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November 1970

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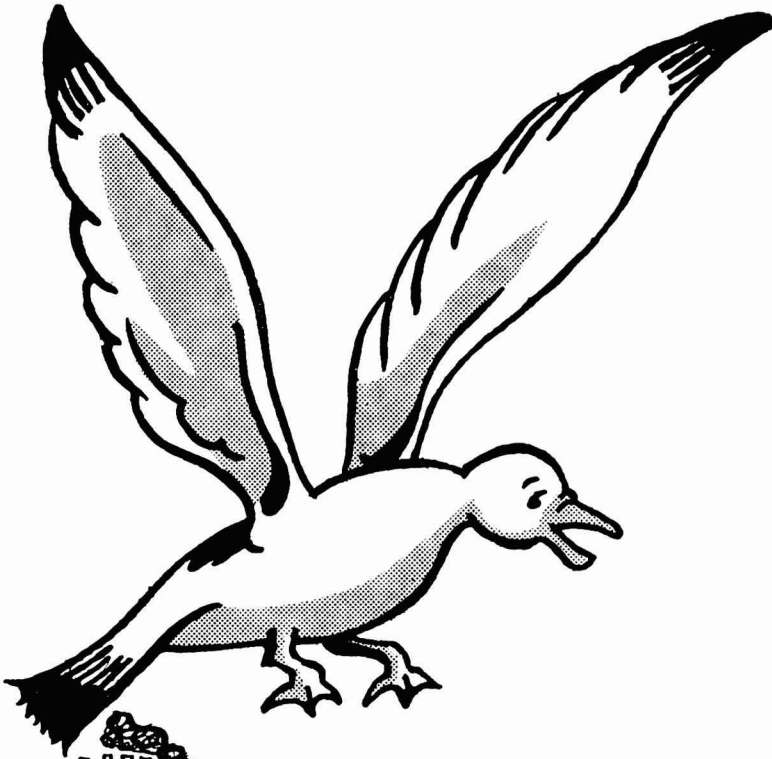
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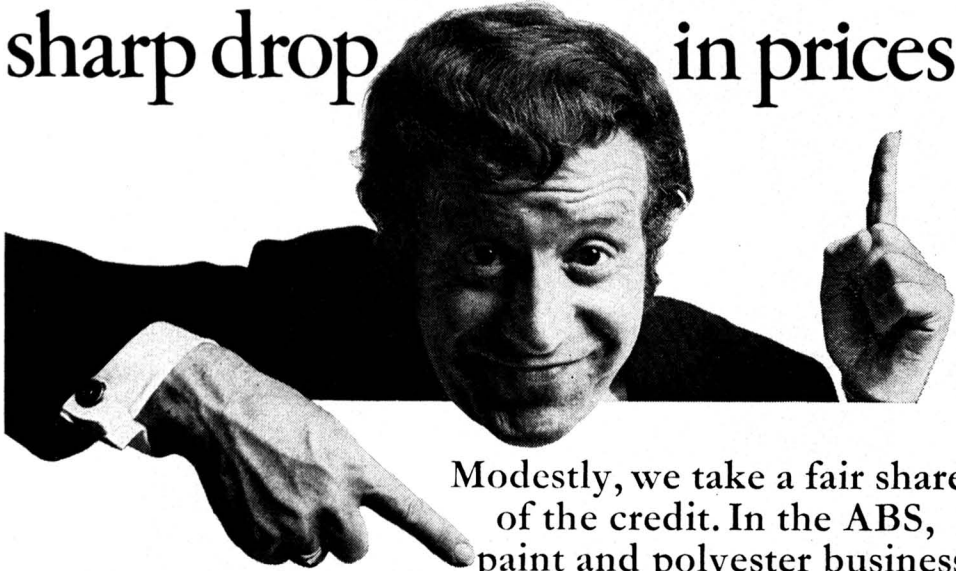
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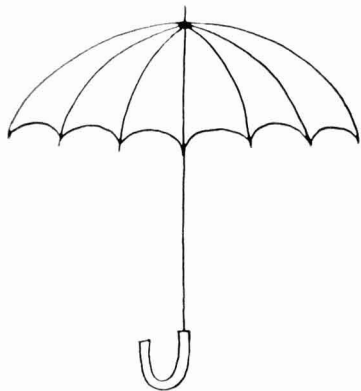
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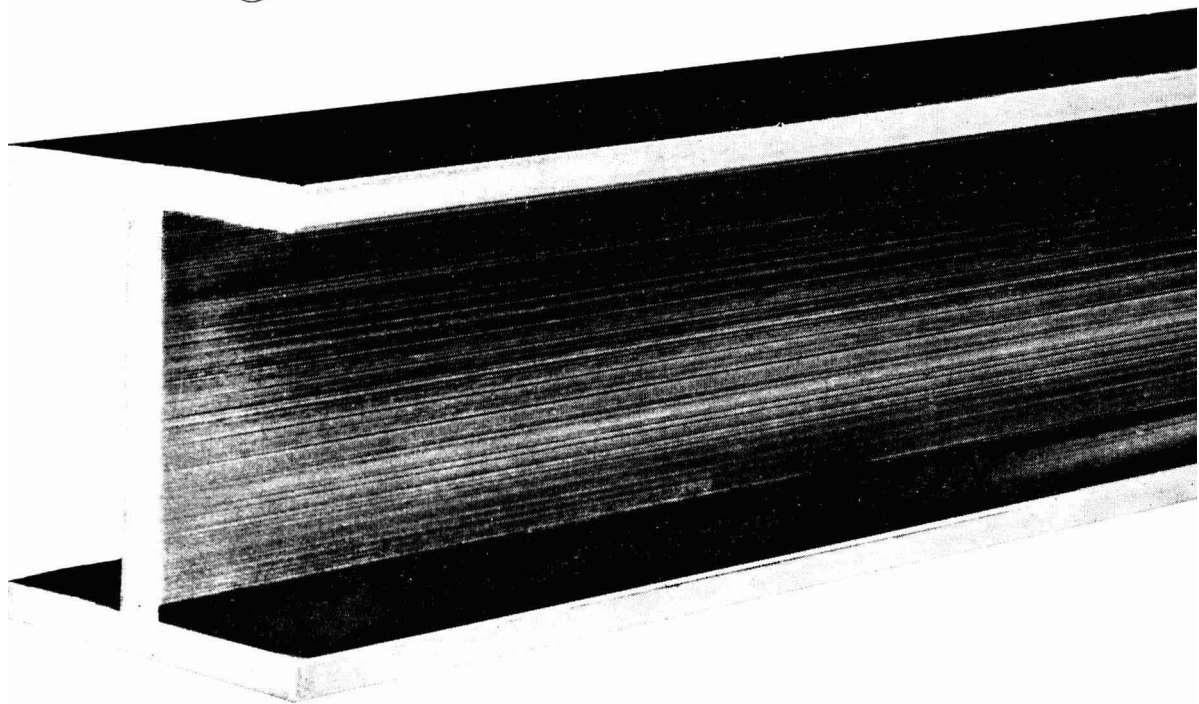
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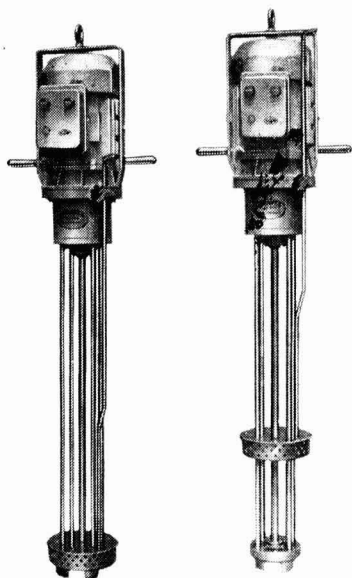
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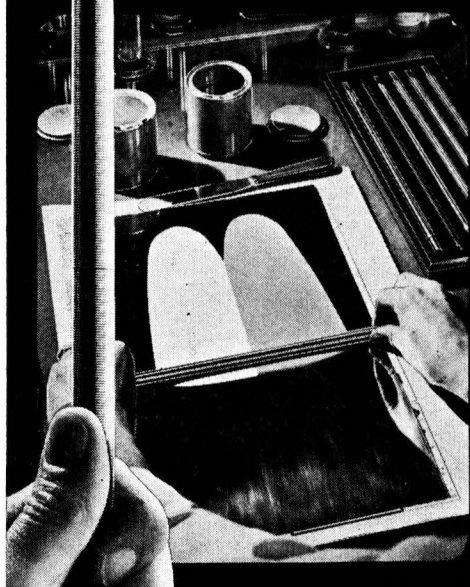
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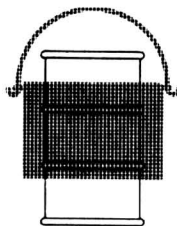
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Transactions and Communications

New resin systems for use in coil-coating applications*

By W. J. Lanigan and L. A. Tysall

Shell Research Ltd., Egham Research Laboratories, P.O. Box 11, Whitehall Lane
Egham, Surrey

Summary

The paper describes the development of resins based on Cardura E (the glycidyl ester of Versatic 911 synthetic acids) intended to give the required mechanical film properties in alkyd/MF enamels for coil coating applications.

A series of resins based on Cardura E, phthalic anhydride, triethylene glycol and trimethylol propane gave promising results. The corresponding isophthalic acid series gave rather better film properties but some members of the series were unstable.

Laboratory methods of rapid cure are described, based either on an LPG-fired burner or on a special oven. Various schedules are compared. Some examination is made of the possibility of obtaining an adequate cure with some of these resin systems at 120°C. A comparison of results obtained with a hexamethoxymethylmelamine resin with those from a butylated melamine resin is given.

Keywords

| | |
|---|---|
| <i>Binders, resins, etc.</i> | <i>Process and methods primarily associated with application of coatings</i> |
| alkyd resin | coil coating |
| melamine formaldehyde resin | |
| <i>Equipment primarily associated with drying or curing of coatings</i> | <i>Properties, characteristics and conditions primarily associated with dried or cured coatings</i> |
| electric oven | hardness |
| gas oven | flexibility |

Nouvelles résines pour la finition des métaux en rouleaux

Résumé

Cet exposé décrit le développement de résines à base de "Cardura E", (l'esther glycidique des acides "Versatic"—acides synthétiques 9.11), destinées à fournir des émaux du type alkyde/mélanine-formol aux propriétés mécaniques de feuillets exigées pour la finition des métaux en rouleaux.

Une série de résines à base de "Cardura E", l'anhydride phtalique, triéthylène glycol, et triméthylolpropane donnaient des résultats d'avenir. La série correspondante à base de l'acide isophthalique donnait des feuillets ayant d'assez meilleures propriétés mais quelques-uns de la série manquent de stabilité.

On décrit des méthodes laboratoires de durcissement, utilisant soit un brûleur à L.P.G. (gaz à basse pression) soit une étuve spéciale. On y fait comparer de divers systèmes de durcissement. On fait quelque examen de la possibilité d'obtenir un durcissement suffisant à 120°C, dans le

*Presented to the London Section on 12 February 1970.

cas de certains de ces systèmes de résines. On donne une comparaison des résultats obtenus à partir d'une résine à hexaméthoxyméthylmélamine auprès de ceux à partir d'une résine mélamine butylée.

Neue Harzsysteme für den Einsatz bei Walzenlackierung

Zusammenfassung

In diesem Artikel wird die Entwicklung von auf "Cardura" E (dem Glicidylester von "Versaticsäuren" 911) basierenden Harzen besprochen, deren Zweck es ist, den für Coilcoating bestimmten Alkydharz/MF Emaillelacken die erforderlichen mechanischen Eigenschaften zu verleihen.

Eine Serie von auf "Cardura" E, Phthalsäureanhydrid, Triäthylenglykol und Trimethylolpropan basierenden Harzen wies vielversprechende Resultate auf. Die entsprechende Serie mit Isophthalsäure ergab etwas bessere Filmeigenschaften, aber einige der dabei benutzten Harze waren unbeständig.

Laboratoriumsmethoden zur Schnellhärtung auf entweder LPG-befeuerten Brennern oder einem Spezialofen beruhend, werden beschrieben. Verschiedene Zyklen werden verglichen. Geprüft wurde auch die Möglichkeit mit einigen dieser Harze eine ausreichende Vernetzung bei 120°C zu erhalten. Ein Vergleich der Resultate, welche mit einem Hexamethoxymethylenmelaminharz und der, welche mit einem butylierten Melaminharz erhlten wurden, wird gezogen.

Новые смольные системы для применения в покрытии обмоток

Резюме

Статья описывает развитие смол основанных на «Кардюре» Е (глицидный эфир синтетических кислот «Версатик» 911) предназначенных для получения требуемых механических качеств пленки в алкидных меламино-формальдегидных эмалях для применения в покрытии обмоток.

Ряд смол основанных на «Кардюре» Е, фталиевом ангидриде, триэтиловом гликоле и триметиловом пропане дал обнадеживающие результаты. Соответствующая серия смол изофталевой кислоты дала несколько лучшие пленочные свойства, но некоторые смолы этой серии оказались неустойчивыми.

Описываются лабораторные методы быстрой сушки, основанные на горелке на жидком пропане или на специальной печи. Сравнивается несколько различных режимов. Анализируется возможность получения надлежащей сушки с некоторыми из этих смольных систем при 120°C. Прилагается сравнение между результатами полученными с гексаметоксиметилмеламиновой смолой и результатами полученными с бутиломеламиновой смолой.

Introduction

Cardura* 30 is a well-known alkyd resin based on highly-branched synthetic acids in the C₉₋₁₁ range (Versatic* 911 is the grade commonly used). One of its main methods of use is in conjunction with melamine formaldehyde (mf) resins to form a binder for baking enamels. It is widely used in coil-coating because it has some very attractive features—outstandingly good exterior durability, colour and colour retention on overbake. It gives much better chemical resistance than normal alkyds. However, for those applications which require a particularly good hardness/flexibility combination it is not very suitable, as shown in Table 1.

The performance is inadequate with respect to the bend and reverse impact tests. It was decided to attempt to formulate resins having improved mechanical properties.

Table 1
Typical properties of a Cardura 30/mf enamel
compared with likely coil coating requirements

| | König pendulum hardness | Pencil hardness | I-T bend | Erichsen slow penetration | Reverse impact BS 3900 |
|--|-------------------------|-----------------|----------|---------------------------|------------------------|
| Probably minimum requirement | 100 sec | H | Pass | 7 mm | 100 mils |
| Cardura 30/ Beetle BE 670† enamel (Convection oven baked 30 min at 150°C) | 140 sec | H | Fail | 7.7 mm | 25 mils |

Alkyd: MF = 80:20. Catalyst: 0.2 per cent of *p*-toluene sulphonic acid (PTSA) calculated on total resin solids, equivalent to 1 per cent by wt calculated on amino resin solids. Pigment: Titanium dioxide RCR-3 (British Titan Products Ltd.). Pigment: binder = 0.7:1 by wt. Substrate: 20 SWG polished vapour degreased mild steel (Pyrene Gold Seal panels).

*Cardura and Versatic are Shell registered trade marks.

†Hexamethoxymethyl melamine (HMMM) resin. British Industrial Plastics Ltd.

Part I: Preliminary work on alternative resins

Chemical nature of Versatic acids

Before describing the composition of alternative resins, attention must be drawn to one chemical property of the synthetic acids used which gives a special feature to the formulation and preparation of the resins. The acids are largely tertiary and therefore, because of steric hindrance, they react markedly more slowly than do the superficially similar acids derived from natural oils. The consequence of this is that calculations of average functionality for a Cardura type resin formulated on conventional lines can be very misleading, since they rest on the implied assumption that all possible reactions will proceed at about the same rate. Since it is the monofunctional component which is slow-reacting, the system is effectively higher in functionality than it seems at first sight and is correspondingly more prone to gelation. Even where gelation is avoided, the performance obtained is disappointing.

In practice this difficulty is avoided by formulating, not on the basis of the synthetic acids themselves, but on their glycidyl esters. Cardura E is the glycidyl ester of Versatic 911 and it is from this material that the alkyd resin Cardura 30 is made.

Some variants of Cardura 30

A number of variants of Cardura 30 were prepared to give preliminary guidance. These involved very drastic changes in some cases. They fall into three series, details of which are shown.

Series A: Part replacement of phthalic anhydride. This involved part (25 per cent molar) replacement of phthalic anhydride (PA) by di-acids which, it was hoped, would improve performance in bend and impact tests. Compositions are given in Table 2.

Table 2
Molar composition of series A resins

| | Cardura 30 | Resin A1 ¹ | Resin A2 | Resin A3 ² |
|---|---------------|--------------------------|-------------|--------------------------|
| Phthalic anhydride | 1.0 | 0.75 | 0.75 | 0.75 |
| Adipic acid (HOOC (CH ₂) ₄ .COOH) .. | — | 0.25 | — | — |
| Azelaic acid (HOOC (CH ₂) ₇ .COOH) .. | — | — | 0.25 | — |
| 12-hydroxy stearic acid (CH ₃ (CH ₂) ₅ CH.OH (CH ₂) ₁₀ .COOH) | — | — | — | 0.25 |
| Cardura E | 0.75 | 0.6 | 0.6 | 0.45 |
| Glycerol | 0.325 | 0.4 | 0.4 | 0.3 |

Notes

¹ Resin A1 is in fact Cardura 40, an established variant showing somewhat better performance in impact tests than Cardura 30. It was thought that still further improvements might be effected by extending this principle by using still longer chain di-acids.

² The ratios are intended to give the same hydroxyl: carboxyl ratio as in resins A1 and A2.

Results from this series were not encouraging. There was some improvement in impact resistance—but only with Resin A3 was the required minimum of 100 units obtained and here the film was unacceptably soft—"B" on the pencil scale.

Series B: Complete replacement of phthalic anhydride. It is generally held that aromatic rings tend to give hard and inflexible structures; alternative anhydrides were therefore examined. Compositions are given in Table 3.

Table 3
Molar composition of series B resins

| | Cardura 30 | Resin B1 | Resin B2 | Resin B3 |
|------------------------------------|---------------|-------------|-------------|-------------|
| Phthalic anhydride | 1.0 | — | — | — |
| Tetrahydrophthalic anhydride | — | 1.0 | — | — |
| Hexahydrophthalic anhydride | — | — | 1.0 | — |
| Succinic anhydride | — | — | — | 1.0 |
| Cardura E | ← (0.750) → | | | |
| Glycerol | ← (0.325) → | | | |

Resin B1 and B2 gave some improvement in impact resistance but only at the expense of hardness—in other words the overall balance of physical properties was not more attractive. Resin B3 gave a very large improvement in impact resistance—up to 250 mils, the limit of the instrument, (beyond this point the momentum of the striker is insufficient to give full penetration with the steel panels used in these tests). With one particular mf a "pass" was obtained in the 1-T bend test. However, here the films were very soft indeed—3B on the pencil scale. It was decided that the results did not justify further study, particularly since this succinic variant tended to gel during cooking.

Series C: Variations in polyol. Here glycerol was replaced by either a diol or a tetrol. Average functionality was kept constant so that the excess hydroxyl varied fairly widely through the series. Compositions are given in Table 4.

Table 4
Molar compositions of series C resins

| | Cardura 30 | Resin C1 | Resin C2 | Resin C3 |
|------------------------------------|---------------|-------------|-------------|-------------|
| Glycerol | 0.325 | — | — | — |
| Monoethylene glycol (MEG) | — | 0.325 | — | — |
| Diethylene glycol (DEG) | — | — | 0.325 | — |
| Diglycerol (DG) | — | — | — | 0.325 |
| Phthalic anhydride | ← (1.0) → | | | |
| Cardura E | ← (0.75) → | | | |
| Hydroxyl excess (per cent) | 24 | 7.5 | 7.5 | 40 |

None of the stoving enamels obtained from these resins gave the required all-round properties, which is hardly surprising in view of the drastic formulation changes made. However, the DEG variant (resin C2) gave a pass in the difficult 1-T bend test at a pencil hardness of HB, though the enamels were very slow curing. It was decided to pursue this theme, but C2 is not an attractive resin as it stands, having too low an excess hydroxyl content. A series of resins based on mixtures of diol and triol was therefore formulated (see below). At this point the triol component was changed from glycerol to trimethylol propane (TMP) in the hope of obtaining better chemical resistance properties. Since it was clear that only a limited proportion of diol could be used, triethylene glycol (TEG) was preferred as likely to give better performance in the flexibility tests than DEG.

Before describing the work with this series of resins it is desirable to consider the methods of cure.

Method of cure

Conventional oven cures, such as the 30 minutes at 150°C used in the ordinary way with Cardura 30/mf enamels, are not appropriate to coil coating applications. For example, on this schedule, a line running at 100ft per minute, which is not particularly fast, would require an oven over half mile in length and is obviously unacceptable. In practice the oven in such a case will be about 100ft in length and cure will be effected in about one minute, moreover a large proportion of solvent must also be removed during this stoving operation since lengthy flash off times cannot be tolerated either. This rapid curing is brought about by a vigorous movement of hot air which also serves to keep atmospheric concentrations of solvent vapour below the explosive limit. Even so, about 100ft of metal must be suspended during stoving, and the air blast helps to support it. Cure schedules of this type cannot be defined in terms of time at a steady temperature and are therefore normally expressed as peak metal

temperature after a quoted time. Oven conditions would, in general, need to be changed whenever the type or thickness of metal was changed.

Since reactions in alkyd/mf enamels are not very clearly understood it cannot be assumed that the film properties obtained in such a rapid stoving operation will be the same as those in a conventional box oven. It was essential, therefore, in this work to have some means of rapid cure; however, conventional oven cures were also included in most cases in order to obtain the comparison.

In most of the work described herein, rapid cure was obtained by placing the coated panel at a fixed distance from a propane-fired Schwank burner. The rise in metal temperature was measured using a blank panel fitted with a chrome/alumel thermocouple. The general arrangement is shown diagrammatically in Fig. 1 and the time/temperature relationship in Fig. 2. Provided

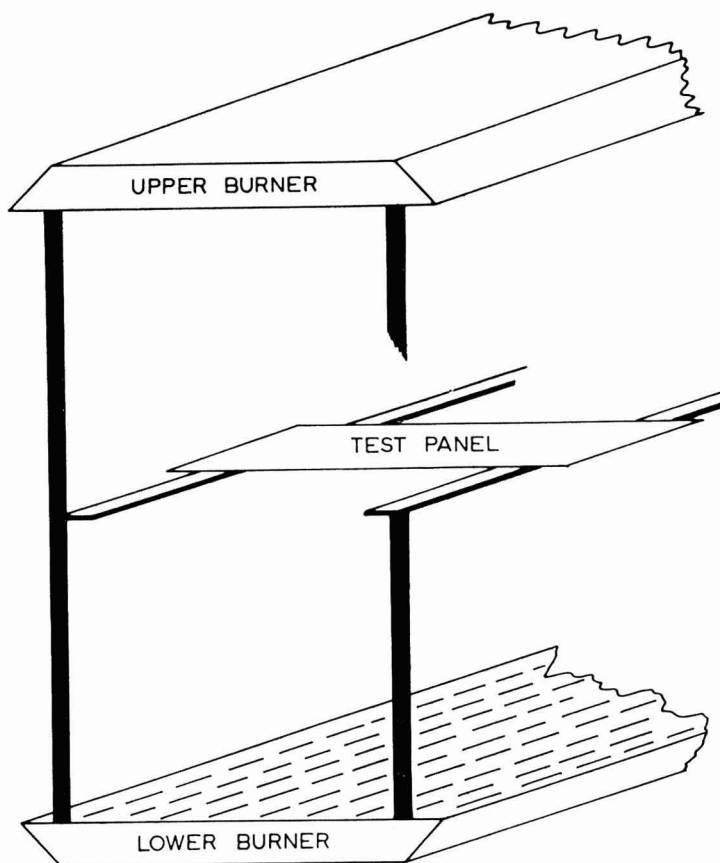


Fig. 1. Diagram of "Schwank" LPG stoving rig

that adequate time was allowed for warming up (about 15 minutes was sufficient) this arrangement worked fairly well. However, in the early stages of the programme a single burner was used and this gave rather inconsistent results owing,

it is thought, to the influence of draughts in the laboratory. It will be noted that no additional blower is used, but the burner surfaces, which are themselves at about 825°C, provide a vigorous thermal movement. There was no difficulty owing to solvent vapours catching fire with the flash off periods used, usually approximately 10 minutes. Nor was bubbling a problem at normal film thicknesses up to, say 35 μ . It was expected that it would be necessary to add a proportion of higher-boiling solvent, such as isophorone, but this proved not to be the case.

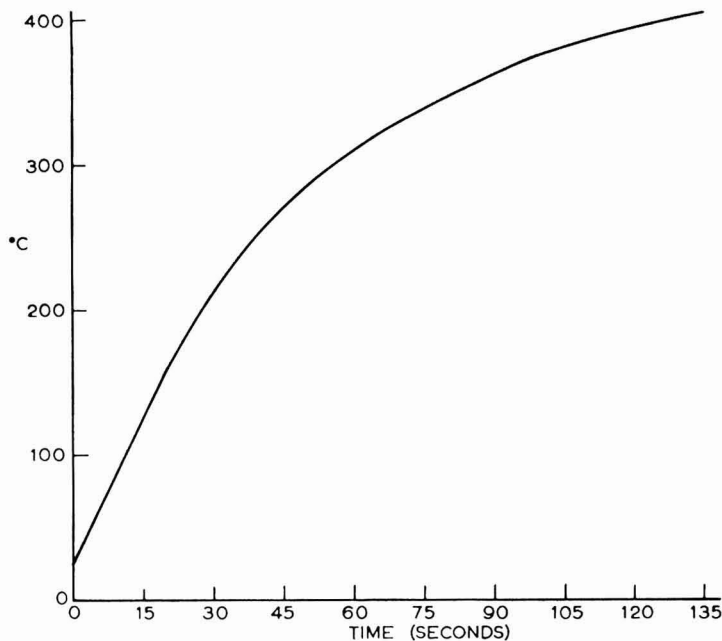


Fig. 2. Time/temp relationship for test panel in "Schwank" LPG stoving rig

In the later stages of the work an American-made Blue M oven (Manufacturers—Blue M Electric Company, Illinois, USA) has been examined. This is electrically heated and provides a vigorous air movement. As originally delivered, it was fitted with a conventional door opening to full oven width and height. Temperature measurements showed a considerable drop when the door was opened momentarily. A "letter box" type of door was therefore designed and fitted, and this almost completely eliminated the problem. Fig. 3 shows the time/temperature relationship for this oven. Fig. 4 shows the temperature drop when the door is opened for five seconds and the corresponding drop when the "letter box" is fitted. This modification made it necessary to deal with panels one at a time, but this is not a problem with the short baking times involved. Indeed it is easier to maintain a fixed flash-off time by working in this way. (Flash-off time is normally one minute. Again it has not been found necessary to use high boiling solvents).

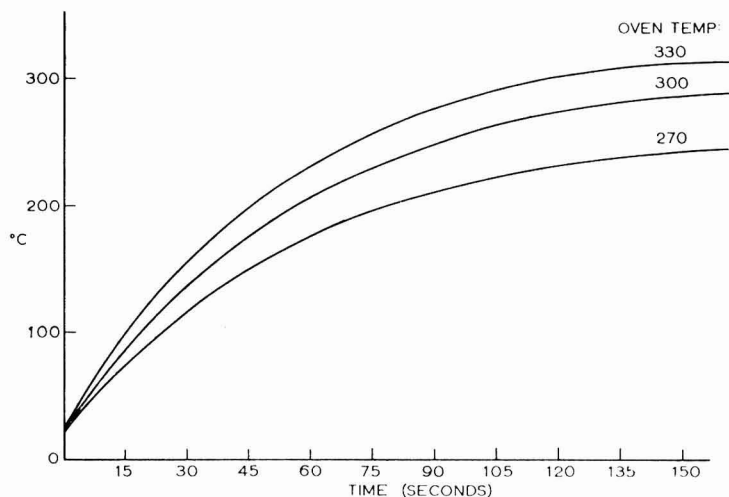


Fig. 3. Time/temp relationship for test panel in "Blue M" stoving oven

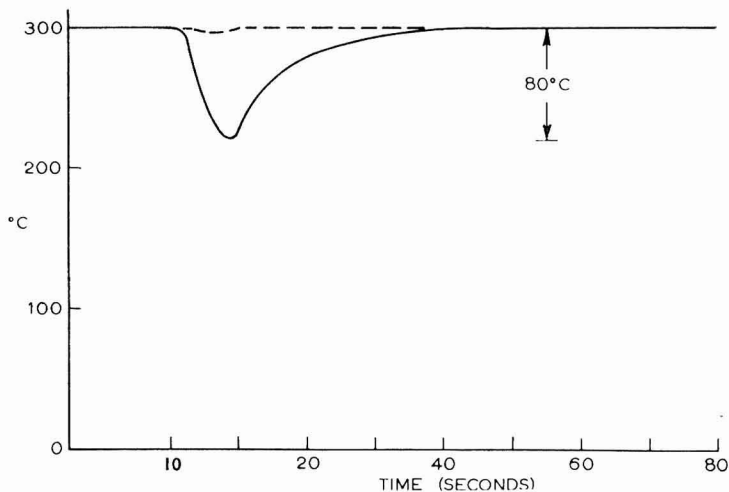


Fig. 4. Effect of opening door for 5 seconds on air temp of "Blue M" oven

Part II: Resins based on diol/triol mixtures and phthalic anhydride—(series D)

Series D resins: General

A series of five resins was formulated, based on different mixtures of TEG and TMP. Compositions are given in Table 5; note that TEG: TMP ratios are expressed in terms of equivalents *not* in terms of moles.

These resins have the same hydroxyl excess (15 per cent) and therefore differ somewhat in their average functionality. They were cooked to an acid value of about 14 mg KOH/g.

Table 5
Molar compositions of series D resins

| | Resin D1 | Resin D2 | Resin D3 | Resin D4 | Resin D5 |
|------------------------------|----------|----------|----------|----------|----------|
| Phthalic anhydride | (1.0) | | | | |
| Cardura E | (0.5) | | | | |
| TEG | 0.488 | 0.390 | 0.325 | 0.260 | 0.163 |
| TMP | 0.108 | 0.174 | 0.217 | 0.260 | 0.325 |
| Ratio (equivs) diol:triol .. | 3:1 | 3:2 | 1:1 | 2:3 | 1:3 |

The mechanical properties obtained from films of alkyd/mf enamels are given in Table 6 and shown diagrammatically in Fig. 5; it was felt that the properties could be more easily judged in this way than from columns of figures. In this type of diagram, the results of hardness tests are plotted upwards from the middle line and the results of flexibility tests downwards. The target level of performance (see Table 1) is of equal length for all tests. Thus in the upward ("hard") direction a König value of 100 is plotted at the same level as a pencil hardness of "H". Higher and lower values are then plotted according to the scales shown. Similarly, in the downward ("flexible") direction an Erichsen slow penetration value of seven is plotted at the same level as a BS 3900 value of 100. Further, the Erichsen value of seven is as far from the zero line (middle line of the diagram) as is the König value of 100 in the opposite direction—so

Table 6
Film properties: Series D resins¹

| | Resin | | | | |
|------------------------------|-------|-----|-----|-----|-----|
| | D1 | D2 | D3 | D4 | D5 |
| König hardness | 81 | 118 | 137 | 148 | 178 |
| | 66 | 103 | 122 | 147 | 177 |
| Pencil hardness | H | F | H | H | H |
| | F | F | H | H | H |
| 1-T bend | F | F | F | F | F |
| | P | P | F | F | F |
| Erichsen slow penetration .. | 8.8 | 8.3 | 7.1 | 7.3 | 6.8 |
| | 9.8 | 9.2 | 8.8 | 8.6 | 7.2 |
| Reverse impact (BS 3900) .. | 125 | 150 | 75 | 25 | 12 |
| | 175 | 200 | 150 | 50 | 12 |

¹Paint formulation and substrate details as in Table 1.

Upper figure is for Schwank cure; lower figure is for box oven cure (30 minutes at 150°C).

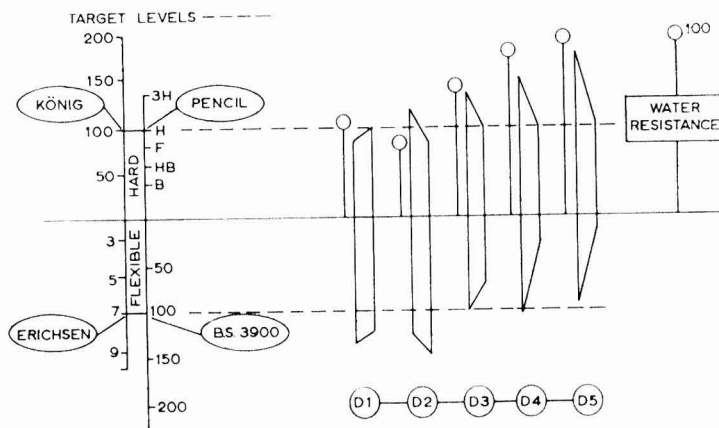


Fig. 5. Film properties: series D resins

that equal "value" is given to all target levels, whether "soft" or "hard." This type of diagram has its dangers; the equating of values from different tests cannot really be justified and the use of a scale of equal steps for pencil hardness values is questionable, to say the least. But the general comparisons between the different resin systems can be seen at a glance and this is very convenient. In particular, it is easy to see how near to the overall targets a particular system has come. Two points of detail in this series of diagrams require comment. First, in Figs. 5 and 7 results of a water immersion test are included as a simple indication of chemical resistance; this was assessed on a 0 to 100 scale indicating the overall performance during the 90 days of test (there is no accepted performance requirement for this test). Secondly, from Fig. 8 onwards the Erichsen slow penetration test is replaced by the "I-T" bend test; this was because it was found in the early stages of the work that almost all the systems studied met the target level of seven for the Erichsen test.

From Fig. 5 the formulation trends for the series D resins can be followed; it can be seen that D1 lacks hardness while D4 and D5 lack flexibility. Resins D2 and D3 are fairly close to the required properties though they fail the I-T bend test (at this time this was treated as a simple pass or fail test and has therefore been omitted from the diagrams.)

A comparison of Schwank and box oven cure results is given in Fig. 6. Oven cure gives slightly softer and more flexible films but the differences are not great.

More detailed study of resins D2 and D3

Since D2 and D3 gave the most promising results, they were selected for a more detailed study. Although the work was mainly based on likely performance requirements for coil-coating applications, it was thought possible that resins of this type would be of some general interest. Accordingly, variations in alkyd/mf ratio and in catalyst loading were studied to see how far the properties were lost when the stoving temperature was dropped to 120°C. Tables 7 and 8 show

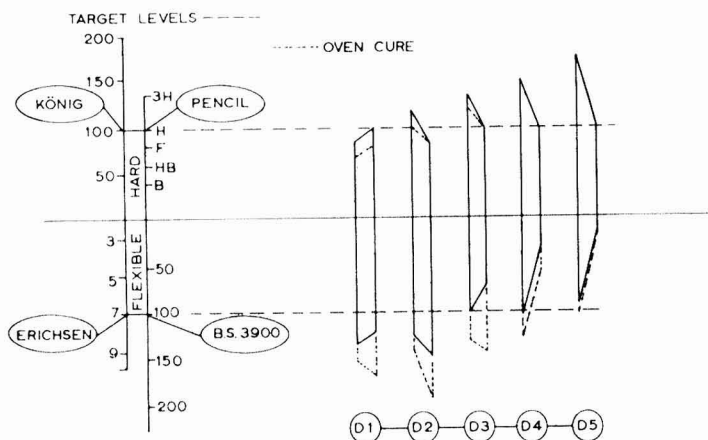


Fig. 6. Series D resins: comparison of "Schwank" v oven cure

Table 7
Comparison of film properties at 150°C and at 120°C (resin D2)

| Thirty min at (Stoving temp) | 150°C | 120°C | | | | | |
|---------------------------------------|-------|-------|-----|-------|------|-------|-----|
| | | 90/10 | | 80/20 | | 70/30 | |
| Alkyd/MF | 80/20 | 90/10 | | 80/20 | | 70/30 | |
| Catalyst loading ¹ | 0.2 | 0.4 | 0.8 | 0.4 | 0.8 | 0.4 | 0.8 |
| König hardness | 103 | 58 | 79 | 74 | 107 | 44 | 92 |
| Pencil hardness | F | HB | HB | HB | HB/F | HB | HB |
| 1-T bend ² | P | P | P | P | F | P | F |
| Erichsen slow penetration | 9.2 | 10 | 10 | 10 | 10 | 10 | 10 |
| Reverse impact (BS 3900) | 200 | 250 | 250 | 250 | 250 | 250 | 200 |

Notes

- ¹ Per cent PTSA on total resin solids.
- ² The 1-T bend test is on a simple "pass" or "fail" basis, as in the earlier section.
- P = Pass F = Fail

Table 8
Comparison of film properties at 150°C and at 120°C (resin D3)

| Thirty min at (Stoving temp) | 150°C | 120°C | | | | | |
|---------------------------------------|-------|-------|------|-------|-----|-------|-----|
| | | 90/10 | | 80/20 | | 70/30 | |
| Alkyd/MF | 80/20 | 90/10 | | 80/20 | | 70/30 | |
| Catalyst loading ¹ | 0.2 | 0.4 | 0.8 | 0.4 | 0.8 | 0.4 | 0.8 |
| König hardness | 122 | 82 | 104 | 93 | 124 | 64 | 111 |
| Pencil hardness | H | HB | HB/F | HB/F | F | HB | F |
| 1-T bend ² | F | P | F | P | F | P | F |
| Erichsen slow penetration | 8.8 | 10 | 10 | 10 | 9.8 | 10 | 9.3 |
| Reverse impact (BS 3900) | 150 | 250 | 100 | 200 | 150 | 175 | 200 |

Notes

- ¹ Per cent PTSA on total resin solids.
- ² The 1-T bend test is on a simple "pass" or "fail" basis as in the previous section.
- P = Pass F = Fail

the results for D2 and D3 respectively. (It was found that very soft films (König test) were obtained at a catalyst loading of 0.2 per cent PTSA; only higher catalyst loadings were therefore examined fully). With resin D2 it can be seen that the 80/20 alkyd/mf ratio gives the most generally attractive results; at a catalyst loading of 0.8 per cent PTSA the overall properties are quite close to those obtained at 150°C. Unfortunately this system had rather poor storage stability. At 0.4 per cent PTSA the films were noticeably softer.

With resin D3 a rather similar picture emerges. The 80/20 ratio gives the best results generally. At 0.8 per cent PTSA results are fairly close to those obtained at 150°C, but again storage stability is rather poor. At 0.4 per cent PTSA films are somewhat softer but there is a gain in flexibility and a "pass" in the I-T bend test.

Summarising, it appears that, if some sacrifice of storage stability can be tolerated, results can be obtained at 120°C which are not greatly inferior to those at 150°C.

Part III: Resins based on diol/triol mixtures and iso-phthalic acid—(series E)

Series E resins: General

Resins parallel to the D series were prepared (series E) using iso-phthalic acid (IPA) in place of phthalic anhydride. This work is not complete, but the results of the early stages are presented as a matter of interest. The molar compositions of E1 to E5 correspond to those of D1 to D5 (see Table 5) and are therefore not given here. Results of mechanical tests and water immersion are given in Table 9 and Fig. 7, results for Series D resins being included for comparison in the diagram. It can be seen that rather better all-round properties are obtained in the mechanical tests and there is a notable improvement in water resistance.

Table 9
Test results for series E resins
(Schwank burner: 60 seconds)

| | Resin | | | |
|-----------------------------------|-------|------|------|------|
| | E1 | E2 | E3 | E4 |
| König hardness | 134 | 149 | 168 | 172 |
| Pencil hardness | H | H/2H | H/2H | H/2H |
| I-T Bend test | Fail | Fail | Fail | Fail |
| Erichsen slow penetration | 7.5 | 7.9 | 8.0 | 8.0 |
| Reverse impact (BS 3900) | 125 | 175 | 140 | 140 |

However, it was not possible to cook resin E5 on a laboratory scale (1kg) because of gelation. With resin E4 it was necessary to stop at an acid value of about 16 instead of the normal 12-15; enamels made from this resin had poor storage stability. Resin E3 gave no difficulties in the laboratory but gave a stringy resin when a pilot scale (20kg) cook was attempted. E2 was satisfactory in laboratory use and in a pilot plant cook. E1 was satisfactory in the laboratory; no pilot batch has been attempted but, from the formulating trends in this series,

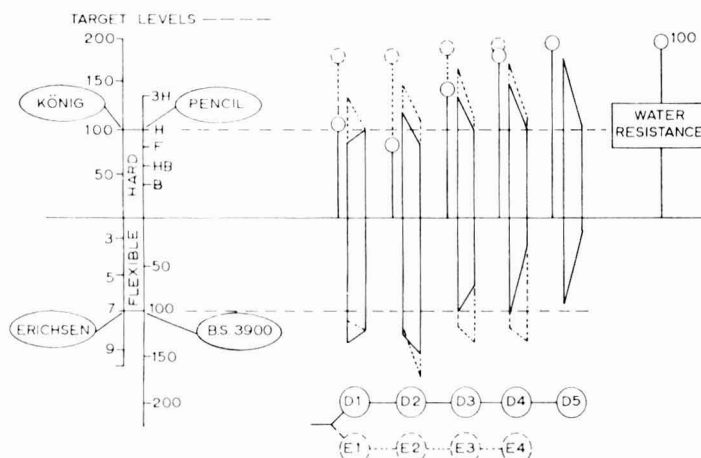


Fig. 7. Film properties: comparison of series D and series E resins

it would be expected to behave satisfactorily. Differences of this sort are often encountered when phthalic anhydride is replaced by iso-phthalic acid; they can be explained by an increased tendency to etherification due to the use of free acid in place of anhydride. It is sometimes stated that the functionality of IPA is not 2 but 2.2; this is difficult to interpret and lacks any theoretical justification. Moreover, even if it were a useful guide in formulating conventional alkyds it would not necessarily be so in the work described here, where an epoxy compound is present. The authors have preferred, therefore, to tackle this problem on a simple trial and error basis and will proceed to lower functionality modifications of the higher members of the E series. It is not possible to say whether the rather more attractive film properties are due to the higher (effective) average functionality or to the use of IPA as such.

Cure schedule studies with series E resins

It was decided to compare Blue M oven schedules with those used previously. Mechanical film properties were therefore measured after the following cure schedules:

- (i) box oven (30 minutes/150°C),
- (ii) Schwank burner (60 seconds),
- (iii) "Blue M" oven, 2½ minutes (air temperature 305°C),
- (iv) "Blue M" oven, 1½ minutes (air temperature 305°C),
- (v) "Blue M" oven, 1 minute (air temperature 305°C).

Resin E1 was omitted as being likely to give soft films. The Erichsen slow penetration test was dropped for this series: instead the "T-bend" test was included and extended to include up to "3-T" so as to be better able to cover a range of behaviour for the systems studied. So far only one type of mf resin (HMMM) had been studied; it was thought that it might be interesting to include a butylated mf resin and Maprenal 5428* was selected, as it was originally

*Cassella Farbwerke Mainkur AG

stated by its manufacturers to be suitable for coil-coating applications. It was used as recommended, without addition of catalyst.

Figs. 8 to 13 compare the different cure schedules for each resin system. Generally, the HMMM type mf resin (Beetle BE 670) gives best results at 1½ minutes, or between 1½ and 2½ minutes, in the Blue M oven. The butylated mf resin (Maprenal 5428) is generally best suited by the 2½ minute schedule. It is usually possible to choose a Blue M schedule which gives results similar to those obtained on the Schwank burner.

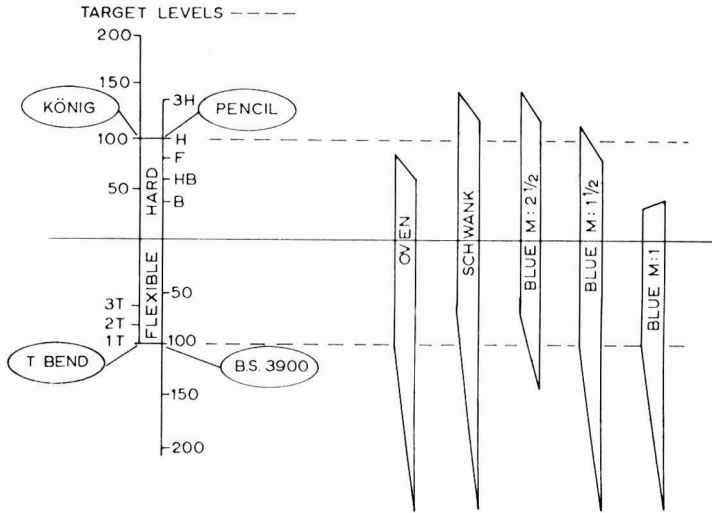


Fig. 8. Comparison of cure schedules: resin E2: "Beetle" BE 670

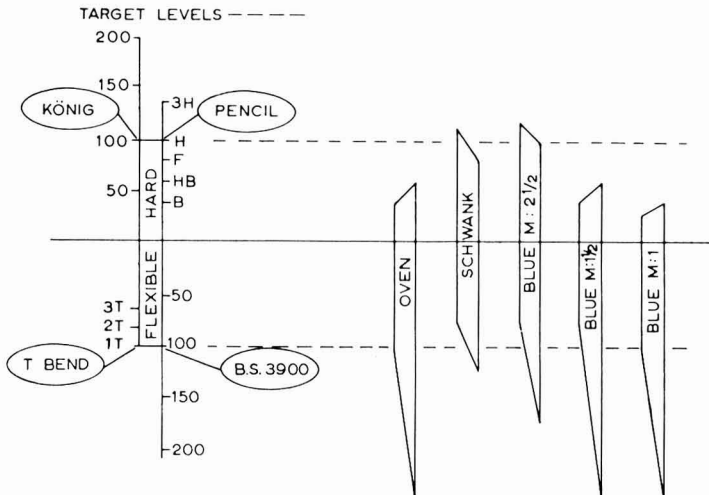


Fig. 9. Comparison of cure schedules: resin E2: "Maprenal" 5428

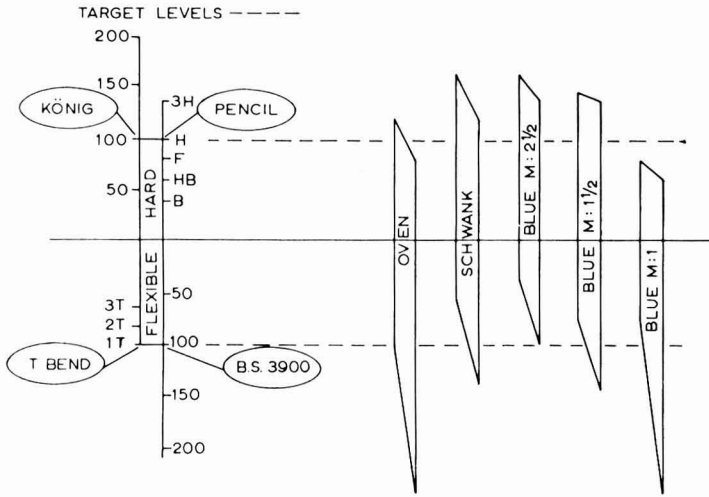


Fig. 10. Comparison of cure schedules: resin E3: "Beetle" BE 670

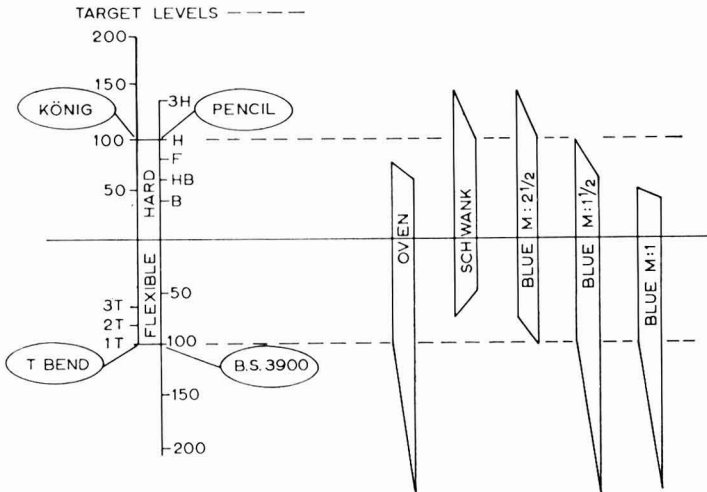


Fig. 11. Comparison of cure schedules: resin E3: "Maprenal" 5428

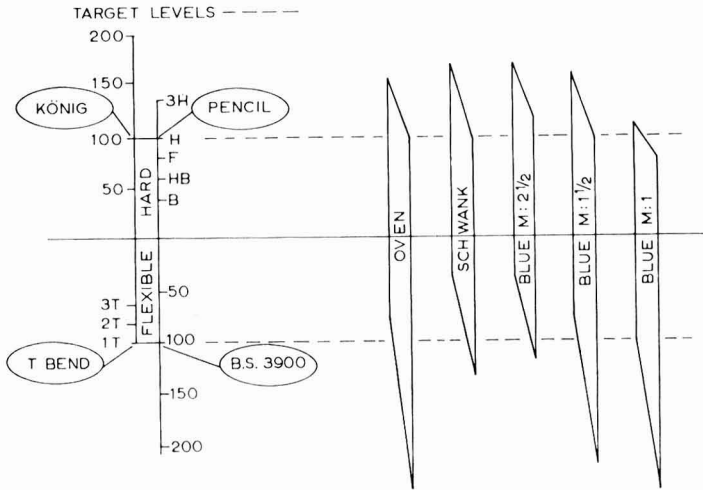


Fig. 12. Comparison of cure schedules: resin E4: "Beetle" BE 670

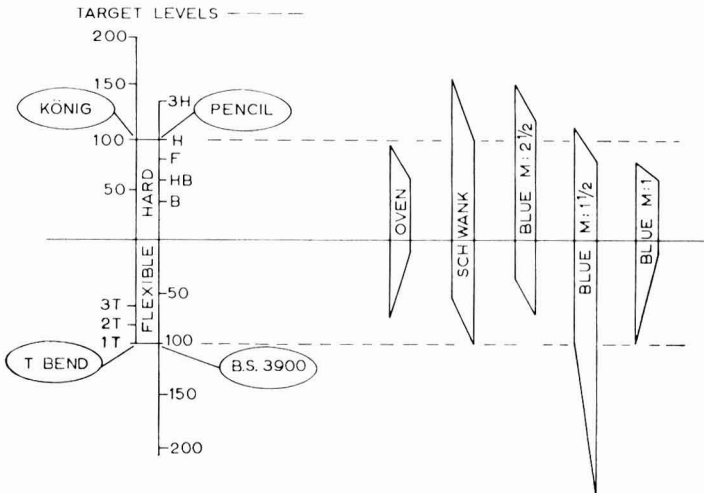


Fig. 13. Comparison of cure schedules: resin E4: "Maprenal" 5428

Figs. 14 and 15 compare the two mf resins after box oven and Schwank cure respectively. The butylated mf resin gives softer films and does not generally show a corresponding gain in the flexibility tests. The position is complicated in the case of the box oven because most of the impact resistance values fall at the limit of the test method (250mils).

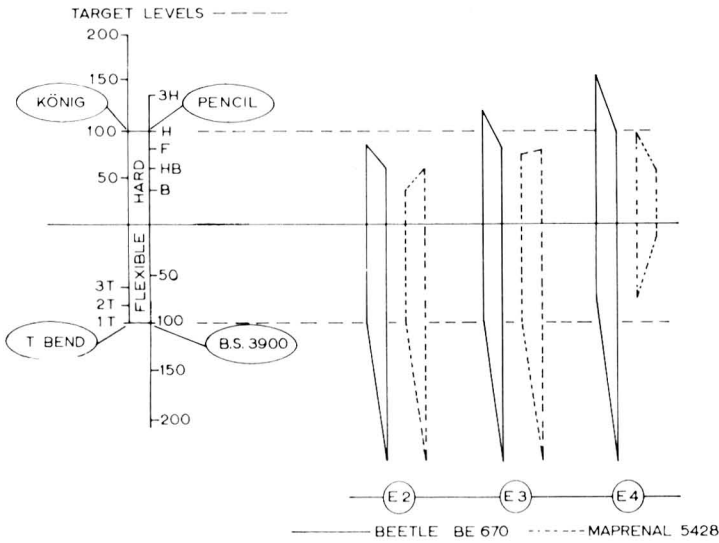


Fig. 14. Series E resins: comparison "Beetle" BE 670 and "Maprenal" 5428

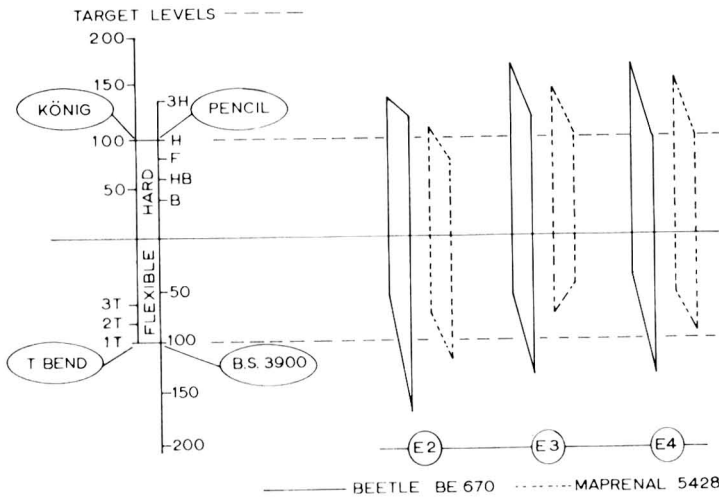


Fig. 15. Series E resins: comparison "Beetle" BE 670 and "Maprenal" 5428 ("Schwank" cure)

Comparison of the two mf resins is less simple for the Blue M schedules. Fig. 16 shows the 2½ minute case and Fig. 17 the 1½ minute. Since Maprenal 5428 seems generally to require a heavier stoving schedule than Beetle BE670, the two resins are compared in Fig. 18 on the basis of 2½ minutes and 1½ minutes respectively. Taken together, these three figures support the general conclusion for the oven and Schwank cures, namely that the butylated mf tends to give rather softer films without much compensating gain in other properties.

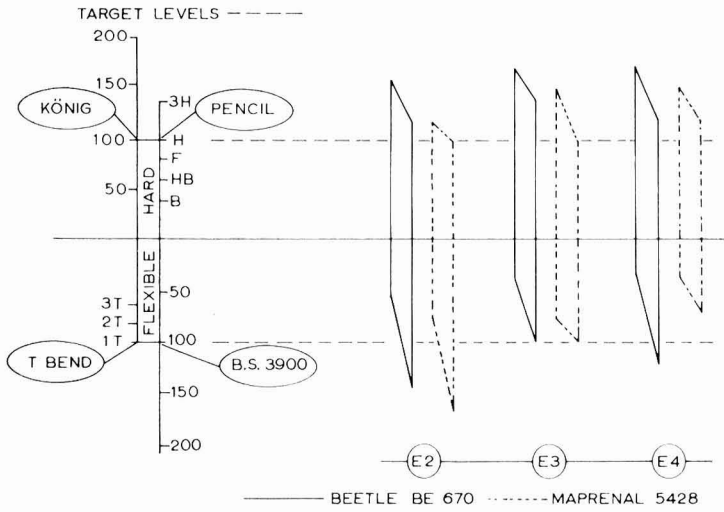


Fig. 16. Series E resins: comparison "Beetle" BE 670 and "Maprenal" 5428—"Blue M" cure: 2½ mins

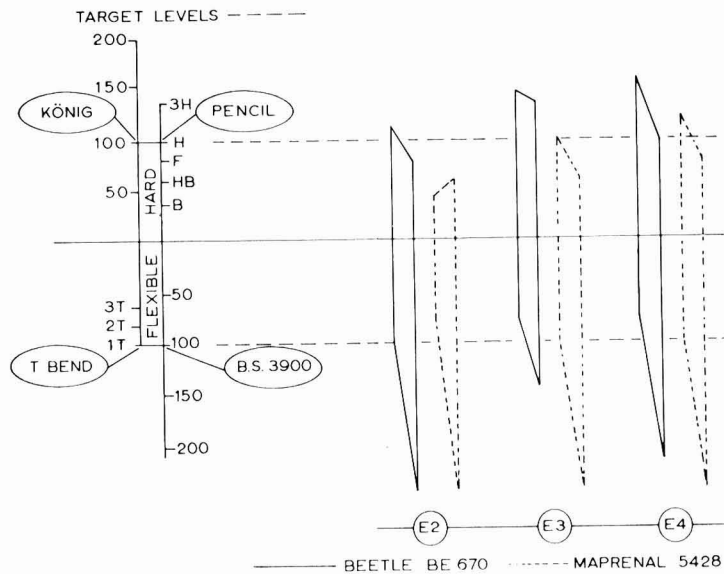


Fig. 17. Series E resins: comparison "Beetle" BE 670 and "Maprenal" 5428—"Blue M" cure: 1½ mins

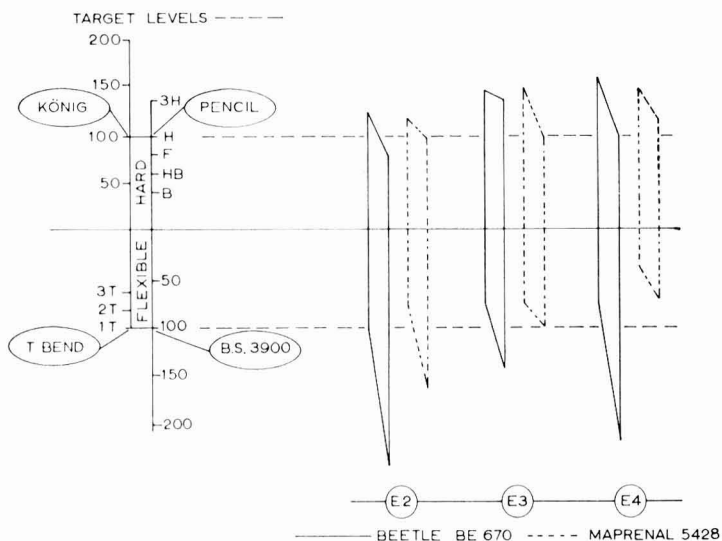


Fig. 18. Series E resins: comparison "Beetle" BE 670—"Blue M" cure (1½ mins) and "Maprenal" 5428—"blue" M cure (2½ mins)

General conclusions and future plans

Some of the resins described above give stoving enamels which come near to the required levels of mechanical properties. Indeed in many cases these levels are comfortably exceeded except for the 1-T bend test.

Nearly all the resins studied have had the same hydroxyl excess and acid value. This was in order to keep the volume of work within reasonable bounds in the early stages of the programme. It is intended in future work to vary these factors so as to locate optimum compositions derived from the chosen raw materials. Meanwhile, it is hoped that the resins described in this paper will give some indication of interesting areas of study.

Acknowledgment

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[Received 15 April 1970]

Discussion at the London Section

MR J. R. TAYLOR asked whether there was any effect of ageing on the physical properties quoted. Did the films become more brittle?

MR TYSALL said that there had been some falling off in the various properties after a month's storage, but this was less than had been expected.

MR N. R. FISK commented on the speaker's use of "above and below the line" diagrams to present information in a highly condensed form, and asked whether this could also be used to present results on gloss/opacity, another pair of properties that had to be a compromise and could never both be obtained at a maximum.

MR TYSALL replied the method could be applied to any pair of opposing properties.

MR P. WHITELEY commented that the work demonstrated that the coating industry had a lot of arbitrary test methods.

MR TYSALL agreed, and said it could sometimes be very misleading to lump together various tests as though they were measuring some single property; for example, "flexibility."

MR R. W. DOREE asked about the general formulation of paints used in the evaluation.

MR TYSALL said that all were glossy white paints, and were made by ball milling; the pigment/binder ratio was 0.7:1 by weight. A surface treated rutile titanium dioxide was used. The paints were examined as 1mil films.

MR M. J. ZISSELL said that the panels had been spun. Could the same solvent mixture be used as for coil coating?

MR TYSALL considered that he was not in a position to comment on the condition in a full scale coil-coating line, but said that he did not think that a change in solvent mixture would be necessary. He had looked at the possibility of building a laboratory scale coil-coating line, but had concluded that it would be a long and expensive exercise, and that it was likely that conditions would not closely parallel those on a full scale line.

MR ZISSELL asked whether a direct comparison had been made between these experimental resins and commercially available ones.

MR TYSALL said he had not made such a comparison.

The aluminium vinyl for ships' bottoms

By W. A. Anderton

Defence Research Establishment Pacific, Victoria, British Columbia, Canada

Summary

The effect of pigmentation on the performance of vinyl systems applied to steel when immersed in sea water with cathodic protection is discussed. In particular, aluminium pigment is compared to red lead, not only under sea water immersion, but also when alternated between this condition and fresh water immersion. The effect of variations in concentration of the aluminium pigment and of the thickness of the aluminium vinyl primers is described. Performance results of several ship trials where the aluminium vinyl system has been used as a bottom system are included. It is proposed that the aluminium pigment is more important in determining the performance of the system under cathodic protection than the binder, provided that the latter is resistant to alkaline attack. The effect of other metallic pigments in the vinyl primer is also described.

Keywords

Types and classes of coating

aluminium paint
ship bottom paint
vinyl coating

Prime pigments and dyes

aluminium pigment
red lead

Properties, characteristics and conditions primarily associated with dried or cured films

cathodic protection

Les systèmes vinyle—poudre d'aluminium pour la protection des carènes de navires

Résumé

On discute l'effet qu'exerce la nature du pigment sur le rendement des systèmes vinyliques appliqués à l'acier cathodiquement protégé, lors de son immersion en eau de mer. En particulier, on fait comparer le poudre d'aluminium auprès du minium, non seulement pendant une période d'immersion dans l'eau de mer, mais également pendant les périodes alternées d'immersion en eau de mer et en eau douce. On décrit l'effet des variations de la concentration en poudre d'aluminium et de l'épaisseur des feuillets de primaires vinyliques contenant de poudre d'aluminium. On mentionne les résultats au point de vue du rendement de plusieurs essais effectués sur navires, dans le cas où le système vinyle-poudre d'aluminium a été appliqué à la carène. On suggère que le poudre d'aluminium exerce une influence plus importante que celle du liant en ce qui concerne le rendement du système sous les conditions de protection cathodique, pourvu que le liant soit résistant à l'attaque alcaline. On décrit aussi l'effet d'autres pigments métalliques sur le rendement de la primaire vinylique.

Das Aluminium-Vinylharzsystem für Schiffsböden

Zusammenfassung

Die Auswirkung der Pigmentierung auf die Bewahrung von Vinylharzsystemen auf Stahl, wenn Immersion in Meereswasser sowie Kathodenschutz erfolgt, wird besprochen. Vor allem wird Aluminium als Pigment mit Bleimennige verglichen, und zwar nicht nur, wenn in Meereswasser, sondern auch wenn abwechselnd daren und in Süßwasser getaucht. Es wird auseinandergesetzt, wie sich Variationen in Konzentrationen des Aluminiumpigmentes, sowie unter-

schiedliche Dicken des Aluminiumvinylharzprimers auswirken. Ebenfalls werden Angaben über die Bewährungsresultate anhand von Versuchen an mehreren Schiffen gemacht, bei denen das Aluminium-Vinylharzsystem am Schiffsboden aufgetragen worden war. Es wird postuliert, dass das Aluminiumpigment bei der Beurteilung der Leistungsfähigkeit des System bei der Beurteilung der Leistungsfähigkeit des Systems bei gleichzeitigem Kathodenschutz wichtiger, als das Bindemittel sei, vorausgesetzt, dass dieses alkalienbeständig ist. Ebenfalls wird die Auswirkung anderer Metallpigmente in Vinylharzprimern beschrieben.

Алюминиево-винильная система для днищ судов

Резюме

Обсуждается влияние пигментации на эксплуатационные качества виниловых систем применяемых на стали при погружении в морскую воду с катодной защитой. В частности алюминиевый пигмент сравнивается со свинцовым суриком, не только в погружении в морскую воду, но также при чередовании этого процесса с погружением в пресную воду. Описывается влияние изменений в концентрации алюминиевого пигмента и толщины алюминиево-виниловых грунтовок. Прилагаются результаты ряда судовых испытаний с применением алюминиево-виниловой системы в качестве системы для днищ. Выражается мнение что алюминиевый пигмент является более важным в определении эксплуатационных качеств системы при катодной защите чем крепитель, при условии что последний устойчив против щелочи. Описывается также влияние других металлических пигментов в винильной грунтовке.

Introduction

It has been demonstrated¹ that, if a properly formulated aluminium pigmented vinyl anticorrosive primer* is substituted for the red lead vinyl primer which has been used on the bottoms of cathodically protected ships of the Canadian Armed Forces, the modified bottom system is superior to the red lead system in maintenance of adhesion. The system as used on these ships consists of one coat of wash primer applied to blast-cleaned steel, enough coats of the vinyl anticorrosive primer to give a minimum cumulative thickness of 125 microns, and an additional 75 microns minimum of vinyl antifouling paint. There is a tendency for the red lead primer to lose adhesion near bare areas and for the adhesion loss to spread progressively farther from the bare area with time. If the loosened film is torn off by the ship's motion, the paint coating at the edge of the new bare area becomes susceptible to further loss of adhesion and extensive stripping may occur.

Extensive laboratory trials, using the products of several manufacturers, have been conducted on the aluminium vinyl system. The DREP Qualification Procedure² has been used in the evaluation of these systems. Laboratory work has shown that a properly formulated aluminium vinyl system is resistant to adhesion loss at potentials of $-1,200$ mV \dagger , which few bottom systems will withstand.

Several ship trials have confirmed the superior performance of the aluminium vinyl system.

Suggested mechanisms which explain the performance of the aluminium vinyl system have been previously described¹.

*Canadian Government Specifications Board specification 1-GP-122b, type 3 describes a satisfactory aluminium vinyl primer.

\dagger All potentials referred to silver-silver chloride reference electrode.



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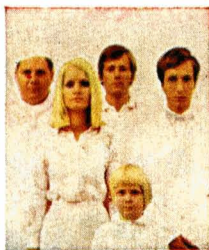
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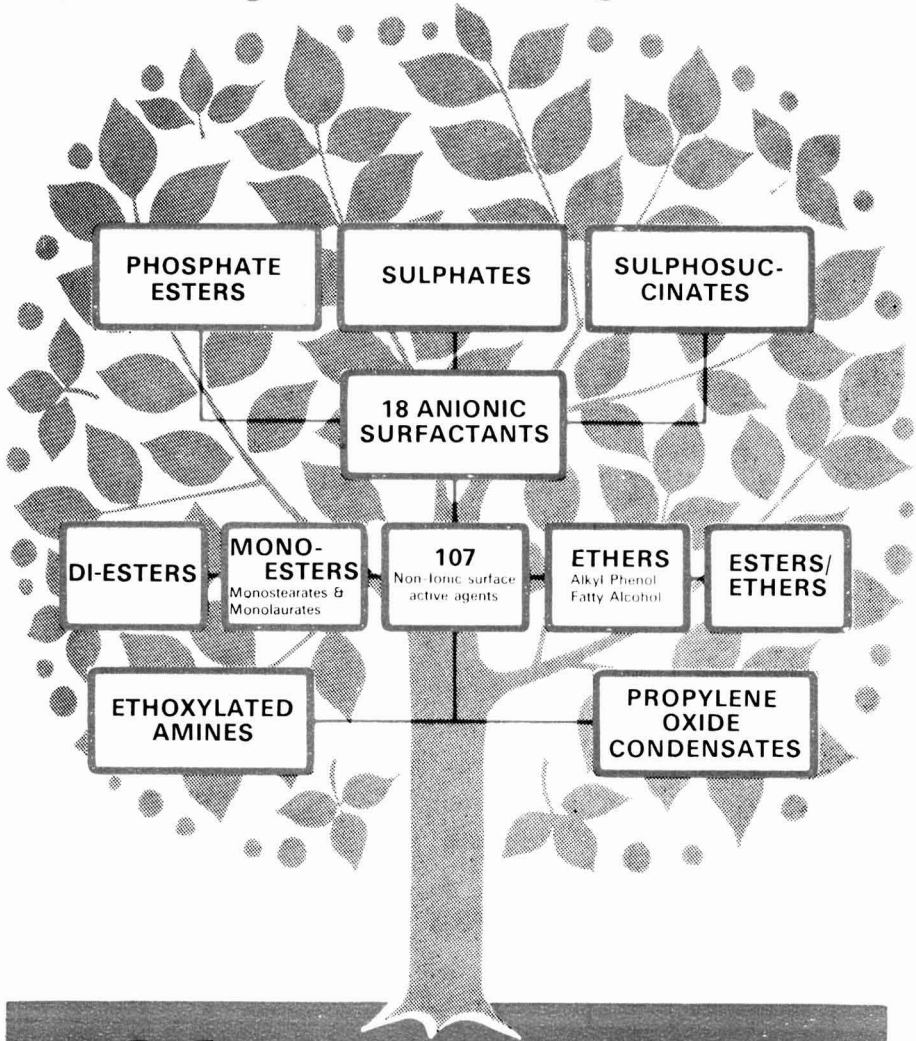
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Effect of the type of pigment in vinyl anticorrosive primers

Laboratory trials—sea water

Red lead vs aluminium in vinyl anticorrosive primers: Effects of cathodic protection on a vinyl system can be illustrated in the following manner. Apply a

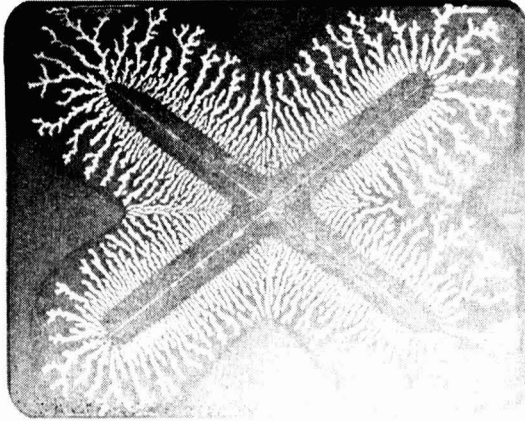


Fig. 1

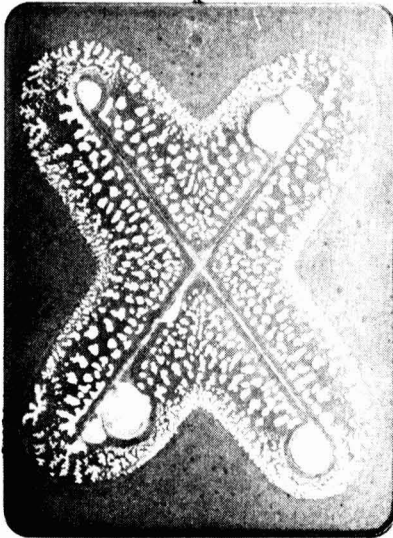


Fig. 2

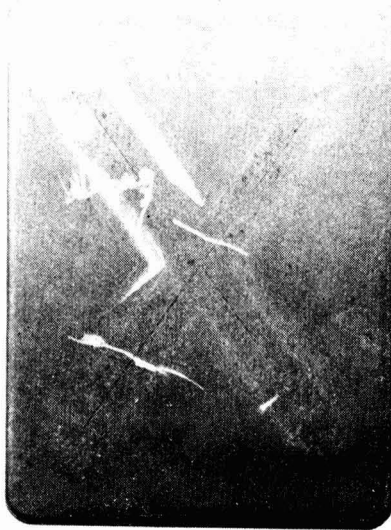


Fig. 3

Fig. 1. Pattern around X-cut after cathodic protection for 3 months at $-1,200$ mV (vs Ag/AgCl) on $3\text{in} \times 4\text{in}$ mild steel panels with the system: one coat of wash primer and 3 coats of unpigmented vinyl

Fig. 2. Scored, stripped panel with the red lead vinyl system after 3 months at $-1,200$ mV (vs Ag/AgCl)

Fig. 3. Scored, stripped panel with the aluminium vinyl system after 3 months at $-1,200$ mV (vs Ag/AgCl)

coat of wash primer to a blast cleaned steel panel, followed by three coats of unpigmented vinyl. Cut through the coating to steel to introduce a bare area. (In the author's work a standard X-cut is made with a sharp scalpel.) Immerse the panel in sea water with cathodic protection at $-1,200$ mv. After a period of immersion, a band of discoloration will develop adjacent to the cut, and the area of discoloration will increase progressively with time. Leave the panel immersed under these conditions for a month or more. When removed, a pattern will become apparent, as illustrated in Fig. 1. In the area of the pattern, adhesion to steel is destroyed. Analysis of the white material forming the pattern has shown it to be sodium phosphate. Phosphorus is only a minor constituent of sea water, so phosphate must have come from the phosphoric acid included in the wash primer. There is little sodium present in the initial coating materials. This must have come from the sea water.

If this experiment is repeated, substituting the full red lead vinyl system for the unpigmented vinyl coating, and if the vinyl topcoats are stripped off by solvent solution, it will be found that a similar pattern of sodium phosphate has developed (Fig. 2). Again, adhesion will have been lost in the pattern area.

Now, if the experiment is again repeated with the aluminium vinyl system, it will be found after solvent stripping that, if the immersion time is the same in each case, and if the aluminium vinyl primer is the same thickness, there is a smaller discoloured area. Moreover, there will be no pattern of sodium phosphate, and adhesion will be maintained (Fig. 3).

Metallic pigments other than aluminium in vinyl anticorrosive primers: A vinyl system with a zinc vinyl primer of the same pigment volume concentration as the aluminium vinyl used as a standard (about 18.5 per cent aluminium by volume of the dried film) was immersed for 100 days at $-1,000$ mV. At the end of this period, adhesion was good and the coating unblistered. The average current for the group was $17 \mu\text{amp}$.

When a panel of the group was immersed for an additional two months at $-1,200$ mV, adhesion was lost on most of the scored side.

A similar system, except that the anticorrosive primer was pigmented with stainless steel at the same pigment volume concentration, also resisted adhesion loss and remained unblistered for 100 days at $-1,000$ mV. The average current for the group at the end of this period was $120 \mu\text{amp}$. This is a relatively high current, and may be the result of the electrical conductivity of the coating. There was an appreciable conductivity between points on the surface which were bared of antifouling paint.

This system quickly lost adhesion when protected cathodically at -1200 mV.

Laboratory trials—alternate immersion in fresh and sea water

Because it had been suggested that ships sailing in fresh water as well as sea water were more susceptible to stripping of their bottom paints than ships sailing exclusively in sea water, a laboratory investigation was carried out.

Standard scored panels, some with red lead vinyl system, and others with the aluminium vinyl system, were immersed alternatively in tap water and sea water.

Whilst they were immersed in sea water, they were protected cathodically at $-1,000$ mV. Cathodic currents were measured at the beginning and end of periods of sea water immersion. The panels were alternated weekly for the first three months and then monthly until removed after one year.

There was no evidence that this treatment resulted in more serious loss of adhesion than did continuous sea water immersion. After one year the adhesion of the aluminium vinyl system was good right up to the score, but that of the red lead system had been destroyed for a distance of about $\frac{1}{2}$ in from the score.

At the end of the year there were more pitted areas along the score with the red lead than with the aluminium vinyl system. (Pits formed during fresh water immersion.) The maximum pit depths measured were 125 microns with the red lead system and 75 microns with the aluminium vinyl system. When stripped, a thin line of adherent rust remained along the score on the aluminium vinyl panels. No adherent scale was found on the red lead panels.

With the aluminium vinyl panels, the measured currents ranged from 6.8 μ amp to 23 μ amp, with a ratio of maximum to minimum values of 3.4. With the red lead systems, the minimum and maximum values respectively were 11 and 75 μ amp giving a ratio of 6.8. With both systems, there was a tendency for the current to rise after fresh water immersion and fall during sea water immersion, but there were exceptions to this.

To summarise:

there was no evidence that alternate immersion in fresh and sea waters was more destructive to bottom coatings than continuous immersion in sea water,

the aluminium vinyl system maintained adhesion but there was some adhesion loss with the red lead system,

score pitting was more prevalent with the red lead system than with the aluminium system,

the average cathodic currents were higher and their range greater in the case of the red lead system.

Ship trials

HMCS Skeena: This was the first test ship. The bottom was quartered, with the aluminium vinyl system in alternate quarters and the red lead system in the remaining quarters.

The bottom was inspected after the ship had been 30 months out of dock. Figs. 4 and 5 illustrate the performance of the paint system at this docking. The bottom was generally in good condition in all quarters but the aluminium vinyl system was superior in stripping-prone areas such as the boottop zone and areas adjacent to the anodes. The total thickness of both systems ranged from 150 to 225 microns, with an average of 175 microns. This is less than the presently specified thickness.

HMCS Antigonish: This ship and all those subsequently mentioned had the aluminium vinyl system applied to the entire bottom area.

Antigonish was drydocked after 26 months afloat. At this time the bottom system was in very good condition, as illustrated in Fig. 6.

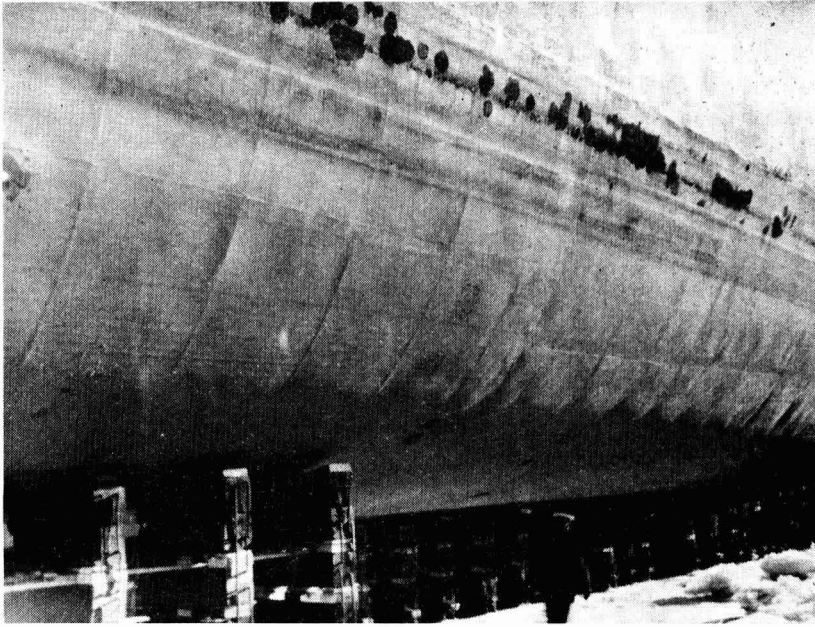


Fig. 4

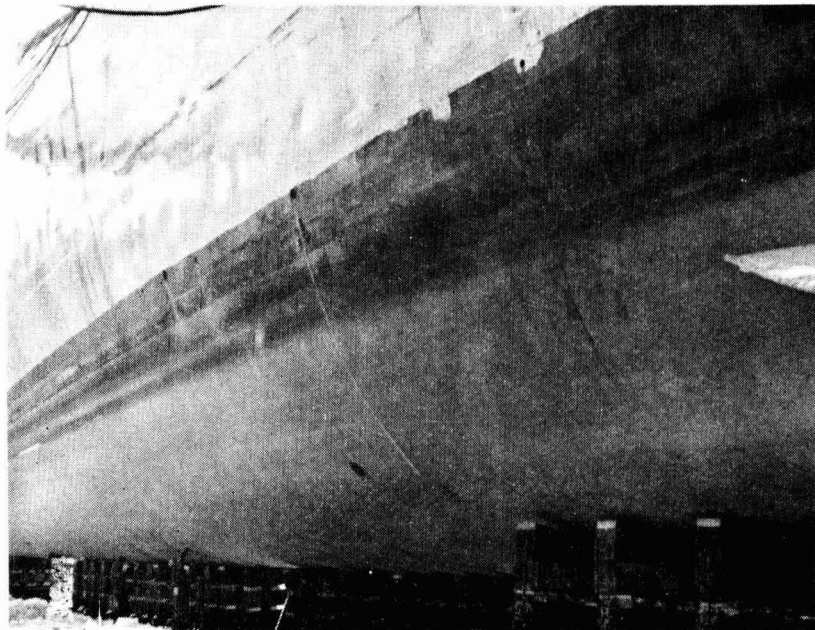


Fig. 5

Fig. 4. HMCS Skeena. This is a red lead vinyl quarter. Note the stripping in the boottop area

Fig. 5. HMCS Skeena. This is an aluminium vinyl quarter. Compare the boottop area of this quarter with the red lead quarter illustrated in Fig. 4

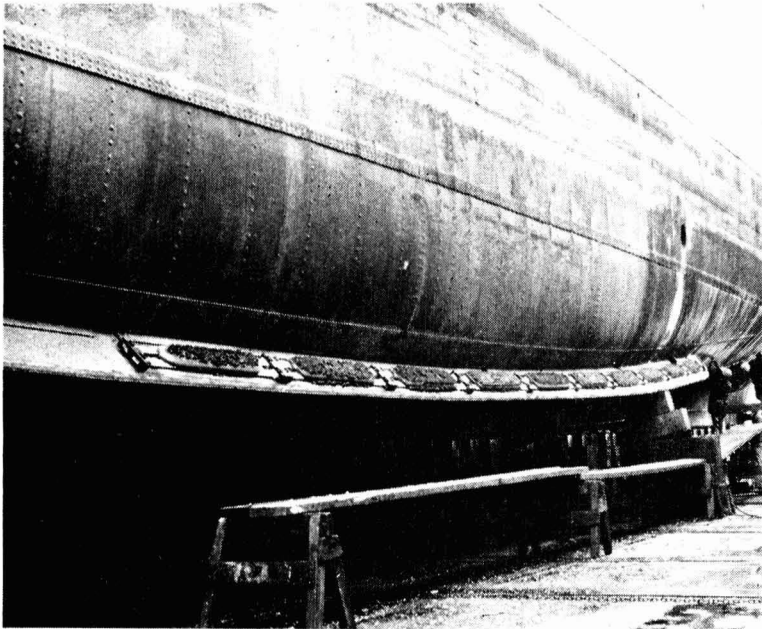


Fig. 6

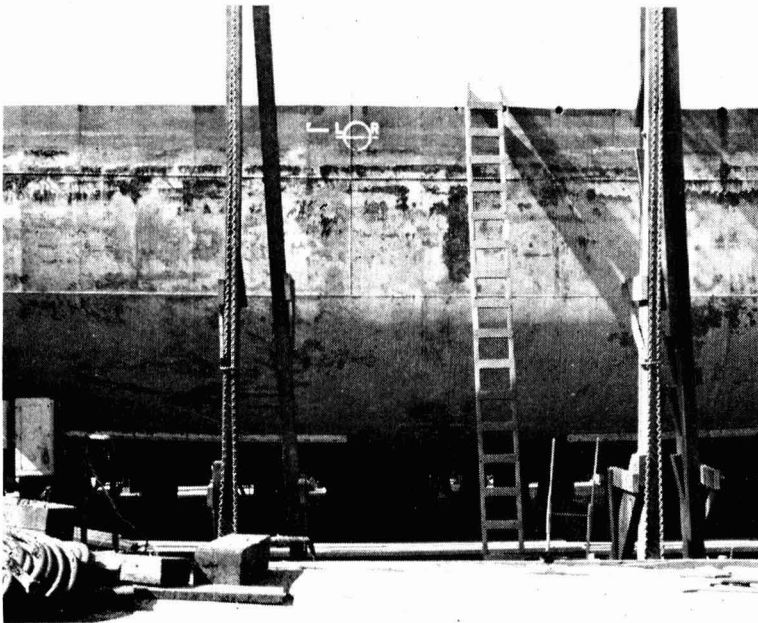


Fig. 7

Fig. 6. HMCS Antigonish. This photograph of the bottom with the aluminium vinyl system was taken after ship had been 26 months out of dock

Fig. 7. CNAV Endeavour. Port side after 9 months out of dock

RCMP Patrol Craft Victoria: After 13 months out of dock, the aluminium vinyl system was in good condition, with less than half a square foot of bare area observed. No blistering was noted, but it was estimated that 1 to 2 per cent of the bottom area was affected by copper conversion³. There was a small amount of bare area on the rudders, and it was judged that this was the result of cavitation.

CNAV Endeavour: An aluminium vinyl system was initially applied to the Endeavour, but it was applied very thinly. Measured thicknesses ranged from 75 to 150 microns for the system, with the average about 115 microns. When a film from the ship was examined under the microscope, it was found that the anticorrosive layer was extremely thin, perhaps less than 12 microns.

The bottom was inspected after nine months. At this time there were many intercoat blisters between the anticorrosive and antifouling layers, and also many patches of copper conversion³. The aluminium vinyl adhered strongly to the steel. Fig. 7 shows the condition of the paint on the port side of the vessel.

HMCS Yukon: After 20 months out of dock, the aluminium vinyl system was in excellent condition. Except for rudders, A-brackets, and boottop area, there was no stripping, and even in these difficult areas it was minor. There was less than 25 square feet stripped from the boottop area. The port after area is illustrated in Fig. 8.

The ship was again docked after an additional ten months. At this time the bottom system was still excellent. Some copper conversion was found near anodes and around the junction of A-brackets and hull. Minor stripping was noted on A-brackets. The after area is illustrated in Fig. 9.

HMCS Mackenzie: Mackenzie, with a red lead vinyl system on its bottom, was examined after 30 months out of dock. There was extensive stripping and blistering, with approximately 5 per cent of the bottom area bare. Copper conversion was also noted, particularly between the keel and bilge keel on the starboard side. The condition of the after end at this docking is illustrated in Fig. 10.

The condition of the bottom of Mackenzie at this docking was poorer than is normally observed on a red lead vinyl system after this period out of dock. Nevertheless, it illustrates the extensive stripping of the red lead vinyl system which can occur.

Effect of aluminium pigment in binders other than vinyl

The aluminium pigment seems to be more important than the binder in determining the successful performance of the aluminium vinyl system. Aluminium pigmented primers other than vinyl have been successful with regard to maintenance of adhesion.

A system including an aluminium pigmented bituminous primer has also given satisfactory performance with potentials in the range of oxygen dependence. However, at $-1,200\text{mV}$ there is a tendency for the film to be disrupted near a bare area, as shown by the panel on the right in Fig. 11. The

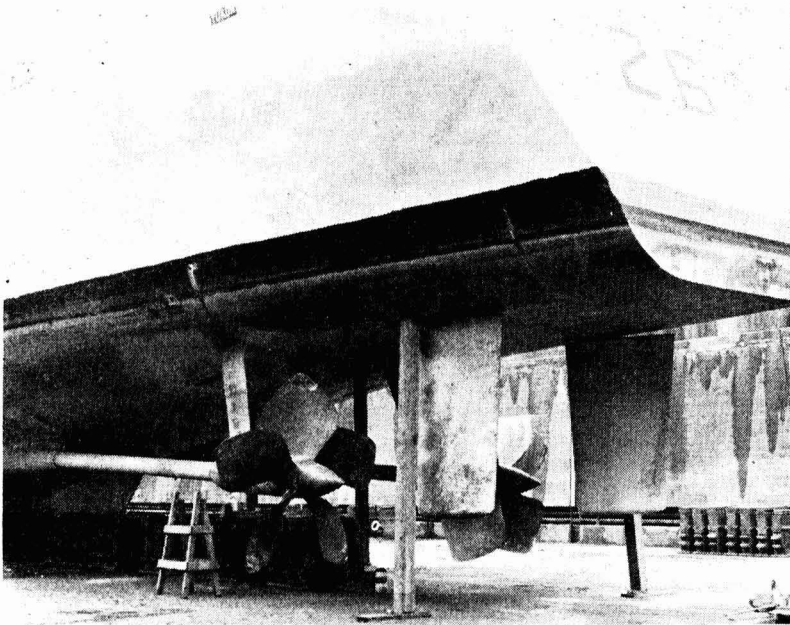


Fig. 8

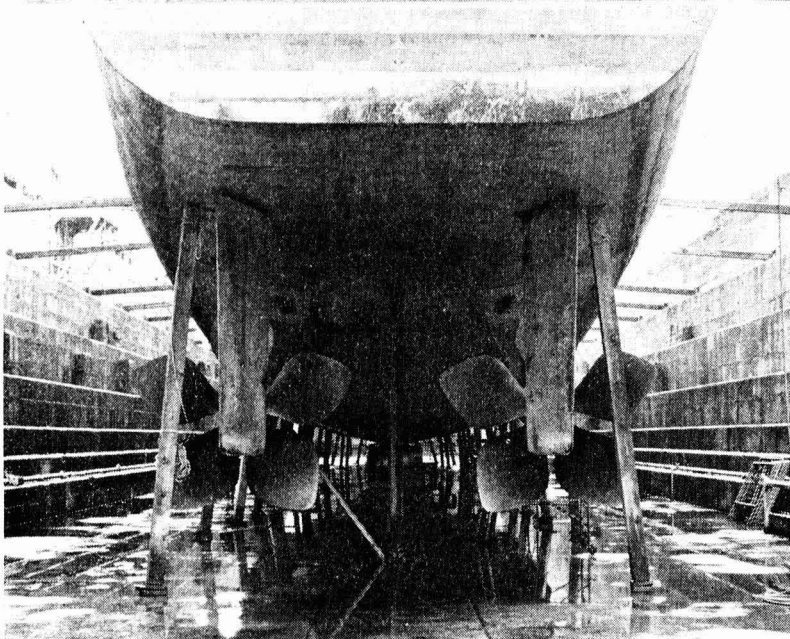


Fig. 9

Fig. 8. HMCS Yukon 20 months out of dock. Note the near absence of stripping on A-brackets, rudders and shafts

Fig. 9. HMCS Yukon 30 months out of dock. Stripping in after area still minimal

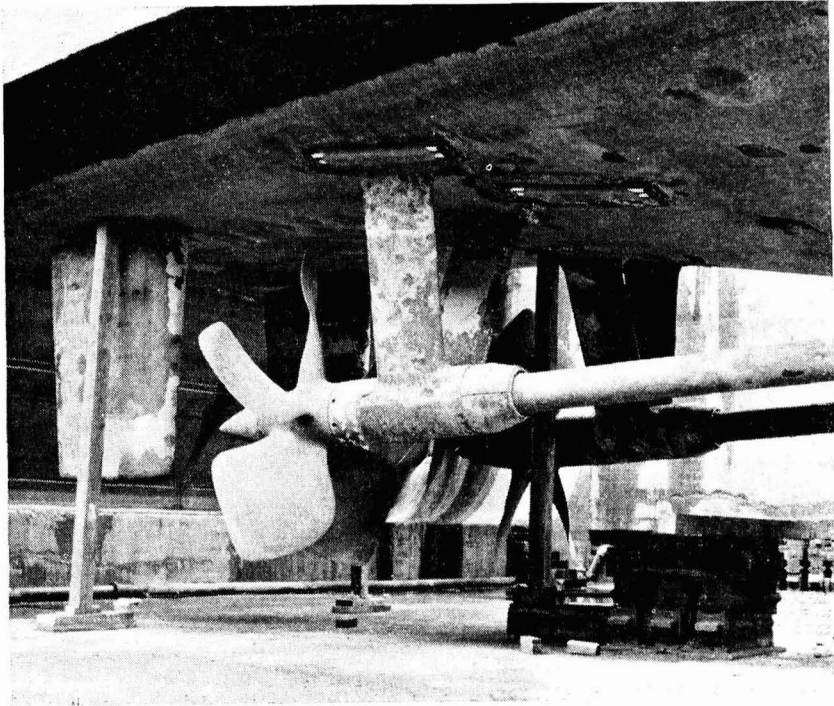


Fig. 10. HMCS Mackenzie 30 months out of dock. Bottom coated with red lead vinyl system

panel on the left has been stripped. Since there is a tendency for aluminium in these primers to be oxidised to aluminium oxide near a bare area, it is assumed that the volume increase of the oxidised pigment particles is responsible for the disruption in this primer and that the vinyl film under these conditions has sufficient strength to withstand such strains. An increase in thickness of the vinyl film has been noted near bare areas on panels where the aluminium has been oxidised.

Also, better adhesion has been achieved with cathodic protection using an aluminium pigmented bituminous epoxy primer compared to its unpigmented counterpart. The systems compared were:

- (a) two coats unpigmented bituminous epoxy;
- (b) one coat aluminium bituminous epoxy,
one coat unpigmented bituminous epoxy,
one coat vinyl antifouling;
- (c) two coats of aluminium bituminous epoxy,
one coat vinyl antifouling.

The first system has been included although it was prepared for another study. Consequently it lacks an antifouling coat.

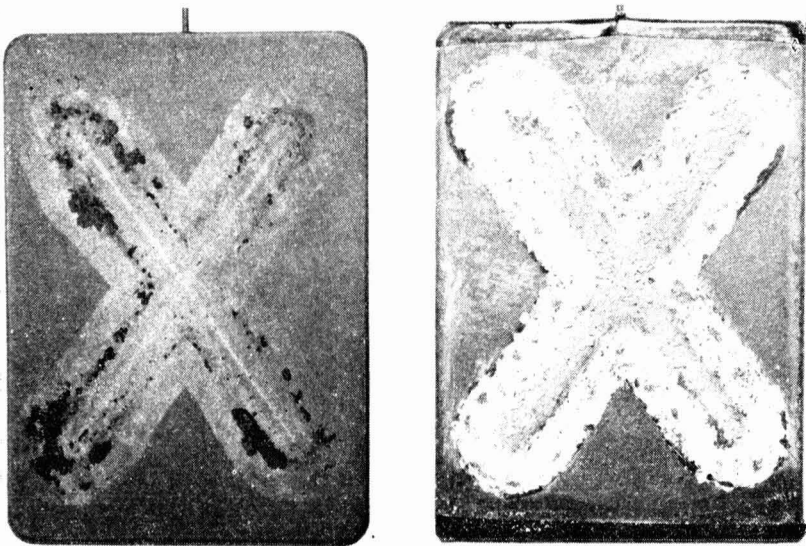


Fig. 11

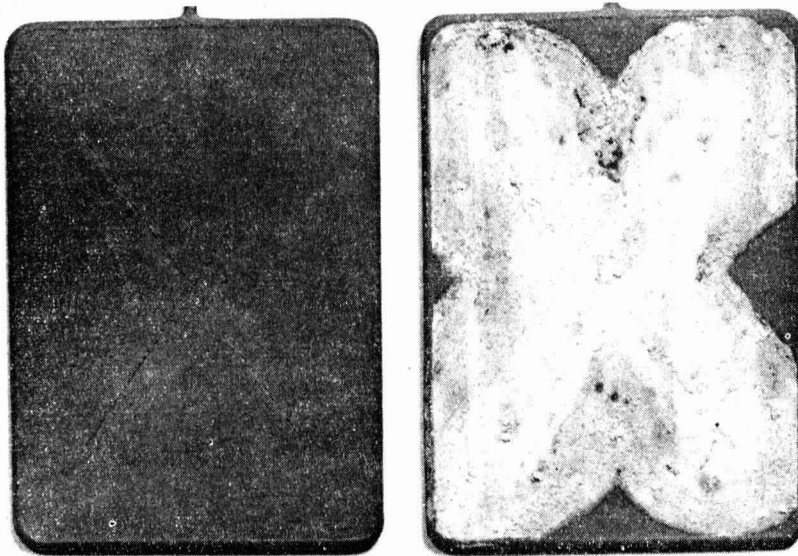


Fig. 12

Fig. 11. The aluminium bituminous system after immersion at $-1,200$ mV for 3 months. Panel on the left has been stripped

Fig. 12. System with 2 coats of aluminium vinyl. Panel on left at $-1,000$ mV, panel on right at $-1,200$ mV

At $-1,000$ mV, there was loss of adhesion with system (a) for about $\frac{1}{2}$ in from the score after 100 days, but the adhesion of systems (b) and (c) was good. At $-1,200$ mV there was little aluminium seen in the coating within $\frac{7}{32}$ in from the score with system (b). There was a cohesion loss within this region but the coating clung to steel on probing with a scalpel. System (c) was similar, but the

area affected was up to $\frac{9}{32}$ in from the score. It was judged that system (b) was the best, being marginally superior to system (c) at $-1,200\text{mV}$.

Effect of variation of aluminium concentration of vinyl anticorrosive primers

A series of aluminium vinyl primers was produced in the laboratory, each member varying only in the concentration of aluminium. As a normal concentration, the reference formula of 1-GP-122b, type 3 which contains about 31 per cent by weight of aluminium in the dried film was selected. This primer and others with $\frac{1}{4}$, $\frac{1}{2}$, $1\frac{1}{2}$ and 2 times the normal concentration of aluminium were produced. Panels were prepared with each of the laboratory produced primers included in the vinyl system:

- one coat wash primer
- two coats of one of the laboratory produced vinyl primers
- one coat vinyl antifouling.

These systems were subjected to the portion of the DREP Qualification Procedure² requiring cathodic protection.

All primers maintained good adhesion for 100 days at $-1,000\text{mv}$ except for the one at one quarter the normal concentration, and this was borderline. Average cathodic currents for the groups in order of increasing aluminium concentration were 9.1, 18, 3.6, 4.4, $3.2 \mu\text{amp}$. There seems to be a tendency for lower currents at the higher aluminium concentrations.

This work shows that the aluminium vinyl primer is effective over a wide range of aluminium concentrations.

Effect of variation in thickness of the aluminium vinyl coating

Standard mild steel panels were grit blasted and coated with the systems:

- one coat wash primer
- x coats of aluminium vinyl primer (1-GP-122, type 3)
- one coat vinyl antifouling.

where $x = 2, 5, 10, 15,$ or 25 .

After being scored with the standard X-cut, one group of each of these systems was immersed in sea water with cathodic protection at $-1,000\text{mV}$ and a similar group of each at $-1,200\text{mV}$.

After 100 days immersion, the panels were examined. Representative panels of each group are illustrated in Figs. 12 to 16 inclusive. The results are given in Table 1. Where blisters were noted on panels which were protected cathodically at $-1,200\text{mV}$, they were dry, indicating that they may have been produced by hydrogen gas. Also, under all of them, a layer of aluminium vinyl remained on the steel. All panels protected cathodically at $-1,000\text{mV}$ were unblistered and had good adhesion.

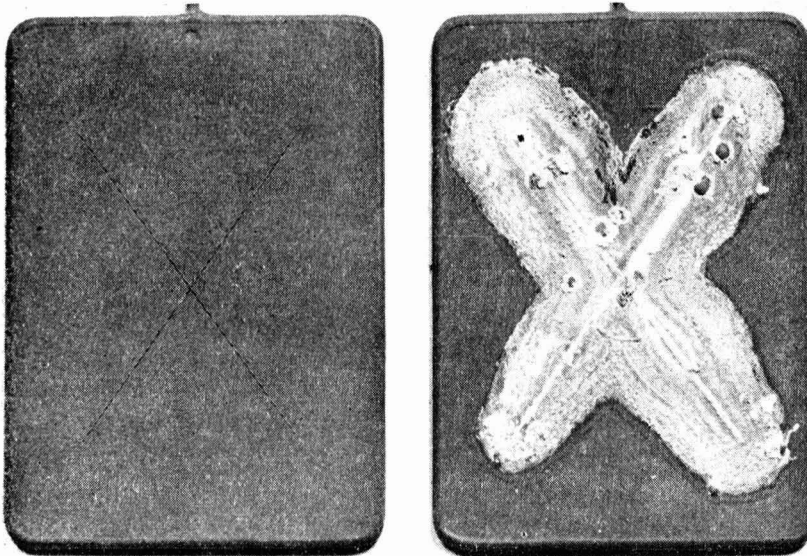


Fig. 13

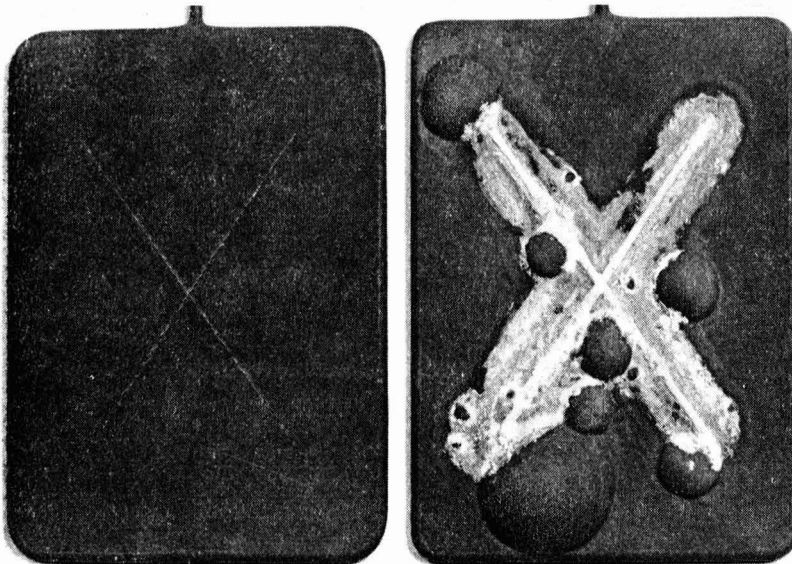


Fig. 14

Fig. 13. System with 5 coats of aluminium vinyl. Panel on left at $-1,000$ mV, panel on right at $-1,200$ mV

Fig. 14. System with 10 coats of aluminium vinyl. Panel on left at $-1,000$ mV, panel on right at $-1,200$ mV

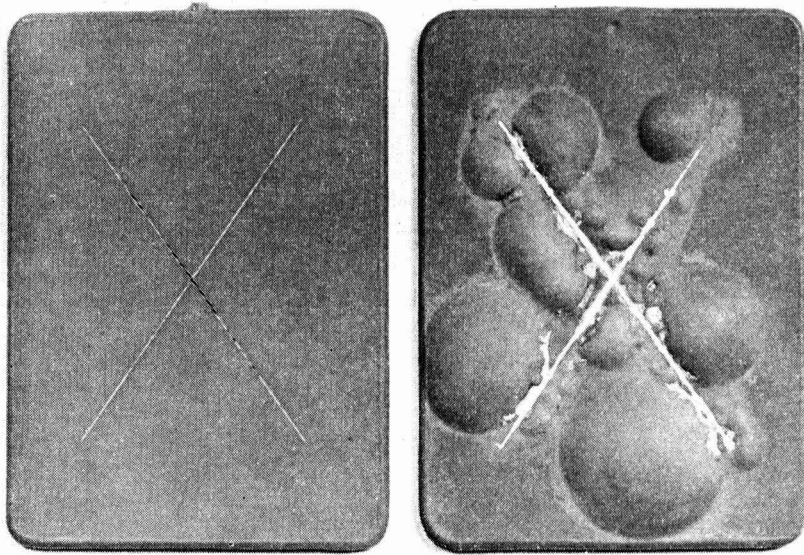


Fig. 15

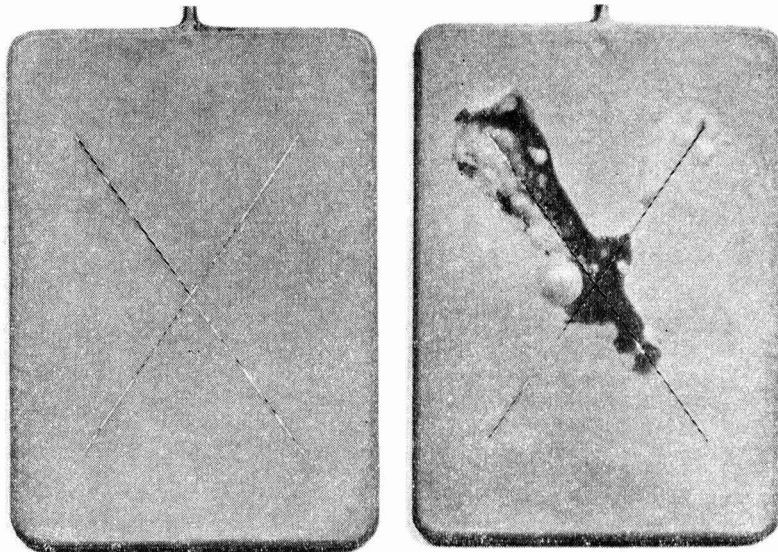


Fig. 16

Fig. 15. System with 15 coats of aluminium vinyl. Panel on left at $-1,000$ mV, panel on right at $-1,200$ mV

Fig. 16. System with 25 coats of aluminium vinyl. Panel on left at $-1,000$ mV, panel on right at $-1,200$ mV

Effect of variations in type of vinyl binder

The vinyl resin used in 1-GP-122, type 3 is a copolymer of vinyl chloride, vinyl acetate and vinyl alcohol. It is resistant to alkaline attack.

If the vinyl resin used in the anticorrosive primer were susceptible to alkaline attack, it would be expected that a system which included this primer would be unsatisfactory for use on cathodically protected steel.

Such a system (one coat of wash primer and two coats of anticorrosive primer) on standard scored panels was immersed for 100 days at $-1,000\text{mV}$. The resin used in the anticorrosive primer was susceptible to alkaline attack, since a dibasic acid was interpolymersed with vinyl chloride and vinyl acetate in the resin molecule. Adhesion was lost on the face of the panel at the wash primer surface and there were blisters near the score up to $\frac{1}{2}$ in in diameter. The panels are illustrated in Fig. 17.

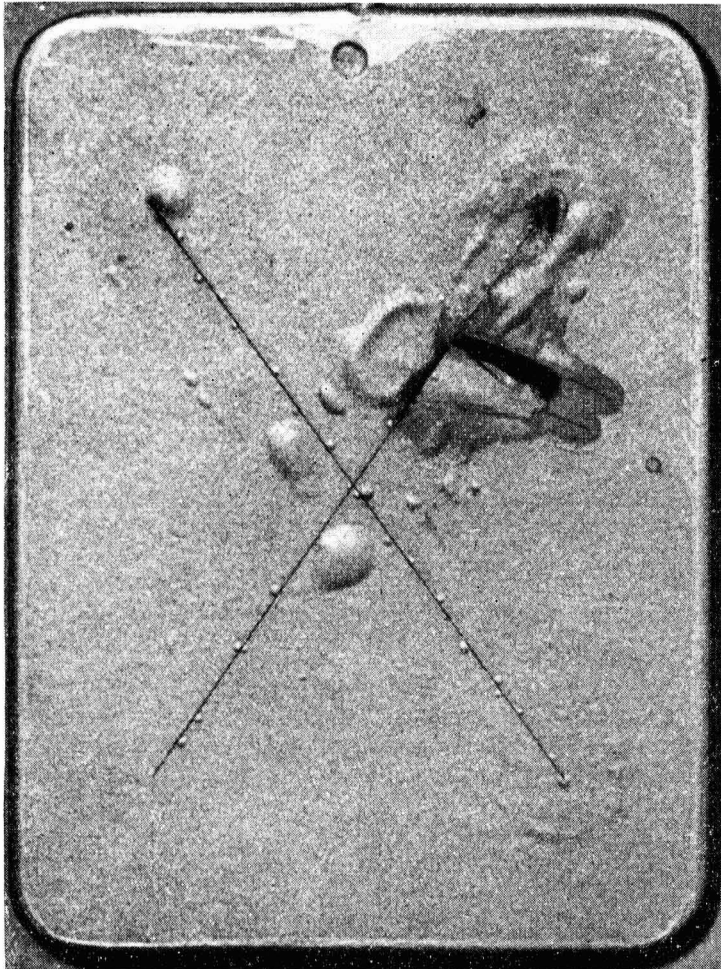


Fig. 17. Aluminium vinyl system with binder of anticorrosive primer susceptible to attack by alkali

Table 1
Panels with varying thickness of aluminium vinyl primer

| No. of coats of Al vinyl* | Average cathodic current of group (μ amp) | | Remarks | |
|---------------------------|--|-----------|---|---|
| | -1,000 mV | -1,200 mV | -1,000 mV | -1,200 mV |
| 2 | 7.8 | 3,500 | Panels of all groups had good adhesion and were unblistered | A band of calcareous deposit to about $\frac{3}{4}$ in from score. Aluminium oxidised to about $\frac{1}{8}$ in from score. Unblistered. Good adhesion right up to score. |
| 5 | 4.7 | 1,600 | | A band of calcareous deposit to a max. of $\frac{3}{4}$ in from score. Deposit less dense than for 2 coat system. A few small dry blisters along score. Good adhesion to score where unblistered. |
| 10 | 2.0 | 650 | | There were a few dry blisters along score and one about $1\frac{1}{4}$ in diameter. Some cohesion loss near score. |
| 15 | 2.0 | 270 | | There was a band of blisters along the score. Blisters greater than 1 in diameter were observed. A narrow band of calcareous deposit near score. Some cohesion loss near score. |
| 25 | 1.4 | 3.3 | | There was some lifting of coating, blistering and cohesion loss near score. |

*The dry film thickness of the aluminium vinyl was 25 microns per coat.

Conclusions

The following conclusions were reached as a result of the described experimental work.

The resistance to loss of adhesion by the aluminium vinyl system, when applied to steel which was protected cathodically in sea water, was superior to that of the red lead vinyl system and to all other systems which were evaluated. This superiority has been demonstrated in the laboratory and also on the bottoms of naval ships.

The aluminium pigmented anticorrosive primer included in this system was effective over a wide range of aluminum concentrations.

The effectiveness of the primer in resisting loss of adhesion with cathodic protection seems to be due to the pigment rather than the binder. However, the binder should have sufficient strength to resist the strains which may occur at more negative potentials.

The only primers evaluated that resisted loss of adhesion at potentials sufficiently negative for hydrogen evolution were pigmented with aluminium.

The aluminium vinyl system maintained adhesion during alternate immersion between sea water with cathodic protection and fresh water.

The binder used should be resistant to alkaline attack. Some vinyl resins do not have sufficient resistance.

With the aluminium pigmented vinyl primer varying in thickness between 50 and 625 microns, all systems resisted adhesion loss and remained unblistered after 100 days of cathodic protection at $-1,000\text{mV}$. This performance supports the hypothesis previously presented⁴ of oxygen scavenging by the aluminium pigment.

With a potential of $-1,200\text{mV}$, the system was unblistered when the thickness of the anticorrosive primer was 50 microns, but at greater thicknesses up to 375 microns there was blistering of increasing severity. With a thickness of 625 microns, loss of adhesion occurred near the standard X-cut. Cathodic deposits and cathodic current decreased as thickness of the aluminium pigmented primer increased. This also supports a previously presented hypothesis⁴.

[Received 23 February 1970]

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An assessment of some commercial insecticidal paints*

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Summary

The RAAF requested the examination of a commercially available insecticidal paint in respect of insecticidal activity, general paint properties and any particular problems associated with its use.

The commercially available paint, together with similar products from other manufacturers, was tested and found to be of little value in killing houseflies but to have good general paint properties. There are no particular problems associated with its use except that the direct contact between foodstuffs and surfaces painted with insecticidal paint is undesirable. Similar remarks apply to other insecticidal paints tested.

Keywords

Biologically active agents

γ -benzene hexachloride
insecticide

Une appréciation de quelques peintures insecticides de commerce

Résumé

La RAAF (L'Armée de l'air Australienne) a demandé l'examen d'une peinture insecticide de commerce, à l'égard de son efficacité insecticide, et de ses propriétés générales, et également de la possibilité des difficultés liées à son utilisation.

La peinture de commerce, ainsi que des produits semblables en provenance d'autres fabricants, a été examinée et l'on l'a trouvée de petite valeur pour tuer les mouches, mais de posséder de bonnes propriétés de peinture. Il n'y a pas de problèmes particuliers en ce qui concerne son utilisation, sauf le contact direct entre les aliments et les surfaces revêtues de peinture insecticide que l'on devrait en éviter. Des observations pareilles s'appliquent aux autres peintures insecticides que l'on a examinées.

Beurteilung einiger Insektiziden Anstrichfarben des Handels

Zusammenfassung

Die königliche australische Luftwaffe (RAAF) verlangte die Prüfung einer im Handel befindlichen insektiziden Anstrichfarbe hinsichtlich ihrer insektiziden Aktivität, allgemeinen Eignung für Anstrichzwecke, sowie irgendwelcher mit ihrem Einsatz verbundener besonderer Probleme.

Diese Farbe wurde gemeinsam mit ähnlichen von anderen Erzeugern geprüft, wobei festgestellt wurde, dass sie nicht viel nützte um Zimmerfliegen zu vernichten, dass sie aber gute Anstrichmitteleigenschaften besaßen. Hinsichtlich ihrer Anwendung bestehen keine besonderen Probleme ausser, dass direkte Berührung von Lebensmitteln mit Flächen, die mit insektiziden Farben gestrichen sind, unerwünscht ist. Ähnliche Beobachtungen treffen auf andere geprüfte insektizide Anstrichmittel zu.

*This paper was issued as Technical Note 137 of Defence Standards Laboratories. It is published by kind permission of the Chief Superintendent.

Оценка некоторых коммерческих инсектицидных красок

Резюме

Австралийские военно-воздушные силы обратились к нам с просьбой проанализировать коммерчески доступную инсектицидную краску по отношению к ее инсектицидным свойствам, ее общим красочным свойствам и каким либо существующим особым проблемам связанным с ее применением.

Коммерчески доступная краска вместе с однородными продуктами других изготовителей, была испытана и было обнаружено что она не особенно пригодна для уничтожения комнатных мух, но обладает хорошими общими красочными свойствами. Не было обнаружено каких либо особых проблем связанных с ее применением, за исключением того факта что непосредственный контакт между пищевыми продуктами и поверхностями окрашенными инсектицидной краской нежелателен. Те же замечания применимы также и к другим испытанным инсектицидным краскам.

Historical background

The idea of using paint to repel or to kill insects is not new. Apart from the presence of an insecticidal or insect-repellant additive, the colour of paint films has been suggested as a means of repelling or trapping insects.¹ It was thought that buildings might be kept relatively free from flies by painting the rooms with certain colours, particularly blue. The ultra-violet reflectance of the paint probably affects the apparent colour to the fly's eye but other factors such as odour and temperature may have an equal effect.^{2, 3}

In 1943, it was suggested that additions of citronella, cedar oil or pine oil to paint would prevent insects settling on the paint film before it dried.⁴ The post-war success of DDT (dichlorodiphenyltrichlorethane) in insect and pest control led to its being incorporated into conventional paints but, apart from some minor use in distempers, it was not generally successful when used in paint.^{5, 6} Styrene dibromide was suggested in 1944 as an insect-repellant additive for paints but never achieved popularity.⁷ Insecticidal paints are used for the protection of plants on plantations, etc., but are usually fairly conventional materials with insecticides added.^{8, 12} They may be used to prevent crawling insects from attacking foliage by painting a ring round the trunk near the ground.

In 1946, the problem of conferring insecticidal properties on paints received more serious study and the importance of the solubility of the insecticide in the paint film and of its crystallisation on the surface of the film began to be recognized.⁹ Urea-formaldehyde resins were found to be useful for the preparation of crystalline insecticidal blooms on the surface of lacquer films.¹⁰ In 1948, Imperial Chemical Industries patented the use of benzene hexachloride, containing a significant proportion of the γ -isomer, in paint.¹¹ Also about that time, the Colonial Insecticides Research Team of the U.K. began work which resulted in the patenting of the use of amine resins (e.g. urea-formaldehyde resins) as film formers for insecticidal paints.^{13, 14, 19} Special lacquers based on urea-formaldehyde and alkyd resins containing various insecticides such as "Aldrin", "Dieldrin", (both manufactured by Shell Chemical Company), γ -benzene hexachloride and DDT were introduced for specialised uses.^{15, 16, 17} However, these lacquers contained powerful solvents of objectionable odour which attacked old paint films, while the addition of pigments adversely affected the crystallisation of the insecticide on the surface and thus the insecticidal efficiency. Some lacquers were shown to increase the fire risk to wood²¹ and

others to cause contamination of foodstuffs.²² These difficulties tended to limit the use of these materials, the development of which has been described.²⁰

Despite the use of special media with generally unsuitable paint properties, toxicity problems and doubtful effectiveness, work continued on the development of insecticidal paints in many countries.^{23, 24, 25, 26} In 1957-8, the Colonial Pesticides Research Committee claimed to have improved on the performance of the "standard" urea-formaldehyde type of formulation.²⁷ The Russians have claimed to have developed paints for shipboard use.²⁸ The "standard" type was still, in 1960, being claimed as a "new" concept in residual insect control,²⁹ but independent assessment indicated that these materials still had weaknesses.³⁰ Investigations showed that their effectiveness in tropical climates may be less than in temperate zones.³¹

Some novel approaches to the problem of preparing insecticidal paints have been made by Nagase & Co. and S. A. Progil who have developed organo-metallic compounds^{32, 33} and by A. P. Ferris and N. McKenzie who attempted to develop a medium both inherently insecticidal and capable of film formation.³⁴ The basic difficulty with this latter approach is that while large molecules are required to form films, insecticidal activity appears to be confined to relatively small molecules.

The development of commercial insecticidal paints for the retail trade has proceeded along more conventional lines, that is by the addition of commonly available insecticides to ordinary paints, up to 0.5 per cent of "Lindane" (γ -benzene hexachloride) being commonly used. An independent assessment of some commercially available latex paints in the U.K. showed that the paints were of doubtful efficiency against flies or mosquitoes.³⁵ On the other hand, an Australian ship trial indicates that a commercially available insecticidal paint shows promise for controlling cockroaches.³⁶ However, this trial was not strictly controlled and insect control may be more feasible on a ship isolated at sea than on land, where insects can move in from other breeding areas.

Experimental work

Work has been done at D.S.L. to assess the effectiveness of some locally-available insecticidal paints. This work was carried out at the request of the RAAF, which was considering the use of insecticidal paints in messes, barracks, etc., especially in tropical areas. The paints tested are listed below.

Materials tested

1. White latex paint, insecticidal, described as "insect-proofed". Available only on special request from the manufacturer.
2. White latex paint, insecticidal, commercially available.
3. White latex paint with the addition of 0.5 per cent "Lindane", available only on special request from the manufacturer.
4. White satin enamel, insecticidal, commercially available.
5. White latex paint free from insecticide. This paint was included in the tests as a control.

General paint tests

The tests carried out are shown in Table 1.

Table 1
General paint tests

| Test | Paint 1 | Paint 2 | Paint 3 | Paint 4 | Paint 5 |
|---|--------------|--------------|--------------|--------------|--------------|
| Colour | white | white | white | white | white |
| Gloss | flat | flat | flat | semi-gloss | flat |
| Appearance | satisfactory | satisfactory | satisfactory | satisfactory | satisfactory |
| Application properties | satisfactory | satisfactory | satisfactory | satisfactory | satisfactory |
| Non-volatile content percentage by weight | 49.8 | 55.2 | 62.5 | 69.1 | — |
| Weight per gallon, lb | 14.0 | 13.8 | 15.6 | 13.9 | — |
| Surface dry (hr) | 0.3 | 0.1 | 0.2 | 1.1 | 0.2 |
| Hard dry (hr) | 2 | 2 | 2 | 2 | 2 |
| Application of insecticidal paints over conventional paints | satisfactory | satisfactory | satisfactory | satisfactory | satisfactory |
| Application of conventional paints over insecticidal paints | satisfactory | satisfactory | satisfactory | satisfactory | satisfactory |

Insecticidal tests

Two coats of each material were applied to two 12in × 6in hardboard panels, allowing an overnight drying period between coats. One set of painted panels was allowed to age for 14 days and the other for 10 months before testing for insecticidal activity. Both sets included the non-insecticidal paint as a control.

After ageing for their respective periods, each panel was placed in a separate fly-box, constructed of clear acrylic sheet, 15in × 15in × 10in (see Fig. 1). The panel was held flat by runners against one vertical wall of the box. Adequate



Fig. 1. Fly boxes: left, containing paint panel; right, paint panel absent

ventilation was provided by wire-mesh lids, and milk, sugar and water were provided as food.

Approximately 50 live common house-flies (*musca domestica*) were introduced into each box, and the percentage of dead flies was determined daily. The tests were carried out at $25 \pm 1^\circ\text{C}$ and at relative humidity of 50 ± 5 per cent.

Results were as shown in Table 2. Table 3, derived from Table 2, shows the percentage dead minus the corresponding percentage dead in the control box.

These tests were carried out in accordance with the recommendations of Mr. D. Bracey of the ICI Agricultural Research Laboratories, Merrindale, Victoria.

Practical trial

In February 1967, a count was begun of the number of dead flies found daily in a men's lavatory containing three toilets and a urinal. The number of dead flies found daily between 1 February and 30 April 1967 varied from 5 to 7 per day. In May 1967, the lavatory was painted throughout with the commercially available insecticidal satin enamel. On 1 June the daily count of dead flies was resumed and continued until 31 August. The average number of dead flies found daily varied from 4 to 7 per day. This test cannot be regarded as strictly controlled because the seasons varied for the "unpainted" and "painted" period and because windows were sometimes open and sometimes closed. Further, the insecticidal paint may have repelled flies which died somewhere else than in the lavatory. However, the test is considered to be of some interest in that no startling differences were found in the number of dead flies found daily.

Discussion

The insecticidal paints exhibit the same behaviour as conventional paints in respect of general paint properties. There appear to be no particular problems relating to their use, except that direct contact with foodstuffs is not recommended. Drying time, application properties and appearance are satisfactory and there are no difficulties in applying insecticidal paints over conventional paints or in applying paints over insecticidal paints.

The biological results indicate that the paints are ineffective for killing flies. The percentage kill is relatively low, the speed of kill is slow and such insecticidal activity as is present initially, falls off after ten months ageing, after which time the paints are, insecticidally, virtually useless. In practice the paint films might be washed and this would probably further decrease their effectiveness.

According to the tests carried out, the order of insecticidal activity for the paints tested was as follows:

| 14 days ageing | 10 months ageing |
|------------------------|------------------------|
| 1. Latex paint, no. 1 | 1. Latex paint, no. 1 |
| 2. Latex paint, no. 3 | 2. Latex paint, no. 3 |
| 3. Satin enamel, no. 4 | 3. Latex paint, no. 2 |
| 4. Latex paint, no. 2 | 4. Control, no. 5 |
| 5. Control, no. 5 | 5. Satin enamel, no. 4 |

Table 2
Insecticidal tests on wall paints

| Paint No. | Description | Ageing period of painted panel | Percentage dead of newly hatched musca domestica (common house-fly) after the following number of days exposure to painted panels | | | | | | | | | |
|-----------|-------------------------------------|--------------------------------|---|----|----|----|----|----|----|----|----|----|
| | | | 1 | 2 | 3 | 4 | 7 | 8 | 9 | 10 | | |
| 1 | White latex, insecticidal | 14 days | 14 | 30 | 32 | 34 | 34 | 36 | 36 | 36 | 36 | 36 |
| 2 | White latex, insecticidal | 14 days | 0 | 8 | 12 | 14 | 16 | 16 | 16 | 16 | 16 | 16 |
| 3 | White latex, insecticidal | 14 days | 12 | 22 | 24 | 26 | 26 | 28 | 28 | 28 | 28 | 28 |
| 4 | White satin enamel | 14 days | 3 | 8 | 15 | 20 | 27 | 27 | 27 | 27 | 27 | 27 |
| 5 | Control white latex, no insecticide | 14 days | 0 | 0 | 0 | 0 | 0 | 2 | 2 | 2 | 4 | 8 |
| 1 | White latex, insecticidal | 10 months | 2 | 6 | 10 | 12 | 16 | 16 | 16 | 18 | 18 | — |
| 2 | White latex, insecticidal | 10 months | 0 | 2 | 5 | 5 | 9 | 9 | 9 | 10 | 10 | — |
| 3 | White latex, insecticidal | 10 months | 6 | 9 | 9 | 9 | 11 | 11 | 11 | 11 | 11 | — |
| 4 | White satin enamel | 10 months | 0 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | — |
| 5 | Control white latex, no insecticide | 10 months | 2 | 2 | 2 | 2 | 2 | 9 | 9 | 9 | 9 | — |

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All the paints tested, except the control, were said to contain 0.5 per cent of "Lindane" (γ -benzene hexachloride). The commercially available materials were claimed to contain a special additive medium to ensure effective release of the insecticide. This special medium, if present, is of doubtful value because the commercially available materials gave the poorest results. Although all the paints lost insecticidal activity, the satin enamel lost relatively the most and this may be caused by oxidative hardening, which latex paint films do not suffer.

The manufacturers of the commercially available paints, in a private communication,³⁷ state that laboratory testing of insecticidal paints can be misleading, particularly if the test panel is too small. Using their statements of minimum lethal dosage and insecticide availability, the panels used in the tests contained enough insecticide to kill approximately 200 flies and 50 flies were used for each test. They also state that unequal dosage can occur if too many insects are confined on too small a panel. The authors consider that the use of a relatively large panel in a relatively large box overcomes this difficulty. The susceptibility of various insect populations may affect testing results and perhaps the formulation of insecticidal materials. Local manufacturers appear to have concluded that Australian insects are more resistant to "Lindane" than English insects because the Australian commercially available paint contains approximately three times as much insecticide, "Lindane," as the English equivalent (see however Ref. 31).

Conclusion

It is doubtful whether any advantage would be obtained by using presently available insecticidal paints for fly control. The paints may be more effective against other types of insects, particularly crawling insects, and we are informed that a trial carried out in the wardroom pantry of HMAS "Kimbla" shows some promise for cockroach control. Insect control is possibly more feasible on a ship where there is a good chance of reducing the insect population because insects cannot move in from other breeding areas as quickly as they can on land. However, other testing authorities have found these paints to be of little value, and such activity as they do possess appears to be lost on ageing.

[Received 1 April 1970]

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Solvent retention in phenolic varnish films

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Summary

When coatings are air-dried, small amounts of solvent are retained in the film because drying takes place most rapidly at the surface. Hence, coatings that dry the fastest trap the most solvent, and evacuation, even at high vacuum, does not remove all the retained solvent. Removal is accomplished only after several cycles of water absorption and desorption.

The amount of solvent trapped in oil-modified coatings is probably not large enough to have much effect on the physical properties of coatings. When the total solvent removed by both evacuation and desorption is calculated on the basis of the air-dried film weight, 15- and 20-gal tung oil phenolic varnishes contained 0.91 and 1.04 per cent solvent, respectively. This is much lower than the quantities retained in cellulose nitrate and vinyl lacquers. The slowest drying varnish tested, 40-gal dehydrated castor, retained 0.56 per cent solvent.

The amount, however, is sufficient to change drastically the water absorption values obtained when precise measurements are made on coatings that do not absorb much water. This effect will be discussed in detail in a second paper concerned with clear coatings for exterior wood.

Keywords

Types and classes of coating
phenolic varnish

Properties, characteristics and conditions
primarily associated with dried or cured films
solvent retention

Process and methods primarily associated
with analysis measurement and testing
gas chromatography
infra-red spectroscopy

La rétention de solvant aux feuil de vernis phénolique

Résumé

Pendant le séchage à l'air des revêtements, de petites quantités de solvant sont retenues dans le feuil, puisque le séchage se produit plus rapidement à la surface. Par conséquent des revêtements qui séchent le plus rapidement, attrapent le plus de solvant, et l'évacuation, même sous vide poussé, n'enlève pas tout le solvant retenu. L'enlèvement ne s'accomplit qu'après plusieurs cycles d'absorption d'eau suivi par désorption.

La quantité de solvant attrapée en revêtements modifiés par huile n'est pas probablement assez important d'exercer beaucoup d'influence sur les propriétés physiques des revêtements. Lorsqu'on calcule la quantité totale de solvant enlevée à la fois par évacuation et désorption, et basée sur le poids du feuil sec, des vernis phénoliques de longueur en huile de 15 et de 20 gallon contiennent respectivement de 0,91 et 1,04 pour cent de solvant. C'est beaucoup moins que les c'est quantités retenues par des peintures à base de nitrocellulose ou vinyliques. Parmi les vernis examinés, celui qui sèche le moins vite, de longueur en huile de ricin déshydratée de 40 gallon, retenait de 0,56 pour cent de solvant.

Pourtant, cette quantité est suffisante pour changer gravement les chiffres d'absorption d'eau mis en évidence par des mesures précises effectuées sur des revêtements qui n'absorbent pas beaucoup d'eau. On discutera cet effet au cours d'un exposé subséquent ou l'on considèra des revêtements clairs pour la boiserie à l'extérieur.

Lösungsmittelretention in Filmen von Phenolharzlacken

Zusammenfassung

Bei Lufttrocknung von Lacken werden geringe Lösungsmittelmengen im Film zurückbehalten, weil Trocknung am schnellsten an der Oberfläche vor sich geht. Daher fangen solche Anstrichmittel, die am schnellsten trocknen, die grösste Menge Lösungsmittel ein, und Entlüftung, selbst unter hohem Vakuum, beseitigt zurückgehaltenes Lösungsmittel nur unvollständig. Die völlige Entfernung wird lediglich nach wiederholten Zyklen von Wasserabsorption und -Desorption ermöglicht.

Bei ölmodifizierten Lacken ist die Menge zurückgehaltenen Lösungsmittels wahrscheinlich nicht gross genug, um die physikalischen Eigenschaften derselben wesentlich zu beeinflussen. Berechnet auf Grund des luftgetrockneten Filmgewichtes enthielten "15- und 20-Gallonen"-Holzöl-Phenolharzlacke 0,91 bzw. 1,04% Lösungsmittel nach Entfernung des gesamten Lösungsmittels sowohl durch Evakuierung als auch Desorption. Diese Werte liegen wesentlich niedriger, als die von Nitrozellulose- und Vinylharzlacken zurückgehaltenen Mengen. Der am langsamsten trocknende der geprüften Lacke, ein 40-Gallonen Rizinenollack, hielt 0,56% Lösungsmittel zurück.

Die Menge genügte doch schon, um die Wasserabsorptionswerte, welche man erhält, wenn exakte Messungen an Lacken, die nicht viel Wasser absorbieren, vorgenommen werden, drastisch zu ändern. Diese Wirkung wird ausführlich in einem zweiten Artikel, der sich mit wetterbeständigen Klarlacken für Aussen befasst, besprochen werden.

Сохранение растворителя в фенольных лаковых пленках

Резюме

При воздушной сушке покрытий небольшие количества растворителя сохраняются в пленке, так как сушка происходит наиболее быстро на поверхности. Поэтому покрытия которые высыхают наиболее быстро, улавливают наибольшее количество растворителя и эвакуация, даже при высоком вакууме, не удаляет всего сохраняемого растворителя. Удаление осуществляется только после ряда циклов поглощения и десорбции водой.

Количество растворителя улавливаемого в покрытиях модифицированных маслом по всей вероятности недостаточно чтобы повлиять на физические свойства покрытий. При расчете общего растворителя удаленного путем эвакуации и десорбции, на основании веса пленки высушенной воздухом, найдено что 15-ти и 20-ти галлоновые тунговые, масляные, фенольные лаки содержали 0.91 и 1.04 процентов растворителя соответственно, что намного ниже чем количества удерживаемые в нитроцеллюлозных и виниловых лаках. Наиболее медленно высыхаемый из испытанных лаков, 40-ка галлоновый дегидратированный кастор, сохранил 0.56 процентов растворителя.

Это количество, однако, достаточно чтобы существенно изменить значения водной абсорбции, полученных при проведении точных измерений на покрытиях которые не поглощают много воды. Этот эффект будет обсуждаться в подробности в добавочной статье посвященной прозрачным покрытиям для дерева в наружном применении.

Introduction

The rapid drying of lacquers occurs because of the fast evaporation of the solvents used in their formulation. To reduce lacquers to application viscosity, a solvent content of 70 to 80 per cent is required. Nevertheless, the lacquer coating is dry to the touch within a few minutes at room temperature, although a small amount of solvent is trapped within the film in the course of the fast drying. Even after the film has apparently dried, the retained solvent takes a very long time to evaporate completely, and this influences coating properties such as water absorption, hardness and other mechanical properties.

The Los Angeles Club¹ studied the effect of solvent release on hardness of lacquer films and observed that cellulose nitrate, although the fastest to harden, retained the most solvent. It was concluded that rapid hardening is due not

only to rapid solvent evaporation but also to other physical characteristics of the resin, in view of the greater solvent retention. Unplasticised vinyl lacquers, dried in air and under vacuum, retained 10 and 7 per cent solvent, respectively, whereas plasticised vinyl films retained less². Scherzinger³ evacuated lacquer films at elevated temperatures to remove solvents that would not leave the film under normal conditions and analysed them by gas chromatography. He also found measurable amounts of solvent in an acrylic film exposed outdoors for 2½ years. The evaporation of solvents from a dried film depends mainly on the rate of diffusion of solvents through the film. Residual solvents can be recovered by heating the film under vacuum⁴.

Murdock and Wirkus⁵ used radioactive tracer techniques and found that polymer films have a finite capacity to retain even very volatile solvents for a fairly long period. The capacity for solvent retention depends on factors such as the nature of the polymer, the type and concentration of modifiers and plasticisers, the volatility and type of solvents, the film thickness, and the mode of curing. Using carbon-14 tagged solvents, Hays⁶ could detect the presence of less than 0.01 per cent toluene in an acrylic film. He found considerable amounts of solvent retained in polymethacrylate films even under rigorous drying conditions. Several workers⁷⁻¹⁷ have studied the effect of high and low boiling point solvents on the rate of evaporation from lacquer coatings using different methods of measurement. Some have attempted to correlate solvent evaporation with drying, hardening, and application properties of such coatings.

Most of the methods and types of equipment for measuring the evaporation rate of solvents are used with freshly applied films. A thin-film evaporometer fitted with dehumidifying and temperature control devices has been commonly used for such determinations^{11, 12, 18}. Highly sensitive techniques were recently employed to detect the presence of solvents in a coating after outdoor exposure for fairly long periods^{3, 6, 19}.

The drying of oil-containing coatings differs from that of lacquers, and the release of residual solvents from them has not been studied in detail. When an oil-modified alkyd or a phenolic resin coating is dried under normal room conditions, the film first loses weight from evaporation of solvents. This is followed by a steady gain in weight owing to the absorption of atmospheric oxygen and concurrent polymerisation^{9, 10, 16, 20}. The more oil a coating contains the longer it takes to attain the stage of "touch dry." Hence, most of the solvents evaporate and only small amounts are trapped in the film. Short oil varnishes should be intermediate between lacquers and long-oil varnishes.

It is the purpose of this study to determine the retention and release of solvents trapped during air-drying of phenolic resin varnishes containing different types and amounts of drying oils. Because of the strong retention of trace amounts of solvents, it is not possible to use only high vacuum to measure solvent retention. It has been found in this laboratory that retained solvents are removed when the films are subjected to water absorption and desorption cycles. This paper reports the effect of oil on the retention of solvent by phenolic varnishes. Temperature and vapour pressure were controlled, unlike the water immersion tests commonly used in the paint industry.

Materials and procedure

Apparatus

The apparatus used for determining solvent retention in the dried free film is based on the McBain-Bakr sorption balance²¹. The film is suspended freely from a highly sensitive quartz spring (1mm extension \approx 0.4mg) in a long, wide, glass tube. The part of the tube holding the film is immersed in a thermostatic water bath controlled at $20 \pm 0.008^\circ\text{C}$. In one unit, four such tubes are fixed to a manifold connected to the vacuum line, a micromanometer, a vacustat and the water vapour source. The latter is immersed in another thermostatic bath so that the pressure of the vapour introduced in the system can be varied by raising or lowering the temperature of the second bath. Extension of the quartz spring is measured by cathetometer to 0.001cm and vapour pressure is determined by the micromanometer to 0.001in of mercury.

Materials

The phenolic varnishes used in the studies are listed in Table 1. Varnishes were prepared by heating the oil to 110°C to dissolve the resin and the mixture was heated to 240 to 260°C . Time of heating was controlled as much as possible to get a product of viscosity C—D (Gardner-Holt scale), when diluted to 50 per cent solids content.

Table 1
Composition of paraphenylphenolic varnishes

| NRP No. | Oil content | | | Volatile content | | Varnish properties | |
|---------|-------------|-----------------|-------------|------------------|-----------------|--------------------|---------------|
| | Type | Approx. length* | % on solids | Aromatic solvent | Mineral spirits | % solids | G-H viscosity |
| 1,020 | Tung | 15 | 58.3 | 85.3 | 14.7 | 51 | A-B |
| 893 | " | 20 | 66.7 | 33.3 | 66.7 | 50 | C |
| 894 | " | 30 | 75 | 10 | 90 | 50 | D |
| 901 | " | 40 | 80 | — | 100 | 50 | B-C |
| 1,021 | Linseed | 15 | 58.3 | 49.4 | 50.6 | 49.5 | D |
| 902 | " | 20 | 66.7 | 30.6 | 69.4 | 51 | B-C |
| 903 | " | 30 | 75 | 20.2 | 79.8 | 49.5 | D |
| 905 | " | 40 | 80 | 10 | 90 | 50 | C-D |
| 1,022 | Soya | 20 | 66.7 | 28.6 | 71.4 | 50 | B |
| 1,023 | " | 40 | 80 | 34.7 | 65.3 | 50 | C-D |
| 1,024 | Dehydrated | 20 | 66.7 | 33.3 | 66.7 | 50 | C |
| 1,025 | Castor | 40 | 80 | 2.6 | 97.4 | 49 | E |

*Imp gal per 100lb resin

Shorter oil varnishes required more aromatic solvent to maintain clarity of dried films. Anti-skinning agent at a level of 0.3 per cent of the total weight was added to the cooled varnishes, which were stored in full containers in a cool room. As additional protection against skinning and to avoid viscosity increases, the cobalt and lead naphthenate driers were not added until shortly before the varnishes were to be used. The drier content as per cent by weight of oil content was 0.2 per cent lead and 0.02 per cent cobalt for the 15-gal tung oil

varnish, 0.3 per cent Pb and 0.03 per cent Co for the 20-gal tung, and 0.5 per cent Pb and 0.05 per cent Co for all others.

Procedure

Varnish films of uniform wet thickness were drawn down on 0.001in tin foil, using a blade of 2 mil clearance and a Gardner Laboratory film applicator. The films were air-dried in a dust-free room at $23 \pm 2^\circ\text{C}$ and 50 ± 2 per cent RH for three weeks. Free films obtained by amalgamation of the tin foil were dried under the same conditions for at least another three weeks before use. Films were cut into 1in squares and, after weighing, were mounted on a platinum loop and suspended freely from a quartz spring. The expanded length of the spring was measured and the system was evacuated below one micron pressure until the film attained constant weight. Most of the coating films reached almost constant weight after 48 hours under high vacuum. For subsequent work this was taken as the initial weight of the film.

Before admitting water vapour to the system, the water source was degassed intermittently. Repeated evacuation of the source removes traces of dissolved gases from water, so that only pure vapour is used in the tests. By controlling the temperature, water at a fixed vapour pressure is admitted to the system. In most cases, the water absorption equilibrium was reached within 24 hours, but the system was generally left for 48 to 72 hours before the final readings were taken. The corresponding gain or loss in the weight of the film from water absorption or desorption was measured with the cathetometer. To prevent condensation of water vapour on the film, tests were kept below 100 per cent RH. Desorption was followed by lowering the vapour pressure in the system by reducing the temperature of the vapour source in steps.

Analysis of retained solvents

The weight of the samples suspended from the quartz springs was not large enough to permit recovery of the retained solvents. In a separate experiment, pieces of free film (dry thickness 30 to 32μ) weighing approximately 4g were suspended on stainless steel hangers in a large desiccator. The desiccator was connected to the vacuum line via a cold trap. The system was pumped to below 1μ pressure for 72 hours, water vapour was then introduced in the desiccator at room temperature, and film pieces were left in water vapour atmosphere for 72 hours. The system was again evacuated; water vapour and traces of volatile products removed from of the film were collected in a specially designed cold trap. This cycle was repeated twice. The small, narrow tube in the bottom of the cold trap was dipped in liquid nitrogen and the upper part of the trap was warmed with a hot air blower so that any vapours it contained were condensed in the small tube, which was then sealed off. The tube contained water and a small quantity of organic matter. For analysis the tube was cut and covered with a rubber cap. About 0.05 to 0.1 ml carbon tetrachloride was injected and shaken gently to dissolve the organic material. The solution in carbon tetrachloride, being heavier than water, settled to the bottom of the tube and could be drawn out with a syringe whenever required for analysis. The organic matter recovered from the film in the course of water absorption-

desorption cycles was analysed by gas chromatography and infra-red spectroscopy.

Results

Loss in weight from evacuation

When the free films that had been dried for at least six weeks were first subjected to vacuum in the absorption apparatus, loosely-held solvents and oxidation products diffused out of them. As a consequence, the films lost weight, but constant weights were again attained after about 72 hours. Weight losses in percentages of air-dried film weight are shown in Table 2. It may be seen that the faster-drying tung oil varnishes lost more weight than did those made with other oils. Constant weight under vacuum was used as the basis for all subsequent weight changes.

Table 2
Initial weight loss on exposure to high vacuum
(Per cent by weight of air-dried film)

| Type of oil | | | | | Per cent weight loss | | | | Oil mean |
|-------------|----|----|----|----|----------------------|-------|-------|-------|----------|
| | | | | | 15gal | 20gal | 30gal | 40gal | |
| Tung | .. | .. | .. | .. | 0.602 | 0.621 | 0.541 | 0.462 | 0.557 |
| Linseed | .. | .. | .. | .. | 0.561 | 0.537 | 0.460 | 0.422 | 0.505 |
| Soya | .. | .. | .. | .. | — | 0.475 | — | 0.403 | 0.439 |
| DHC | .. | .. | .. | .. | — | 0.535 | — | 0.356 | 0.446 |

Loss in weight from water absorption-desorption

After removal of volatile material by high vacuum, there remains a certain amount of material held more strongly in the inter-molecular spaces of the film. This was gradually removed by repeatedly saturating the film near 99 per cent RH and then desorbing the water. The weight losses at the end of each absorption-desorption cycle are given in Table 3, and representative weight loss curves are shown in Fig. 1. Again, the fast-drying tung oil varnishes have a higher loss and take longer to reach equilibrium than do the slower drying varnishes. In Fig. 1, the dehydrated castor varnish maintained approximately the same weight during the last four cycles, the linseed varnish for the last three, and the tung varnish for the last two cycles. The 20-gal tung* lost slightly more weight than the 15-gal tung, probably because of the higher drier content, and lost considerably more than the 30- and 40-gal varnishes. With linseed varnishes in which drier concentration was uniform, the losses were inversely related to oil content. After six cycles, even the fastest-drying varnishes had practically ceased to lose weight. This means that water absorption values measured in the seventh cycle should not be affected by the presence of volatile ingredients.

*See Table 1 for the definition of this quantity.

Table 3
 Weight loss of varnish films exposed to water absorption and desorption
 (Per cent by weight of evacuated film)

| Absorp- desorp cycle | 15-gal varnishes | | | 20-gal varnishes | | | 30-gal varnishes | | | 40-gal varnishes | | | |
|----------------------------|---------------------|------------------|-------------|---------------------|---------------|--------------|---------------------|----------------|-------------|---------------------|---------------|--------------|---------------|
| | 1,020 Tung | 1,021 Linseed | 893 Tung | 902 Linseed | 1,022 Soya | 1,024 DHC | 894 Tung | 903 Linseed | 901 Tung | 905 Linseed | 1,023 Soya | 1,025 DHC | Cycle mean |
| 1 | 0.092 | 0.093 | 0.102 | 0.070 | 0.062 | 0.057 | 0.061 | 0.072 | 0.065 | 0.068 | 0.059 | 0.075 | 0.074 |
| 2 | 0.182 | 0.175 | 0.210 | 0.121 | 0.130 | 0.106 | 0.126 | 0.116 | 0.121 | 0.146 | 0.106 | 0.092 | 0.136 |
| 3 | 0.274 | 0.226 | 0.289 | 0.180 | 0.192 | 0.175 | 0.182 | 0.178 | 0.169 | 0.182 | 0.164 | 0.147 | 0.197 |
| 4 | 0.351 | 0.286 | 0.367 | 0.235 | 0.209 | 0.217 | 0.249 | 0.232 | 0.228 | 0.197 | 0.207 | 0.195 | 0.248 |
| 5 | 0.398 | 0.319 | 0.430 | 0.276 | 0.212 | 0.222 | 0.290 | 0.257 | 0.249 | 0.234 | 0.215 | 0.197 | 0.274 |
| 6 | 0.411 | 0.323 | 0.448 | 0.285 | 0.215 | 0.222 | 0.305 | 0.259 | 0.247 | 0.236 | 0.211 | 0.204 | 0.284 |
| 7 | 0.418 | 0.319 | 0.455 | 0.285 | 0.218 | 0.222 | 0.307 | 0.259 | 0.251 | 0.240 | 0.215 | 0.208 | 0.288 |

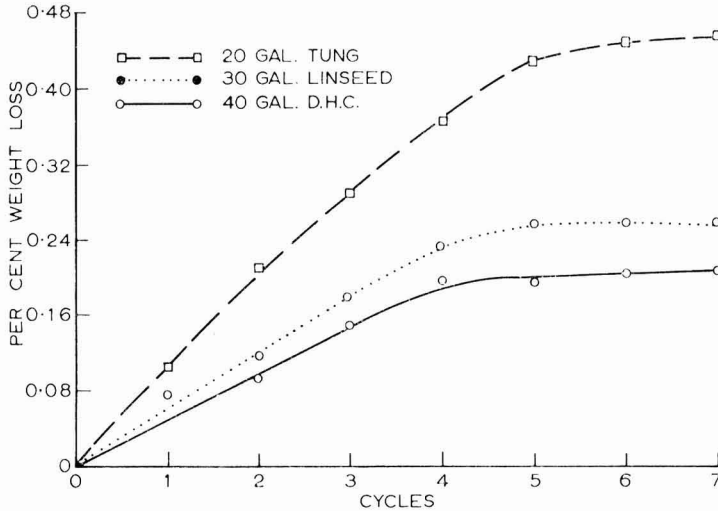


Fig. 1. Loss in weight with water absorption-desorption

Effect of drier content and drying conditions

The quick surface-drying properties of the 20-gal tung varnish seemed to be related to the high weight loss caused by both evacuation and water absorption-desorption. Experiments were therefore carried out to determine whether slower drying might lead to lower weight losses. This was accomplished by reducing the drier content and also by drying in the absence of oxygen.

The drier content in the 20-gal tung oil varnishes was 0.3 per cent Pb and 0.03 per cent Co. The same batch of varnish was used to prepare samples that contained 0.004 and 0 per cent cobalt respectively with 0.3 per cent Pb, and one with no drier at all. The effects of the changes in drier content are shown in Table 4. Films that are slower drying because driers are low or absent exhibit smaller weight losses. Reduction in cobalt, which is generally considered to be a surface drier, has a large effect on the weight loss of the dried and evacuated film. Elimination of lead, which is a "through" drier, has no effect.

Table 4
Per cent weight loss vs drier content

| Absorp-desorp cycle | Drier content (per cent metal on oil content) | | | |
|---------------------|---|----------------------|-----------------|--------------|
| | 0.03% Co 0.3% Pb | 0.004% Co 0.3% Pb | 0 Co 0.3% Pb | 0 Co 0 Pb |
| 1 | 0.102 | 0.072 | 0.063 | 0.081 |
| 2 | 0.210 | 0.181 | 0.142 | 0.148 |
| 3 | 0.289 | 0.248 | 0.215 | 0.201 |
| 4 | 0.368 | 0.289 | 0.263 | 0.282 |
| 5 | 0.430 | 0.351 | 0.304 | 0.341 |
| 6 | 0.448 | 0.395 | 0.365 | 0.348 |
| 7 | 0.455 | 0.400 | 0.365 | 0.352 |

Films of 20-gal tung varnishes containing 0.3 per cent Pb, and 0.03, 0.004 and 0 per cent Co respectively, were placed in a vacuum after a short exposure to air to allow the drying reaction to start, but solvent was removed by vacuum before the film had set. After 18 hours under vacuum (0 to 2in Hg), the films were allowed to dry normally before free films were prepared. The varnishes containing cobalt were, in fact, dry at the end of the vacuum period. The weight losses obtained by subjecting the films to water absorption-desorption are given in Table 5. It may be seen that drying in a vacuum had a much greater

Table 5
Per cent weight loss of films evacuated for 18 hours before normal drying

| % Cobalt | 0.03% | 0.004% | | 0 |
|-----------------------|-------|--------|-------|-------|
| % Lead | 0.3% | 0.3% | | 0.3% |
| Minutes before vacuum | 30 | 30 | 5 | 30 |
| Cycle No. | | | | |
| 1 | 0.091 | 0.063 | 0.048 | 0.059 |
| 2 | 0.143 | 0.157 | 0.109 | 0.094 |
| 3 | 0.223 | 0.157 | 0.117 | 0.124 |
| 4 | 0.263 | 0.176 | 0.109 | 0.171 |
| 5 | 0.293 | 0.251 | 0.137 | 0.190 |
| 6 | 0.308 | 0.251 | 0.158 | 0.204 |
| 7 | 0.315 | 0.240 | 0.158 | 0.209 |

effect in reducing weight loss than did lowering the drier content. For example, a film containing 0.004 per cent Co that was exposed to air for only five minutes, lost less weight than one with no cobalt that was left in air for 30 minutes.

Identification of recovered products

The carbon tetrachloride solution of the volatile material obtained from larger pieces of varnish film was subjected to gas-liquid chromatography using two different columns. In one series of tests, the stationary phase was Carbowax 1,540 on 110 to 120 mesh Anakrom AS. The 9ft column was maintained at 100°C with an inlet temperature of 160°C. In other tests, a 150ft capillary column treated with Ucon 550-LBX was used with a programmed temperature rise of 2°C per minute. Comparisons were made with chromatograms obtained under the same conditions from a 4 per cent solution of mineral spirits in CCl₄. More information was deduced from the capillary column results. The sample exhibited peaks corresponding to those for decane, undecane, dodecane and tridecane, which are found in mineral spirits. Many very small peaks not detected in the reference solvent chromatograms were present in those from the sample.

The sample solution was also cast on a sodium chloride plate and its infra-red spectrum obtained with a grating-equipped spectrophotometer. The largest absorptions occurred at wavelengths assigned to CH_2 and CH_3 groups and alkane chains. Expansion of the absorption scale indicated small amounts of carbonyl compounds. It was concluded that the recovered material was chiefly composed of hydrocarbons similar to those in mineral spirits, with trace quantities of ketones from the oxidation products of the film.

Discussion

The results show that solvents are trapped in air-dried varnish films, especially those that surface dry rapidly. This entrapment occurs because, after application, the surface becomes viscous and then immobile, owing to solvent evaporation and oxidative polymerisation. Meanwhile, because it takes time for solvent to diffuse out and oxygen to diffuse in, the coating in contact with the substrate is still liquid and contains solvent. Once the surface becomes dry to touch, solvent release follows the laws of diffusion through solids^{22, 23, 24}. Such diffusion is directly proportional to the vapour pressure difference across the film and inversely proportional to the thickness. Solvent retained in a coating applied to an impermeable substrate will, therefore, diffuse through the film until equilibrium is reached between its vapour pressure within the film and that in the local environment.

Because there is, for practical purposes, no solvent present in the atmosphere once the bulk of the solvent has evaporated, diffusion should continue until no solvent is left in the film. Escape of the last few per cent of the solvent is, however, very slow because resistance to diffusion increases as the film solidifies and because the vapour pressure difference across the film is low. Forces of attraction, such as hydrogen bonding between the solvent and film components, may be strong enough to counteract the vapour pressure differential. For these reasons, solvents may be detected in coatings even after outdoor exposure for more than two years^{3, 6}.

Evacuation of the air-dried film speeds up attainment of the equilibrium that would ultimately be reached in air by removing air molecules, which slow down solvent evaporation. When free films are used, both sides are available for diffusion and this assists in rapid attainment of equilibrium. Part of the observed weight loss is due to removal of water absorbed when the film was maintained at 50 per cent RH. In normal curing, slow-drying coatings do not reach the touch-dry and hard-dry stages for several hours, and this longer drying period allows more time for solvent to evaporate from the film. Hence, the loss in weight due to evacuation is less for phenolic varnishes prepared with soya, dehydrated castor, and linseed oils than it is for the rapid-drying tung-oil varnishes. In varnishes made with the same oil there is more solvent trapped in the short-oil varnishes, where solvent evaporation plays an important part in the drying process, than in the long-oil varnishes.

When the evacuated film is subjected to almost 100 per cent RH, water diffuses into the film until it is saturated at equilibrium. There is probably some swelling because the water interferes with hydrogen bonding between polar components of the film. Water molecules would also displace hydrogen-bonded solvent because water is more polar than most organic solvents²⁵. In addition,



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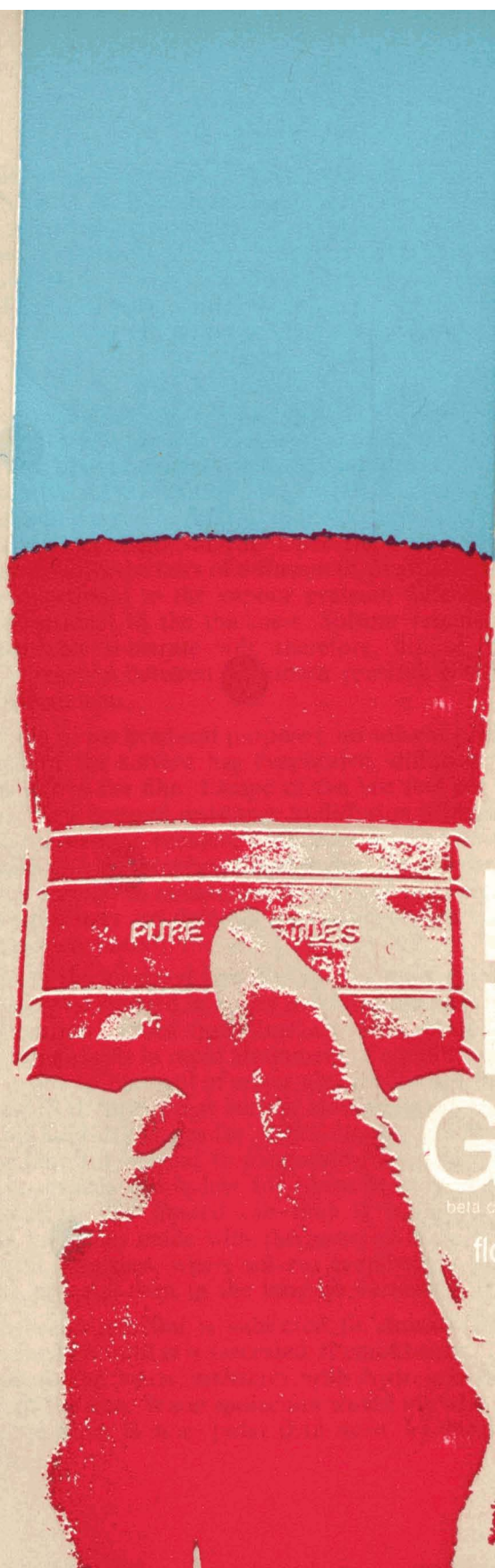
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retained solvent would dissolve in the absorbed water in proportion to its distribution coefficient between water and the dry film. When the external water vapour pressure is lowered and desorption takes place, the swollen condition of the film and the displacement of trapped solvent allows more of the solvent to escape than is the case with simple evacuation. The release of some of the solvent provides added space for water to be absorbed during the next absorption cycle. The additional water causes more swelling and more solvent is lost on the second desorption. This continues in subsequent cycles until all solvent is removed and the true dry weight and water absorption values of the film are obtained. The same relation between fast-drying and solvent retention was obtained with water absorption-desorption as with the evacuation tests.

The results of weight losses from absorption-desorption of films of short-oil tung varnishes, the drying of which was retarded because driers were reduced or absent or because air was removed during the first drying period, also indicate that rapid drying causes solvent entrapment. Reduction or total absence of cobalt drier, which promotes surface drying, slows down the drying rate. This results in the retention of less solvent in the dry film, as shown by the lower weight loss after the same number of cycles. When films are placed under vacuum shortly after application, there is a marked reduction in subsequent weight losses. This is attributed to the decrease in rate of oxidative polymerisation and also to the faster evaporation of solvents in a vacuum. Film evacuated within five minutes of preparation consequently showed the lowest retention of solvents of all the varnishes tested.

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Errata

Owing to circumstances beyond our control, proofs of the paper by Beresford published in the September issue of the *Journal* were not corrected by the author before publication.

Three errors have now been pointed out.

1. The illustrations for Figs. 4 and 5 were transposed.
2. Equation (9), page 813 should read

$$\frac{A_B - a}{A_B} R_K + \frac{a}{A_B} R_L = R_C$$

3. In reference 5, Guild is the author, and therefore should not appear in italics.
-

Next month's issue

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

"The formulation of fungus resistant paints IX Influence of the primer and of the pigments causing chalking," by *E. Hoffmann and R. R. Couper*

"Evaluation of the effect of the steel base and polyethylene coating properties on the bond strength of the system polyethylene coating steel base," by *J. Kupfova*

"Applications of silicas and silicates in the paint industry," by *A. Elbrechter and L. Muller-Fokken*

"Water absorption of phenolic varnish films," by *M. Yaseen and H. E. Ashton*

"Paints for high speed aircraft," by *C. E. Hoey*

Determination of the phosphoric acid content of the acid component of etch primer paint by flame emission spectrophotometry

By **W. N. Elliott** and **R. A. Mostyn**

Chemical Inspectorate, Royal Arsenal, London, S.E.18

Summary

Phosphoric acid in the acid component of etch primer paints is determined by measurement of the emission intensity of the HPO molecular species at 528nm in a cool hydrogen-nitrogen diffusion flame. Results are compared with those given by standard titrimetric methods.

Keywords

Types and classes of coating
etching primer

Miscellaneous paint additives
phosphoric acid

*Process and methods primarily associated
with analysis, measurement and testing*
flame spectroscopy

Dosage de la teneur en acide phosphorique du composant acide d'un "etch-primer" au moyens de la spectrophotométrie de flamme

Résumé

On a dosé la teneur en acide phosphorique du composant acide des "etch-primers" par la mesure de l'intensité de l'émission à 528 nm. des espèces moléculaires de HPO dans une flamme de diffusion d'hydrogène- azote du type tiède. On fait comparer les résultats auprès de ceux que rendent des méthodes titrimétriques usuelles.

Bestimmung des Phosphorsäuregehaltes Mittels Flammenemissions-Spektralanalyse der Säurekomponente von Washprimer

Zusammenfassung

Die in der Säurekomponente von Washprimer enthaltene Phosphorsäure wird durch Messung der Emissionsintensität der molekularen HPO Spezies bei 528 nm in einer kühlen Wasserstoff-Stickstoff Diffusionsflamme gemessen. Resultate werden mit dem durch Urtitermethoden erhaltenen verglichen.

Определение содержания фосфорной кислоты в кислотной части травильной грунтовочной краски при помощи пламенной спектрофотометрии

Резюме

Фосфорная кислота в кислотной части травильных грунтовочных красок определяется измерением интенсивности выделения молекулярного вида HPO при 528 нанометрах в водородно-азотовом диффузионном пламени. Результаты сравниваются с результатами полученными стандартными титрометрическими методами.

Introduction

Difficulty has been encountered in the estimation of the phosphoric acid content of etch primers* by titration with standard alkali; the problem is the selection of a satisfactory indicator for the second equivalence point¹, together with the fact that the colour change corresponding to the third neutralisation stage is too weak for reliable visual estimation. Various indicators have been suggested for titration of phosphoric acid to the second equivalence point at pH 9.7¹: with phenolphthalein, which has a colour change in the pH range 8.3–10.0 and an apparent indicator constant $pK_{In}^1 = 9.6$, the error has been reported as several per cent¹. The thymolphthalein colour change, in the pH range 8.3–10.5 with $pK_{In}^1 = 9.3$, has been claimed as satisfactory¹, and a mixed indicator of one part α -naphtholphthalein with three parts of phenolphthalein, having a colour change at pH 8.9 (approximately), has also been reported as suitable; a mixed indicator of one part α -naphtholphthalein and two parts phenolphthalein has also been quoted².

It was felt that a direct, and independent, phosphorus determination might suggest which indicator was to be preferred for titration to the second equivalence point, and a convenient procedure appeared to be that described by Dagnall et al³, who have determined phosphorus by flame emission spectroscopy with a cool nitrogen-hydrogen flame. The technique was well suited to the range of phosphoric acid concentration (3 per cent–20 per cent), likely to be encountered in etch primer formulations.

The phosphoric acid employed in such formulations has been variously described as 85 per cent⁴, 88 per cent minimum^{5,6} and 90 per cent by weight, and with a density of 1.68 to 1.75 g.cm⁻³. In Service stores, etch primers complying with specification DEF 1,408⁷ will normally be used; here, the phosphoric acid is specified as 85 per cent by weight. By relating the phosphorus content, as determined by the flame emission method, directly to the phosphoric acid content, it is suggested that a simpler formulation can be derived.

Experimental

Apparatus

The present work was performed on a Unicam SP.900 flame spectrophotometer, fitted with the standard propane burner head. Responses were measured on a 10mV potentiometric recorder.

Reagents and materials

Analytical grade *o*-phosphoric acid is used as the primary standard; an accurate 0.01M solution (310 μ g.ml⁻¹ as phosphorus) is prepared by dilution. Laboratory grade *n*-butanol and *iso*-propyl alcohol are used to investigate the flame background emission. Hydrogen and nitrogen gases are from the normal cylinder supplies.

Procedure

Approximately 1ml of the etch primer sample, accurately weighed, is transferred to a 100ml graduated flask and diluted to volume with distilled water, shaking thoroughly to obtain complete miscibility of the alcohols and water. Aliquots

*Etch primer paints are supplied as 2-pack materials, a "base" and an "acid component." The text refers exclusively to the analysis of the acid component.

(A ml) of this solution are transferred to each of four 100ml graduated flasks, and respective additions of 0, 1, 2 and 5ml of the standard phosphoric acid solution made before dilution to volume. The size of the aliquots may be varied according to the phosphoric acid contents of the sample; ideally, the phosphorus content of the undoped sample dilution should be of the order $3 \mu\text{g}\cdot\text{ml}^{-1}$. The doped sample dilutions will contain additions of 3.1, 6.2 and $15.5 \mu\text{g}\cdot\text{ml}^{-1}$ P respectively.

The solutions are nebulised into the hydrogen-nitrogen flame, with water as the solvent "blank" between successive sprayings, and with the following instrumental conditions:

| | |
|--------------|---|
| Wavelength | 528nm |
| Slit width | 0.2mm |
| Gain setting | 5.5 |
| Bandwidth | 3 |
| Nitrogen | 15psi. on "air" intake of SP.900 |
| Hydrogen | 2cm pressure on "fuel" intake manometer of SP.900 |
| Burner head | 1cm below entrance slit. |

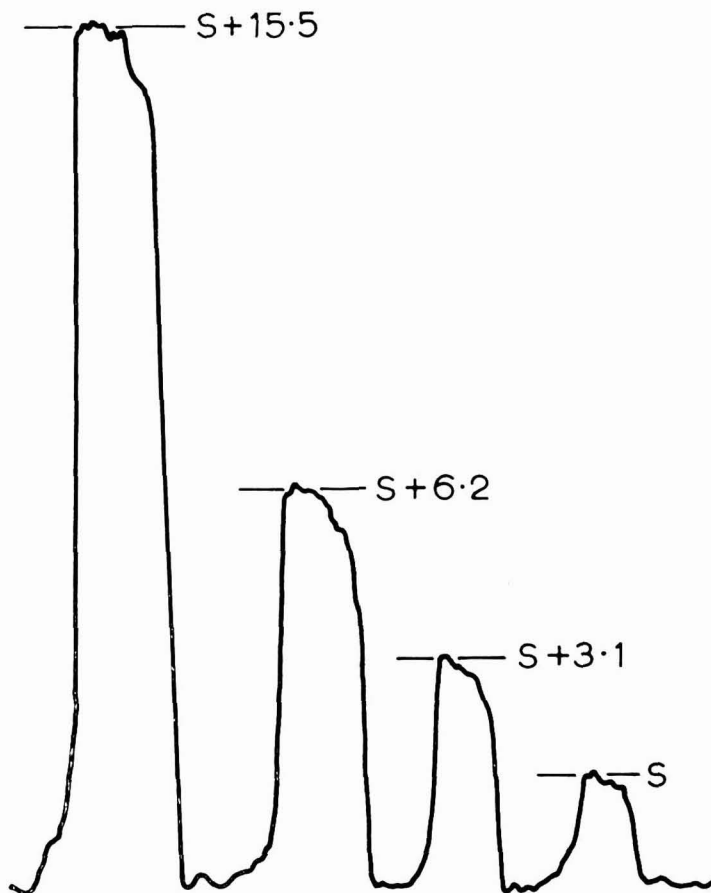


Fig. 1. Typical recorder tracings

The average response for triplicate sprayings of each of the four solutions is recorded and a graph constructed relating peak height and added phosphorus concentration. The phosphorus content of the sample is derived from the intercept on the concentration axis. Fig. 1 shows a series of recorder traces from a typical sample run and Fig. 2 illustrates the evaluation procedure.

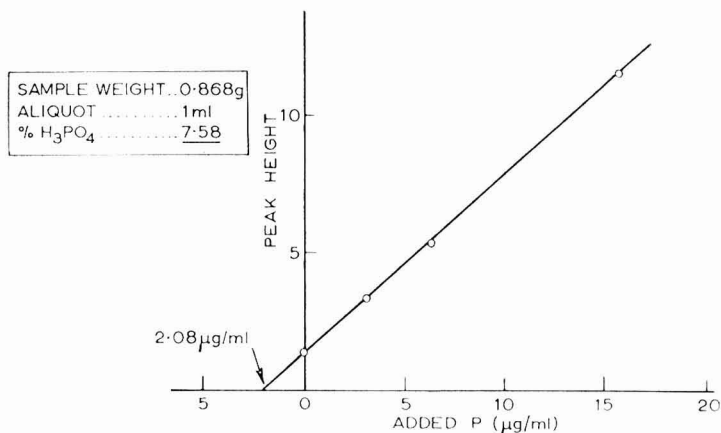


Fig. 2. Calibration graph and sample evaluation

Calculation

From the phosphorus content of the sample dilution, the phosphoric acid content of the etch primer is given by:

$$\begin{aligned} \% \text{H}_3\text{PO}_4 &= \frac{\text{P found } (\mu\text{g/ml}) \times 100 \times 100 \times 98 \times 100}{\text{Sample weight (g)} \times A \times 31 \times 10^6} \\ &= \frac{\text{P found } (\mu\text{g/ml}) \times 3.16}{\text{Sample weight (g)} \times A} \end{aligned}$$

where A is the aliquot taken (in ml) for the second dilution.

Results

Comparative results on three samples are shown in Table 1. It can be seen from the results of the titrimetric experiments that no one indicator system is entirely satisfactory, and the choice devolves upon sharpness of end-point, coupled with any preference the operator may have for a particular colour change.

The flame photometric results were found to show a precision of the order ± 2 per cent of the phosphoric acid content. There was no difficulty in assessing the result, with the proviso that instrumental conditions must be such that the calibration graph is linear over the working concentration range of about 0-30 $\mu\text{g/ml}$ phosphorus.

Table 1
Comparison of flame photometric and titrimetric methods

| Method | % Phosphoric acid Sample | | |
|--|-----------------------------|------|-----|
| | 1 | 2 | 3 |
| A. Titrimetry ^(a) with indicator: | | | |
| (1) 0.2% thymol blue | 6.7 | 14.0 | 2.9 |
| (2) phenolphthalein/ α -naphtholphthalein (2:1) | 7.0 | 14.4 | 3.2 |
| (3) phenolphthalein/ α -naphtholphthalein (3:1) | 6.9 | 14.2 | 3.0 |
| (4) phenolphthalein/thymolphthalein (1:1) | 6.5 | 13.7 | 2.8 |
| (5) 0.4% bromo-cresol green | 6.9 | 14.2 | 3.0 |
| B. Flame photometry ^(b) : | 6.9 | 14.0 | 2.7 |

(a) Mean of three determinations.

(b) Mean of eight determinations.

Discussion

No background interference from the alcohols in the etch primer was found at the dilution levels used in the flame photometric method, but it was found desirable to nebulise water for 1-2 minutes between samples to eliminate any memory effect due to residual phosphoric acid.

Although the work was carried out on a Unicam SP.900 flame photometer, very simple instrumental systems could well be equally satisfactory for this application, e.g. a system comprising an atomiser, burner, selective wavelength filter, photocell and read-out device.

Whilst titration to a potentiometric end-point would eliminate the difficulties associated with observing colour changes, the cool-flame photometric technique is of interest as providing an entirely independent, and specific, method for the estimation of phosphoric acid. The fact that no foreign acids will be recorded is an advantage to be balanced against the slightly longer time involved; results can be calculated directly as actual phosphoric acid present.

Acknowledgment

The authors wish to thank Mr C. F. Bush for helpful discussions and for the provision of various samples.

[Received 25 April 1970]

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Correspondence

Sir,—I was most interested to read Mr Arnot's letter in your June issue, in which he poses the question "to whom should one turn in order to obtain expert advice on the use of paint testing instruments?"

There are several independent consulting chemists fully qualified to give this advice. The Royal Institute of Chemistry provides in its "Directory of Independent Consultants," names of those who are active in the surface coating field. Such consultants are very frequently called upon to give an independent opinion on matters relating to surface coatings and Mr Arnot may rest assured that those specialising in this field will perform this task without any axe to grind.

Yours faithfully,

A. S. Freeborn.

15 June 1970

*50, Blackbrook Lane,
Bickley, Bromley, Kent.*

Note: We apologise for the delay in publishing this letter.

Reviews

A TREATISE ON ADHESION AND ADHESIVES, VOLUME 2—MATERIALS

EDITED BY R. L. PATRICK. New York: Marcel Dekker, Inc., 1970. Pp. xv + 554, price \$32.50.

The second volume of the "Treatise on adhesion and adhesives" deals with "Materials," the first volume having been concerned with the theoretical considerations of adhesion. A final volume will deal with the technology. The first volume has already been accepted as an important contribution to the available knowledge on adhesion. The second volume, although less controversial than the first, will become of equal importance and the ultimate trilogy will become an essential part of any adhesives library.

The aim of the editor in this volume was to present as complete as possible a coverage of the materials used in adhesives. The multiplicity of materials and systems combined with the problems of deriving a clear demarcation between the subject areas makes this a task of no small degree of difficulty. He has selected a number of outstanding scientists, who have contributed informative and interesting papers which will appeal both to students and chemists possessing a basic knowledge of the problems of adhesion.

The early chapters of this volume are concerned with thermosetting adhesive systems. "Epoxide adhesives" by H. Dannenberg and C. A. May is an excellent survey of epoxide adhesives and includes information not only on the physical and organic chemistry of the epoxide resins and their curing systems, but also on the principles of formulation and the application of the adhesives. The information is presented in a concise and logical manner and will be of great assistance to the reader.

The section entitled "Thermosetting adhesives" by L. T. Eby and H. P. Brown is a comprehensive coverage of the thermosetting resins that are now available to the adhesive industry. As is to be expected, there is a slight overlapping of information with the previous chapter, but this is necessary to achieve completeness. It is unfortunate that phenolic and amino resin systems have merited only scant coverage, since they represent a very large percentage of the total thermosetting resin adhesive production. Other thermosetting adhesive systems are dealt with fully and the applications described clearly indicate the growing future for this class of material.

The chapter on "Elastomeric adhesives" by W. C. Wake gives a very good coverage of the subject, clearly demonstrating the depth of knowledge of the author both in respect of the theoretical and the practical aspects.

"Pressure sensitive adhesives" are dealt with by C. A. Dahlquist, who describes in great depth the physical testing and theories of pressure sensitive adhesives. Unfortunately, he omits details of the basic materials and typical formulations used in adhesives of this type, so that this section tends to be unbalanced. Extreme competitiveness in this branch of the adhesive industry, not unnaturally, often restricts the disclosure of such detailed information.

Practical aspects of fibre adhesion are well discussed in the chapter by H. T. Patterson, "Fibre adhesion." The extent of the discussion of the variables

concerned in fibre adhesion clearly indicates the author's extensive knowledge on the subject. This chapter will be of great interest to all concerned with the problems of fibre adhesion, particularly now that non-woven fabrics are finding increased uses and applications.

"Soldering, brazing and welding" by F. H. Bair was of particular interest to the reviewer. The subject is presented clearly and in perspective and is a valuable reminder to adhesive chemists who often tend to disregard this aspect of metal to metal adhesion.

Aspects of glass resin adhesion are dealt with by S. Breland in his chapter on "Glass resin adhesion in filament wound structures." This subject, whilst appealing mainly to the specialist, is presented in easily-read form and will be of interest to student and expert alike.

The chapter on "High temperature adhesion" by H. Levine, although omitting some aspects of high temperature structural adhesives, covers very well the aspects in which the author has been intimately concerned in his own investigations. The increasing complexity of adhesives for high temperature use makes this subject a very specialised aspect of adhesion, albeit one of increasing importance. The concise presentation will assist readers to understand fully this sophisticated aspect of adhesives.

A comprehensive survey of the types of thermoplastic resins used in the adhesives industry is presented by R. A. Weidener. The information includes methods of polymerisation, together with details of the formulation of adhesive systems. A wide variety of ethylenic polymers is described and, therefore, the depth of information given is, of necessity, limited.

The final chapter "Preparation of ultraclean substrate surfaces" by V. Ponec should be of interest to all concerned with adhesion, since the contamination of the surface substrate is one of the major reasons for adhesive failure in bonded systems. A number of the methods described are of academic interest, although they will be of great assistance to chemists investigating adhesion to the more difficult surfaces.

The omission of a section on natural resin adhesive systems is unfortunate, since it would have made this particular volume truly comprehensive in its coverage. This does not, however, detract from the quality of the work.

The basic aim of the editor was to provide a comprehensive coverage of the materials in the adhesives industry making use of outstanding experts in their field; this aim has been achieved.

The reviewer looks forward to the publication of the final volume of the trilogy and feels sure that the complete work will become the standard treatise on adhesion and adhesives.

D. L. G. CHILDS

KINETICS AND MECHANISMS OF POLYMERISATION: VOLUME 1. VINYL
POLYMERISATION. PART 2

BY G. E. HAM (EDITOR). New York: Marcel Dekker Inc., 1969. Pp. xiii + 416.
Price: £10 14s 0d.

This eagerly awaited book completes the editor's coverage of vinyl polymerisation, and his readers will now, equally eagerly, be awaiting the volumes on ring

opening and condensation polymerisation. If they are as good as this, they will be well worth waiting for.

The mechanism of emulsion polymerisation is authoritatively treated in some 130 pages by Vanderhoff and three other chapters of the general review type deal with anionic polymerisation (Morton), mechanisms of cationic polymerisation (Zlamal) and radiation-induced polymerisation (Tabata). The remaining chapters are of the specialised, topical, type which dominated Part I of this volume. Fowler discusses the elucidation of emulsion polymerisation mechanism based upon copolymer studies; Stryker, Mantell and Helin review the relatively little known area of ethylene polymerisation in emulsion; Smith treats in considerable depth the mechanism of stereospecific polymerisation of propylene.

It is the general review chapters which will be of greatest interest to readers of this *Journal*, and many will feel that the book is worth buying for Vanderhoff alone. Certainly, this reviewer has not seen a more comprehensive and critical survey of emulsion polymerisation mechanism as it is understood today.

References, largely to the literature of the mid-'60s, are abundant; production is excellent; misprints are few; the index, usually a target for criticism, is less than adequate.

This reviewer, at least, will be a happier man when he has the complete series in his possession.

A. R. H. TAWN

Manchester Section

Modern machinery for the manufacture of inks and paints

A lecture to Student Members on "Modern machinery for the manufacture of inks and paints" was given on 16 September 1970 by Mr D. P. Sullivan of D H Industries Ltd. The meeting was held under the chairmanship of Mr J. Mitchell, the Hon. Student Activities Officer, at the Manchester Literary and Philosophical Society, George Street, Manchester. There was an attendance of 110 Members and guests.

Mr Sullivan introduced his lecture by outlining the past, present and future manufacturing techniques which were used or likely to be adopted by the ink and paint industries.

In the past, the surface coatings industry was one which involved both high manufacturing and labour costs, coupled with a very slow rate of production. At the present time, it was characterised by its extremely slow growth rate.

It was felt that the major initial step in reducing the overall cost of manufacture lay in the introduction of the slurry technique for pigment dispersion in ball mills. The necessity of adequate premixing prior to the addition of the mill base to the mill was stressed and, for this purpose, the introduction of dissolvers and cavitation mixers had greatly increased the efficiency of the manufacturing process.

The introduction of the sand mill in the late forties was stated to represent the major single advance which had been made in pigment dispersion techniques and the history of the development of this type of mill was outlined. The latest type of totally enclosed sand mill was discussed; its ability to handle fairly high viscosity mill bases represented a significant advance in production rates.

With the improvement in the quality of pigments, it was now possible to process the mill base in high speed mixers, and the lecturer outlined the processes involved in this type of dispersion.

The necessity for suitable filling machinery to handle both bulk and small scale manufacture was discussed, and the savings involved by ensuring that accurate weights and volumes of product were sold were detailed.

Throughout his lecture, Mr Sullivan stressed that it was essential that the surface coatings industry rationalised its manufacturing techniques and obtained adequate profit margins; the perilous state of the industry was instanced by quoting the falling profits of various firms.

In conclusion, Mr Sullivan stated that profit margins could only be held by adopting strict price controls in all sections of the industry and he felt that in the future it would be necessary for the industry to become more and more automated in the manufacture of both raw materials and the finished product, in order to remain competitive with firms in Europe and the rest of the world.

Following a discussion period, a vote of thanks to the lecturer was proposed by Mr R. Aldred.

Information Received

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

Bayer Chemicals Limited has recently published a leaflet entitled "Bayer polyurethanes for industry," giving an outline of the range and uses of its urethane products.

New accessories that provide digital read-out and print-out for the *Color-eye* range of spectrophotometer-colorimeters have recently been introduced by the Colour Systems Division of **Kollmorgen Corporation**. Use of the digital read-out module, and the *ASR-33* teletypewriter, claim Kollmorgen, will substantially increase the quantity of sample measurements, as well as removing the possibility of error involved in recording visual readings.

The Chemical Industries Association has now published the "U.K. chemical industry statistics handbook 1970," giving full breakdowns of the economics, production and sales, and manpower of this country's chemical industry, and making comparisons with other UK industries and overseas chemical industries. Copies of the handbook are available from the CIA at £1 10s 0d per copy.

Scott Bader Company Limited has developed a new intumescent fire-retardant paint, which obtained a Class I rating at the first attempt when tested for surface spread of flame under BS 476. Full details of the new paint, which is based on the company's *Polidene* vinylidene chloride copolymer emulsions, are contained in Technical Leaflet No. 536: "Polidene intumescent fire-retardant paint."

A new development for the wide angle photosedimentometer has recently been announced by **Microscal Limited**. A scanning device can now be supplied which permits the continuous recording of the optical density of the sedimenting suspension as a function of its height, thus reducing analysis times.

Microscal has also introduced an improved type of exposure cell for its light-fastness tester. The new cells are rectangular in shape, measuring 6in × 2in × 1in, and can incorporate water cooling facilities if required. Up to 12 cells of this type can be exposed in the light-fastness tester at one time.

It has recently been announced that a new *Gasil* plant, to be built at **Joseph Crosfield & Sons Limited's** Warrington facility, will have a much larger capacity than the old plant, and will allow for expansion of sales over the forthcoming years. The *Gasil* range of specially treated micronised silica gels has many applications, notably the production of eggshell and semigloss paints. New applications are continually being investigated, say Crosfield.

A 52-page report on the international conference "Lead and zinc through the 70's" has been published by the **Zinc and Lead Development Associations**. About 250 delegates attended the conference in May, and it is claimed that the report provides an informative look, through the eyes of experts, at the future for lead and zinc in the decade ahead.

A new range of coating thickness meters for non-magnetic coatings applied to ferrous substrates has been introduced by **Elcometer Instruments Limited**. The *Minitecor* is 4.7in × 3.7in × 1.7in in dimensions, with a separate probe, various types of which are available for different applications. The instrument uses a small magneto-resistor to

measure the magnetic flux changes occurring when a small magnet is separated from a ferrous metal surface. Signals proportional to coating thickness are amplified by a silicon microcircuit and indicated directly in metric or imperial units. Three models are available, with different scale ranges, as well as the *Ferritector*, which is scaled to indicate the ferrite content of stainless steels directly in the range 0-10 per cent and 10-25 per cent.

"Additives for paints, pigments and printing inks" is the title of a booklet issued by **Armour Hess Chemicals Limited**. Intended to assist the chemist in the application of the company's products, the booklet considers in detail the use of cationic and amphoteric surfactants as dispersing and softening agents, as well as suggesting other applications for *Armour* chemicals.

A greatly extended programme of "Innovation studies" is planned by **Arnold Services**, it has recently been announced. A list of 34 titles, all multi-client studies of new or less-developed fields, is available; six authors, said to be well known for their original thinking, carried out the work.

Plastanol Limited has now issued a revised booklet summarising the properties of its styrene and toluene modified alkyd resins. The revised version has been published, say *Plastanol*, because of the large demand for the first edition.

A range of seven books dealing with instrumented analytical techniques has been published by **Pye Unicam Limited**. Written by specialists on the *Pye Unicam* staff, the books cover many chromatographic and spectrophotometric methods.

Glassolac is a new paint repair system introduced by **General & Industrial Paints Limited** for the spot repair and re-spraying of metallic car enamels. The system involves the use of a base metallic enamel followed by a special lacquer. Applied wet-on-wet, *Glassolac* saves time in eliminating rubbing down between coats and final polishing, and thus also eliminates the danger of shearing the metallic pigment during the polishing process.

Farbwerke Hoechst AG has recently issued a reprint of the paper "The flow behaviour of printing inks" by H. Pahlke, which was published in *Paint Technology*. Copies are available from **Hoechst Chemicals Limited**.

Hoechst has also issued: data sheets on *Macamoll WH*, a flexible resin specially designed for plasticising *Maprenal TTX*, and *Macrynal 5481*, a polyfunctional acrylic resin containing hydroxyl groups, recommended for cross-linking with polyisocyanates; and a technical information sheet on matching RAL shades in plasticised pvc film and sheeting with *PV Fast* and *PV* pigments.

An automatic analysis system, *Datachrom One*, based on the **Digital Equipment Company's PDP-11/20** computer has been introduced by **Instem Limited**.

The *Datachrom One* operates by computer analysis and digital print-out of information from gas chromatographs. The system also controls the instrument, via "chromatographers desks," control points containing a teletypewriter and operator's control panel. Up to 32 chromatographs can be handled on each desk, and up to four desks, in separate laboratories if required, can be linked to the central computer.

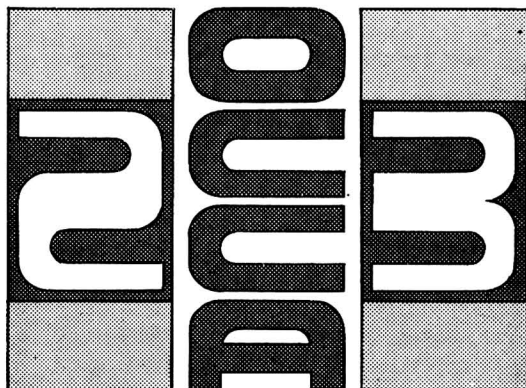
It has recently been announced that **Bush Beach & Segner Bayley Limited** has been appointed sole selling agent in the UK for the *Kolorit* range of paint tinters, manu-

factured in Sweden by **AB Henning Persson Farg**, and imported by the Swedish company's wholly owned subsidiary **Kolorit UK Limited**.

The *Kolorit* range, based on eight principal colours, is claimed to be non-drying, thus eliminating skinning, and to be suitable for tinting almost any shade in practically all types of surface coating system produced by the paint, lacquer and adhesives industries.

Badische Anilin- & Soda-Fabrik AG has added two new products to the *Neozapon* range of dyes. The new shades, *Neozapon Orange 3R* and *Neozapon Fire Red BL*, are claimed to have brilliant shade, good solubility in alcohols, glycol ethers, esters, and ketones, and good fastness properties.

The capacity of the trimethylol propane plants at the Krefeld-Uerdingen works of **Farbenfabriken Bayer AG** will reach the 24,000 tons/year level at the end of this year, it has recently been announced. A future expansion to a capacity of 36,000 tons/year is planned.



Technical Exhibition

21-25 June 1971

Early space applications high

Since the circulation of the Invitation to Exhibit, many applications for space at OCCA 23, to be held at the Empire Hall, Olympia, from 21-25 June 1971, have been received.

In view of the fact that the closing date for applications is not until 1 December 1970, this early response shows that companies have taken heed of the success of OCCA 22, and promises an even larger exhibition for 1971.

Not least of the factors influencing the continuing increase in size of the exhibition has been the move to Olympia last year. Both exhibitors and visitors found the new venue easily accessible from all parts of London, as can be seen from the map opposite, and this was reflected in the increase in the number of people who attended the exhibition, in spite of the fact that it was only possible to open for

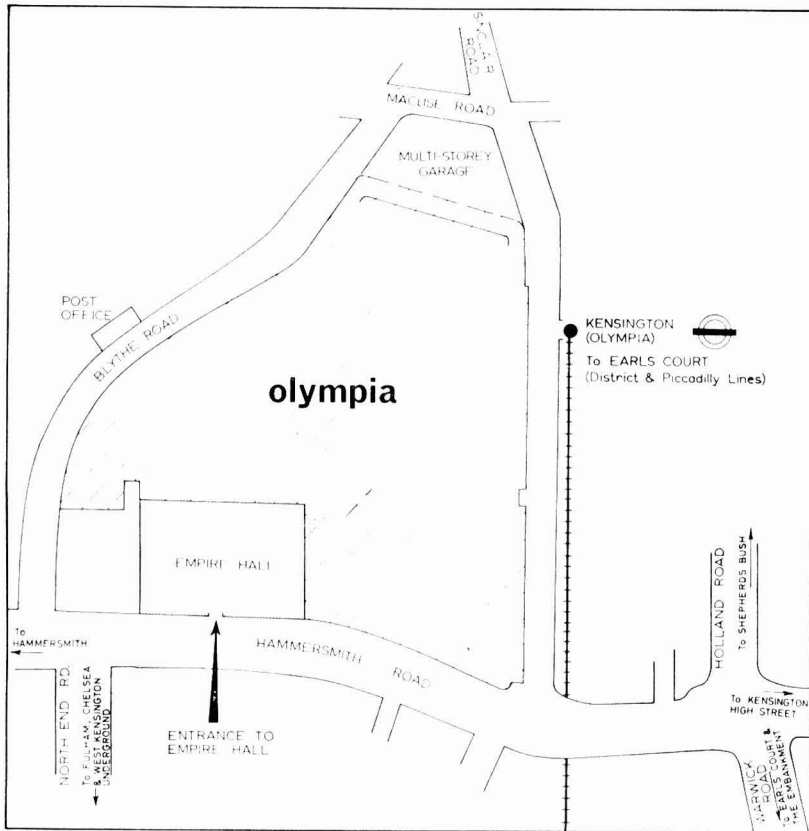
four days, owing to a restriction in the tenure of the lease.

Next year a longer lease has been negotiated, and it will be possible to open for five days. The extension of opening hours in 1970 proved so popular that it is to be retained, making OCCA 23 the longest ever exhibition in terms of hours of opening. Details are shown below.

| | | |
|-----------|---------|-------------|
| Monday | 21 June | 15.30-18.30 |
| Tuesday | 22 June | 09.30-18.30 |
| Wednesday | 23 June | 09.30-18.30 |
| Thursday | 24 June | 09.30-18.30 |
| Friday | 25 June | 09.30-16.00 |

As already mentioned, the closing date for applications for space is **1 December 1970**. However, in view of the response to date, any company considering applying for space would be well advised to do so as soon as possible. Applications should be addressed to the Director & Secretary, at the address on the cover of this *Journal*.

How to get to Olympia



1. For those travelling by road, there are car parking facilities available in the multi-storey garage, the entrance to which is from Maclise Road.
2. Visitors arriving at the West London Air Terminal may board District Line trains at Gloucester Road Underground Station to Earls Court, from which station a special Underground train is available to Olympia, running at 10-15 minute intervals.
3. Olympia can be reached from main line stations by travelling on the Underground to Earls Court, which is on the District or Piccadilly Line, and changing to the special train.
4. There are a number of bus routes which also serve Olympia:
 Bus Nos.: 9, 27, 28, 49, 73, 91, 207A and 270.
 Green Line Coaches Nos.: 701, 702, 704, 705, 714 and 716A.
5. There is a Motorail Terminal at Olympia and those wishing to transport their cars should contact British Rail.

Association Conference, 4-8 May 1971

Surface properties and appearance

The technical programme for the Association's 1971 Conference, to be held at the Palace Hotel, Torquay, from 4-8 May, has now been arranged by Mr A. R. H. Tawn, the Association's Hon. Research and Development Officer.

Details are given below.

Wednesday morning, 5 May

T. R. Bullett (Paint Research Station) "Keynote Address: The changing face of paint."

P. Whiteley and G. W. Rothwell (Building Research Station) "Appearance and performance factors in coatings for buildings."

K. McLaren (ICI Ltd., Dyestuffs Division) "Colour specification by visual means."

Wednesday afternoon, 5 May

Management session, to run parallel with the workshop sessions.

P. Bennett (Chemical and Allied Products Industry Training Board) "Research and development—recruitment, education and training."

R. R. Davidson (Welwyn Hall Research Association) "The mechanism of discovery and innovation."

A. G. North (Cray Valley Products, Ltd.) "Financial evaluation of research projects."

Conference papers and authors

Summaries of most of the papers and biographies of the authors appeared in

Keynote Address: The changing face of paint by T. R. Bullett

Modern paints are, intrinsically, amongst the most durable of building materials; erosion rates, expressed as loss in thickness per year of unpainted steel, wood, brick and concrete, in urban atmospheres are all many times that of a good average

Thursday morning, 6 May

Dr K. H. Reichert (Forschungsinstitut für Pigmente und Lacke e.V) "Gas chromatographic investigations of interaction forces between binder and solvent in paint films."

L. A. Tysall and Dr D. H. Scharer (Shell Research, Ltd.) "Film appearance and its dependence on solvent formulation; a systematic approach."

R. P. Bates (National Lead Company) "Basic lead silichromate pigments—facts about them."

Thursday afternoon, 6 May

D. G. Dowling and D. F. Tunstall (British Titan Products Co., Ltd.) "Opacity of roller coatings:

Part I—Practical aspects; Part II—Theoretical analysis."

Friday morning, 7 May

J. R. Taylor and H. Foster (BP Chemicals (UK) Ltd.) "Several factors affecting appearance and properties of thermosetting acrylic enamel films."

J. H. Colling, Dr W. E. Craker, Dr J. Dunderdale and Dr M. C. Smith (Laporte Industries, Ltd.) "The relation between gloss and dispersion in acrylic paint films."

Dr W. Carr "Effect of pigment dispersion on the appearance and properties of paint films."

the October issue. The remainder are given below.

paint film. New coating materials of even higher durability are now coming into use and, when applied under controlled conditions to properly prepared surfaces to ensure lasting adhesion, may be expected to maintain integrity for 20,

30 or more years. But integrity is not enough; the primary function of paint is decoration, so that the useful life of a coating is only the period for which it maintains a satisfactory appearance. "Loss of face" will increasingly become the main reason for repainting.

The paper will review the ways in which a coating can change in appearance. There are external factors, such as retention of dirt, yellowing by tobacco smoke, the effects of other atmospheric pollutants, contamination by fungi and algae. Susceptibility to such factors and, perhaps more important, ease of cleaning is a function of paint composition. Building design can do much to reduce these troubles.

There are also internal changes in coatings leading to alterations in surfaces, such as the rearrangement of material around pigment particles that results in hazing, irregular shrinkage when retained solvent is finally lost and shrinkage due to weathering effects that normally precedes chalking. Finally, colour change in relation to pigment, pigment/medium interaction, exposure to light and ultraviolet radiation will be considered. An important problem, not yet entirely resolved, concerns assessment of colour changes. The new PRA fibre optics colorimeter will greatly facilitate measurement, but further study of methods for expressing colour differences in units correlating with visual judgment is desirable.

Mr T. R. Bullett obtained a BSc Special (Physics) degree at University College, London. He is now head of the physics division at The Paint Research Station, where his work has covered many aspects of paint testing. He is a Fellow of the Institute of Physics and a Fellow and Council Member of the Institution of Corrosion Technology.



Mr T. R. Bullett

The relation between gloss and dispersion in acrylic paint films by J. H. Colling, W. E. Craker, M. C. Smith and J. Dunderdale.

After obtaining his BSc in Chemistry at Manchester University, Mr J. H. Colling joined the Basic Research Group of Laporte Industries Limited in 1966. Initially, his work concerned optical properties of surface coatings, specialising in the study of gloss phenomena. Following this he investigated the photochemical degradation processes in paint films. Currently he is using rheological methods to investigate the dispersion of titanium dioxide in aqueous and non-aqueous media.



Mr J. H. Colling

After taking a physics degree at Durham University, Dr W. E. Craker stayed on to study the mechanical properties and phase change kinetics of polymerised sulphur. He was awarded his PhD in 1953. Following three years teaching in the RAF he joined British Plaster Board and worked on the rheology of plaster slurries and the dehydration of gypsum.

Dr Craker joined the Basic Research Group of Laporte Industries Limited in 1962 and initially worked on the optical properties of pigment and paint films. In 1968 he was appointed Section Manager in the Basic Research Group and is responsible for a range of problems involving the physics and chemistry of paint and pigment. In addition to this he has worked on the statistics of process control.



Dr W. E. Craker

After taking chemistry at the Trent Polytechnic, Dr M. C. Smith went on to Nottingham University where he worked with the Colloid and Surface Chemistry Group and used the light scattering technique to study the micellisation of sodium dodecyl sulphate in binary liquid mixtures. He was awarded his PhD in 1970.

Since October 1969 he has been working in the Basic Research Group of Laporte Industries Limited, mainly on optical properties of surfaces and the hiding power of emulsion paint systems.



Dr M. C. Smith

After service with the RAF, Dr J. Dunderdale graduated from University College, London, and continued to his PhD for studies in infra-red spectroscopy.

In 1954 he entered the Research and Development Section of the British Oxygen Company Ltd., and worked for a year on purification of inert gases. He then spent two years at the Research Department of the Distillers Company, Ltd., working on the application and development of infra-red and mass-spectrometric techniques. In 1957 he joined the Physical Section of the Research Department of British Titan

Products Company, Ltd., and was subsequently appointed Section Manager; during this period he was essentially concerned with small particle physics and surface properties.

In 1962 Dr Dunderdale joined the CSIRO and was engaged on the study of reactions in flames and the formation of fireside deposits in boilers. He was also concerned with the application and development of X-ray techniques both for these problems and for the examination of mineral matter in coals.

In 1965 he joined the Research Department of Laporte Industries Limited at Stallingborough, in charge of the Basic Research Section, and was appointed Divisional Research and Development Manager in 1967.



Dr J. Dunderdale

Research and development—recruitment, education and training by P. Bennett

Mr P. Bennett is a Senior Training Officer with the Chemical and Allied Products Industry Training Board. His main responsibilities are for the training of all technical staff in the industries within scope of the Board. A graduate of London University, he was for a number of years with the Plastics Division of ICI, first in the research department and later in education and training.



Mr P. Bennett

Financial evaluation of research projects by A. G. North

Mr A. G. North is a Londoner by birth, and was educated at Bromley Grammar School and London University, from which he graduated with an honours degree in chemistry. After graduation, he went to the Harvard Business School, where he completed a business management course. Since 1948, Mr North has served with Cray Valley Products Limited, in a variety of positions from laboratory assistant to his current position as Technical Director and Assistant Managing Director.



Mr A. G. North

Jordan Award

This award was instituted by the late Mrs M. R. Jordan in memory of her husband Dr L. A. Jordan, who was President of the Association 1947-1949 and who died in December 1964.

The Committee invites applications for the second award of £100 which it is hoped to present at the Torquay Conference 4-8 May 1971.

The rules of the Award are appended below.

1. The Award will be made for the best contribution to the science or technology of surface coating by a member of any nationality working in either the academic or industrial field who is under the age of 35 at the date of application.

2. The final date for submission of applications will on this occasion be 1 January 1971.

3. The selection of the recipient of the Award will be made by a Committee

under the Chairmanship of the Association's Hon. Research and Development officer.

4. There will be two methods of application. First, by the submission of a paper describing original work by the candidate which is offered for publication in the *Journal* or has been so published during the two years prior to the closing date for application. The alternative method will be by recommendation by a superior for work which for reasons of commercial secrecy cannot be published; in this case the candidate will be expected to submit a dissertation on a topic relating to his work and demonstrating his superior knowledge of the principles thereof. The Award is for *individual* merit and clear evidence of the candidate's own contribution will be required if a paper is offered under joint authorship.

5. Applications should be addressed to the Director & Secretary at the Association's offices.

London Section

One-day symposium on pigment surface characterisation

A one-day joint symposium, having the theme "The characterisation of pigment surfaces", will be held in the Department of Chemistry, Brunel University, Acton, on Wednesday 25 November, starting at 10 a.m. It has been organised by the Colloid & Surface Chemistry Group, Society of Chemical Industry, and the London Section of OCCA.

The meeting should be of considerable interest, since both the theoretical and more practical aspects of the subject will be discussed. In addition, delegates will also have the opportunity of seeing the surface chemistry laboratories of Brunel University.

The proceedings will open with a paper by Prof. K. S. W. Sing of Brunel University entitled "Assessment of area and porosity of pigment surface" and will be followed by "The chemical characterisation of pigment surfaces" by Prof. G. D. Parfitt of British Titan Products Co. Ltd.

Following lunch, there will be two further papers: "The characterisation of organic pigment surfaces" by Dr G. Eulitz and Dr K. Merkle of Farbwerke Hoechst AG, and "The characterisation of carbon black surfaces" by Dr D. Dollimore of the University of Salford.

Further details and application forms can be obtained from Prof. K. S. W. Sing, Department of Chemistry, Brunel University, Woodlands Avenue, Acton, London W3.

South African Section

The Section held its first meeting of the session on 4 June, when Mr G. C. Burgess presented a paper entitled "Titanium dioxide pigment design with relation to the chloride process." The next meeting was to be held on 30 July, when Professor Hamilton of the Paint Research Institute was to give a lecture entitled "The research programme of the Institute."

Third National Convention

The Third National Convention is to be held on 11-13 September at the Cathedral Peak Hotel in the Drakensberg area. The theme of the Convention is "The principles of electrophoretic deposition of coatings." The Section Committee feel it particularly encouraging that enthusiasm and support for the Convention is now such that four of the

five lecturers have been obtained locally. The full programme of lectures is:

"The physical chemistry of electrophoresis" by Prof. J. W. Bayles, Professor of Physical Chemistry, University of Natal.

"Water soluble resins as used in paints suitable for electrophoresis" by Mr R. Crawford, of Cray Valley Products, Isipingo, Natal.

"Pigments and pigmentation of paints suitable for electrophoresis" (Speaker to be arranged).

"Equipment aspects and quality control of electrophoresis baths" by Dr Nikoli, of Herbert Evans, Durban.

"General formulation aspects of paints suitable for electrophoresis" by Mr T. Edwards, of Dulux, Alberton, Transvaal.

News of Members

Mr A. R. H. Tawn, an Ordinary Member attached to the London Section, and the Association's Hon. Research and Development Officer, has recently returned from a tour of the USA. During the tour he lectured to the Pittsburgh and Houston Societies of the Federation of Societies for Paint Technology, and to the Paint Research Institute's Annual Meeting at Columbus, Ohio, and on these occasions conveyed the greetings of the President and Council.

Mr Tawn has also been recently elected a Fellow of the Institute of Metal Finishing.

Mr D. P. Godden, an Ordinary Member attached to the Irish Section, has been appointed to the board of The Walpamur Company (Ireland) Limited.

Mr P. Redmond, a Student Member attached to the Irish Section, has been awarded a pass with credit in the examination for the Ordinary Certificate in Printing Ink of the City and Guilds.

PI Symposium

The Reinforced Plastics Group of the Plastics Institute is to organise a symposium entitled "Surface coating of plastics and metals in the automotive industry." Six papers are to be given at the symposium, which is to be held at the Civic Hall, Solihull, Warwickshire, on Thursday 12 November.

Courses at the Polytechnic of the South Bank

A series of courses on various aspects of chromatography has been arranged by the Polytechnic of the South Bank.

The first "Chromatography: theory and practice" commenced on 23 October. The remainder are:

"Practical chromatography," to be held on six successive Friday evenings, commencing 8 January 1971,

"Liquid chromatography," a three-day course to be held on 24-26 February 1971,

"Gas chromatography," a three-day course to be held on 31 March—2 April 1971,

"Gas chromatography," a course of six lectures to be held on Friday evenings, commencing 30 April 1971.

All courses include lectures and practical work, and full details are available from: The Secretary, The Polytechnic of the South Bank, Borough Road, London SE1.

SCI Colloid and Surface Chemistry Group Symposium

The Colloid and Surface Chemistry Group of the SCI is to hold a symposium on "Particle growth in suspensions," on 24-26 April 1972 at Brunel University (London).

The objective of this symposium is to consider changes in size and habit of particles in suspension that are influenced by internal and external factors, and to discuss the effect of these changes on the properties and uses of the suspensions.

The Organising Committee invites papers dealing with the ageing of all types of suspensions in which a liquid forms the continuous phase, and covering such

aspects as (a) measurements of changes in particle size and habit and of associated physical properties of suspensions, (b) changes associated with additives, (c) Ostwald ripening and related phenomena, and (d) polymorphism in crystallisation and precipitation.

Abstracts (not more than 500 words) are required by June 1971 and should be sent to the Secretary, Professor G. D. Parfitt, British Titan Products Co. Ltd., Billingham, Teesside. The complete papers will be required by December 1971 so that preprints may be issued to members attending the conference. All the papers will be published by the Society of Chemical Industry as a monograph.

Urethanes Group of the I.R.I.

In view of the increasing production and use of urethane chemicals and end products, the Institution of the Rubber Industry has formed a new Urethanes Group. Operating on a national basis, the new group will work in close collaboration with the existing I.R.I. sectional groups.

Section Officers and Committees 1970-71

Scottish (Eastern Branch)

Chairman: P. A. Gower, c/o Lorilleaux & Bolton Ltd., Eclipse Works, Sighthill, Edinburgh, 11.

Immediate Past Chairman: G. H. Hutchinson, ARIC, AFInstPet, c/o A. B. Fleming & Co. Ltd., Glasgow Road, Edinburgh, 12.

Vice-Chairman: R. Webster, 37 Iona Street, Edinburgh, 6.

Hon. Secretary: J. W. Brunton, 20 Cramond Terrace, Edinburgh, 4.

Hon. Treasurer: R. Harvie, 8 Deanpark Crescent, Edinburgh, 4.

Hon. Publications Secretary: J. H. Stewart, AHWC, LRIC, 49 Dregghorn Loan, Edinburgh, 13.

Hon. Auditor: D. I. Muirhead, c/o Wm. Sim & Sons (Paints) Ltd., 40 Jane Street, Edinburgh, 6.

Committee:

A. McLaren, 4 Hermitage Park, Edinburgh, 6.

G. A. Pringle BSc, ARIC, 3 House O'Hill Grove, Blackhall, Edinburgh, 4.

P. R. Phillips, 10 Craigcrook Park, Blackhall, Edinburgh, 4.

J. J. Traynor, 114 Cuikew Terrace, Penicuik, Midlothian.

C. G. Cochrane, BSc, c/o Craig & Rose Ltd., Leith Walk, Edinburgh, 6.

Wellington

Chairman: T. W. Slinn, BSc, c/o Balm Paints (NZ) Ltd., PO Box 30366, Lower Hutt, Wellington, New Zealand.

Hon. Secretary: M. D. Taylor, c/o Pinchin Johnson & Co. (NZ) Ltd., PO Box 14-064, Kilbirnie, Wellington, New Zealand.

Hon. Treasurer: A. J. Mayne, MSc, c/o Polychem (NZ) Ltd., PO Box 9141, Wellington, New Zealand.

Hon. Publications Officer: G. P. Cryer, BSc, Atlantic Union Oil Co. (NZ) Ltd., PO Box 38073, Petone, New Zealand.

Representative on Council: G. Willison.

Committee:

R. Bockhop, Swift & Co. (Trading) Pty. Ltd., PO Box 1002, Wellington, New Zealand.

M. D. Thompson, 12 Reading Street, Karori, Wellington, New Zealand.

R. M. Sinclair, MSc, 169 Riverside Drive, Lower Hutt, Wellington, New Zealand.

R. A. Ness, c/o Mobil Oil, PO Box 38073, Petone, Wellington, New Zealand.

D. J. Wilson, c/o Robert Bryce & Co. Ltd., 19 Lower Tory Street, PO Box 3747, Wellington, New Zealand.

G. L. Willis, 35 David Crescent, Karori, 5, Wellington, New Zealand.

Register of Members

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

Ordinary Members

ALLDRITT, COLIN, "Colene," East Park Avenue, Darwen, Lancs. (*Manchester*)

BOOTH, MARTIN WILLIAM, c/o General Trading Co., Paints Division, PO Box 1079, Kuwait, Arabian Gulf. (*Overseas*)

CAVE, MICHAEL RUSSELL, LRIC, The Walpamur Co. Ltd., Darwen, Lancs. (*Manchester*)

KENYON, JEFFREY, 22 King's Road, Blackburn, Lancs, BB2 4PX. (*Manchester*)

WILSON, HUBERT HORNBY, The Walpamur Co., Paint Division, Research Labs., Darwen, Lancs. (*Manchester*)

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.

Monday 2 November

Hull Section: "Protective coatings for gas pipe lines and storage vessels" by Dr J. T. Harrison of the Gas Council, to be held at the Bullock Lecture Theatre, Hull College of Technology at 7.00 p.m.

Wednesday 4 November

Scottish Section—Eastern Branch: "Metrication" by Mr F. Mundy. Joint Lecture with BPBMA to be held at the Carlton Hotel, North Bridge, Edinburgh at 6.45 p.m.

Tuesday 10 November

London Section—Southern Branch: "Modern adhesives" by Dr W. A. Leef of Borden Chemicals Limited, to be held at the Pendragon Hotel, Clarence Parade, Southsea at 7.00 p.m.

West Riding Section: "Zinc rich paints" by Mr B. Jones of Amalgamated Oxides Limited, to be held at the Griffin Hotel, Boar Lane, Leeds at 7.30 p.m.

Wednesday 11 November

London Section: "The significance of glass transition temperatures of paint films" by Mr J. L. Prosser of the Paint Research Station, to be held at the new extension building of the Borough Polytechnic, Borough Road, London SE1 at 7.00 p.m.

Newcastle Section—Student Group: "Flame retardant paints" by Mr A. G. Walker of Associated Lead Manufacturers Limited, to be held at the Newcastle Polytechnic, Ellison Place, Newcastle upon Tyne at 3.00 p.m.

Thursday 12 November

Midlands Section—Trent Valley Branch: "Electro-painting" by Mr J. R. Bourne of Mebon Limited. A Joint Meeting with the Institute of Metal Finishing to be held at the Department of Transport Technology, Loughborough University at 7.30 p.m.

Newcastle Section: "Addition copolymers of the vinyl esters of branched chain fatty acids for cure with isocyanates" by Mr P. de Carpentier of Koninklijke/Shell Plastics Laboratorium, Delft, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne at 6.30 p.m.

Scottish Section: "Applications of silicas and silicates in the surface coatings industry" by Mr L. Muller-Fokken of Degussa, to be held at the St. Enoch Hotel, Glasgow at 6.00 p.m.

Friday 13 November

Manchester Section: "Olefine route to new paint latices" by Mr J. A. Wall

of BP Chemicals Limited, to be held at the Bolton Institute of Technology, Deane Road, Bolton at 6.30 p.m.

Thursday 19 November

Thames Valley Section: "Wallpaper" by Mr A. O. Sutherland of ICI Wallpapers Limited, to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks at 7.00 p.m.

Friday 20 November

Irish Section: "Urethanes" by Mr A. C. Jolly of Synthetic Resins Limited, to be held at the Clarence Hotel, Wellington Quay, Dublin at 8.00 p.m.

London Section: "Ladies Night" at the Criterion-in-Piccadilly, London W1 at 7.30 p.m.

Midlands Section: "Gloss and semi-gloss latex paints" by Mr G. Willison of British Titan Products Limited, to be held at the Chamber of Commerce House, 75 Harbourne Road, Birmingham 15 at 6.30 p.m.

Monday 23 November

Auckland Section: "Ladies Night" at the Crystal Room, Commercial Travellers Club, Remuera, Auckland.

Wednesday 25 November

London Section: "Characterisation of pigment surfaces." Joint Symposium to be held with the Colloids and Surface Chemistry Group, Society of Chemical Industry, to be held at Brunel University at 10.00 a.m.

Friday 27 November

Bristol Section: "Industrial training" by Mr H. R. Peel of the Chemical and Allied Products Industry Training Board, to be held at the Royal Hotel, Bristol at 7.15 p.m.

West Riding Section: Annual Dinner and Dance at the Crown Hotel, Harrogate.

Thursday 3 December

Midlands Section—Trent Valley Branch: "Safety in the paint industry"

by Dr L. E. Euinton HM Medical Inspector of Factories, to be held at the British Rail School of Transport, London Road, Derby at 7.00 p.m.

Newcastle Section: "Coal tar based surface coatings" by Dr D. McNeil of the Coal Tar Research Association, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne at 6.30 p.m.

Monday 7 December

Hull Section: "The value of gel permeation chromatography for the design of alkyd resins" by Mr H. Olley and Dr L. A. O'Neill of the Paint Research Station, to be held at the Bullock Lecture Theatre, Hull College of Technology at 7.00 p.m.

Tuesday 8 December

West Riding Section: "Milling—a variable in ink performance" by Mr J. Groom of Sandoz Products Limited. Joint Meeting with the Institute of Printing, to be held at the Griffin Hotel, Boar Lane, Leeds at 7.30 p.m.

Wednesday 9 December

Newcastle Section—Student Group: "Marine fouling" by Dr A. O. Christie of the International Paint Company Limited, to be held at the Newcastle Polytechnic, Ellison Place, Newcastle upon Tyne at 3.00 p.m.

Thursday 10 December

London Section: "Addition copolymers of the vinyl ester of branched chain fatty acids for use in electrodeposition paints" by Dr W. J. van Westrenen of Koninklijke Shell Plastics Laboratories, Delft, and Mr W. H. M. Nieuwenhuis of Koninklijke Shell Laboratories, Amsterdam; to be held at the East Ham Technical College, High Street South, London E6, at 7.00 p.m.

Scottish Section: "Development of gloss paints in the twentieth century" by Mr I. R. McCallum and Mr M. Devine of P. W. Hall Limited, to be held at the St. Enoch Hotel, Glasgow at 6.00 p.m.

Friday 11 December

Irish Section: "Ladies Night" to be held at the Clarence Hotel, Wellington Quay, Dublin at 8.00 p.m.

Manchester Section: "Chloride titanium dioxide pigments—their value" by Mr J. S. Jordan and Mr F. D. Robinson of Laporte Industries Limited, to be held at the Liverpool Building and Design Centre, Hope Street, Liverpool 1 at 6.30 p.m.

Wednesday 16 December

Scottish Section—Eastern Branch: "Modern developments in titanium" by Mr G. Willison, of British Titan Products Limited, to be held at the Carlton Hotel, North Bridge, Edinburgh at 7.30 p.m.

Oil and Colour Chemists' Association

President: A. S. FRASER

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 (with a Southern Branch), 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 (I.I.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.

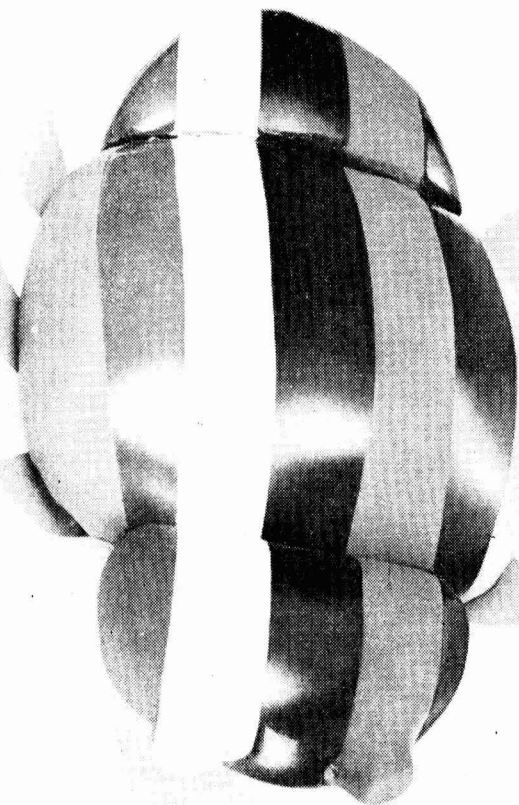
Part 3 : " Convertible Coatings," Pp. 318, 35s.

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, EC2V 7AB.



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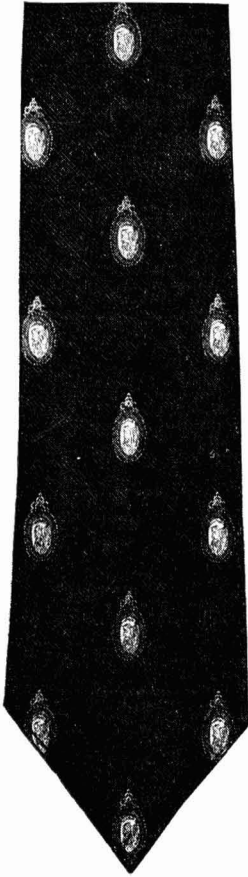
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The tie is blue terylene, with the Association's insignia woven in red and gold silk.

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

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

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



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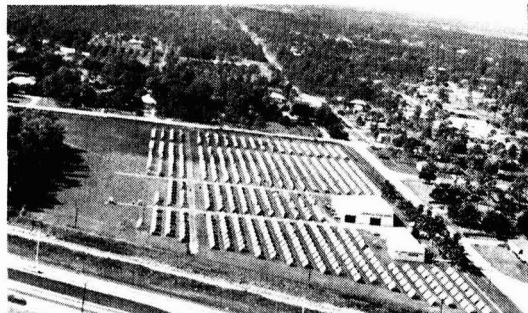
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