 Copal ester gum varnish $$ 5.0 4.0 $2.1-2.4$ 4.0 3.5 $1.8-2.0$ 30 $50/50$ Long alkyd/1:2 pure phenolic 6.5 4.5 $3.0-3.3$ 5.8 4.0 $3.0-3.1$ 1.6 31 $50/50$ Med. alkyd/1:2 pure phenolic 6.5 4.5 5.5 4.1 $2.9-3.0$ 1.9 32 $1:2$ Penta rosin ester tung varnish 5.0 4.0 $2.8-3.0$ 2.0 4.8 4.0 $2.1-2.3$ 33 Linseed stand oil $(22-23)$ $$ 4.8 3.4 $2.2-2.6$ 6.0 4.0 $2.8-3.0$ 2.0		1.4 P osin modified phenolic	5.0	4.0	2.5-5.0	2.0	5.5	4.5	2.0-2.9	1.5-1.0	1.4
271:4Rosin modified phenolic varnish5.54.02.5–2.8–3.01.85.54.22.5–3.02.2281:4Copal ester varnish5.64.02.8–3.12.15.03.82.0–2.51.8291:6Copal ester gum varnish5.04.02.1–2.44.03.51.8=2.03050/50 Long alkyd/1:2 pure phenolic7.05.03.8–4.53.0–3.35.84.03.0–3.11.63150/50 Med. alkyd/1:2 pure phenolic6.54.55.54.12.9–3.01.9321:2 Penta rosin ester tung varnish5.04.02.8–3.02.04.84.02.1–2.333Linseed stand oil (Z2-Z3)4.83.42.2–2.66.04.02.8–3.02.0	20		5.0	4.0	24.25	2.0	5.0	35	18.23		1.4
varnish5.54.02.5–2.8–3.01.85.54.22.5–3.02.2281:4 Copal ester varnish5.64.02.8–3.12.15.03.82.0–2.51.8291:6 Copal estergum varnish5.04.02.1–2.44.03.51.8–2.03050/50 Long alkyd/1:2 pure phenolic7.05.03.8–4.53.0–3.35.84.03.0–3.11.63150/50 Med. alkyd/1:2 pure phenolic6.54.55.54.12.9–3.01.9321:2 Penta rosin ester tung varnish5.04.02.8–3.02.04.84.02.1–2.333Linseed stand oil (Z2-Z3)4.83.42.2–2.66.04.02.8–3.02.0	27	1.4 Posin modified phenolic	5.0	4.0	2.7-2.5	2.0	5.0	5.5	1.0-2.5		1.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	21	varnish	55	4.0	25-28-30	1.8	55	42	25.30	2.2	1.6
29 1:6 Copal estergum varnish 5.0 4.0 2.1–2.4 4.0 3.5 1.8–2.0 30 50/50 Long alkyd/1:2 pure phenolic 7.0 5.0 3.8–4.5 3.0–3.3 5.8 4.0 3.0–3.1 1.6 31 50/50 Med. alkyd/1:2 pure phenolic 6.5 4.5 5.5 4.1 2.9–3.0 1.9 32 1:2 Penta rosin ester tung varnish 5.0 4.0 2.8–3.0 2.0 4.8 4.0 2.1–2.3 33 Linseed stand oil (Z2-Z3) 4.8 3.4 2.2–2.6 6.0 4.0 2.8–3.0 2.0	20	1.4 Copal ester varnish							20-25	1.8	1.7
30 50/50 Long alkyd/1:2 pure phenolic 7.0 5.0 3.8–4.5 3.0–3.3 5.8 4.0 3.0–3.1 1.6 31 50/50 Med. alkyd/1:2 pure phenolic 6.5 4.5 5.5 4.1 2.9–3.0 1.9 32 1:2 Penta rosin ester tung varnish 5.0 4.0 2.8–3.0 2.0 4.8 4.0 2.1–2.3 33 Linseed stand oil (Z2-Z3) 4.8 3.4 2.2–2.6 6.0 4.0 2.8–3.0 2.0	20	1:6 Copal estergum varnish			21-24				1.8-2.0	1.0	1.6
31 50/50 Med. alkyd/1:2 pure phenolic 6.5 4.5 32 1:2 Penta rosin ester tung varnish 5.0 4.0 2.8–3.0 2.0 33 Linseed stand oil (Z2-Z3) 4.8 3.4 2.2–2.6 6.0 4.0 2.8–3.0 2.0	30	50/50 Long alkyd/1:2 pure phenolic				3.0-3.3			3.0-3.1	1.6	1.5
32 1:2 Penta rosin ester tung varnish 5.0 4.0 2.8–3.0 2.0 4.8 4.0 2.1–2.3 33 Linseed stand oil (Z2-Z3) 4.8 3.4 2.2–2.6 6.0 4.0 2.8–3.0 2.0		50/50 Med, alkyd/1:2 pure phenolic									1.5
33 Linseed stand oil (Z2-Z3) 4.8 3.4 2.2–2.6 6.0 4.0 2.8–3.0 2.0	32				2.8 - 3.0	2.0				,	1.6
	33				2.2-2.6					2.0	1.8
						2.8					2.0
35 4 Linseed stand: 1 tung oil 5.2 4.0 2.8–3.2 2.0 4.4 3.8 1.8–2.4 1.9											1.7

Table 1Details of structural paints

Pa

Table 2

		Dry film thickness (in \times 10 ³)								
aint	Composition of medium	Orig	ginal	1968	(43F)	Original		1968 (44P)		
No.		3x	2x	3x	2x	3x	2x	3x	2x	1 x
36	4 Linseed stand:1 DCO	6.6	4.4	4.0-4.2	2.5-3.0	5.5	4.0	3.0-3.1	1.9	1.5
37	4 Linseed stand:1 tung stand	6.0	3.8	2.8 - 3.5	2.2	5.5	3.8	2.4-2.8	1.5	1.3
38	3 RLO:1 linseed stand	5.5	4.0	2.6 - 2.9		5.5	3.6	1.8-2.4		1.0-1.
39	1 DCO stand:4 linseed stand	6.0	4.3	3.5 - 3.8	2.0-2.3	5.6	3.8	2.8-3.0	1.8	1.2
40	Linseed stand oil (U-V)	8.0	5.0	4.2-4.3	2.1-2.3	6.0	4.2	2.9-3.2-3.5	2.0	1.3
41 42	Long linseed alkyd 22% PA Long DCO linseed alkyd 18%	4.5	4.0	2.8 - 3.0	2.1	4.4	3.9	2.2–2.4	1.8	1.6
	РА	5.3	3.8	2.9 - 3.5	2.3-2.4	4.3	3.0	1.9-2.1	1.7	1.0
43	Penta soya long alkyd 24% PA	5.0	4.1	2.8 - 3.4	2.0 - 2.8	4.8	4.0	3.0	2.1	
44 45	Long marine oil alkyd 24% PA 50/50 RLO/linseed penta alkyd	5.8	4.3	3.5-3.8	2.8	5.0	4.0	2.5-3.0	1.7–1.8	
	23 % PA	5.8	4.4	3.5 - 3.9	2.2-2.4	5.0	4.0	2.5-2.8	1.8	
46	50/50 Med. linseed alkyd/RLO	5.0	4.2	3.5 - 4.0	2.9 - 3.0	5.0	3.1	2.8-3.0	1.5 - 1.6	
47	4 Linseed stand:1 RLO	5.0	4.5	1.9-2.2	1.9	4.9	4.0	2.0	1.5	0.99
48	1:6 Copal ester varnish									
49	4 Linseed stand:1 RLO	5.0	3.7	1.8 - 2.1		4.5	3.5	1.8		1.0-1.
50	1 Tung stand:4 L. stand	4.5	3.7	2.0 - 2.1	20.21	4.8	3.2	1.4-1.8		0.8-0.
51	Penta linseed alkyd 20% PA	4.2	3.5	2.6-2.9	2.0-2.1	4.5	3.8	2.5-3.0	1.8	
52	Medium length alkyd	4.0	3.5	2.5 - 3.0	2.3	4.0	.3.4	1.9-2.2-2.9	2.0	
53	Sunflower penta alkyd 23% PA	4.8	4.0	2.8 - 3.0	2.0-2.4	4.3	3.7	2.3-2.9	1.8 - 2.0	
54	Styrenated oil	5.3	3.8	3.1-3.3	1.8-2.0	6.0	4.2	3.4-4.0	1.9 - 2.0	
55	Med. alkyd/chl. rubber/LSO	5.7	4.0	3.9-4.0	2.0-2.5	5.3	4.0	2.8-3.0	2.0	
56 57	Vinyl modified alkyd 1:2 Pure phenolic/chl. rubber	6.5 4.5	4.7 3.5	2.0-2.3		7.0	4.3	4.4-5.0	3.0-3.5	10
58		4.5 5.2	4.0	2.0-2.3		5.8	4.0	2.1		1.8
59	1:2 Pure phenolic varnish Styrenated oil	5.2	4.0	3.3-3.6	2.3	5.0	4.5	1.8		1.6
60	Aluminium mod. long soya alkyd	5.0	4.0	3.8-4.0	2.0-2.2	5.0	3.9	2.9-3.0	1.5-1.6	
61	Long linseed alkyd 22% PA	6.0	4.3	5.6-4.0	2.0-2.2	5.5	4.4	3.0-3.4	2.1-2.5	
62	Long penta linseed alkyd 20% PA	5.0	4.0	3.4-3.5	2.2-2.5	5.2	4.2	3.0-3.5	2.1-2.5	
63	Long DCO linseed alkyd 18%	5.0	7.0	5.4 5.5	2.2 2.3	3.2	7.2	5.0-5.5	2.1-2.5	
05	PA	6.0	4.5	3.8 - 4.0	2.6-3.0	6.3	5.2	4.0-4.5	3.0-3.1	
64	Penta soya alkyd 24% PA	5.5	4.5	3.4-3.7	2.5-2.6	6.6	4.7	4.4 4.5	3.0-3.1	
65	Sunflower penta alkyd 23% PA	5.2	4.4	3.8-4.0	2.8	4.8	3.9	3.0-3.5	1.9-2.0	
66	Long marine oil alkyd 24% PA	4.8	3.6	3.3-3.5	2.2-2.4	5.0	4.0	3.0-3.1	1.9-2.0	
67	50/50 RLO/linseed penta alkyd			010		2.0		0.0 0.1	2.0	
	23 % PA	6.3	4.5	4.4-4.5	2.5 - 3.0	6.0	4.6	4.0-4.3	2.6	
68	50/50 RLO/long DCO alkyd	6.0	4.8	4.0-4.2	3.0-3.4	5.0	4.0	3.2-3.6	2.1	1
69	50/50 Med. linseed alkyd/RLO	4.2	3.6	2.8-3.0		4.8	3.7	1.5		1.5
70	1:2 Pure phenolic (tung)	6.0	4.4	1.8 - 2.2		5.8	4.5	2.8-3.0	1.8 - 2.2	

Details of structural paints

indicated by 3x, and one coat on primer indicated by 2x. Thicknesses as measured in 1968 are also given. The series with red lead as primer is denoted by the series no. 43P while 44P denotes the series on a zinc chromate primer. Where excessive erosion of the top coat has exposed the primer, thicknesses for the latter have been included.

The steel panels were all rated in four groups. Group I consisted of those panels where virtually no perceptible difference existed between the three-coat and two-coat systems. In the case of the red lead primed system Groups II to IV indicated three stages of increasing rust on the two-coat system, so that Group IV virtually only retained the three-coat system in good condition. On the zinc chromate primer there was considerably less rust and Groups II to IV consisted mainly of increased film loss so that Group IV represented virtually a total loss of the top coat on the two-coat system exposing the primer in good condition, while erosion had started on the three-coat system.

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Series No.	43P	43P	44P	44P	42A	42A	
Colour	Grey	Red oxide	Grey	Red oxide	Grey	Red oxide	
Primer	Red lead	Red lead	Zinc cl	chromate Wood		Primer	
Substrate	Steel	Steel	Steel	Steel	Saligna	Saligna	
<i>Group I</i> Pure alkyds	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	62 63 64 65 66 67 68 56	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	61 62 63 64 65 66 67 68 69 56	1 41 42 51 60	56	
Group II	28 30 40	69	51		44 46	68	
Pure alkyds	60 60	8 9 10	25 39 40	4 5 6	31 40	00	
		11 20 21	54	7 8 9 10 11	51 40		
Group III Pure alkyds	41 51		52 58		2 43 45	61 62 63 64 65 66	
r are any as	3 24 26 27 36 39 54 55	6 7 12 13 14 15 18	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	15 18 19 20 21	25 30	01 02 00	
<i>Group IV</i> Pure alkyds	23 25 29 32 33 34 35 37 38 47 49 50 52 58 59 70	4 5 16 17 19 22	26 29 33 38 49 50 70	12 13 14 16 17 22	33 34 35	67	
Group V					3 36 37 52 54 57	69	
Group VI					70	8 10 11 12 13 20 21 22	
Missing panels (believed in bad condition)	31 48 57 70	61	47 48 59		23 24 26 27 28 29 32 38 39 47 48 49 50 53 59	4 5 6 7 9 14 15 16 17 18 19	

Table 3Performance rating of structural paints

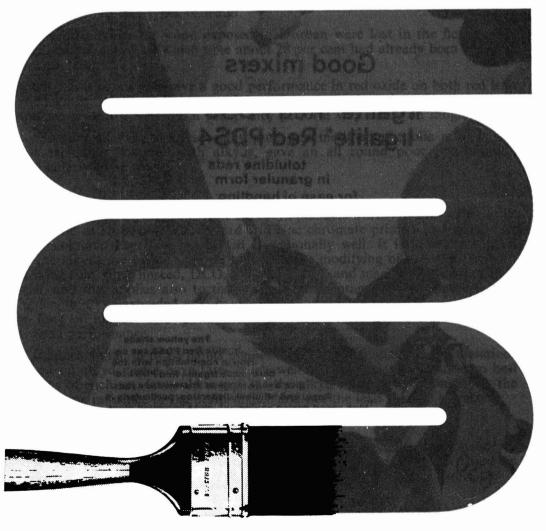
The wooden panels were arbitrarily grouped into six groups according to their condition, and for purposes of comparison with the steel panels, Groups I, II, and III seem to compare well with Group I of the steel panels.

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Discussion of results with structural steel paints

An analysis of the results indicates that the pure alkyd paints and oil extended alkyds form the majority of the six best groups almost to the exclusion of other types. Even where alkyds are modified with other types, such as in paint nos. 20, 21, 30, 31, 55, and 56, the alkyd influence is evident.

In the case of the wood panels, the first three groups are dominated by the alkyd types. However, the results on saligna give a false impression of the performance of these paints on wood, because, in the case of South African pine and Oregon pine, there was a considerable number of failures at five years because of cracks in the wood, so much so that both series on these woods were removed after seven years. It is most significant that, on the saligna wood which has exhibited remarkable weatherability, the paints have lasted well. The greater majority of failures, even on saligna, appear to have their origin at the bottom of the panel, and it is reasonable to conclude that, with a better design of the exposure racks to provide more effective drainage, the performance would no doubt be better. This was, in fact, a contributing factor to the early failure on the other types of wood.

The three series on wood exposed in Durban were lost in the floods after four years exposure at which time about 28 per cent had already been removed due to failure.

Oil paints as a group give a good performance in red oxide on both red lead and zinc chromate primers on steel, but the grey paints perform poorly on steel and worse on red lead. As a group they perform very badly on saligna wood.

Virtually all varnishes, especially pure and modified phenolic resin based, but excluding mixtures with alkyds, gave an all round poor performance, particularly so on wood.

The alkyd resin based paint

The exceptional performance of the alkyd paints is worthy of further analysis. On wood or steel, both as red lead and zinc chromate primers and in light or dark colours, they have performed exceptionally well. It is found that most of the alkyds are of the long oil type, but the modifying oil has not played a striking role, since linseed, DCO, soya, sunflower and marine oils fared equally well, and this applies also to the glycerol and pentaerythritol types. Medium oil length alkyd extended with linseed oil admixtures gave similar performance to long oil alkyds. The special aluminium modified long oil alkyd also gave a good performance.

It appears that, of those paints pigmented with lead titanate, the formulations based on alkyd media have fared quite well and were classed in the two best groups of each set. It would seem that the alkyd medium also constitutes the over-riding influence in the performance and not the lead titanate pigment.

Alkyd resins based on marine oils

Since the foregoing results have illustrated the remarkable performance of alkyds, it will be interesting to examine the performance of paints based on fish oil alkyd resins. Details of these paints and resins are given in Table 4.

Paint	97 DA	Alashal	%	Oils	Performance	Dry film thickness (in \times 10 ³)
No.	% PA	Alcohol modif.	Fish	Linseed	grouping in Pretoria	
1	24	Glyc.	100	0	3	5.5
2	24	Glyc.	75	25	2	4.8
3	24	Glyc.	50	50	3	4.3
4	24	Glyc.	25	75	2	5.3
5	24	Glyc.	0	100	3	4.1
6	20	Penta	100	0	2	6.3
7	20	Penta	50	50	2	4.8
8	20	Penta	0	100	3	5.0
9	31	Glyc.	100	0	1	5.2
10 11 12	31 31 31	Glyc. Glyc. Glyc.	50 0 75	50 100 25	1 1	4.5 5.0 5.1
13	28	Penta	100	0	1	4.8
14	28	Penta	75	25	1	4.8
15	28	Penta	50	50	1	5.2
16 17 18	28 25.5 24	Penta Glyc. Penta	0 0 100	100 100 0	1 1 3	4.2 5.1

Table 4Fish oil modified alkyd resin paints

All the paints consisted of green enamels made to the same pigment : binder ratio.

After 13.8 years' exposure, the two-coat system over the zinc chromate primer is still in excellent condition. The grouping in three groups indicates (a) no visible difference between one and two coats, (b) slight erosion of the single coat, and (c) appreciable corrosion in groups 1, 2, and 3 respectively.

The paints do not differ very considerably in their comparative performance and, therefore, the important conclusion is to note the exceptionally good performance of the group over such a long period.

Tall oil alkyd resin paints

In order to investigate the outdoor performance of tall oil modified alkyd resins, six enamels were exposed on clean cold-rolled steel and *pinus radiata* and Oregon pine (Douglas fir) in Pretoria and Durban. The two alkyd resins were based on 24 per cent phthalic anhydride and about 60 per cent tall oil with a rosin content of 4 per cent, and the enamels consisted of, two white, a red oxide, deep green, pastel blue and cream, colour samples.

One and two coats were applied over zinc chromate primer (SABS 679, Type I) on steel, and over wood primer (SABS 678, Type III) for wood.

The following observations and conclusions were made at the end of the tests.

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(a) Failure by flaking affects all panels, but the degree of flaking is worse on *pinus radiata* than on Oregon pine both in Pretoria and Durban, even for some three-coat systems.

(b) A particular type of ring checking is evident to a greater or lesser extent on all panels, but the rings are larger and more numerous on the Pretoria panels.

(c) After 4.5 years' exposure in Durban, all six enamels were a total failure on Oregon pine and *pinus radiata* except for the red oxide and green, of which both one and two coats were in good condition on *pinus radiata* in the case of the former and the two coat system of the green was in good condition.

(d) In Pretoria, after five years' exposure, red oxide, green and cream fared best on *pinus radiata*, and red oxide, pastel blue and cream were the best on Oregon pine.

(e) After 6.5 years the three-coat system on the steel panels in Pretoria are in excellent condition, with only very fine checking just visible under $80 \times$ magnification for the four pale colours only. The two-coat system is perceptibly in a slightly poorer state. After a similar period the panels in Durban show some evidence of rust on the edges, but are still in good condition.

Commercial enamels

A series of 35 commercial enamels were exposed ten years ago to establish their performance characteristics. As far as general appearance is concerned these products are in a very good condition on steel, and reasonably good on wood, which again was saligna. Table 5 gives the condition of the films listing the defects from microscopic examination.

The important aspects of these results are, first, the good performance over a ten year period and, secondly, the appreciably better performance on steel, compared to that on wood.

Here again, then, is further evidence of a similar nature to that obtained for structural paints, namely of inherent weather resistance on a solid substrate. Only photomicrographs can adequately illustrate the impossible physical task expected of films, which are of a few thousandths of an inch in thickness, of containing the physical forces released in wood during warping, and bridging cracks when formed in order to prevent the entrance of water and to protect the wood from decay.

Zinc chromate primers

In order to comment on the performance of zinc chromate primers, the results of a series of 21 zinc chromate primers which were exposed in Pretoria and Durban are reviewed. These primers were all formulated at a PVC of between 35 and 40 per cent, and based on different media, which included long and medium oil alkyds, and varnishes of modified and pure phenolic resins and of mixtures of these with alkyds. At the same time 11 commercial primers were exposed with this series. All primers were coated with one coat of chrome oxide green enamel based on a long oil pentaerythritol linseed alkyd.

After 9.5 years' exposure in Pretoria, about half these panels showed some signs of rust. The exposure of five panels was continued and, after 15 years, these are in remarkably good condition.

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Table 5 Commercial enamels

Paint	Colour	Film failure in Pretoria after 10 years				
No.	Colour	on steel	on wood (saligna)			
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22	Maroon Yellow Red Blue Green Grey Dark green Light green Orange Grey Brown Turquoise Blue Pale grey Red Cream Blue Primrose Maroon Yellow Orange Blue	Severe erosion X12 Isolated line checks (6) Removed at 3.5 years. Erosion Removed at 3.5 years. Erosion Nil Nil Nil X12 Medium dense blistering Nil X12 Checking (4) X12 Checking (4) X12 Line checking (8); X50 crowsfoot chedes X12 Big cracks; severe erosion X12 Isolated line checking (6) Line checking (8) crowsfoot checks	Complete failure Line checking (2) (Failed at 3 years) (Failed at 4 years) Nil Checking (2) Nil Isolated line checking (6) Isolated line checking (6) Line and crowsfoot checking (2) Isolated line checking (6) Checking (4) Line cracking (6) Line checking (8) Crowsfoot checking (8), line checking (6) Line checking (8) Line and crowsfoot checking (4-6) Line and crowsfoot checking (6-8)			
23 24 25 26	Green Blue Pale grey Orange	Nil Nil X12 Checking (4) X12 Checking (<8)	Isolated line checking (8) Nil Line cracking (6), crowsfoot checking (4) Line and crowsfoot checking			
27 28 29 30 31 32 33 34 35	Blue Green Cream Grey Green Brown White Cream Orange	Nil Nil Nil Nil X12 Checking (8) Nil X12 Crowsfoot cracks (2) X12 Isolated line checks (8) X12 Line and crowsfoot check (6)	(4-6) Isolated line checking (<8) Nil Nil Checking (2), isolated cracking Checking (2) Line and crowsfoot checking (8) Complete failure Line checking (6-8) Line and crowsfoot checking (2)			

It would appear that, on clean rust-free steel, zinc chromate primers, formulated at 35-40 per cent PVC and a minimum of 50 per cent zinc chromate pigment, give exceptional performance in Pretoria under an alkyd enamel, and that the primer's performance is not critically affected by a wide variation in the composition of the medium.

The position in Durban is quite different; after 3-3.5 years' exposure, all the panels exhibited fine rusting, accompanied by blistering and very fine flaking, and in some cases checking or cracking. The severity of the corrosion effect on

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panels with long exposure can only be adequately indicated by photographs. A primer with multiple protective coats performs measurably better in Durban than with a single top coat.

Aluminium paints

Numerous tests in the past have repeatedly confirmed the exceptional durability of aluminium pigmented paints. The example chosen here is a series exposed on kin sand blasted mild steel panels, coated with all the different classes of red lead primers provided by SABS 312, and including an alkyd based zinc chromate primer and three commercial red lead primers. All these paints were coated with the same varnish based aluminium paint.

Results show that, after eight years in Durban, the primers with two coats of aluminium paint were still giving good service, while the zinc chromate primer and a few others still gave good protection and were in good condition after 14.5 years in Pretoria. This illustrates the type of performance that can be expected of both types of primers and with aluminium paint.

PVA based emulsion paints

On sound substrates, the long-term film performance of pva paints is characterised by slow chalking of the film and eventual failure by erosion.

A single example is mentioned here, namely of a series exposed for a period of 12.5 years in Pretoria. These paints still retained an appreciable thickness of the original film, and serve to emphasise the durability of pva emulsion paints.

The life of paint films

Throughout this paper, many examples have been given of numerous types of architectural paints and continuous reference has been made to the exposure periods involved and the resultant performance achieved. One object has been to emphasise the unusually long life obtained with many of these coatings during panel exposures, not only in Pretoria, but also in Durban. Secondly, the intention has been to illustrate in clear terms the amazing durability of South African paints under severe conditions of exposure.

The possibility now exists that these results may be regarded as only of academic interest, since the results are based on laboratory "pampered" exposures which differ considerably from the hard facts of service tests and use. It must therefore be pointed out that these tests and results nevertheless irrefutably illustrate the inherent weather resistance and life potential of ordinary paint coatings even to conditions to some extent accelerated (45 degree exposure).

The question now arises that, if these results and the foregoing information are to be accepted, why such performance in practice cannot be achieved regularly and as a matter of course. The answer quite clearly is ascribable to the relevant prevailing conditions in practice, and most likely concerns the following:

(a) condition and cleanliness of the substrate, particularly that of steel.

(b) the change of the substrate with weathering and age, particularly in the case of wood.

(c) methods of coating application and what is achieved in comparison with what is specified.

(d) practical and realistic difficulties relevant to the coating and protection of structures.

(e) the thickness of paints applied and the number of coats used.

The next question is whether South African paints are unnecessarily good and durable. Many may regard this question as ridiculous in the light of their general experience with paint, but the reply to the question may, quite sensibly be in the affirmative. Experience has irrevocably proven that good coating performance can only be obtained from a clean, solid and sound substrate, and the reason to use durable material is defeated by bad practice. Therefore, unless all the important aspects of protection are scrupulously adhered to, one may never attain the advantages offered by good coatings.

The information presented shows that there is adequate proof that exceptionally long and lasting protection can be obtained in the South African climate by ordinary paints, especially if proper attention is given to the substrate and especially, and again this must be emphasised, to an adequate number of coats and proper overall film thickness throughout.

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Epoxy resin floor finishes in South Africa*

By L. Muller

African Bitumen Emulsions, P.O. Box 44, Jacobs, Natal, South Africa

Summary

The application of epoxy resin systems in flooring is reviewed with particular reference to South African practice.

Key words

Types and classes of;

coating epoxy finish floor finish surface concrete metal wood

Finitions aux résines époxydes pour sols en Afrique du Sud

Résumé

On passe en revue l'utilisation des systèmes à résine époxyde pour la finition des sols à l'égard particulier de l'usage en Afrique du Sud.

Epoxidharz—Bodenbeschichtungen in Südafrika

Zusammenfassung

Die Anwendungsmethoden für Bodenbeschichtungen mit Epoxyharzsystemen wird mit besonderer Berücksichtigung der in Südafrika üblichen Praktiken besprochen.

Эпокси-смольные отделки полов в Южно-Африканском Союзе

Резюме

Рассматривается применение эпокси-смольных систем для полов, в частности по отношению к их практическому применению в Южной Африке.

Introduction

The protection of industrial concrete floor toppings against chemical attack and mechanical damage has presented problems for many years. With the introduction of epoxy resins into this country some 12 years ago, the first major breakthrough in solving some of these problems was realised.

Early observations made on the various characteristics of these materials, such as adhesion to various substrates, abrasion resistance and chemical resistance, tended to make one think that here at last was something that would be a "cure all."

^{*}Presented to the Second National Convention, South African Section, Durban, 18-20 October 1968.

However, this optimism was short lived, as the many test panels applied to floor surfaces produced almost as many failures. Then started the hard uphill battle once again to establish the limiting factors of the various formulations and application techniques. This led invariably to an investigation of the subbase as, in most cases, failure was caused by lack of bond or weak sub-bases. This possibly produced the first real understanding of epoxy applications as floor finishes.

In most cases, these early epoxy applications were applied to screeds or concrete bases that had been in service for many years and had become impregnated with various types of oils, fats, chemicals etc., which were being manufactured or used in the particular industries. Due to lack of experience at the time, little thought was given to cleaning methods. Tests carried out on these bases soon showed that a new approach to base cleanliness and soundness was necessary. The idea that treating existing floors was, in fact, false economy, had to be presented to the various customers and hence today exists a situation where an experienced contractor can make a visual inspection of a base and, with almost 100 per cent certainty, be in a position to say whether or not an epoxy system will adhere sufficiently well to the base in question.

Types of flooring systems

Multiple paint coats

The simplest form of epoxy flooring is the multiple coat system. This is achieved by the application of two or more coats of a solvent-borne epoxy material, preferably to a well screeded floor. The application is by brush, roller or spray gun, and a suitable curing time is allowed between coats to avoid trapping solvent. Ambient temperature conditions are most important in deciding overcoating time. The completed system, properly formulated and applied, gives a smooth surface with high chemical resistance, suitable in areas where spillage of chemicals or oils are encountered but not for heavy traffic. Foot traffic and rubber-tyred wheels would be acceptable.

Stipple finish

This is usually a two-coat system, using a primer followed by a solvent-free epoxy compound, suitably formulated to give some degree of thixotropy. The application may be initially by brush followed by a lambswool roller to create the stipple effect, or may be squeegee-applied followed by roller. This system gives a heavier coating than the above and is also more non-slip due to the stipple effect. Resistance to mechanical and chemical damage is good. It performs very well in canteens and kitchens.

Aggregate sandwich

In this case, similar techniques are used as in multiple coat flooring, except that a suitably graded aggregate is applied to either the first or the second coat while wet, depending on the desired effect. Usually, the aggregate is applied into the wet second coat which is allowed to cure, the excess being swept away, and one or two top coats applied. The system gives excellent non-slip properties, and good abrasion and mechanical resistance together with good chemical resistance. Solvent-free epoxy coatings may also be used in this application to

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give a heavier final flooring system. The choice of the type used is dependent on the conditions to which the floor will be subjected. The application may be by brush, roller or squeegee, depending on the system used.

Self-levelling

These materials are always solvent free, and are formulated to give dilatant properties and exceptional air-bubble release. The application can be by either squeegee or notched trowel, and once the material has been applied, it flows out leaving an extremely smooth finish. These systems can be formulated to give a high thickness build or can, in fact, be applied using suitable spray equipment. They are usually applied in areas where chemical or mechanical resistance is required together with aesthetic appeal.

Aggregate-filled, trowel-applied

These systems are applied by trowel, and may be finished with an epoxy paint coat if desired.

- (a) In one procedure a solvent-free epoxy compound is mixed with a suitably graded clean sand. Optimum tensile and compressive strengths are obtained using approximately 14 per cent of binder by weight. These systems are usually applied to a previously primed base and trowelled on to give a final thickness of approximately $\frac{3}{16}$ in. Field tests have shown that it is not advisable to apply these systems in thicknesses below $\frac{3}{16}$ in under conditions of severe mechanical attack, as this invariably leads to failure of the system. This system is suitable for high chemical resistance and fairly heavy mechanical resistance.
- (b) The same epoxy resin formulation may be used, but with steel aggregate in place of sand. This type of flooring is ideally suited to areas of limited chemical attack but very high mechanical damage. An example of this would be a drum-filling plant where heavy drums are rolled across the floor.
- (c) As in (a) and (b), but using coloured terazzo chips as aggregate. This type of flooring obviously is only required where aesthetic appeal is primarily required, and therefore not a great deal of this type of flooring is used.

Certain application difficulties are experienced in applying these trowelled finishes and, for the inexperienced artisan, the first lesson to be learned is that, being non-self-levelling, it is very easy to trap air while applying these systems. This usually shows itself as a blister which, once created, is extremely difficult to put right, and therefore great care should be exercised to avoid this and also to avoid leaving an "open textured" surface which will allow the ingress of chemicals etc. These floors should not be used at elevated temperatures as differential expansion between the flooring material and the substrate causes failure.

Tile joints

In cases where operating conditions are beyond the limits of epoxy floor systems, quarry or similar tiles have been used with great success in conjunction with an epoxy system. The tiles may be bonded to the concrete using an epoxy resin compound, and the joints between the tiles pointed with an epoxy system. The pointing may be an aggregate-filled epoxy, but need not necessarily be so. Excellent results have been obtained with these systems.

Preparation of sub-base

Concrete

In some cases it is possible to use an epoxy system on a previously used concrete base. Depending on the type of contamination, solvent/detergent mixes have been found to be adequate. Sand blasting has also been found to be effective. However, in most cases it is necessary to remove the existing topping and to apply a new screed. Depending on the type of floor finish to be applied, this may be a wood- or steel-float finish.

Acid washing has created a storm of protest from many authorities, but tests have shown that, if used correctly, various concentrations of hydrochloric acid give excellent results as a surface preparation for concrete prior to applying an epoxy finish. If any doubt exists regarding the soundness or cleanliness of a base, it is recommended that a trial area be treated to test adhesion. Rising dampness through concrete bases has been a common cause of adhesion failure of epoxy floor finishes, and it is recommended that some form of test be carried out to check this prior to applying the epoxy.

Other surfaces

In most cases these are metallic or wood. In the case of metallic surfaces, sandblasting is recommended. For wood, mechanical sanding is preferred.

[Received 12 November 1968]

Next month's issue

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

"Electron probe analysis in the investigation of surface coating problems," by *P. Whiteley, K. E. Fletcher and G. W. Rothwell.*

"The influence of the solvent and the substrate on the water vapour permeability of films," by R. Katz and B. F. Munk.

"Effect of inhibiting pigment in high-build chlorinated rubber systems for underwater use," by T. F. Birkenhead.

"The formulation of zinc oxide latex paints," by E. Hoffmann and A. Saracz.

Correspondence

SIR,—May I refer, although somewhat belatedly, to a paragraph on p. 839 of the *Journal* for last September where the President, when conferring the well-deserved Honorary Membership on Dr Keenan, is reported as saying "Dr Keenan had been the first President to visit the USA and establish what had since developed into a very close liaison between the Association and the Federation of Societies of Paint Technology."

I well remember Dr Keenan's visit to the USA, and I should indeed be sorry if any words of mine were taken to detract in the slightest degree from the valuable work he did in bringing about close co-operation between the Association and the Federation of Paint and Varnish Production Clubs of the USA when he attended their Meeting at Atlantic City in 1946.

As a matter of historic interest and accuracy however I should like to refer to one aspect of my visit to the USA and Canada in 1927, particularly as it was not mentioned in the Journal at the time though published in the USA. This was some years before the formation of the Paint and Varnish Production Clubs in the USA and was when I was the Immediate Past President of the Association.

In that capacity I attended the Scientific Sessions and the Banquet of the Paint and Varnish Division of the American Chemical Society held in connection with the Annual Meeting of the latter at Richmond, Virginia, in April 1927. I was given a very friendly and cordial reception, being their "Guest of Honour" at the Banquet and replying to the toast of "The Guests." I gathered from many informal talks with prominent members attending the Meeting that they all had a high regard for the Oil and Colour Chemists' Association and took a lively interest in its activities as reflected in its Journal.

References to OCCA and to my attendance at the above Meeting were made in the weekly periodical "Paint, Oil and Colour Review" (published in Chicago) for 21 April 1927 and again (following my visit to Chicago) in the issue for the 9 June, when it refers to OCCA as "a very active and successful body which has done much to foster the spirit of co-operation and to show the need and value of scientific research."

On my way up from Virginia I stayed off at Washington where I visited the US Bureau of Standards and the USA Paint Manufacturers Educational Bureau of Research, and had friendly and interesting talks with Dr Walker, Head of the Paint and Varnish Division of the Bureau of Standards and Dr H. A. Gardner, of the Paint Manufacturers' Research Bureau. As the first Honorary Editor of the *Journal* I had, from the outset, sent copies regularly to each of the above in return for their own publications, abstracts of which were published in the *Journal*.

Incidentally, in my capacity as member of council of the Society of Chemical Industry, I attended the Annual Convention of Canadian Chemists at the Chateau Frontenac, Quebec, at the end of June; a very large gathering indeed on a grand scale. I was one of three speakers who replied to the toast of "The Guests" at the Convention Banquet, the first being the Governor of Quebec Province. Very few of those attending the Convention were connected with the Paint and Allied Industries, a significant reflection I think of the scientific status of these industries some forty odd years ago compared with what it is today.

Yours faithfully,

H. Houlston Morgan.

Reviews

PLASTICS RHEOLOGY

By R. S. Lenk, London: Maclaren and Sons Ltd., 1968. Pp. xxv + 214, 80s.

The first six chapters of this book are on the flow of viscoelastic melts, beginning with a rheological introduction and going on to flow defects and extruder screw design. There follow two chapters on the deformation and strength of solids and one on dynamic testing, analysed largely in electrical terms.

There are many serious misprints, for instance equation 9.7 contains three and on page 5 there is a drawn out confusion between v (velocity) and v (kinematic viscosity). However, my main criticism centres on the large number of misleading statements. Thus for instance a power law liquid is given a Newtonian viscosity, shear stress and shear rate are confused, the importance of time dependent effects is underestimated and compliance is defined generally as the reciprocal of modulus. Some of these statements are later qualified and corrected, but they must lead to confusion in the mind of the reader.

P. LAMB

Organic Photochemistry-2

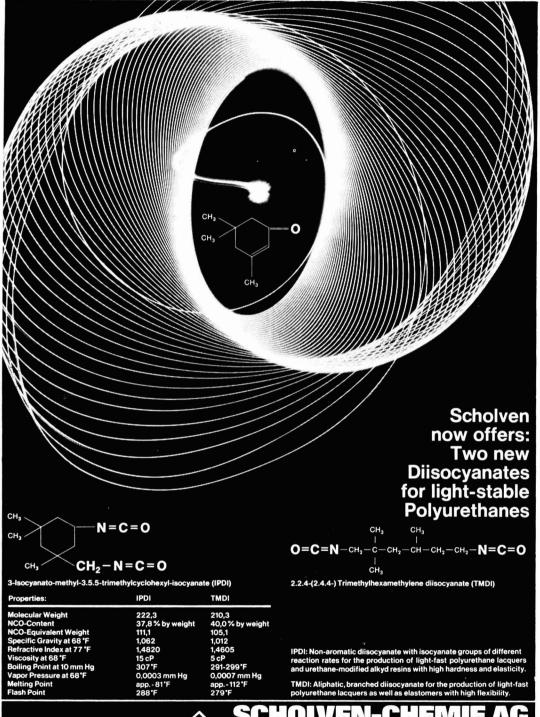
IUPAC Division of Organic Chemistry. London, Butterworths, 1968. Pp. viii + 200, price 25s.

This volume comprises the plenary lectures presented at the Second International Symposium on Photochemistry held in 1967 at Entschede, The Netherlands, reprinted from *Pure and Applied Chemistry* 1968, Vol. 16, No. 1, and bound in hard covers. As is well known, IUPAC plenary lectures represent some of the most authoritative reviews and reports of recent work available in the world literature, and their reputation is well upheld in this series.

Photochemistry, long of the greatest importance to the colour side of the coatings industry, has been studied to an increasing extent in recent years in relation to film curing and degradation. The printing ink technologist, no doubt already keeping abreast with high speed plate-making techniques based on photochemical principles, cannot be unaware of the threat to impression methods represented by the latest developments in photoelectric and related reprographic processes. Notwithstanding the reluctance of the chemical industry to adopt photochemical methods of synthesis in the past, the latest improvements in reactor design seem likely to encourage the development of photochemical polymerisation processes. It would be imprudent, therefore, for the forward-looking coatings scientist to ignore the researches reported in this book just because they appear to be centred on systems and reactions generally remote from his erstwhile experience.

Nevertheless, it must with regret be said that little of obviously direct applicability to the coatings field can be seen in the substance of these lectures. For the most part, they report studies in basic photochemical reaction mechanisms, and a rather long extrapolation is needed before their application to coatings systems can be envisaged.

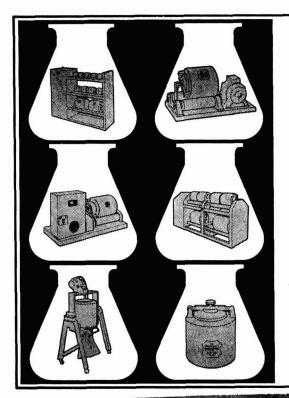
Readers of this *Journal* are most likely to be interested in the papers by Prinzbach on photochemical reactions with non-conjugated dienes, Bryce-Smith on photoaddition and photoisomerisation reactions of the benzene



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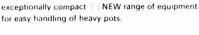
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REVIEWS

ring, Stephenson & Hammond on fluorescence quenching by conjugated dienes, Rigaudy on photo-oxidation of aromatic compounds, and Bartlett *et al.* on cycloaddition to conjugated dienes. The two papers by Schaffner and by Yates on reactions of cyclic ketones are also of interest. All these provide food for much thought and speculation, and they provide a testing exercise in forward thinking for the man whose job it is to shape the technology of the future.

A. R. H. TAWN

BRITISH POLYMER JOURNAL

J. G. GREGORY, Editor. London: Society of Chemical Industry Vol. 1. No. 1. January 1969. Annual Subscription: to members of SCI £4, to non-members £8.

This is not so much a review as a welcome to a worthy contemporary. As the Society's President states in his message to readers, the first number of a new journal is an event of some importance. We would add that this is even more true when the subject matter is polymers, which has for so long been served predominantly by journals of overseas origin. Whilst the stated intention is to assemble in the new journal many of the kinds of paper hitherto published in the *Journal of Applied Chemistry* and the Society's Monographs, we have no doubt that this venture will lead to a substantial increase in the volume of polymer science literature published in this country. Financial viability is always a problem when a learned society takes such a plunge, and we wish the *British Polymer Journal* every success.

Papers appearing in the first issue are as follows:

Modulus and damping of polymers in relation to their structure.

by J. Heijboer.

Molecular weight determinations on polymers by electron microscopy. by D. V. Quayle.

Melamine-formaldehyde resins. 1. An examination of some model compound systems.

by I. H. Anderson, M. Cawley and W. Steedman.

Isolation of dinuclear dihydroxydiphenylmethanes and trinuclear novolacs (triphenylols) from phenol-formaldehyde condensations.

by W. H. Moss and Elsie Moss.

Peel adhesion of PVC to steel.

by J. C. Sherlock and L. L. Shreir.

Wax crosslinking with dicumyl peroxide.

by A. Brink and F. Dressler.

Studies on anion-exchange resins. IV. Chelating properties of anion exchangers prepared from melamine and commercial cashew nut shell liquid.

by B. D. Dasare and N. Krishnaswamy.

HON. EDITOR

The theory of functionality: Part II By A. R. H. Tawn

Cray Valley Products, St. Mary Cray, Kent

Bifunctional reactions between complementary reactants

This is typified by the polyesterification of a dihydric alcohol with a dicarboxylic acid. The first reaction step may be depicted thus:

 $\begin{array}{ccc} HOOC-A-COOH+HO-B-OH \longrightarrow HOOC-A-COO-B-OH \\ monomer & monomer & dimer \end{array}$

The resultant dimer is a hydroxy acid which can now react with itself to yield a tetramer and so on, in a sequence of reactions substantially identical with those discussed for ε -hydroxy caproic acid in part 1. In addition, each hydroxy acid species formed can react with a molecule of dicarboxylic acid via its hydroxyl group or with a molecule of diol via its carboxyl group. Three kinds of polymer molecule can thus be identified: those containing equal numbers of diacid and diol moieties, terminated at one end by OH and at the other by COOH; those containing an extra diacid moiety and terminated by COOH at both ends; and those containing an extra diol moiety with both ends terminated by OH. As in the case of ε -hydroxy caproic acid, at all stages of reaction there will be a distribution of sizes due to the random nature of the reaction (any OH group being liable to react with any COOH group) and it will only be possible to speak of an *average* molecular weight or degree of polymerisation. Moreover, provided carboxyl and hydroxyl groups were initially present in equal numbers, the polycondensation can again proceed to an indefinitely high degree. Since reaction of a carboxyl group necessarily requires the reaction of a complementary hydroxyl group, hydroxyl and carboxyl groups always react in equal numbers so, if equal numbers were present at the start. equal numbers must always remain and be available for further condensation whatever the degree of reaction. There is, however, a practical distinction from the case of ε -hydroxy caproic acid. Whereas the hydroxy acid by its very nature furnishes OH and COOH groups in equal numbers, the diol-diacid system requires the reactants to be weighed out in exactly equimolar proportions if strict stoichiometric balance is to be maintained. Any slight excess of alcohol or acid will introduce a number of functional groups which have nothing to react with and which are thus ineffective in building up the size of the polymer molecule. These excess functions act as chain-stoppers. For example, if diol is present in excess, polymer molecules terminated at both ends by OH groups will predominate; there will not be enough COOH-terminated molecules for them to react with, and eventually the reaction will stop. This situation is easily dealt with in terms of functionality theory as will later be seen. For the present however, attention will be concentrated on systems in which complementary functions are present in equal numbers.

Relationship between degree of reaction and degree of polymerisation in bifunctional systems

Consider the intermolecular reaction between bifunctional molecules. Either the hydroxy acid or the diol-diacid type of system may be taken as an example.

Let two monomer molecules react to produce a molecule of dimer

$\text{HO}-\text{R}-\text{COOH}+\text{HO}-\text{R}-\text{COOH} \longrightarrow \text{HO}-\text{R}-\text{COO}-\text{R}-\text{COOH}$

or

$HOOC-A-COOH+HO-B-OH \rightarrow HOOC-A-COO-B-OH$

In both cases, four functional groups were originally present, two have reacted and two remain. The degree of reaction is said to be 0.5 at this (dimer) stage, 0.5 being the fraction of the original groups (4) which have reacted (2) i.e., 2/4.

Suppose a trimer to be formed by reaction of three monomer molecules (the reaction sequence does not matter):

HO-R-COOH + HO-R-COOH + HO-R-COOH

\longrightarrow HO-R-COO-R-COO-R-COOH

Of the six functional groups originally present, four have reacted and two remain. The degree of reaction at the trimer stage is thus 4/6 or 0.66.

It is easily seen that formation of a tetramer involves reaction of six of the eight functional groups present in the four monomer molecules, again leaving two groups unreacted, giving a degree of reaction 6/8 = 0.75 at the tetramer stage.

It is already becoming clear that a simple relationship exists between the degree of reaction and the size of the polymer molecule formed. The size of the polymer molecule is unequivocally defined by the number of monomer molecules it contains. This is called the degree of polymerisation and denoted by the symbol x.

It is now possible to construct a table showing the degree of reaction a corresponding to each degree of polymerisation x.

X	1	2	3	4	5	8	10	20	100	10000
р	0	1/2	2/3	3/4	4/5	7/8	9/10	19/20	99/100	999/1000
р	0	0.5	0.66	0.75	0.8	0.975	0.9	0.95	0.99	0.999

Inspection of this table enables one to deduce that the relationship between p and x takes the form:

$$p = \frac{x - 1}{x}$$

or $p = 1 - \frac{1}{x}$

This is a perfectly general expression for bifunctional reactions in stoichiometric balance, i.e., provided complementary functions are present in equal numbers. It can be deduced more rigorously; it can be extended to systems which are not in stoichiometric balance; and a somewhat similar formula can be derived which is applicable to systems of any functionality. These matters will be dealt with in part 3 of this series. In the meantime the student may like to test his grasp of the simple bifunctional relationship by solving the following.

Exercises

- 1. 1 gram mole of isophthalic acid is reacted with 1 gram mole of propylene glycol.
 - (a) At what degree of reaction will the degree of polymerisation be 75?
 - (b) What will be the degree of polymerisation when 98.5 per cent of the original functions have reacted?
- 2. 1 gram mole of adipic acid (molecular weight 146) is reacted with 1 gram mole ethylene glycol (molecular weight 62).

Calculate:

- (a) the weight of water lost from 100 grams of the original mixture when p = 1.
- (b) the weight of water lost from 100 grams of the original mixture when p=0.85.
- (c) the acid value at p=0.85.
- (d) the degree of polymerisation at p=0.85.
- (e) p and x when the acid value is 20 mg KOH/g.

Information Received

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

It has recently been announced that **Chemische Produkte C. H. Baur GmbH** has taken over as sole importer in Europe for the *Uresolve* range of resin solvents, following the withdrawal of **Urethaanchemie NV** from the field.

Uresolves HF, for cured polyester urethanes and epoxy, *Plus*, for urethanes and silicones, and *Plus SG*, similar to *Plus*, but particularly for use with aluminium parts in the electronics industries, are available from stock.

Elcometer Instruments Ltd. has recently announced the availability of the *Elcometer Mark III*, a redesigned version of the well-known instrument for measurement of coating thickness on metal substrates, metal sorting, hardness determination and crack detection on certain materials.

The power supply of the new instrument is by rechargeable nickel cadmium cells, and repairs are simplified by the use of "plug-in" printed circuit boards.

The new instrument, which is claimed to be lighter, and more stable and sensitive in use than its predecessor, can be used with a wide variety of probes, including a ferret probe for use in pipes and a set of coil probes with diameters from 1/8 to 3in.

Victor Wolf Limited has recently announced the formation of a new associate company in Spain. In collaboration with **Transformaciones Quimico-Industriales SA**, Victor Wolf's sole Spanish agents, a new manufacturing company, **Traquisa-Wolf SA**, has been formed. The company will manufacture certain selected products, some of which are already exported by Victor Wolf, and sell to most countries in the world. It is hoped that the new plant will come on stream in the very near future.

Victor Wolf have also recently published a new 36-page booklet entitled "Wolfamid Polyamide Resins." The booklet consists of three main sections dealing with the various uses of these products, and a section devoted to specification and reference data.

As well as general surface coatings manufacturers, the booklet is said to be of particular interest to those in the field of flexographic inks.

It has recently been announced that **Stanhope-Seta Ltd.** has acquired **Poulten**, **Selfe & Lee Ltd.**, manufacturers of lamp blown scientific glassware, viscometers and hydrometers.

A new product, dihydroxydicyclohexyl propane, has recently been introduced by Farbenfabriken Bayer AG.

The product is supplied in the form of free-flowing, clear, lozenge-shaped particles about 10mm in diameter, and finds use as a hardness promoting diol in surface coatings, for raw materials for adhesives, moulding compounds and textile auxiliaries and finishes, and as an intermediate and auxiliary for plastics.

The formation has recently been announced of Ceilcote UK Ltd., the British subsidiary of the American Ceilcote Company, specialists in corrosion resistant techniques in industrial installations.

The new company, which will cater for the British, Scandinavian and South African markets, will specialise initially in the design, manufacture and installation of corrosion

proof floors, walls and vessel linings, both of monolithic and unit construction. Special cement mortars and grouts for the construction industry will be supplied also.

Ceilcote UK Limited will draw on the 40 years' experience in this field of its American parent, and offers what is claimed to be a unique guarantee against breakdown and on fitness of operation of all its work.

Farbwerke Hoechst AG has recently added *PV Brown HFGG Hostavinyl*, an approximately 40 per cent pigment preparation, to its range of *Hostavinyl* pigments for use in pvc.

As from 1 March 1969 in the UK and at a later date overseas, sales of *Acid 810*, which is used in the production of paint driers, and has applications in alkyd resin manufacture, will be taken over from ICI Ltd., Heavy Organics Division, by Novadel Ltd.

ICI's Billingham plant producing *Acid 810* will close down during the second quarter of 1969, when production will be commenced at Novadel's Gillingham site.

It has been announced that there will be no redundancy as a result of the closing of the ICI plant.

Berger, Jenson and Nicholson Limited and Celanese Corporation of America have recently announced that agreement has been reached for BJN to acquire various Celanese subsidiaries operating in the paint and allied industries on a world-wide basis. These subsidiaries broadly comprise the British Paint (Holdings) Limited group.

At the time of writing, the acquisition is subject to approval by the Ordinary and Preference Stockholders of BJN, the approval of the Debenture Stockholders of BJN to certain alterations under the Debenture Stock Trust Deeds, and the necessary exchange control and other consents.

Plans for increased production at the Barry, Grangemouth and Stroud factories currently producing plastics, was recently announced by **BP Chemicals (UK) Ltd.**

Main products affected are polystyrene, *Rigidex* high density polyethylene, *Breon* nitrile rubber and *Cellobond* brake lining resins.

BP Chemicals has also recently issued five new "Technigrams," "Technigram 110/2" on methoxyhexanone, "Technigram 377/1" on isobutyl acetate," Technigram 371/1" on *Lobosols*, "Technigram 256/2" on ethyl acetate, and "Technigram 321/2" on *n*-butanol, all products in the *Bisol* range.

Stewart Wales, Somerville Ltd. has recently commenced publication of its own house journal "Fact." The journal will be distributed to 15,000 actual and potential customers, and is intended to illustrate the advantages of using specialist surface coatings in preference to conventional paints.

It is claimed that "Fact" is the first publication of its type in this field.

A new iron-zircon coral pink glaze stain, 14 M200, has recently been introduced by Blythe Colours Limited.

The new stain is claimed to be capable of matching most existing pink shades, and to be stronger and more economical in use, have high thermal stability, complete consistency batch to batch, and, owing to its non-metameric nature, to minimise the effects of different lighting conditions.

Scott Bader & Co. Ltd. has recently issued a 16-page booklet on the use of its *Polidene* vinylidene chloride copolymer emulsions. Copies are available from Scott Bader on request.

It has recently been announced that the industrial paint companies of the Ault and Wiborg Group have been reorganised to form Ault and Wiborg Industrial Finishes Ltd.

The new company, which will incorporate Gittings and Hills Ltd., A. Learner and Co. Ltd., Ault and Wiborg Paints Ltd., and Perivale Paint Products Ltd., is intended to make maximum use of the manufacturing and service units within the group, and thus to offer customers service and technical co-operation. The industrial paint activities of Ault and Wiborg (Scotland) Ltd. will be incorporated at a later date.

Midlands-Membership Survey

By D. E. Hopper and L. R. Seaborne

Introduction

There is at the present moment concern in the Association regarding the strength of membership, rate of recruitment, and its role in industry, present and future. During the presidency of Dr S. H. Bell, a document entitled "Forward Thinking" was compiled, and submitted to Section Committees for consideration. The document was duly considered by the Midlands Section at two full committee sessions, and a letter prepared and submitted to Council.

In the light of the document, it was felt imperative that we as a Section should conduct a membership survey, and this report duly records the work conducted, and the results obtained.

A sub-committee was formed to study the statistics, and ideas drawn from the compiled results.

Questionnaire and survey

The membership survey exercise carried out by the Manchester Section on the range and type of membership, duly recorded in *JOCCA* 1968, **51**, 356, was, it was felt, extremely useful, and should be extended to cover the whole of the Association.

In order to standardise the survey it was felt desirable to deviate as little as possible from the form of the Manchester questionnaire. However, several small alterations were made to cater for the local conditions, such as possible replies from the Trent Valley Branch. Basically the questionnaire remained the same, being divided into four main sections:—

Section A.	Personal and company details.
Section B.	Programme organisation.
Section C.	Programme content.
Section D.	Social programme.

The membership questionnaire was despatched to Section members on 9 February 1968, accompanied by a covering letter from the Section Chairman, and a window envelope for the completed replies. The sub-committee forwarded a reminder to all members on 27 February, and a final reminder from the Chairman was despatched on 1 April. In mid April some 133 replies had been received, which represented a 53.9 per cent return. Due to the lack of response to the Chairman's letter of 1 April, it was decided to close the returns at 133 and compile what results had been received.

Summary and conclusions

There were 247 questionnaires posted, 199 to Midlands members and 48 to Trent Valley Branch members. Returns totalled 133, which represented 53.9 per cent of Section membership; the returns were split as follows; 116 Midlands (58.3 per cent) and 17 Trent Valley Branch (35.4 per cent).

The option was given of answering the questions anonymously; however, only 1.5 per cent did so, although there were one or two requests to respect the privacy of the replies.

The membership replies, when compared with the theoretical breakdown, showed some slight deviations, and these are duly recorded herewith:—

	Theoretical	Replies
Junior	2.9%	3.85%
Associate	16.0%	9.85%
Ordinary	80.7%	85.55%
Honorary	0.4%	0.75%

The survey results are thus in fair agreement with these figures, although, as a class, Associate Members have been less responsive than the other classes.

The age distribution shows distinctly that the largest proportion of members (40 per cent) is in the age group 30-40. The 40-50 year group envelops 26 per cent, and 20 per cent were aged over 50 years. Alarmingly, only 13.5 per cent of members are below 30 years old. These facts are very close to those obtained by the Manchester Section, and, similarly, are supported by the fact that over 44 per cent of Midlands Section members have been in industries served by OCCA for more than 20 years, and a further 32 per cent between 10 to 20 years.

Replies to the question on function in which the member was engaged, indicated that most members were engaged in more than one function in their company (230 replies on 133 questionnaires). This is probably most characteristic of smaller companies. In such circumstances, percentages can only indicate in a general way the distribution of occupations. The largest group (45 per cent) was concerned with research and development, and was closely followed in size by the group of members involved with technical service (41 per cent). Production concerned 22 per cent, quality control 15 per cent and analysis 10 per cent. Sales and marketing involved 28 per cent of members and 13 per cent were occupied with other functions, including general administration, costing and buying. No less than 43 per cent claimed managerial or directorial status whilst 17 per cent were representatives. Only 2.7 per cent admitted to positions as assistants or technicians.

Over half of the members worked for firms manufacturing paint, varnish and lacquers (53 per cent) and 8 per cent worked for printing ink manufacturers. Resin manufacture concerned 31 per cent, pigment manufacture 17 per cent, ancillary chemicals 11 per cent and intermediates 8 per cent.

Encouragement was given to two thirds of the membership by their respective companies, the remaining third finding their companies indifferent to OCCA. The companies also paid subscriptions in the same ratio, indicating the accuracy of this section of the report.

At this stage of the report, it is noted how remarkably close some of the findings are to those of the Manchester Section. Companies obviously gave varying support towards OCCA activities, and the survey indicates that 84 per cent of members were given time to attend Technical Meetings or Symposia of direct interest. The Biennial Conference is, of course, completely different, and only 26 per cent were allowed time to attend. Questions on programme organisation have shown that only 18 per cent attended five to six meetings a year, and 41 per cent attended only one or two meetings. Reasons given for not attending lectures were given by 46 per cent as lectures of no particular interest and 39 per cent had insufficient spare time.

In assessing lecture venues, facilities, frequency, day and time it was found that members were distinctly creatures of habit. The one change 41 per cent of members would like to see was that of refreshment facilities (bar) being to hand.

Committee had for some time wondered whether a midday lecture would be preferable, with lunch, but this was definitely rejected by 87 per cent of members. A substantial majority (82 per cent of those replying) were largely satisfied with the existing balance of programme, but there was also strong support for more lectures on organisation/management, application, fundamentals, materials and manufacture. The idea of panel evenings was favoured by 47 per cent whilst a film evening was requested by 32 per cent.

The present Social Programme (Section D) was shown to be extremely satisfactory, 56 per cent attending social activities, and 80 per cent fully endorsed the programme content. Despite this "carte blanche," only a third of the members regularly attended the annual dinner and dance; reasons for not attending were very few, and rather random.

Acknowledgement

Acknowledgement is made to the Manchester Section Committee who provided a copy of the questionnaire used in their survey. It is of interest that the two surveys have produced such very similar results.

The authors would also like to thank those members of Midland Section who replied to the questionnaire; without such co-operation the survey would not have been possible.

Hull

Developments in emulsion polymers

Mr E. A. Brown, Hull Section Chairman, introduced Mr K. A. Safe, of Vinyl Products Ltd., to the fourth meeting of the current session held at the College of Technology, Hull, on 6 January, to speak on developments in emulsion polymers.

Mr Safe briefly outlined how the use of emulsion polymers in the paint industry had started with vinyl acetate homopolymers and how these had been superseded by vinyl acetate copolymers. Recently, developments had been made mainly in the directions of increased opacity and of lower cost paints for interior use only. It was possible that some of the newer types of polymer might be used for the latter purpose and find quick acceptance if some cost advantage were obtained.

The available monomers were considered in three groups, those giving hard homopolymers, such as styrene, vinyl acetate and methyl methacrylate, those giving soft homopolymers, such as butadiene, butyl acrylate, ethylene, and those giving special properties, such as acrylamide, acrylic acid. For comparative purposes the current cost of these monomers was considered in US cents per pound. The properties conferred on the dried film by these monomers were briefly considered, and it was pointed out that the hard monomers required softening, either by the use of an external plasticiser, such as dibutyl phthalate, or by copolymerisation with a monomer from the group giving soft homopolymers. The range of copolymers based on combinations of the above monomers which were commercially available was considered, and it was concluded that the polymer types readily available and worthy of serious consideration were methyl methacrylate copolymers, styrene copolymers and vinyl acetate homoand co-polymers. The vinyl acetate polymers were considerably cheaper than the all acrylic polymers and probably also than the styrene-acrylic copolymers.

It is claimed that the new acrylic and styrene-acrylic emulsions had a higher pigment binding power than the vinyl acetate emulsions, and if, for this reason, a lower content of the former emulsions could be used in the formulation of a paint, this might offset their higher cost. It had been decided that this possibility was worthy of investigation and, after considering a number of possible methods of assessing the binding power, it was decided that the resistance to wet rubbing was probably the most realistic. The method demonstrated at the 1968 OCCA Exhibition was adopted, which consisted

of casting a film of the paint concerned on a sheet of vinyl chloride/vinyl acetate copolymer ("Flovic"), drying for 24 hours under controlled conditions and weighing accurately. The film was then subjected to a standard number of strokes (500) on a scrub testing machine, washed and redried for 24 hours under the same conditions and reweighed. The loss in weight gave the weight of film removed. It was found that if a series of paints of increasing PVC and based on the same binder, was tested by this method, the loss in weight (between 0.01 and 0.02g) remained remarkably constant until a critical PVC was reached, after which the weight loss suddenly increased to over 0.1g. The results were reproducible and the critical point was always very clear.

This method was used to test a wide range of commercially available emulsion polymers, which were made up into a series of paints of increasing PVC. In all cases a small, almost constant, weight loss was shown until the critical point was reached, after which a rapid increase in the weight lost occurred as the PVC increased. The emulsion types fell into clear cut bands; the worst vinyl acetate copolymer was better than the best vinyl acetate homopolymer, the worst all-acrylic was better than the best vinyl acetate copolymer, and the worst styrene-acrylic was better than the best all-acrylic copolymer. It was of interest to note that a vinyl acetate-ethylene copolymer fell into the general class of vinyl acetate copolymers.

The results suggested that all-acrylics and styrene-acrylics did have a better pigment binding power than the vinyl acetate polymers. Since the investigation had been limited to paints for interior use, it was considered that a paint having a PVC just below the critical break point, as assessed above, would be adequate; but before any cost comparisons could be made the question of opacity had to be considered. The opacity was measured by applying a 0.003in thick wet film to a standard black and white opacity card and measuring the contrast ratio over the two halves of the card after 24 hours drying. Reasonably satisfactory results could be obtained by carefully checking the wet film thickness and carrying out a number of replicate tests.

In order to establish a standard of opacity, a range of commercial emulsion paints was examined and it was found that good quality general purpose paints gave a contrast ratio averaging around 95 per cent, whilst the more recently introduced higher opacity paints were about 97 per cent.

The physical properties of the range of emulsions used in the investigation were studied, but did not show any useful correlation with the scrub tests. When the cost of these emulsions was considered, it was noted that the low specific gravity of the solid styrene-butyl acrylate copolymer brought its cost on a solids/volume basis guite close to that of the vinyl acetate-2-ethylhexyl acrylate copolymer. Each of the emulsions studied was made up into a series of paints, ranging from 40 per cent to 90 per cent PVC. Formulation was on a volume basis, since paints were sold and applied on this basis. A coated rutile titanium dioxide was used as the sole pigment and whiting as the sole extender throughout the series. Sodium polyphosphate, as dispersant, and ethyl hydroxyethyl cellulose, as thickener, were each used at constant ratios by volume to the total pigment. Coalescing solvent was used, where necessary, to give film formation at 5°C. In each series the volume of titanium dioxide in the dry film was kept constant throughout the range of PVC's, so that when applied at constant spreading rate, the volume of titanium dioxide per unit area of film remained constant. Throughout the series the volume of volatile matter (water plus coalescing solvent) remained constant at 60 per cent.

The first series contained 20 per cent by volume of titanium dioxide on the dried film and scrub tests showed that the PVC at which resistance became poor was below 55 per cent for vinyl acetate copolymers, between 65 per cent and 70 per cent for vinyl acetate-ethylene and for vinyl acetate-octyl acrylate copolymers, between 75 per cent and 80 per cent for the all-acrylic copolymers, and between 85 per cent and 90 per cent for styrene-acrylic copolymers.

These results must be considered in conjunction with the opacity values of the paints. Here it was found that the opacities at any particular PVC were in the reverse order of the pigment binding power of the polymers. Vinyl acetate homopolymer, the worst pigment binder, gave the highest opacity. All the emulsions used could provide paints which exceeded the 95 per cent contrast ratio level and which were still scrub resistant, but only the all-acrylics and the styrene-acrylics would reach the 97 per cent level at 75 per cent and 85 per cent PVC and still remain scrub resistant. However, these last two emulsions were over pigmented at 20 per cent titanium dioxide for the 95 per cent contrast ratio, whereas the others were under pigmented for the 97 per cent level.

The systems were re-examined at a 25 per cent titanium dioxide by volume content in the dried film. The increase in the pigment made little difference to the scrub resistance, but the vinyl acetate homopolymer almost reached a 97 per cent contrast ratio at about 50 per cent PVC and remained scrub resistant, while the two vinyl acetate copolymers reached this ratio at about 65 per cent PVC. Thus scrub resistant formulations had been obtained which would meet either of the opacity levels. It was necessary to see whether 15 per cent titanium dioxide by volume would enable cheaper formulations to be made with the all-acrylic and the styrene-acrylic emulsions which would meet the 97 per cent contrast ratio level and still be scrub resistant. It was found that this could be achieved at 75 per cent PVC for the all-acrylic and at 85 per cent PVC for the styrene-acrylic emulsions.

Thus formulations had been established for the levels of titanium dioxide and the PVC necessary to give scrub resistant emulsion paints at both the 95 per cent and the 97 per cent contrast ratio levels. The styrene-acrylic emulsions gave the lowest cost paints (8/3d and 9/4d per gallon respectively) on account of their very high pigment binding power.

In the discussion following the lecture Messrs Brown, Robinson, Hasnip, Duggan, Clark and Miss Whitehead took part. A vote of thanks for a most instructive lecture was proposed by Mr E. Armstrong. Twenty-one members and fourteen visitors were present.

Colour sense

The fifth ordinary meeting of the session was held at the Queen's Hotel, Hull on 3 February. This occasion was the "Ladies Night," at which the Chair was taken by Mr N. Lythgoe, who introduced the lecturer, Mr J. Haines of Sissons Bros Ltd.

Mr Haines briefly described the ranges of colours which were known as "cool" and "warm" and those which had the effect of making surfaces to which they are applied "advance" or "recede."

The lecture was well illustrated with a number of colour slides of various rooms and colour schemes. Mr Haines made comments and described how the desired effects had been achieved.

After a break for refreshments, Mr Haines answered a large number of questions from members of the audience, mainly from those requiring advice on their own homes. It seemed that Mr Haines advocated a certain amount of boldness, on the grounds that if a mistake were made it would not last for very long, owing to the modern habit of almost annual redecoration.

A vote of thanks for an interesting and instructive lecture was proposed to Mr Haines by Mr T. A. Fillingham. Twelve members and eighteen visitors were present.

London

Well varied programme of meetings

The first four lectures in the 1968-69 session of the Section have been of a varied nature and have provoked much interest—members from other Sections, including the Midlands, have been present at several of them.

The session began with an excellent talk by Mr A. R. H. Tawn who chose the title "New concepts in polymer architecture." He noted that, compared with 20 years ago, polymer science was now a highly disciplined branch of knowledge. The probe into polymer structure and its relation to properties had been a slow process and there still remained much to be done. There were, he said, possibilities of new molecular shapes and new building methods leading to new polymer species.

There was, for example, the preparation of block and graft polymers by redox reactions and an elegant technique had been developed by which polymerisation could be initiated at halocarbon sites by the use of metal carbonyl catalysts. He mentioned also the comb, ladder and sheet polymers. The ladder-type structure was, for example, of interest in connection with space research and the need for coatings of high heat stability.

There was, he suggested, no reason to confine one's thinking to covalent bonded polymers. Another class that presented interesting possibilities was the ionomers possessing an ionic structure. Then there was the metallocene type structure—might it not be possible to conceive a polymer of this type in which the central metal atom was, say, titanium?

The paper provoked considerable interest and there was, naturally enough, a vigorous discussion. Among the more practical points raised, Mr Tawn was asked if alkyds, in the presence of driers, could be regarded as ionomers with ionic crosslinking through the metal cations. He said that he believed one should regard alkyds as polyelectrolytes and that, on a number average basis, there would always be a number of small molecules present to which the drier metal was bonded.

In his talk, Mr Tawn had described work which had indicated the existence of Ladenburg-benzene (prism structure) and Dewar-benzene in form of hexamethyl derivatives. This led to the question as to whether or not alkyd resin films on irradiation could undergo structural changes which might affect their properties; further, that it would be interesting to prepare alkyds from, say, Dewar-benzene and contrast their properties with conventional products.

Mr Tawn would not be drawn by another question which asked if he would say what the structure of the "ideal" coating polymer might be. He said it was first necessary to relate properties to structure and that, in the paint industry, one did not yet know enough about the properties that were required of such an ideal structure.

The next lecture was given by Mr G. S. Sanders (Urwick Management Centre) and the subject was "Management by objectives in research and development." The basis of his argument was that the major problem in management generally was "organising ambition." In other words, to integrate the objectives of all individuals in an organisation.

This involved setting meaningful corporate objectives (quantified statements in terms of defined profit objectives, return on capital, and so on). It also involved defining carefully the "key tasks" of managers. Having set the objectives for each layer of the management pyramid, one had to review progress, re-assess objectives, up-date targets and so forth at regular intervals.

Similar arguments applied to the management of research and development for which explicit objectives could be set. He also indicated the various key tasks, standards and controls that would have to be set up. The key decision areas in innovative research and development included the objectives at corporate level, management level and bench level under the headings research, development, and pilot plant operation or prototype manufacture.

This was a subject that also provoked a considerable amount of discussion. There was, for example, the view that highly qualified personnel might be subjected to excessive restraints in relation to their professional requirements although Mr Sanders did not believe this was universally true; those engaged on sponsored research, for example, did not appear to suffer in this way.

He also believed it was possible to ration the time spent on specific projects if there were a number of minor projects involved. He did emphasise the need for continual involvement between the various management levels and between management at the same level and this had led to the adoption by some of "project management" in which several groups (production, marketing and R and D) were blended.

He agreed that the problem of a research manager in selecting a project was a difficult one and suggested that a "portfolio" of projects, some of which had a good chance of commercial success, together with others of a more speculative nature, might be included.

A rather different paper was presented by Dr W. C. Wake (Rubber and Plastics Research Association) under the title "Cross-links between paints and adhesives" in which he examined some of the points of similarity between the two products, and covered other aspects, such as the measurement of adhesion.

This raised a number of points in the discussion. For example, could the adhesive failure of a paint film be attributed to the change in the polar nature of the polymer on ageing? Dr Wake suggested that cross-linking, which introduced stresses and shrinkage at the interface, was responsible for loss of adhesion rather than any change in polar nature of the polymer which, in fact, did not change on ageing.

Asked why it was that old paint films were so difficult to wet, Dr Wake said the surface of the film would have lost its polar nature due to the adsorption of dirt and fatty acids (the latter would be orientated to present a non-polar surface). In any case, he said, an organic acid surface had a very much lower surface energy than that of a metal oxide layer. Answering a further question on this point, he said that with increased —COOH groupings the possibility of forming water-in-oil emulsions decreased.

The fourth lecture in the session was on "Gel permeation chromatography," given by Mrs S. M. Rybicka (Paint Research Station). She described the application of GPC to the study of polymers used in the paint industry and explained the technique, noting that commercial GPC equipment contained chromatographic columns, packed with beads of crosslinked polystyrene gels of graded pore size. Molecules dissolved in organic solvents were separated depending on the extent to which they penetrated into the gel particles, which offered different internal volumes to molecules of different sizes.

Polymers that had been studied by this technique included epoxy resins, phenolic resins and stand oils, all of which consisted of a series of well separated components; acrylics and pva and pvc resins which gave very symmetrical molecular size distribution curves; and alkyds which gave a very broad distribution of molecular sizes.

GPC had been used to follow the polymerisation process, to compare polymers obtained by different polymerisation methods, to follow the copolymerisation process, and so on.

The discussion was concerned especially with particular aspects of the technique. It was also stressed that one had to exercise care in interpreting the results of GPC

determinations in terms of molecular weight. This might be especially true where, as in alkyds, several chemically different molecular species might be present. Much depended on the shape (i.e. compactness or otherwise) of the molecules under examination.

This meeting was one of two that were being held at East Ham Technical College during the session. This is a venture that was started in the 1967-68 session and proved to be a great success, in that members working in East London found it easier to attend than the meetings in central London. It was also encouraging that a number of students from the College attended; one of them, Mr D. Howell, proposed the vote of thanks to the lecturer. DFF

Manchester

Emulsion paints: instrumental aids to binder selection

As a result of the Section survey conducted in 1968, the meeting on 10 January was held in Bolton, and an excellent response resulted, over 100 members and guests attending. The venue was the Swan Hotel, and the lecturer, Dr C. Bondy of Revertex, presented a paper entitled "Emulsion paints: instrumental aids to binder selection."

Dr Bondy opened by stating that unwarranted assumptions were often made about the speed and extent of film integration in emulsion paints. He described a technique by which the change in these properties could be followed; the rate of water penetration of a film could be followed by measuring resistance changes, which showed that film impermeability was sometimes not reached after one week's ageing. Two coats of a commercial gel latex paint showed rapid water penetration, one coat of a styrene/ acrylic paint showed very slow penetration. These results indicated that film formation followed a mechanism different from that generally described and that an impermeable coat required weeks of ageing rather than days. Many of these paints had satisfactory scrub resistance at an early stage; this raised doubts about scrub testing. It had been found that wetting a film, or dry rubbing, did not affect water penetration as measured by resistance changes, but that wet rubbing delayed the onset of water penetration. Dr Bondy suggested that high scrub figures produced from relatively new films were to some extent artifacts.

Other uses for the resistance/water penetration technique were: determination of CPVC, above this figure the penetration rate increased rapidly, and prediction of resistance to efflorescence, where a direct link with water penetration had been found and it was considered that the emulsion type influenced efflorescence much more than paint formulation.

A modified measurement technique, that of surface resistance, could predict mud cracking, which was likely to occur if a high resistance was found at a given water content. Tensile tests used to measure film integration from surfactant stabilised and protective colloid stabilised latices indicated different mechanisms of film formation, the first by direct fusion of polymer particles, the second by the colloid "glueing" together particles which would not become fused. Coalescing solvents had been found to be retained in films for up to 80 days, as shown by greater elongation under stress. This effect was larger for colloid stabilised than for surfactant stabilised emulsions.

Other physical methods were described by Dr Bondy, including the determination of film attrition on outdoor exposure. After a short time a steady rate was obtained which, by extrapolation, could predict long term behaviour. Finally, reference was made to the use of light scattering tests on latices, from which mean particle diameters and information on size distribution could be obtained.

The large audience plied the lecturer with a considerable number and variety of questions and finally the vote of thanks, proposed by Mr D. Stewart, was carried with enthusiasm.

Midlands

High speed coating of packaging materials

On 17 January the Midlands Section met at the Winston Restaurant, Edgbaston, Birmingham, for an informal dinner, followed by two papers on "High speed coating of packaging materials." Mr C. H. Morris was in the chair and the speakers were Dr T. Williams and Mr D. McFarlane.

Dr Williams said that the British Steel Corporation in South Wales produced a million tons of tin-plate annually. A large proportion of this was lacquered before can manufacture by roller coating from a solution of 30 per cent solids. The tin-plate was normally lacquered as sheets $2ft \times 3ft$, then stacked and passed through an oven for ten minutes. The coating thickness varied from 2-3 microns for epoxy-phenolics up to 8 microns for oleoresinous materials. Of recent years there had been interest in coil lacquering but there was a technology gap between what could be achieved and what was required. The difficulty was that curing times were too long for efficient and economic operation.

At BISRA the possibility of using glow-discharge polymerisation as an alternative to thermal curing had been examined. Reaction was fast, giving uniform non-porous coatings, but control of the process was unsatisfactory. The process could be regarded as having two basic stages, the first being adsorption of monomer on to the electrode and the second stage being polymerisation or cross-linking. The adsorption stage was replaced by a vapour deposition method and glow discharge was replaced by electron bombardment in vacuum for the polymerisation stage.

Vapour deposition of organic materials was very similar to the well-known process for vacuum deposition of metals and involved short-path evaporators like those developed for molecular distillation.

For electron bombardment in vacuum, the lacquered surface was brought into vacuum, whereas with normal electron-beam curing the electrons were brought out from vacuum through a window. The processes were complementary rather than competitive. Air radiation required an acceleration of 100-150kV to overcome the resistance of the window plus 25kV for each thou film thickness. Its efficiency for thin coatings was low whilst vacuum radiation, having no window losses, was much more efficient. For thicker coatings the cost of curing in vacuum was small compared to the cost of getting the sample into and out of the vacuum. The relative costs of the two processes were also influenced by the speed of the coil.

Air radiation was restricted to materials which were not of great interest to can manufacturers. The vacuum technique was much more powerful, and coatings like epoxy and Novolaks could be cured at very high speeds without curing agents. The technique could be used with hot-melt and solventless systems.

The problems associated with getting strip into and out of vacuum had been solved. Some eight lines for metal evaporation were processing strip at speeds up to 1,000ft/ min. The strip passed through a series of double rolls backed by compartments progressively evacuated to 200mm, 1mm, 5×10^{-2} mm and 10^{-4} mm. Suitable guns for producing electron beams had also been developed for heating strip in vacuum prior to metal deposition.

A simulator for coating trials had been built and consisted of a drum, to which panels were attached, revolving inside a tank. Speeds equivalent to 60ft/min had been attained and it was hoped to achieve speeds of 600ft/min.

Mr McFarlane said that at the British Steel Corporation other methods of applying organic materials were being examined. The use of lacquers with 30 per cent solids involved the removal of very large amounts of solvents at the speeds required.

Roller coating was effective at speeds up to 600ft/min but this was near the limit at which the film became discontinuous. It entailed the use of solvents but it gave the possibility of using the rolls as seals for the vacuum system.

Direct and off-set gravure permitted higher solids contents than roller coating but different weight coatings would require different rollers. Use of an application head with pressure-fed lacquer had the disadvantage of excessive wear of the unit head.

Curtain coating was very promising but it required solutions; hot melt systems gave too high a film weight. Electrostatic spray entailed a large number of spray units to achieve the required capacity and also deposited on the back of the strip. Electrodeposition on coils raised problems due to non-conductivity of lacquers and was restricted to using the same system on both sides of the strip.

The vacuum evaporation method was unsuitable for pigmented coatings, and did not permit stencilling or leaving a strip of bare metal for soldering. However, a bare metal strip was not required if tin-free steel was used with nylon polymers as sealants.

To assess the degree of cure of samples, five methods were employed. These were AID hardness, scotch-tape adhesion, MEK solubility, wedge bend and crown-cork test.

After a discussion period, Mr D. Penrice proposed a vote of thanks to the speakers.

L.R.S.

Newcastle

Wallpaper, its development, manufacture and design

The fourth meeting of the present session was held in the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne on Thursday 2 January 1969. This was a joint meeting with the National Federation of Master Painters and Decorators, and on this occasion a paper was presented by Mr Corless and Mr Jones of Wallpaper Manufacturers Limited, entitled "Wallpaper, its development, manufacture and design."

Mr Corless traced the history of wallpaper from the late 15th century, when wallpaper was produced by hand, to the present day with its high speed printing methods. He stated that block printing of wallpaper was used until 1826, when the first attempts were made to machine-print using copper engraved rollers, but this was not successful and it was left to Potter, in 1839, to patent the first successful technique using a letterpress-type machine. Embossed papers were introduced in the early part of this century and Heidmann printing, in which the embossing and printing was done simultaneously, followed in 1948.

Then Mr Jones, with the aid of slides, gave a guided tour of a wallpaper factory showing the types of printing, the design stage, the techniques used for preparing the rollers, the checking of the design and finally the types of machines used to apply the ground, print and gloss coatings and the embossing and duplexing equipment.

After question time, in which Messrs Connor, Skjonnemand, Coulson, James and Clark took part, Mr Wall thanked the lecturers warmly for giving such an interesting talk.

A.L.

Scottish

Investigations of the rheological behaviour of emulsion paints

The first meeting of the New Year for the Scottish Section was held on 16 January in the Whitehall Restaurant, Glasgow, and was addressed by Dr F. Wagener, of Titangesellschaft, mbh, who took as his subject "Investigations of the rheological behaviour of emulsion paints."

JOCCA

Dr Wagener first showed how manufacturers of titanium dioxide had kept up with other advances in emulsion paint technology by introducing special grades of pigment with better optical properties. This was achieved by coating with materials such as alumina and silica, which kept the particles well separated, and reduced the "crowding effect" of larger particles of extender. Such treated pigments had higher oil absorption and specific surface than the ordinary grades, and therefore had different rheological properties.

These properties were important to the paint manufacturer, who achieved best dispersion at high solids content and low viscosity, and to obtain the optimum with these contradictory demands, a specific amount of surfactant was needed. This could be found by plotting wet point/flow point curves, obtained by titrating powder samples with a range of solutions of varying concentrations of the surfactant sodium polyphosphate. As the concentration increased, wet points and flow points decreased and converged, and at this point of convergence it was considered that the pigment was fully dispersed with excess of neither surfactant nor water. Different pigments or pigment mixtures naturally showed different convergence points. The special grade of titanium dioxide needed more water and surfactant than the ordinary grade; if extender was added this was still the case, but the two convergence points had moved closer together. If mill bases predicted by this method were used in manufacturing practice, some difficulties due to thixotropy occurred, but these could be overcome by the addition of a few per cent of water or thickener solution, and did not affect the value of this method.

Dr Wagener then discussed the relationship between viscosity, water content and surfactant demand. He showed curves of viscosity against percentage surfactant for different water contents, and in each case a minimum viscosity was attained at a specific surfactant level which, in the case of the standard grade pigment, was unaffected by solids concentration. With the special grade, the surfactant level for minimum viscosity varied with the solids concentration and was in all cases higher than that for the standard grade, and the final dispersions showed higher viscosities, indicating a higher water demand by this pigment. It was notable that if such curves were drawn for mixtures of extender and pigment, again the properties of standard and special grades came closer together.

In practical cases it was very important to ensure that sufficient surfactant was present to ensure stability of the final paint. The emulsions used to let down this mill base were, to the user, of unknown composition, and unless the titanium dioxide surfaces were fully saturated before emulsion addition, the stabilisers and emulsifiers from the latter could be absorbed on to the pigment surface with bad effect.

The higher viscosities shown by the special grades of titanium dioxide were of course important to the final paint. They permitted reduced thickener quantities, or increased water contents, without destroying the structure of the paint necessary for application properties. The viscosities of practical paints were not Newtonian, and it was notable that paints made from the special grade diverged further from Newtonian properties than those from the standard grade, having higher yield values and less steep, more curved viscosity curves (rheograms). Dr Wagener indicated that such non-Newtonian flow, which led to structuring, conferred better application properties on the paint, and that this topic was the subject of continuing investigation.

In answer to questions, Dr Wagener stated that future work could try to relate application properties to rheogram shape. Structure was affected by the type of emulsion used, being lowest with styrene/butadiene, higher with pva/pvc copolymers and higher still with polyvinyl propionate. He emphasised that materials coated on to the pigment surface had more effect on optical properties than similar materials added at the same percentage as extenders, although there was no evidence that all of this coating material was firmly attached. Added extender had less deleterious effect on

the optical properties if its particle size was lower than that of the titanium dioxide, but in that case the flow properties tended to suffer. The higher viscosity of the special grade was not due to a greater number of particles; the particle diameter was much the same, but specific surface was much higher, denoting greater surface irregularity. The durability of paints made from special grade titanium dioxide was if anything better than that from ordinary grade, in spite of the extra surfactant content needed.

In proposing the vote of thanks, Mr A. MacLean made the point that not only were technical developments important, but also the communication of them to industry at large, and congratulated Dr Wagener on his success with both aspects.

J.D.E.

Eastern Branch

Colour computers

The second ordinary meeting of the Session, with Mr G. H. Hutchinson in the chair, was held in the "Wee Windaes" Restaurant, Edinburgh, on Wednesday 20 November, when Mr P. Foote of the Paint Research Station spoke on "Colour computers."

Mr Foote said that colour was defined not in terms of the actual visual sensation but by the quantities of the three standard primaries which would produce the same visual sensation. The colour could be measured either by spectrophotometry, followed by the application of appropriate weighting factors to the various wavelengths, or by colorimetry, using an instrument designed to apply the weighting factors automatically.

It was then shown how data on the absorption and scatter coefficients of pigments could be derived from spectrophotometric measurements. These could be fed into a computer and used to predict the formulation required to match a specified colour or to obtain tinting factors for use in the correction of the match. Slides were shown to illustrate these and other points during the lecture.

In his vote of thanks Mr C. Cochrane recalled his visit to the PRS in its early days, before warmly congratulating the lecturer on his excellent paper.

Crime prevention

The third ordinary meeting of the session, with Mr G. H. Hutchinson in the chair, was held in the "Wee Windaes" Restaurant, Edinburgh, on Wednesday 18 December, when Detective Inspector Elliott of the Edinburgh City Police spoke on "Crime prevention."

Inspector Elliott commenced by saying that millions of pounds were lost through crime every year, and, in many cases, the cause could be traced to thoughtlessness or carelessness. Security had to be tackled deliberately and not half-heartedly, remembering that prevention was much easier than detection.

Firstly, one person should be made solely in charge of security. In making security arrangements, the value of the contents of the premises must be considered. For example, high value contents such as gold, silver and copper necessitated high security, which could be achieved by the use of good quality burglar alarms and safes. Safes should be preferably of the combination type, having, therefore, no key hole.

The protection of the actual premises was then considered. There should be only one entrance which should be watched, and the identity of anyone entering the building checked. All other doors should open outwards, should have no keyhole on the outside and should be reinforced by metal sheeting. Locks should be at least five-lever types where they could be opened from the outside; if they were single-side locking, they were nearly unpickable. When padlocks were used they should be of the close-shackle type. The security of windows and rooflights was considered. Windows, in high value premises, should have bars, which should always be on the inside. The bars could be built into a swinging frame secured by a padlock. This would allow the framed bars to be swung aside from the inside, to allow exit in case of fire. Glass bricks were a solution to the problem of making a window presentable and at the same time secure. All rooflights should have wire mesh on the inside. Also, access to the roof should be made difficult. The building should have no handgrips, ladders should not be left lying about, and the pipes on the side of the building should be treated with anticlimb paint.

In conclusion, Inspector Elliott dealt with cash security, advocating payment by cheque where possible. Visits to the bank should be made daily by able-bodied employees and the route and time should be varied.

After a stimulating question period Mr R. Webster proposed the vote of thanks.

J.H.S.

Thames Valley

Some recent developments in marine painting

This meeting was held on 16 January at the Royal White Hart Hotel, Beaconsfield, at the usual time of 7.00 p.m. The talk was given by Mr A. McIntosh of the Shell Laboratories, Egham.

Mr McIntosh began by saying that the last few years had seen a revolution in shipyard techniques and materials, a process that was still continuing. A number of influences were at work, all of which had contributed to this rapid change. Among them were increasing vessel size, smaller crew numbers, faster turn-round, demands for longer service life, cathodic protection, improved paint performance, which encouraged better surface preparation, and reductions in the thickness of the steel.

He next touched on the generally accepted principles of hull and tank painting for high performance. The usual steps were to grit blast, shop prime, weld and reprime, assemble on slipway, apply bottom and boot top paints to thickness of 250-300 microns, apply topsides paints and superstructure paints and finally to decide the appropriate type of system for the tanks which might have to carry chemicals, solvents, oils etc.

The various paints in use today were described. Primers no longer needed to function for long periods since "production line" under-cover construction was now much more common. Thus zinc rich two-pack epoxy paints were now lower in zinc content than hitherto and a wider latitude in total formulation was permitted. For the hull, protection by coal tar epoxy paints had proved very successful, while for topsides, polyamide/epoxy paints were preferred. However, shorter construction times had led to demands for higher build and fewer coats, the ultimate being a single coat application of up to 250 microns thick. To obtain the best build implied the use of liquid epoxy resins and this in turn demanded the use of a solvent or diluent to give workable viscosities.

Some interesting work had been done in the speaker's laboratory on tracing the degree of cure analytically by means of infra-red reflectance spectra of films deposited on aluminium foil. Peaks appeared at 11.0 and 12.1 microns due to the epoxide and the aromatic nucleus respectively. The epoxide content of the film was monitored by the ratio :

 $R = \frac{\text{Intensity of 11.0 micron peak}}{\text{Intensity of 12.1 micron peak}}$

and hence it was possible to deduce per cent epoxide by referring to the specimen of an uncured blend of the same system. The method was also of value in determining

the extent of failure that may be directly attributable to solvents retained in the cured film.

Mr McIntosh gave a very useful run down on available equipment which he backed up with colour slides, during which the Graco Hydracat equipment was described in some detail.

Other marine compositions not dependent on the epoxide reaction were mentioned. These included polyurethanes with good low temperature characteristics, zinc silicate paints useful in certain tank linings and catalysed polyester/styrene compositions needing two-spray equipment for their application.

Finally in a forecast for future surface coating activity he said that

- (a) primers would need less emphasis on their long term protective character,
- (b) hull paints would tend toward higher build per coat and rely on two-component spraying,
- (c) topsides paints would show an increasing use of epoxy base coats and urethane topcoats,
- (d) tank linings might develop along competitive lines, that is, two-component solventless epoxies, high solids/minimum solvent epoxies, and zinc silicate paints, with the first system probably predominating.

After an interesting question period Mr B. Jacob gave a warm vote of thanks.

R.E.G.

Report of Council Meeting

The meeting of Council on Tuesday 28 January at Wax Chandlers' Hall, Gresham Street, London, EC2 was attended by 22 members with the President, Mr F. Sowerbutts, in the Chair.

The Council were saddened to hear of the death of Mr A. J. Gibson (President 1938-40) on 11 November 1968 and as a mark of respect members stood in silence for a few moments. An appreciation of his work, written by Mr G. Copping, was published in the January issue of the *Journal*.

The President gave a brief account of visits, which he and Mrs Sowerbutts had made during the course of a private sea cruise, to the South African, Auckland and Wellington Sections and to the Oil and Colour Chemists' Association Australia. The visits had been very successful and they had been extremely well received. The Council passed a vote of thanks to Mr and Mrs Sowerbutts for their work on behalf of the Association on these occasions.

The Council decided to institute a Commendation Award for outstanding and long service to the Association, particularly at Section level. It was also decided that the first recipient of this award would be Mr W. J. McWaters, who had been Hon. Treasurer of the Bristol Section for over twenty years, and had rendered considerable assistance in the setting up of the Irish Branch of the Bristol Section (now the Irish Section).

The Draft Annual Report of the Council for 1968 was accepted and this will be circulated to members in due course with other papers in connection with the Annual General Meeting, which will be held on 20 June 1969 at the Grand Hotel, Eastbourne, at 2.15 p.m.

In order to strengthen the relationship between Council and the Sections in South Africa and New Zealand, it was decided that one Vice-President should always be appointed from South Africa and one from New Zealand, possibly alternating between the Sections in the latter country.

It was reported that applications were being received for places at the 1969 Conference, to be held in Eastbourne, and that invitations were being extended in the usual way to the Presidents of FATIPEC, the Federation of Scandinavian Paint & Varnish Technologists, and the Federation of Societies for Paint Technology.

Council were informed that the Conference papers had been received and biographies of the authors and summaries appeared in the January issue of the *Journal*.

The arrangements which were in hand for the Exhibition in March were reported, and Council was pleased to learn that this would be the largest ever staged. In addition to the usual facilities at the Exhibition, the European Liaison Lecture, organised by the London Section, would take place on the Thursday evening. A full report of the Exhibition will appear in the May issue of the *Journal*.

A full report on the meeting of the Publications Committee held on 27 November 1968 was received. Discussion had taken place on the use of key words in papers, on the second editions of Part I and II of the Paint Technology Manuals, which were available at the end of January 1969, and on papers for the *Journal*.

Changes and vacancies amongst OCCA representatives on a number of BSI Committees, and on the Technical Training Board for the Printing Ink and Roller Making Industry, the East Ham Technical College Advisory Committee, and the SDC Terms and Definitions 1969 (4)

Committee had arisen. Names were put forward to represent the Association on these bodies.

It was reported that, owing to the reorganisation of their examination syllabuses, the City and Guilds of London Institute would now award the F. W. Clarke Memorial Prize to the best candidate for the Paint Technician's Certificate, not, as previously, on the results of the Advanced Paint Technology examination.

From a recommendation made by the Working Party on Forward Thinking, Council agreed that, since Mr I. S. Moll had had to relinquish the chair of the

North of England OCCA Golf Trophy

The West Riding Section is to organise a tournament for the North of England OCCA Golf Trophy at the Pannal Golf Club, Harrogate, on Friday 9 May 1969.

The tournament, which will be run as a Stapleford competition, playing to 7/8 of lowest club handicap, will commence at 1.30 p.m., with high tea and presentation of prizes in the clubhouse at 6.45 p.m. Buffet lunch will be available at the clubhouse from 12.15 onward.

The entrance fee, which includes lunch, tea, and green fees, is $\pounds 2$ 10s, and wives and girlfriends are welcome to join the party for high tea at a cost of 15s.

The West Riding Section Committee has presented a cup for the tournament, as an eternal trophy, and replicas will be provided for the winner on each occasion.

Scottish Section

Annual Dinner Dance

The Annual Dinner Dance of the Scottish Section was held in the Kintyre Suite of the Central Hotel, Glasgow, on Friday 17 January. Guests, to the Working Party owing to business commitments, Mr A. S. Fraser, President Designate, should succeed him. A report was received from this Working Party, but it was not possible for the Working Party on Education, Training and Qualifications to report to this Council meeting. It would report at the meeting in February.

Reports were received of Section activities, and Council noted with regret that, for reasons of health, Dr H. A. Hampton, who had represented South African Section on Council for many years, had informed the Section that he could no longer do so.

The Pannal Club lies on a glorious stretch of moorland to the south of Harrogate, within a hundred yards or so of the main Leeds-Harrogate road, and is thus easily reached from most of northern and central England. The 6,738 yard course, used for many major tournaments, is acknowledged as a test of a high standard, and its setting is beautiful, with Wharfedale and Almscliffe Crag to the West, Crimple Valley, with its viaduct, made famous by a Turner painting, to the North, and the plain of York, with the Minster, to the East.

Members interested should apply to Mr D. Young, Hon. Social Secretary of the West Riding Section, who will be pleased to arrange hotel accommodation in Harrogate for any member who wishes to stay overnight, or for the whole weekend.

number of some 250, were welcomed by the Chairman of the Scottish Section, Mr James Miller, and Mrs Miller, and by the President of the Association, Mr Frank Sowerbutts, and Mrs Sowerbutts.



(Left to right): standing, Mr R. Adam (Chairman, Irish), Mr R. H. Hamblin (Director and Secretary), Mr R. H. Wheeler (Chairman, London), Mr G. H. Hutchinson (Chairman, Scottish, Eastern Branch), Mr J. Miller (Chairman, Scottish), Mrs Hutchinson, Mrs Silver, Mr F. Sowerbutts (President), Mr L. H. Silver (Chairman, West Riding), Mr D. M. James (Chairman, Newcastle), Mr D. Morris (Chairman, Midlands). Seated: Mrs Adam, Mrs Wheeler, Mrs Miller, Mrs Sowerbutts, Mrs James and Mrs Morris

After an excellent dinner-identification as usual being obscured by a Gaelic menu-Mr Miller proposed the toast to the Guests, mentioning, in particular, Mr and Mrs Sowerbutts, Mr Hamblin (Director and Secretary), and Chairmen of Sections and their ladies, as follows: Mr and Mrs G. H. Hutchinson (Scottish, Eastern Branch), Mr and Mrs R. Adam (Irish), Mr and Mrs D. J. Morris (Midlands), Mr and Mrs R. N. Wheeler (London), Mr and Mrs L. Silver (West Riding) and Mr and Mrs D. M. James (Newcastle). Referring to the banner, "Ceud mile failte air na cairdean a Sasunn," which has graced the top table for the past few years, he revealed that the burden of its message was a traditional and warm Gaelic welcome to our guests from across the border, and that, in spite of previous propaganda, it had nothing whatever to do with parking restrictions on bicycles outside the hotel. Thus easily are embryonic legends brought to an untimely end! Mr Miller continued with an extremely witty speech,

which was very highly appreciated by the company, and there is little doubt that the tenor of the subsequent proceedings was largely set at this point. Replying on behalf of the guests, Mr Sowerbutts maintained the opening high spirits and mentioned, in particular, his recent world tour undertaken on behalf of the Association. Tradition was maintained when the haggis was piped in by Pipe Major Lawrie of the City of Glasgow Police Pipe Band. A minor delay in the arrival of the haggis was apparently due to the fact that, this year, it was of the tail-less variety and that the normal method of capture, by the application of an alkali metal halide at the appropriate locus, was thus rendered extremely difficult. Pipe Major Lawrie having proposed a suitable "Slainte Mhath" and a brief interval having been declared by the Chairman, dancing proceeded forthwith and continued unabated, until one o'clock the next morning arrived to the surprise and dismay of everyone.

Another success? Without a doubt!

Obituaries



J. A. Frome Wilkinson

Mr J. A. Frome Wilkinson

We regret to record the death in February of Mr J. A. Frome Wilkinson at the age of 77, a Past President of the Association.

Educated at Kings College School, Wimbledon, Mr Wilkinson took the BSc degree in chemistry at Kings College, London, in 1912 and the AIC degree by examination in food and drugs in the same year.

After serving as assistant to Mr E. Hinks, Public Analyst for Surrey, for one year he joined the Department of the War Department Chemist at the outbreak of World War I and served in various capacities in that Establishment, becoming Assistant Director during World War II. In 1943 he joined the Controller of Chemical Research and Development in the Ministry of Supply as Assistant Director where he remained until his retirement from public service in 1951.

Mr Wilkinson, together with H. H. Morgan, J. Newton Friend, Noel Heaton, L. A. Jordan and others, was one of the very early band of chemists working in the broad field of paint who did so much to lay the foundations on which the Oil and Colour Chemists Association, as we now know it, was built. He was Hon. Editor of the *Journal* from 1924-28, President of the Association from 1932-34 and a Vice-President from 1934-36.

Mr Wilkinson is survived by his wife and a son. A kindly and ever courteous man, the paint industry benefited from his knowledge, and he will be sorely missed by all who had the privilege of knowing him.

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Mr A. H. Whitaker

It is with regret that we record the death, on 7 February, of Mr A. H. Whitaker, an Honorary Member of the Association, at the age of 72.

Mr Whitaker was a Chairman and a Managing Director of James Anderson & Co. (Colours) Ltd., until his retirement in 1961 after 31 years service with the company.

He was the prime mover in the formation of the Scottish Section of the Association in 1933, and for 27 years was associated with the running of the Section in several capacities, including that of Chairman. He also served as a Vice-President of the Association in 1951-53, and was made an Honorary Member in 1956.

Mr Whitaker leaves a widow, and a son, Mr P. J. Whitaker, who is wellknown and active in OCCA affairs, and who is at present a marketing executive with J. R. Geigy SA in Basle.

News of Members

Mr J. E. Armstrong, an Ordinary Member attached to the Midlands Section, and Mr G. F. Caffery, an Ordinary Member attached to the London Section, have recently joined the UK latices sales staff of BP Plastics. Mr Armstrong will cover the Midlands and South-west, and Mr Caffery London and the South-east.

Dr G. D. Parfitt, an Ordinary Member attached to the Midlands Section, has been appointed Assistant Research and Development Manager at the Central Laboratories of British Titan Products Company Limited.

Mr L. W. Robson, an Ordinary Member attached to the London Section, has relinquished his post as General Sales Manager of British Titan Products Co. Ltd., to concentrate his attention on Titanium Intermediates Limited, of which he is Chairman.

Mr H. L. Salter, an Ordinary Member attached to the London Section, has been appointed Marketing Manager, European Economic Community, of Laporte Industries Limited.

Mr K. Kallman, an Ordinary Member attached to the Manchester Section, has been elected to the board of International Colloids Limited. Mr Kallman was previously in charge of technical sales for International Colloids.

Mr T. Graham, an Ordinary Member attached to the Manchester Section, has been elected a Fellow of the Royal Institute of Chemistry.

Conferences and Symposia

Surface area determination

A symposium on surface area determination is to be held jointly by the SCI and IUPAC on 16-18 July 1969, at the School of Chemistry, University of Bristol. Accommodation has been arranged at a nearby Hall of Residence. A provisional programme has been arranged, and copies, together with full information on registration and accommodation, are available from Professor D. H. Everett, at the School of Chemistry, University of Bristol.

Illumination

The northern section of the Colour Group are to hold a half-day symposium on illumination on Wednesday 9 April, at the Geigy lecture theatre, Heald Green, at 2.30 p.m.

Four papers are to be given, with a short break for refreshment.

Any Member of the Association who is interested is invited to attend.

G. D. Ch-Congress

The 43rd Congress of the German Chemical Society working party "Paints and pigments" is to be held in Bad Ems (West Germany) from 7 to 10 May 1969. Programmes and registration forms are available from Dr H. Rechmann, c/o Titangesellschaft mbH, 509 Leverkusen, West Germany, Postfach 80/90.

Electropainting

An "International Symposium on Electropainting, organised by *Surface Coatings* journal, is to be held at the Criterion-in-Piccadilly, London, from 28 to 30 October 1969.

The symposium, claimed to be the first of its kind, is directed at potential endusers of the electropainting technique. Further information may be obtained from the Editor, *Surface Coatings*.

New coatings and new coatings raw materials

The eleventh Annual Symposium on "New coatings and new coatings raw materials," organised by the North Dakota State University, Polymers and Coatings Department, is to be held at the Fair Hills Resort, Pelican Lake, near Detroit Lakes, Minnesota, USA, from 2 to 5 June 1969.

The programme is split into two subsymposia, one on "Radiation curing and new methods of film application, containing 6 papers, and one on "Film structure and instrumentation techniques" containing 11 papers.

Transport has been arranged between the University, in Fargo, North Dakota, and the symposium, and this is included in the enrolment fee of \$60.00.

Full details are available from the Polymers and Coatings Dept., North Dakota State University, Fargo, North Dakota 58102.

Education, training and communication in corrosion control in engineering

A joint conference of the Institute of

Corrosion Technology, the British Joint Corrosion Group and the Corrosion and Protection Association, with the above title, is to be held at the University of Sheffield on 10 and 11 April 1969.

The aim of the conference is to examine the efforts that are being made to reduce the cost of corrosion through proper education of technologists, training of technicians and dissemination of information.

Full details and application forms are available from the Conference Secretariat, British Joint Corrosion Group, 14 Belgrave Square, London SW1.

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

BANKS, ALLEN HARTLEY, BSc, 11 Cornhill Avenue, Gosforth, Newcastle-on-Tyne, (Newcastle) NE3 2ST. BOWER, HAROLD HELLAWELL, BSc, 46 Maple Road, Baguley, Manchester. (Manchester) BROWN, CHRISTOPHER PHILIP, Pinchin Johnson Paints Ltd., Henrietta House, 9 (London) Henrietta Place, London, W1. BROWN, DONALD, BSc, PhD, B.P. Chemicals (UK) Ltd., B.P. Plastics Department (Manchester) Barry House, Beech Road, Hale, Altrincham, Cheshire. BROWN, PETER THOMAS, "Wulfruna," Westley Waterless, Nr. Newmarket, Suffolk. (London) (Scottish) BRUNTON, JOSEPH WILLIAM, 20 Cramond Terrace, Edinburgh, 4. CHANCEY, RALPH STANLEY, The Standard Manufacturing Co. Ltd., Water Street East, St. Johns, Newfoundland, Canada. (Overseas) CORNELL, ROBERT MORLEY, BA, MA, 40 Bothwell Road, New Addington, Croydon, (London) Surrey. (Scottish) COWLTER, JAMES, 1 May Road, Glenburn, Paisley, Scotland. COX, JEFFREY HENRY, BSc, Cromford Colour Co. Ltd., Cromford, Matlock, Derby. (Midlands-Trent Valley) CRUDEN, JOHN MCNAB, BSc, 20 Edmunds Tower, Harlow, Essex. (London) DANDO, VIVIAN CHARLES OWEN, BSc, LIRI, 91 Heatherstone Avenue, Dibden Purlieu, (London-Southern) Southampton SO4 5LE. EDLIN, ANTHONY SINCLAIR, 85 Nethercote Gardens, Shirley, Solihull, Warks. (Midlands) EVANS, EDWARD MICHAEL, BSc, PhD, B.P. Chemicals (UK) Ltd., Hayes Road, (Bristol) Sulley, Penarth, Glam. FRANKLIN, MICHAEL JOHN BARRY, BA, 8 Greenfield Drive, Eaglescliffe, Co. Durham. (Newcastle) GRIBBLE, PETER RONALD, 175 Clarence Road, Windsor, Berks. (Thames Vallev) HICKS, GLYN, BA, "Highlight," Upper Court Road, Woldingham, Surrey. (London) HOSSACK, JAMES, BSc, PhD, 44 Roebank Road, Beith, Ayrshire, Scotland. (Scottish) (London) HOWELL, IAN DAVID, 28 Francis Road, Horndean, Hants.

JENKINS, GORDON WILLIAM, 54 Campbells Green, Birmingham 26. (Midlands) KERR, GEORGE RALSON, 23 Carsegreen Avenue, Paisley, Scotland. (Scottish) KYNASTON, GEOFFREY EDWARD, 16 Graham Avenue, Whickham, Newcastle-on-Tyne (Newcastle)
LLOYD, DAVID CHRISTOPHER, BSc, LIRI, Anchor Chemical Co. Ltd., Clayton Lane Manchester 11. (Manchester
MCGARRITY, JAMES, Geigy (UK) Ltd., Hawkhead Road, Faisley, Scotland.
(Scottish) MCKAY, ROBERT BRUCE, BSc, PhD, ARIC, 44 Woodlands Grove, Kilmarnock, Ayrs (Scottish)
MCMILLAN, WILLIAM DENIS, BSc, 12 Ashwood Avenue, Sale, Cheshire.
MEREDITH, M. J. R., 15 Poplars Road, Buckingham, Bucks. (Thames Valley) Moss, NoEL SYDNEY, 2 Pennystone Road, Saffron Walden, Essex. (London) REYNOLDS, JOHN HENRY, BSc, "Southover," 18 Mountfield, Prestwich, Lancs. M25 5EJ. (Manchester)
SAUNDERS, CHRISTOPHER, Water End, Park View, Hockley Heath, Warks. (<i>Midlands</i>)
SAVAGE, ROBERT JOHN, 7 Abbots Road, Haverhill, Suffolk. (London) SHANKLAND, IAN MCINTOSH, 29 Thornwood Drive, Paisley, Renfrewshire, Scotland
SMITH, DAVID DORMAN, 294 Mosspark Drive, Glasgow, SW2.(Scottish)STUBBINGS, ALEC WALTER GEORGE, 31 Prospect Close, Hounslow, Middx.
(London) TODD, JOHN ERIC, 49 Branksome Road, Heald Green, Cheadle, Cheshire.
(Manchester)
 VAN DER HAUW, Tj, Drs. Chemistry, Noury & Van der Lande N.V. Bibliotheek, PO Box 10, Deventer, Holland. (Overseas) WILTSHIRE, JAMES PHILLIP, BA, PhD, Research and Development Department, ICI (Paints Division), Wexham Road, Slough. (Thames Valley) WOOD, RICHARD GRAHAM, BSC, 9 Woodlands Road, Willerby Road, Hull. (Hull)
WOOD, ROBIN, BScTech, AMCST, 126 Shepherds Bush Road, London, W6. (London)
Associate Members
MCINTOSH, FREDERICK TOSH, 59 Bailie Drive, Bearsden, Glasgow. (Scottish) MCNEILL, MAURICE EDWARD, 33 Oakbank Road, Perth, Scotland. (Scottish) NAQVI, SYED WAHID HUSSAIN, BSc, 32 Warrington Avenue, Slough, Bucks.
(Thames Valley)
SIMPSON, ROLAND THEODORE, 19 West Walk, Yate, Bristol. (Bristol)
Student Members
AYRE, THOMAS RICHARD, 14 Crown Gardens, Hyndland, Glasgow. (Scottish)
BANNON, MICHAEL FRANCIS, 274 Drumchapel Road, Glasgow, W5. (Scottish) CONROY, MICHAEL JOHN, 282 Farnborough Road, Castle Vale, Birmingham 35.
(<i>Midlands</i>) DUNSTER, ROGER FREDERICK, 45 Jordan House, Blossom Grove, Bromford, Birmingham 34.
FULTON, ALEXANDER FRASER, 10 Archerhill Avenue, 7-4 Knightswood, Glasgow, W3.
(Scottish)
GILBERT, GORDON, 18 Hutton Drive, Linthouse, Glasgow, SW1.(Scottish)GILL, ALAN GORDON, 7 Fereneze Avenue, Clarkston, Glasgow.(Scottish)
LYNE, JEFFREY STUART, 46 Green Lane, Coleshill, Birmingham. (<i>Midlands</i>)
SPENCER, ANTHONY LEE, 12 Rossall Avenue, Chapelfields, Radcliffe, Lancs.
(Manchester)

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Forthcoming Events

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

Wednesday 2 April

Manchester Section—Student Group. "New Polymer for Emulsion Paints" by Mr A. C. Fletcher of Vinyl Products Ltd., to be held at the Manchester Literary & Philosophical Society at 4.30 p.m.

Thursday 3 April

Newcastle Section. Annual General Meeting, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Friday 11 April

Scottish Section. Annual General Meeting to be held at the St. Enoch Hotel, Glasgow, at 5.30 p.m., followed by the Annual Smoking Concert at the Eglinton Arms Hotel, Eaglesham.

Monday 14 April

London Section—Southern Branch. Annual General Meeting, to be held at the Keppels Head Hotel, The Hard, Portsmouth, at 7.30 p.m.

Thursday 17 April

Midlands Section—Trent Valley Branch. Annual General Meeting, to be held at the Midland Design and Building Centre, Mansfield Road, Nottingham at 7.00 p.m. Followed by "Colour and Design," by Mr D. J. Healey of ICI Ltd., Fibres Division. Film: "Colour Sense."

Friday 18 April

Irish Section. "Metrication and what it means," to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m. *Manchester Section.* Annual General Meeting, to be held in the Pavilion Suite, Lancashire County Cricket Club, Old Trafford, Manchester 16, at 6.30 p.m.

Tuesday 22 April

West Riding Section. Annual General Meeting, to be held at the Griffin Hotel, Boar Lane, Leeds, at 7.30 p.m.

Wednesday 23 April

Scottish Section—Eastern Branch. "The use and development of PVA Emulsions in the field of Paper Coatings, Paints and Adhesives," by Mr R. A. C. Kuenzli of Resinous Chemicals Ltd., to be held in the Wee Windaes Restaurant, High Street, Edinburgh, at 7.30 p.m.

Thursday 24 April

London Section. Annual General Meeting, to be held at the Criterionin-Piccadilly, London W1, at 6.30 p.m.

Friday 25 April

Bristol Section. Annual General Meeting, to be held at the Royal Hotel, Bristol, at 7.15 p.m.

Midlands Section. Annual General Meeting, to be held at the Winston Restaurant, Balsall Heath Road, at 7.00 p.m.

Friday 16 May

London Section—Southern Branch. Social Evening with Hovercraft Trip to Isle of Wight.

Oil and Colour Chemists' Association

President : F. SOWERBUTTS, B.SC. TECH.

The Oil and Colour Chemists' Association was formed in 1918, to cover paint, printing inks, pigments, varnishes, drying and essential oils, resins, lacquers, soaps, linoleum and treated fabrics, and the plant, apparatus and raw materials useful in their manufacture. In 1924 it absorbed the Paint and Varnish Society. The stated purpose of the Association is to promote by discussion and scientific investigation the technology of the industries concerned with the above-mentioned products, and to afford members opportunity for the interchange of ideas. This is achieved by the regular holding of ordinary meetings at which papers are presented, and the organisation of annual technical exhibitions, biennial conferences, educational activities and practical co-operative experimental work. Details of these activities are given in the Journal of the Oil and Colour Chemists' Association, which is published monthly, and whose pages are open to receive communications and other pronouncements on scientific and technical matters affecting the members of the Association and the industries concerned. The Association's meetings also afford opportunities for members to meet informally and socially.

There are Sections of OCCA in Auckland, Bristol, Hull, Ireland, London, Manchester, the Midlands (with a Trent Valley Branch). Newcastle upon Tyne, Scotland (with an Eastern Branch), South Africa (with Branches in the Cape, Transvaal and Natal), Thames Valley, Wellington, and the West Riding, and these are responsible for the conduct of their own local affairs. There is also a General Overseas Section. There is also a close alliance between the Association, the Federation of Societies for Paint Technology in the United States, and the Fédération d'Associations des Techniciens de l'Industrie des Peintures, Vernis, Emaux et Encres d'Imprimerie de l'Europe Continentale (FATIPEC). The Association also maintains cordial relations with the Scandinavian Federation of Paint and Varnish Technicians (SLF).

The five Sections previously maintained by the Association in Australia formed (1.1.68) the Oil and Colour Chemists' Association Australia, having the same aims and activities as, and working in close liaison with, the parent body.

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. Student Membership, which is intended primarily for students, is open without restriction to persons under the age of 21 and to those up to 25 who are following a course of technical study. The annual subscription in each case is five guineas, except for Student Members whose subscription is one guinea. An entrance fee of 10s, is payable by all members. Applications for membership are invited from suitably qualified persons who are engaged or otherwise interested in the industries noted above. Applications, which should be supported by two members of the Association (one of whom must be an Ordinary Member), should be forwarded to the Director & Secretary at the address given below. Application forms and full details of membership may be obtained from the offices of the Association.

PUBLICATIONS

Journal of the Oil and Colour Chemists' Association. Published monthly. Subscription rate to non-members in UK and abroad, £7 10s. p.a. post free ; payable in advance.

An Introduction to Paint Technology (Second Edition with additional chapter), Pp. 187, illustrated, with index, £1 (including postage).

Paint Technology Manuals

- Part 1 : "Non-convertible Coatings," Second Edition, Pp. 343, 36s. Part 2 : "Solvents, Oils, Resins and Driers," Second Edition, Pp. 268, 36s. Part 3 : "Convertible Coatings," Pp. 318, 35s.
- Part 4 : "The Application of Surface Coatings," Pp. 345, 35s.
- Part 5 : "The Testing of Paints," Pp. 196, 35s. Part 6 : "Pigments, Dyestuffs and Lakes," Pp. 340, 35s.

Director & Secretary : R. H. Hamblin, M.A., F.C.I.S., F.C.C.S., Wax Chandlers' Hall. Gresham Street, London, E.C.2.



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introduction to paint technology

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second edition with additional chapter

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

This addition will help the 'Introduction to Paint Technology' to maintain its position as an invaluable aid to young entrants into the industries and to marketing and other personnel requiring a basic knowledge of the principles and techniques of surface coating production and application.

new chapter

The new chapter is subdivided to three sections

resins and media

Including polyester, epoxy, polyurethane resins and developments in water based paints, vinylics, etc.

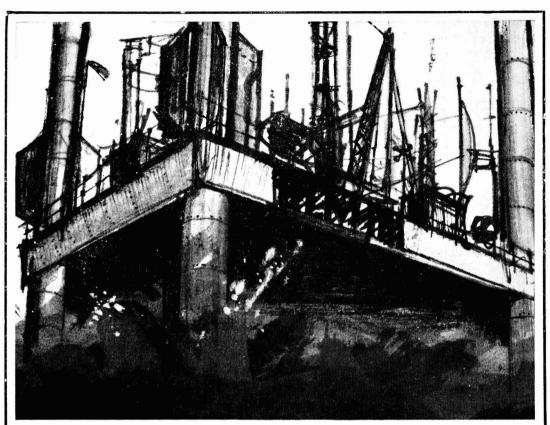
application techniques

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The book contains 204 pages including 11 line diagrams, 8 photographs of common paint defects, and comprehensive index. Copies can be obtained from the Oil and Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London E.C.2, price 20s. (post free).



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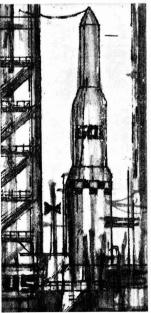
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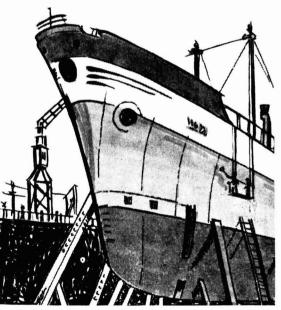
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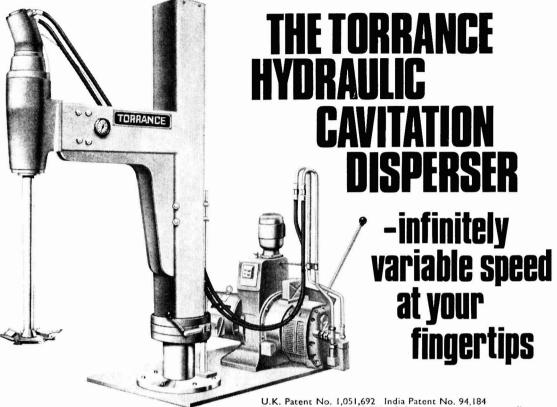
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We've already reminded you of the problems of foam during high speed mixing. The wastage it causes. The adverse effects it has on the quality of the final product.

And we've told you about three of Nopco's top foam killers:

• Nopco* NDW, probably the best all round defoamer in the world today.

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To help you choose the right defoamer for the job, the Nopco Technical Advisory Service is always available for consultation. For full information on this service plus comprehensive literature on the new, extended range of Nopco chemicals for the paint industry, please contact:









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

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

The plaque has the insignia handpainted in red and gold on a blue ground.

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

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

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To : Thresher & Glenny Ltd.,	Lancaster Place, Strand, London, W.C.2. on, please accept my order for the following:
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The South African Bureau of Standards invites applications from suitably qualified and experienced persons for appointment in its Organic Coatings Division in Pretoria.

A B.Sc.-degree or equivalent qualification is required and applicants must have a thorough knowledge of the coatings field. They must also be conversant with industrial manufacturing and related processes, paint raw materials, and end product formulation and properties. The vacancy calls for a senior person who will also be responsible for the preparation of product specifications or for the organizing and directing of this activity.

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M.Sc. Course in Colour Chemistry

Applications are invited for entry to a 12 month postgraduate course commencing October 1969. The course, which will lead to the degree of M.Sc. by examination, will provide instruction in the branches of chemistry of particular concern to those whose interests lie in the field of colour. The course will consist partly of lectures on the chemistry of colour matters, the physical chemistry of absorption, photochemistry, colour physics and the chemistry of natural and synthetic polymers. The remainder of the course will be concerned with practical instruction and a research project. Applicants should normally possess a good Honours degree (or its equivalent) in chemistry or a related subject.

The course is accepted as suitable for the tenure of SRC Advanced Course Studentships. Firms wishing to second members of their staff may reserve places for candidates to be named at a later date.

Applications and enquiries should be addressed to Professor I. D. Rattee, Department of Colour Chemistry and Dyeing, The University, Leeds, LS2 9JT. University of Salford THE STUDY OF SURFACES AND SURFACE-RELATED

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Full details may be obtained from the Administrative Assistant (Short Courses), Room 328/JOCCA, The University of Salford, Salford M5 4WT.

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