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(June 1976)

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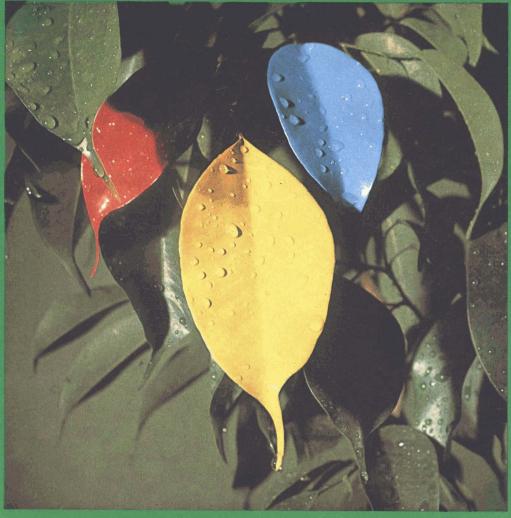
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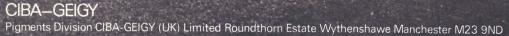
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| Hon. Editor: S. R. Finn, BSc, FRIC, FTSC | Contents | Vol. 59 No. 4 | ļ | | Ap | oril 1976 |
|---|---|---------------|------------|------------|------------------|------------|
| Publications Committee : R. McD. Barrett, BSc, MSc E. H. A. Bishop, LRIC, MICorrT, FTSC R. A. C. Chappell, MRIC | | | | | | |
| F. W. Cole, ATSC F. Cooper, BSc M. T. Cotter C. N. Finlay, ATSC | Transactions and Com High shear rheology | | al paints— | -its ef | ffect o | n |
| P. A. J. Gate, BSc, MRIC, FTSC B. Hulme, MSc, PhD, MRIC R. J. King, BSc, AWP, ATSC A. McWilliam, MRIC, FTSC | rolling and brushi | | ÷ . | ٠ | · | . 115 |
| D. J. Morris A. J. Newbould L. H. Oliver • G. H. Robertson, BSc, PhD F. D. Robinson, ATSC | Interfacial phenome | na in inks . | | <i>W</i> . | Hanse | . 127 n |
| A. T. S. Rudram, FTSC L. H. Silver R. C. Somerville J. R. Taylor, BSc, FRIC, FTSC L. J. Watkinson, MSc, PhD, MRIC, FTSC D. M. Wilson, LRIC | The application of to packaging | UV-curing mat | erials and | · | nolog . D. Lo | . 141 |
| Editorial correspondence should be addressed to the Hon. Editor, <i>JOCCA</i> , 49 Elms Drive, Kirk Ella, Hull HU10 7QH. | Information Received | | | | | . 148 |
| General correspondence should be addressed to: R. H. Hamblin, MA, FCIS, | Reviews | · · · | | i•(| 2. | . 150 |
| Director & Secretary, Oil & Colour Chemists' Association, at the address below. | Section Proceedings | | | ÷ | • | . 151 |
| Tel: 01-908 1086 Telex 922670 (OCCA Wembley) Telegrams: OCCA Wembley Telex | Correspondence . | | | | • | . 153 |
| Assistant Editor: C. A. Tayler, BSc | Notes and News | ж н н | · · | • | ÷ | . 154 |
| Annual subscription to non-members: £20 (\$50), post free by surface mail, payable in advance. | Register of Members | | » · | .•0 | | . 156 |
| Single copies £2 (\$5), post free by surface mail, payable in advance. | Forthcoming events . | | | | · | . 156 |
| Published by | | | | | . – | |

OIL AND COLOUR CHEMISTS' ASSOCIATION Priory House, 967 Harrow Road, Wembley, Middlesex, England HA0 2SF

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Transactions and Communications High shear rheology of architectural paints—its effect on rolling and brushing*

By J. D. Dormon and D. M. D. Stewart

Laporte Australia Limited, 20-22 McPherson Street, Banks Meadow, NSW 2019, Australia

Summary

The high shear rheology of several series of flat latex paints and alkyd undercoats has been measured and related to rolling and brushing application properties.

It has been shown that viscosity at 1000 sec^{-1} is related closely to roller fly-off performance and ease of brushing, as assessed by spreading time. The effect of other rheological parameters, such as

Keywords

Types and classes of coatings and allied products

emulsion paint undercoat

Processes and methods primarily associated with application of coatings and allied products

roller coating

pseudoplasticity and recovery factor on rolling and brushing, has also been discussed and compared with previously published results.

The effects of titanium dioxide pigment grade and the scale up of manufacture have been related to the resulting paint rheology, roller fly-off and brushing properties.

Properties, characteristics, and conditions primarily associated with:

materials in general pseudoplasticity rheological property thixotropy viscosity

coatings during application

brushability

La rhéologie à des vitesses de cisaillement élevées de peintures pour bâtiments—son influence sur les caractéristiques d'application par rouleau ou par brosse

Résumé

On a déterminé la rhéologie à des vitesses de cisaillement élevées de plusieurs séries de peintures-émulsions mattes et de peintures alkydes pour couches intermédiaries et l'on a établi le rapport entre la rhéologie et les caractéristiques de l'application par rouleau et par brosse.

On a démontré que la viscosité à 1000 sec⁻¹ exerce une influence importante sur le dégagement des gouttelettes lors de l'application par rouleau et sur la facilité d'application par brosse où l'on l'apprécie par le temps de recouvrement. On a discuté également l'effet d'autres paramètres rhéologiques, tels que la pseudoplasticité et le facteur de récuperation lors du roulage et du brossage et l'on l'a comparé avec les résultats déjà parus.

On a établi le rapport entre l'influence d'une part du type de pigment de dioxyde de titane et l'augmentation du taux de fabrication et d'autre part de la rhéologie de la peinture qui en résulte, les caractéristiques d'application par brosse et le dégagement de gouttelettes par le rouleau.

Hohe Scherrheologie von Malerlacken—ihr Einfluss auf Malerrollen und Pinselauftrag

Zusammenfassung

Die hohe Scherrheologie mehrerer Gruppen von matten Latexfarben und Alkydharzgrundemaillen wurde gemessen und mit den sich beim Auftragen mittels Malerrolle und Pinsel zeigenden Eigenschaften in Beziehung gebracht.

Es wurde gezeigt, dass Viskosität bei 1000 Sek.⁻¹ in enger Beziehung mit dem als Spreitungszeit bewerteten Abfliegen bei Rollenauftrag, sowie leichter Verstreichbarkeit mit dem Pinsel steht. Ebenfalls

Introduction

Refs. 7, 1-3

In 1967, a method was published⁷ of rheological characterisation of coatings using inexpensive laboratory viscometers, which were available readily. This method, called the "Viscosity profile technique" had its limitations, and it soon became obvious that a sophisticated cone-and-plate viscometer would be necessary for the detailed rheological study of a wide range of surface coatings. besprochen und mit früher veröffentlichten Resultaten verglichen wurde die Wirkung anderer rheologischer Parameter, wie Pseudoplastizität und Erholungsfaktor beim Walzen und Streichen.

Der Einfluss der Titandioxidqualität und der Einfluss besserer Fabrikationsmethoden wurden auf die resultierende Anstrichfarbenrheologie, das Abfliegen von der Rolle sowie die Streichbarkeit bezogen.

Hence a Weissenberg cone-and-plate rheoviscometer was obtained as a means of carrying out such investigations. Examination of the literature revealed a wealth of information on the relationship of low shear rheology to the flow and sagging properties of coatings. There was, however, relatively little published work on the relationship of high shear rheology to brushing properties of paints¹⁻³ and none on rolling properties of architectural paints.

In the course of servicing the paint industry in the Eastern States of Australia during 1972-73, many enquiries were

*Presented at the 16th Annual Convention of OCCA Australia held at Marysville, Victoria, from 20 to 23 June 1974.

received regarding the tendency of architectural paints to fly off a normal hand roller. In view of an apparent commercial interest in this subject and the lack of published work in the high shear rheological areas, it was decided to attempt to relate rheological parameters with both brushing and roller fly-off properties.

Parameters investigated were:

- 1. Viscosity at 10⁴ sec⁻¹ shear rate
- 2. Viscosity at 10³ sec⁻¹ shear rate
- 3. Viscosity at 10 sec⁻¹ shear rate
- 4. Degree of pseudoplasticity at 10³ sec⁻¹ shear rate
- 5. Recovery of viscosity after a specific shearing schedule.

All readings were taken at 25° C and 55 per cent relative humidity (RH).

These parameters were established for a range of flat latex paints and alkyd undercoats using a Weissenberg rheoviscometer and compared with brushability and roller fly-off properties as assessed by several operators.

The effects of scaling up the manufacturing process and changing the grade of TiO_2 used in a flat latex formulation were also examined with relation to rheological properties.

Experimental

Paint manufacture

Each series of paints was made up in the laboratory using a basic formulation modified slightly to obtain varying rheologies (Appendix D). Table 1 shows details of the manufacturing method used for each series.

| Table 1 |
|-----------------------------|
| Paint manufacturing methods |

| | Series A | Series B | Series C |
|---|---------------------|---|---|
| Paint type | Flat latex | Alkyd undercoat | Flat latex |
| Formulation variable | Protective colloid | Synthetic clay and/or soya lecithin | Quantity made. Protective colloid. TiO ₂ grade. |
| Mixer revs (rpm) | 3200 | _ | 3200 |
| Ball mill revs (rpm) | <u> </u> | 100 | |
| Ball mill volume/ internal diameter | — | 1.136 dm ³ 10.5 cm | _ |
| Cavitation blade diameter (cm) | 3.80 | - | 6.8 |
| Pot diameter (cm) | 7.3 | 1 <u></u> 1 | 10.4 |
| Mill base volume (cm ³) | 137 | 474 | 549 |
| Ball mill load ratio: volume of balls to volume of balls plus charge (%) | — | 70:70 | _ |
| Approximate volume of paint produced | 284 cm ³ | 568 cm ³ | 1136 cm ³ |

The basic formulations used in series C were those in series A which performed best and worst for roller fly-off. The titanium dioxide grade used in four of these formulations was then varied in order to ascertain the significance of this factor.

Each paint was allowed to stand for three weeks at 25°C and 50 per cent RH before rheological examination on the Weissenberg rheoviscometer.

Rheological examination

The programme of examination on the rheoviscometer for each series is listed in Table 2.

, Table 2 Programme of examination

| Series A | Series B | Series C |
|--------------------------------------|--|---|
| Flat latex | Alkyd undercoat | Flat latex |
| 89.7 sec ⁻¹ for 3 minutes | 89.7 sec ⁻¹ for 5 minutes | 89.7 sec ⁻¹ for 3 minutes |
| | 8.97—712 19 readings | 8.97-2250 25 readings |
| | 712-8.97 4 readings | 2250—8.97 5 readings |
| | Flat latex 89.7 sec ⁻¹ for | Flat latex Alkyd undercoat 89.7 sec ⁻¹ for 3 minutes 89.7 sec ⁻¹ for 5 minutes 8.97—2250 8.97—712 25 readings 19 readings 2250—8.97 712—8.97 |

Log shear stress was plotted against log shear rate. From this plot, viscosities at different shear rates were determined. The plot was then extrapolated to a shear rate of 10^4 sec^{-1} and viscosities at 10^3 sec^{-1} and 10^4 sec^{-1} (extrapolated value) were assessed from the graph.

The slopes of the plots at $10^3 \sec^{-1}(n)$ were also recorded. These slopes gave an indication of the degree of pseudoplasticity at $10^3 \sec^{-1}$.

At approximately the same time the paints were tested for brushing and rolling according to the methods detailed below.

Assessment of brushing

A standard area of liner-board (as used for facing "Gyprock" or paper-faced plaster board) was sealed using a proprietary flat latex paint (a proprietary undercoat in the case of series B). A 50 cm³ sample of the test paint was brushed out with a new pre-wetted 5-cm brush over this area (423 cm³) using a standard brushing pattern. The time required fully to cover this area was recorded as a rating of ease of brushing. Shorter times were given lower ranking as an indication of easier brushing.

The brush was cleaned and spun dry using 50 strokes of a Mira Spin (Shurline Manufacturing Inc.) brush spinner before the next test was begun.

Roller fly-off test

A 100 cm³ sample of paint was poured into a roller tray ("Rota Cota" tray 35.5×22 cm).

A roller with 0.95 cm long synthetic fibres, and of dimensions 17.2 cm wide and diameter 3.80 cm was then saturated with the paint. The paint was rolled in a standard manner on to 1.54 m² of vertical liner-board (pinned to a backing board) and the fly-off collected on clean brown paper at the bottom of the liner-board. The liner-board was set on to the backing board 122 cm from the floor (Fig. 1). The number and size of paint spots falling on to the brown paper were used as a criterion for roller fly-off. Each paint was then ranked subjectively by four operators for degree of roller fly-off. The paints showing smaller and fewer spots were given lower rankings to indicate better resistance to fly-off.

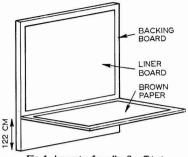


Fig. 1. Apparatus for roller fly-off test

Results and calculations

Series A and B

The Appendices (Tables 6, 8 and 10) show results obtained with the rheoviscometer from the three series of paints.

From this information, a graph (Fig. 2) of log shear stress versus log shear rate was plotted, and the required rheological parameters were recorded for each paint (see Appendices—Tables 7, 9 and 11). A typical log/log plot is shown in Table 8: n is the ratio of log shear stress to log shear rate and relates to the degree of dilatancy or pseudoplasticity of the material under test; values of n greater than unity indicate dilatancy and values less than unity, pseudoplasticity.

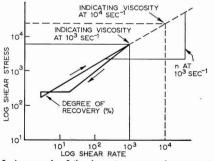


Fig. 2. An example of the shear stress versus shear rate curves, which were plotted from experimental results and used to obtain rheological parameters for each paint

All rheological parameters were then plotted against average brushing and roller fly-off rankings (see Figs. 3-10 in Appendix A and Figs. 11-20 in Appendix B). Relationships were observed by examination of the plots. Spearman correlation coefficients were also calculated in the initial latex series if the graphs indicated a relationship. These were not calculated in sections B and C due to the number of samples in the series. If the rankings varied excessively from one operator to another, the result was not plotted on the graph.

For the purposes of calculating correlation coefficients, the roller fly-off results used were those of the operator (PW), which were closest to the average; the results are listed in Table 3 and a summary of the relationships observed from the graphs appears in Table 4.

Table 3 Correlation coefficient results

| Rheological variable | Spearman r* |
|--|---|
| Viscosity at 10 ³ sec-1 | 0.5 |
| | 0.6 |
| Recovery factor | -0.5 |
| Product of recovery factor | |
| and viscosity at 103 sec-1 | 0.7 |
| Viscosity at 10 ⁴ sec ⁻¹ | +0.3 |
| | +0.5 |
| | +0.5 |
| | +0.7 |
| | -0.5 |
| | -0.5 |
| | |
| and viscosity at 10 ³ sec ⁻¹ | -0.5 |
| | Viscosity at 10 ³ sec ⁻¹ Viscosity at 10 ⁴ sec ⁻¹ Recovery factor Product of recovery factor and viscosity at 10 ³ sec ⁻¹ Viscosity at 10 ⁴ sec ⁻¹ Viscosity at 10 ⁴ sec ⁻¹ Viscosity at 10 ³ sec ⁻¹ Recovery factor Recovery factor Product of recovery factor |

correlation = -1.0 indicates perfect inverse correlation = 0 indicates no relationship (see Appendix E)

 Table 4

 A summary of relationships observed from the graphical results

| Physical variable | Rheological variable | Series A (Flat latex) | Series B (Alkyd undercoat) |
|------------------------|---|------------------------------|-------------------------------|
| Roller fiy-off rank | Viscosity at 10 ⁴ sec ⁻¹ | Inverse trend | No relationship |
| | Viscosity at 10^3 sec ⁻¹ | Very strong inverse trend | Very strong inverse trend |
| | $n \text{ at } 10^3 \text{ sec}^{-1}$ | No correlation | Positive trend |
| | Recovery (%) | Inverse trend | No correlation |
| Brushing rank | Viscosity at 10^4 sec ⁻¹ | Positive trend | Very positive trend |
| | Viscosity at 10^3 sec ⁻¹ | Positive trend | Very positive trend |
| | $n \text{ at } 10^3 \text{ sec}^{-1}$ | Insufficient variation | Inverse trend |
| | Recovery (%) | Positive trend | No correlation |

Series C

Effect of pigment grade on fly-off

The rankings of formulae 24/119/1-4 (paints based on TiO₂, grade I) and formulae 24/119/5-8 (based on TiO₂, grade II) were separately summed and averaged, in order to compare the effect of different TiO₂ grades on fly-off:

| | Grade I | Grade II |
|--------------|---------|----------|
| Rank average | 4.57 | 4.25 |

No significant difference in performance was evident over a range of four formulations.

Effect of pigment grade on brushability

A similar procedure was followed as given above for assessing the effect on fly-off, but average brushing times were summed and averaged:

| | Grade I | Grade II |
|------------------------------|---------|----------|
| Average brush time (seconds) | 55 | 59 |

No consistent difference in performance was evident over the range of four formulations.

Effect of pigment grade on rheology

In some formulations, grade I tended to give lower viscosities than grade II; however, in other formulations the reverse occurred. The same was found for *n*-values and recovery factors.

(See Appendix C, Tables 10 and 11)

Effect of method of manufacture on rheology

An examination of Table 12 (Appendix C) shows that manufacturing on a larger scale gave paints with lower viscosities at higher rates of shear.

Effect of method of manufacture on brushing

An examination of Table 5 indicates that the method of manufacture had little effect on brushability.

Table 5 Variation of brushability

| Formulation | Ave | rage brush time (seconds) |
|-------------|----------|------------------------------|
| Large scale | | |
| 24/119/2 | 60 | |
| 24/119/3 | 54 55 | |
| 24/119/4 | 55 | Average: 56 |
| Small scale | | |
| 30/21/12 | 64 | |
| 30/21/17 | 58 | |
| 30/21/18 | 49 | Average: 57 |

Discussion

Rheological parameters: roller fly-off relationships

The results obtained indicate that both viscosity at 10^3 and $10^4 \sec^{-1}$ and recovery factor play an important part in the roller fly-off properties of flat latex paints. A similar relationship between roller fly-off and viscosity at $10^3 \sec^{-1}$ was observed in the series of undercoats (Fig. 11), however, viscosity at $10^4 \sec^{-1}$ and recovery seemed to have little effect on fly-off performance.

A high pseudoplasticity (n) tends to give worse fly-off performance in the case of the undercoats, but n has little effect on fly-off performance in the case of the latex series. In view of the above, therefore, it can be stated with reasonable certainty that the viscosity at approximately 10^3 sec^{-1} is the rheological property of a paint which relates most closely with roller fly-off performance; that is, the higher the viscosity at approximately 10^3 sec^{-1} the lower will be the tendency for the paint to fly off the roller.

Rheological parameters: brushability relationships

Results obtained in series A indicate that there are relationships between brushability and viscosity (at both 10^4 and 10^3 sec⁻¹) and brushability and percentage recovery in flat latex paints.

Results obtained from series *B* (undercoats) indicate relationships between brushability and viscosity (at both 10^3 and 10^4 sec⁻¹) and brushability and the degree of pseudoplasticity of the paint. The recovery factor and brushability were unrelated in the undercoat series (Fig. 19).

In light of the above, viscosities at 10^4 and 10^3 sec⁻¹ are probably the most important rheological properties affecting brushability. The lower the viscosity at shear rates in the range 10^3 to 10^4 sec⁻¹ the easier will it be to brush out the paint.

Effect of method of manufacture on rheology and brushing of flat latex paint

The fact that the larger scale manufacturing method gave lower viscosities (at high shear rates) than the smaller scale manufacturing method indicates that the larger scale method should give a product which will brush more easily. This, in fact, was not found to be the case. The average brushing times of the larger scale manufactured paints were marginally lower than those of the smaller scale paints, but this difference would almost certainly be within the experimental error of the test method. Presumably, if more samples had been included in the experiment more noticeable brushing differences might have been observed.

Discussion of methods

Roller fly-off

The main disadvantage of this method was the fact that rolling the paint and ranking the fly-off depended upon a subjective assessment. This was overcome to some extent by recording averages of rankings in order to obtain a more general picture of the fly-off ranking. In addition, it cannot be assumed that the operator rolled out each paint in exactly the same manner, even though a standard procedure was followed.

In view of this inherent subjectivity, only "trends" could be observed in the plots of rheological parameters versus ranking. Some plots, however, were found to indicate particularly close relationships (Figs. 3, 5, 11).

Brushing

The disadvantages in the brushing method were similar to those of the fly-off method: subjectivity was the problem.

In series A, the duplication of each set of brushing times and rankings was only moderate. In series B, the duplication of results was much closer than that in series A. In series C, duplication of brushing times was unacceptable, although rankings correlated particularly well. The reason why the undercoats gave better duplication was probably due to the fact that the rheological differences in this series were much greater than the variations in rheology in the latex series.

The large amount of latex paint required to cover the area without significant evaporation of solvent occurring during brushing meant that any variations in brushing were difficult to assess. On the other hand, the amount of undercoat required to cover the area without significant evaporation during brushing was such that brushing differences could be maximised and positively ranked. In other words, a small amount of undercoat could be used and worked in order to cover the area, thus highlighting the brushing differences without evaporation becoming a significant variable in the test.

119

Conclusion

Refs. 1-6

There is a close relationship between roller fly-off and the viscosity at 10^3 sec^{-1} shear rate of architectural latex paints and undercoats.

The brushing properties of architectural latex paints and undercoats bear close relationship to viscosities at both 10^4 and 10^3 sec⁻¹.

Pseudoplasticity at high rates of shear and also recovery factors affect brushing and rolling properties in some paint formulations.

The grade of titanium dioxide pigment used in a flat latex paint affects roller fly-off and brushing in a manner specific to the formulation being used.

The scaling-up of a particular method of manufacture of flat latex paints may influence viscosities at higher rates of shear.

Discussion of conclusions in light of previous work on high shear properties of paints

In 1966 Beeferman and Bergren² plotted brushing viscosities of latex paints against spreading rates (brushability) and made the following comment:

"We can never hope to predict spreading rates exactly with viscosity data alone, because there are too many other variables involved, such as humidity, ventilation, intention of the applicator and temperature of substrate."

In this investigation, the variables quoted above, with the exception of "operator intention", were minimised, since the experiments were performed in air-conditioned laboratories under constant conditions of temperature and humidity. Thus, these variables are not the only ones affecting brushing; on the basis of the current investigation, it has been shown that other rheological variables, such as pseudoplasticity and recovery properties, in addition to brushing viscosity, can also affect brushing properties.

In 1966 Pierce and Donegan¹ qualitively related the brushability with high shear viscosity of four interior latex paints and found the paint with the highest viscosity at high rates of shear was the most difficult to brush. The findings of these investigators were similar to the conclusions on brushability stated in this study. However, in this investigation, strong relationships between viscosities at both 1000 sec⁻¹ and brushability were observed: most authors assume brushing viscosity is of the order of 10 000 sec⁻¹. The evidence from this work shows that not onl α viscosities at shear rates lower than 10⁴ sec⁻¹, but also the degree of pseudoplasticity at high shear rates and the recovery properties can affect the brushability of a paint.

In 1964 Patton³ found that for adequate brushability, flat latex paints must have viscosities of 0.05 to 0.09 N s m⁻² at shear rates of the order of 10⁴ scc⁻¹, and for alkyd paints, the viscosity at this rate of shear should be 0.1 to 0.25 N s m⁻². In this investigation, Patton's results were corroborated in the case of the latex paints. Undercoats with good brushing performance gave similar viscosities, only slightly higher (0.27 N s m⁻²) than those reported by Patton³. However, the latex paints examined by Patton all had similar viscosities at a shear rate of 10⁴ scc⁻¹, yet operators were able to detect differences between the paints.

(References 4-6 are included for further reading on the subject.)

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[Appendices A to E commence on following pages]

Appendix A

Results and calculations for paint series A

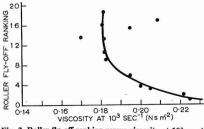
Table 6

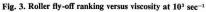
| Formulation number: 30/21/ | 1 | 2 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 17 | 19 |
|---------------------------------|-------|-------|-------|-------|-------|-------|-------|----------|--------|-------------------|-------|-------|-------|-------|--------|-------|-------|------|
| Shear rate (sec ⁻¹) | | | | | | | | Viscosit | y (Nsn | 1 ⁻²) | | | | | | | | |
| 2250 | 0.162 | 0.154 | 0.157 | 0.153 | 0.146 | 0.137 | 0.137 | 0.142 | 0.127 | 0.156 | 0.159 | 0.145 | 0.144 | 0.134 | Splash | 0.136 | 0.133 | 0.15 |
| 1790 | 0.173 | 0.167 | 0.170 | 0.166 | 0.155 | 0.152 | 0.157 | 0.159 | 0.140 | 0.168 | 0.179 | 0,163 | 0.162 | 0.149 | 0.122 | 0.152 | 0.143 | 0.16 |
| 1420 | 0.186 | 0.178 | 0.182 | 0.178 | 0.177 | 0.163 | 0.161 | 0.173 | 0.153 | 0.197 | 0.278 | 0.176 | 0.173 | 0.160 | 0.133 | 0.162 | 0.155 | 0.18 |
| 1130 | 0.200 | 0.192 | 0.197 | 0.192 | 0.188 | 0.177 | 0.174 | 0.192 | 0.165 | 2.217 | 0.219 | 0.191 | 0.189 | 0.175 | 0.148 | 0.175 | 0.167 | 0.19 |
| 897 | 0.217 | 0.211 | 0.215 | 0.214 | 0.202 | 0.192 | 0.192 | 0.210 | 0.179 | 0.241 | 0.240 | 0.210 | 0.208 | 0.192 | 0.149 | 0.192 | 0.186 | 0.21 |
| 712 | 0.239 | 0.234 | 0.235 | 0.232 | 0.227 | 0.215 | 0.213 | 0.228 | 0.183 | 0.264 | 0.262 | 0.234 | 0.226 | 0.213 | 0.163 | 0.207 | 0.192 | 0.23 |
| 566 | 0.261 | 0.255 | 0.256 | 0.255 | 0.246 | 0.216 | 0.219 | 0.238 | 0.203 | 0.294 | 0.285 | 0.238 | 0.232 | 0.219 | 0.177 | 0.216 | 0.211 | 0.24 |
| 449 | 0.261 | 0.269 | 0.266 | 0.263 | 0.254 | 0.237 | 0.241 | 0.263 | 0.223 | 0.303 | 0.294 | 0.260 | 0.254 | 0.245 | 0.195 | 0.237 | 0.235 | 0.26 |
| 357 | 0.287 | 0.292 | 0.294 | 0.291 | 0.280 | 0.261 | 0.266 | 0.293 | 0.250 | 0.338 | 0.322 | 0.288 | 0.280 | 0.272 | 0.214 | 0.261 | 0.261 | 0.29 |
| 283 | 0.315 | 0.319 | 0.325 | 0.318 | 0.309 | 0.290 | 0.300 | 0.329 | 0.277 | 0.378 | 0.357 | 0.322 | 0.308 | 0.304 | 0.240 | 0.290 | 0.290 | 0.32 |
| 225 | 0.348 | 0.352 | 0.356 | 0.364 | 0.348 | 0.318 | 0.329 | 0.369 | 0.324 | 0.418 | 0.393 | 0.358 | 0.342 | 0.338 | 0.267 | 0.327 | 0.327 | 0.35 |
| 179 | 0.384 | 0.388 | 0.396 | 0.404 | 0.388 | 0.358 | 0.369 | 0.408 | 0.362 | 0.464 | 0.432 | 0.396 | 0.385 | 0.344 | 0.277 | 0.365 | 0.365 | 0.42 |
| 142 | 0.435 | 0.435 | 0.441 | 0.451 | 0.431 | 0.366 | 0.415 | 0.465 | 0.401 | 0.528 | 0.480 | 0.440 | 0.423 | 0.423 | 0.310 | 0.382 | 0.397 | 0.44 |
| 119 | 0.444 | 0.464 | 0.464 | 0.474 | 0.453 | 0.413 | 0.437 | 0.529 | 0.432 | 0.580 | 0.536 | 0.472 | 0.447 | 0.444 | 0.341 | 0.423 | 0.431 | 0.46 |
| 89.7 | 0.491 | 0.512 | 0.516 | 0.527 | 0.506 | 0.463 | 0.490 | 0.563 | 0.485 | 0.665 | 0.567 | 0.527 | 0.498 | 0.502 | 0.379 | 0.471 | 0.484 | 0.52 |
| 71.2 | 0.548 | 0.520 | 0.574 | 0.583 | 0.559 | 0.515 | 0.544 | 0.635 | 0.548 | 0.697 | 0.633 | 0.586 | 0.549 | 0.539 | 0.421 | 0.527 | 0.535 | 0.57 |
| 56.6 | 0.594 | 0.649 | 0.628 | 0.648 | 0.629 | 0.576 | 0.618 | 0.760 | 0.622 | 0.784 | 0.698 | 0.653 | 0.613 | 0.627 | 0.477 | 0.594 | 0.599 | 0.64 |
| 44.9 | 0.682 | 0.718 | 0.706 | 0.735 | 0.699 | 0.657 | 0.690 | 0.811 | 0.697 | 0.882 | 0.792 | 0.743 | 0.690 | 0.697 | 0.539 | 0.663 | 0.669 | 0.73 |
| 35.7 | 0.773 | 0.795 | 0.785 | 0.835 | 0.787 | 0.731 | 0.770 | 0.924 | 0.793 | 1.008 | 0.880 | 0.841 | 0.770 | 0.790 | 0.608 | 0.748 | 0.755 | 0.81 |
| 28.3 | 0.876 | 0.882 | 0.884 | 0.934 | 0.884 | 0.812 | 0.873 | 1.050 | 0.910 | 1.150 | 0.992 | 0.943 | 0.873 | 0.884 | 0.690 | 0.855 | 0.855 | 0.91 |
| 22.5 | 0.991 | 1.010 | 1.005 | 1.040 | 0.987 | 0.951 | 0.987 | 1.200 | 1.013 | 1.267 | 1.124 | 1.075 | 1.000 | 1.009 | 0.764 | 0.950 | 0.964 | 1.06 |
| 17.9 | 1.106 | 1.160 | 1.120 | 1.212 | 1.117 | 1.055 | 1.117 | 1.352 | 1.196 | 1.440 | 1.274 | 1.211 | 1.117 | 1.117 | 0.883 | 1.050 | 1.103 | 1.21 |
| 14.2 | 1.275 | 1.330 | 1.310 | 1.331 | 1.232 | 1.197 | 1.254 | 1.528 | 1.324 | 1.620 | 1.449 | 1.370 | 1.268 | 1.310 | 1.000 | 1.170 | 1.233 | 1.37 |
| 11.3 | 1.434 | 1.520 | 1.450 | 1.575 | 1.425 | 1.398 | 1.425 | 1.770 | 1.527 | 1.841 | 1.649 | 1.550 | 1.451 | 1.469 | 1.186 | 1.300 | 1.403 | 1.52 |
| 8.97 | 1.583 | 1.640 | 1.630 | 1.795 | 1.615 | 1.520 | 1.620 | 1.784 | 1.730 | 2.096 | 1.828 | 1.767 | 1.640 | 1.630 | 1.310 | 1.520 | 1.612 | 1.76 |

Table 7

| Formulation number: 30/21, | / 1 | 2 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|--|------------------|------------------|--------------------|----------------------|--------------------|--------------------|----------------------|------------------------|----------------------|-----------------------|-------------|------------------|----------------------|------------------------|----------------------|------------------------|--------------------------|--------------------|
| Viscosity (N s m ⁻²) at 10 ⁴ sec ⁻¹ | 0.094 | 0.088 | 0.095 | 0.097 | 0.835 | 0.086 | 0.075 | 0.081 | 0.076 | 0.085 | 0.095 | 0.082 | 0.084 | 0.074 | 0.065 | 0.075 | 0.075 | 0.084 |
| Viscosity (N s m ⁻²) at 10 ³ sec ⁻¹ | 0.222 | 0.205 | 0.212 | 0.208 | 0.200 | 0.183 | 0.182 | 0.195 | 0.170 | 0.222 | 0.225 | 0.200 | 0.195 | 0.182 | 0.149 | 0.182 | 0.181 | 0.202 |
| Recovery factor (%) + | 15.4 | 9.43 | +9.62 | +1.73 | 0.0 | 2.04 | 0.0 | 1.64 | +3.57 | +5.88 | +6.78 | +5.72 | +7.55 | 0.0 | | +8.17 | 0.0 | +1.75 |
| Pseudoplasticity factor n at 10 ³ sec ⁻¹ | 0.648 | 0.651 | 0.662 | 0.653 | 0.642 | 0.696 | 0.607 | 0.626 | 0.650 | 0.570 | 0.625 | 0.635 | 0.628 | 0.623 | 0.626 | • 0.616 | 0.618 | 0.622 |
| Fly-off ranking—Operator: | | | | | æ., | | | | | | | | | | | | | |
| PW AK IH JD | 2 3 2 2 | 4 2 3 4 | 8 11 12 8 | 16 18 17 17 | 7 8 5.5 6 | 9 9 9.5 9 | 13 14 13 13 | 15 16 15.5 15 | 14 12 14 14 | 12 13 9.5 12 | 1 1 1 | 3 5 4 3 | 5.5 7 5.5 5 | 10.5 10 11 10 | 10.5 6 8 11 | 17.5 17 18 18 | 17.5 15 15.5 16 | 5.5 4 7 7 |
| Average fly-off ranking | 2.25 | 3.25 | (9.75) | * 17 | (6.63) | 9.03 | 13.25 | 15.38 | 13.50 | (11.63) | 1 | 3.75 | 5.75 | 10.38 | (8.88) | 17.55 | 16.0 | (5.88) |
| Brushing time (sec) 21/1/74 | _ | 67.1 | 58 | 47 | 72 | 58 | 58 | 63 | 46 | 81 | 64 | 88 | 83 | 66 | 60 | 51 | 44 | 68 |
| Brushing ranking 21/1/74 | | 12 | 7 | 3 | 14 | 7 | 7 | 9 | 2 | 10 | 10 | 17 | 16 | 11 | 8 | 4 | 1 | 13 |
| Brushing time (sec) 22/1/74 | _ | 69 | 81 | 57 | 65 | 48 | 53 | 63 | 45 | 78 | — | 86 | 68 | 46 | 62 | 65 | 54 | _ |
| Brushing ranking 22/1/74 | _ | 14 | 16 | 6 | 9 | 3 | 4 | 8 | 1 | 15 | - | 17 | 12 | 2 | 7 | 9 | 5 | _ |
| Average brushing time (sec) | \rightarrow | 68 | (69)* | 52 | 69 | 53 | 56 | 63 | 46 | 80 | (64) | 87 | (75) | (56) | 61 | (58) | 49 | (68) |
| Average brushing ranking | | 13 | _ 4 | 45 | _ | 5 | 5.5 | 8.5 | 1.5 | 15 | 10 | 17 | 14 | _ | 7.5 | | 3 | - |

* Results in brackets were not plotted on graphs due to wide ranking differences between operators





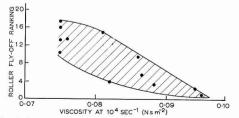


Fig. 4. Average roller fly-off ranking versus viscosity at 10⁴ sec⁻¹

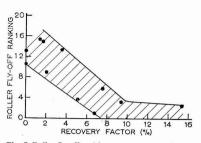


Fig. 5. Roller fly-off ranking versus recovery factory

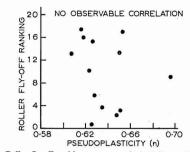


Fig. 6. Roller fly-off ranking versus pseudoplasticity coefficient (n)

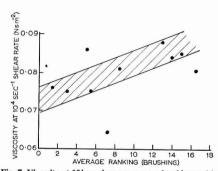


Fig. 7. Viscosity at 10⁴ sec⁻¹ versus average brushing ranking

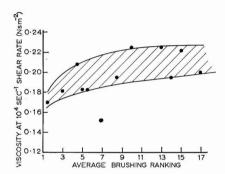


Fig. 8. Viscosity at 10³ sec⁻¹ versus average brushing ranking

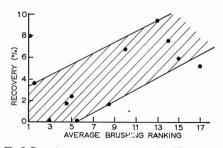


Fig. 9. Percentage recovery versus average brushing ranking

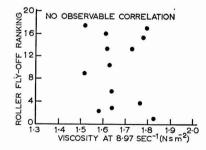


Fig. 10. Average fly-off ranking versus viscosity at 8.97 sec⁻¹

Appendix B

J. D. DORMON ET AL. JOCCA

| Results a | and c | calculations | for | paint | series | B |
|------------------|-------|--------------|-----|-------|--------|---|
|------------------|-------|--------------|-----|-------|--------|---|

| Table 8 | | | | | | | | | | |
|---------------------------------|-------|-------|-------|-------|---------------|----------------------|---------|-------|-------|-------|
| Formulation number: 17/91/ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Shear rate (sec ⁻¹) | | | | S | hear stress (| (N m ⁻²) | | | | |
| 8.97 | 31.0 | 23.6 | 59.0 | 28.0 | 19.2 | 11.2 | 56.0 | 11.8 | 23.6 | 26.5 |
| 11.3 | 38.5 | 29.5 | 68.0 | 29.5 | 22.1 | 19.0 . | 62.0 | 14.8 | 26.5 | 29.5 |
| 14.2 | 45.7 | 35.5 | 82.9 | 34.0 | 25.0 | 23.5 | 74.0 | 17.7 | 29.5 | 35.5 |
| 17.9 | 53.0 | 44.3 | 91.5 | 38.5 | 26.5 | 26.5 | 85.6 | 20.7 | 32.5 | 41.5 |
| 22.5 | 65.0 | 50.0 | 100.0 | 44.3 | 29.5 | 29.5 | 94.0 | 22.2 | 35.5 | 47.2 |
| 28.3 | 73.7 | 59.0 | 118.0 | 44.3 | 32.5 | 35.4 | . 115.0 | 23.6 | 40.0 | 53.0 |
| 35.7 | 85.8 | 71.0 | 142.0 | 53.0 | 27.0 | 38.4 | 127.0 | 26.5 | 46.0 | 62.0 |
| 44.9 | 118.0 | 83.0 | 162.0 | 62.0 | 42.7 | 44.2 | 148.0 | 29.5 | 53.0 | 71.0 |
| 56.6 | 133.0 | 112.0 | 186.0 | 72.2 | 50.0 | 54.5 | 165.0 | 35.5 | 59.0 | 82.8 |
| 71.2 | 148.0 | 124.0 | 222.0 | 84.0 | 60.2 | 65.0 | 198.0 | 42.8 | 71.0 | 97.2 |
| 89.7 | 174.0 | 148.0 | 286.0 | 97.2 | 72.0 | 77.0 | 234.0 | 50.0 | 82.8 | 112.0 |
| 113 | 200.0 | 168.0 | 300.0 | 115.0 | 88.2 | 88.5 | 265.0 | 62.0 | 100.0 | 133.0 |
| 142 | 234.0 | 192.0 | 350.0 | 133.0 | 103.0 | 108.0 | 310.0 | 77.0 | 118.0 | 168.0 |
| 179 | 269.0 | 228.0 | 408.0 | 172.0 | 124.0 | 130.0 | 363.0 | 91.5 | 139.0 | 192.0 |
| 225 | 310.0 | 265.0 | 470.0 | 198.0 | 162.0 | 168.0 | 420.0 | 109.0 | 177.0 | 230.0 |
| 283 | 370.0 | 310.0 | 500.0 | 234.0 | 192.0 | 198.0 | 480.0 | 136.0 | 206.0 | 269.0 |
| 357 | 413.0 | 360.0 | 650.0 | 270.0 | 234.0 | 235.0 | 547.0 | 177.0 | 242.0 | 310.0 |
| 449 | 473.0 | 423.0 | 665.0 | 320.0 | 271.0 | 275.0 | 665.0 | 210.0 | 295.0 | 363.0 |
| 566 | 507.0 | 486.0 | 702.0 | 370.0 | 325.0 | 325.0 | 767.0 | 254.0 | 350.0 | 422.0 |
| 712 | 665.0 | 560.0 | 770.0 | 428.0 | 385.0 | 384.0 | 830.0 | 300.5 | 390.0 | 495.0 |

| Table 9 | | | | | | | | | | |
|---|-----------------------|-----------------------|-------------------------|-----------------------|-----------------------------|-----------------------|--------------------------|-----------------------------|---------------------------|--------------------------|
| Formulation number: 17/91/ 1 | 2 | 3 | 4 | 5 | 6 | | 7 | 8 | 9 | 10 |
| Viscosity at 104sec ⁻¹ (N s m ⁻²) | 0.34 | 0.34 | 0.310 | 0.275 | 0.275 | 0.285 | 0.465 | 0.280 | 0.302 | 0.305 |
| Viscosity at 103sec-1 (N s m-2) | 0.79 | 0.62 | 0.96 | 0.550 | 0.490 | 0.490 | 1.080 | 0.405 | 0.525 | 0.620 |
| Recovery factor (%) | +14.3 | +6.7 | 0.0 | +16.3 | +22.4 | +6.1 | +3.7 | 0.0 | +12.3 | +11.3 |
| Pseudoplasticity factor (n) at 10^3 sec ⁻¹ shear rate | e 0.640 | 0.677 | 0.508 | 0.698 | 0.747 | 0.763 | 0.630 | 0.848 | 0.765 | 0.678 |
| Fly-off ranking—operator: PW AK IH JD Average fly-off ranking | 6 5 6 - 5.50 | 2 4 4.5 3.62 | 1 2 1 2 1.5 | 4 6 4.5 5.12 | 9 8 9.5 10 9.13 | 7 7 7 7 7 | 5 3 2 3 3.25 | 10 9 9.5 9 9.38 | 8 10 8 8 8.50 | 3 1 2 1 1.75 |
| Brushing time (sec) 21/3/74 | 114 | 103 | 140 | 80 | 65 | 78 | 138 | 81 | 90 | 130 |
| Brushing ranking 21/3/74 | 7 | 6 | 9 | 3 | 1 | 2 | 10 | 4 | 5 | 8 |
| Brushing time 25/3/74 | 107 | 108 | 138 | 80 | 81 | 87 | 170 | 67 | 87 | 116 |
| Brushing ranking 25/3/74 | 6 | 7 | 9 | 2 | 3 | 4.5 | 10 | 1 | 4.5 | 8 |
| Average brushing time (sec) | 111 | 105 | 139 | 80 | 73 | 83 | 154 | 74 | 88 | 123 |
| Average brushing ranking | 6.5 | 6.5 | 9 | 2.5 | 2 | 3.25 | 10 | 2.5 | 4.75 | 8 |
| Ranking of average brushing time | 7 | 6 | 9 | 3 | 1 | 4 | 10 | 2 | 5 | 8 |

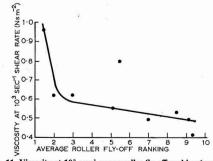


Fig. 11. Viscosity at 10³ sec⁻¹ versus roller fly-off ranking (average)

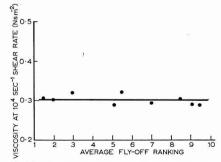


Fig. 12. Viscosity at 10^4 sec^{-1} versus fly-off ranking (average) pseudoplasicity coefficient (n)

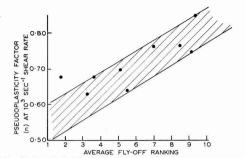


Fig. 13. Pseudoplasicity coefficient (n) at 10^3 sec^{-1} versus average fly-off ranking

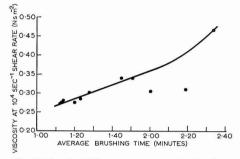


Fig. 15. Viscosity at 10⁴ sec⁻¹ versus average brushing time

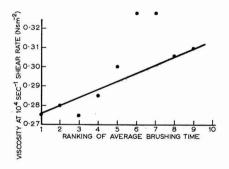
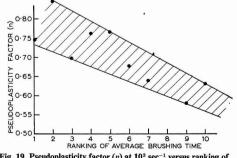
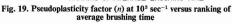


Fig. 17. Viscosity at 10⁴ sec⁻¹ versus ranking of average brushing time





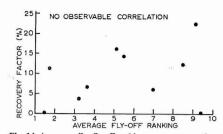


Fig. 14. Average roller fly-off ranking versus recovery factor

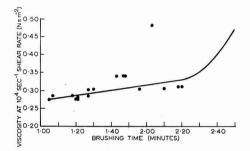


Fig. 16. Brushing time versus viscosity at 10⁴ sec⁻¹

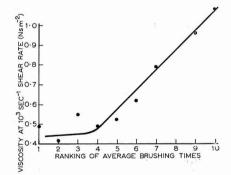


Fig. 18. Viscosity at 10³ sec⁻¹ versus ranking of average brushing times

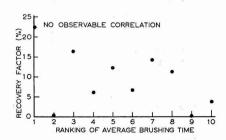


Fig. 20. Recovery factor versus ranking of average brushing time

Results and calculations for paint series C Table 10

| Formulation number: 24/119/ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---------------------------------|-------|-------|-------|-------------|----------------------|--------|-------|-------|
| Shear rate (sec ⁻¹) | | | S | hear stress | (N m ⁻²) | | | |
| 8.97 | 14.7 | 16.4 | 13.9 | 12.5 | 16.6, | 16.5 | 11.7 | 11.9 |
| 11.3 | 16.4 | 18.1 | 16.1 | 15.2 | 18.3 | 17.8 | 13.4 | 13.4 |
| 14.2 | 17.5 | 20.0 | 17.2 | 16.6 | 20.5 | 19.7 | 16.1 | 16.1 |
| 17.9 | 19.2 | 22.2 | 19.2 | 18.0 | 22.2 | 22.0 | 17.2 | 17.5 |
| 22.5 | 21.4 | 24.5 | 20.9 | 20.3 | 24.7 | · 23.9 | 19.4 | 19.4 |
| 28.3 | 23.1 | 26.7 | 22.7 | 22.2 | 27.5 | 26.4 | 22.0 | 22.0 |
| 35.7 | 25.6 | 28.4 | 25.5 | 25.0 | 30.5 | 29.2 | 24.2 | 23.6 |
| 44.9 | 28.4 | 32.0 | 28.3 | 27.8 | 33.5 | 32.0 | 27.5 | 25.9 |
| 56.6 | 32.0 | 35.9 | 32.0 | 30.5 | 37.2 | 36.0 | 30.2 | 30.3 |
| 71.2 | 36.2 | 40.3 | 35.5 | 34.2 | 42.0 | 40.3 | 33.9 | 33.3 |
| 89.7 | 40.0 | 45.0 | 39.1 | 37.5 | 49.7 | 45.2 | 38.3 | 37.1 |
| 113 | 45.0 | 50.0 | 44.6 | 42.0 | 52.8 | 50.5 | 42.5 | 41.5 |
| 142 | 50.9 | 59.8 | 50.0 | 47.0 | 62.4 | 61.0 | 47.5 | 46.5 |
| 179 | 61.2 | 66.7 | 60.0 | 52.9 | 70.4 | 68.0 | 54.5 | 52.0 |
| 225 | 62.5 | 75.1 | 66.8 | 62.3 | 79.0 | 76.2 | 64.0 | 61.0 |
| 283 | 77.8 | 84.4 | 75.0 | 69.0 | 90.0 | 85.0 | 72.0 | 69.3 |
| 357 | 89.0 | 95.9 | 85.0 | 77.8 | 100.7 | 96.0 | 80.8 | 78.0 |
| 449 | 100.1 | 109.8 | 94.2 | 86.0 | 116.0 | 108.0 | 92.0 | 86.0 |
| 566 | 114.0 | 125.1 | 100.7 | 970 | 133.0 | 122.0 | 100.3 | 97.0 |
| 712 | 132.1 | 158.4 | 122.0 | 111.0 | 166.0 | 152.0 | 117.0 | 111.0 |
| 897 | 166.8 | 175.1 | 150.0 | 128.0 | 189.0 | 172.0 | 147.0 | 125.0 |
| 1130 | 191.8 | 200.1 | 170.0 | 158.0 | 220.0 | 197.0 | 166.0 | 155.0 |
| 1420 | 222.4 | 236.3 | 197.0 | 172.0 | 250.0 | 228.0 | 192.0 | 175.0 |
| 1790 | 253.0 | 278.0 | 228.0 | 200.0 | 295.0 | 266.0 | 222.0 | 205.0 |
| 2250 | 300.2 | 333.6 | 255.0 | 240.0 | 345.0 | 308.0 | 258.0 | 245.0 |

Table 11

| Formulation number: 24/119/ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|--------------------|------------------|--------------------|--------------------|--------------------|------------------|-------------|------------------|
| Viscosity at 10 ⁴ sec ⁻¹ (N m s ⁻²) | 0.083 | 0.090 | 0.065 | 0.061 | 0.088 | 0.081 | 0.062 | 0.072 |
| Viscosity at 103sec-1 (N m s-2) | 0.175 | 0.185 | 0.155 | 0.138 | 0.205 | 0.180 | 0.158 | 0.138 |
| Recovery factor (%) | +3.8 | +22.0 | +4.0 | +6.7 | +5.0 | +1.7 | +2.4 | +15.9 |
| Pseudoplasticity factor (n) at 10^{3} sec^{-1} | 0.625 | 0.657 | 0.600 | 0.647 | 0.630 | 0.656 | 0.598 | 0.71 |
| Fly-off ranking—Operator: PW AK IH JD | 2 2 2 2.5 | 4 5 5 4 | 5 3 3 2.5 | 8 8 7 7.5 | 3 7 8 7.5 | 1 1 1 1 | 7 6 6 | 6 4 4 5 |
| Average fly-off ranking | 2.25 | 4.5 | 2.625 | 7.625 | 6.375 | 1 | 6.25 | 4.75 |
| Brushing time (sec) 21/3/74 | 53 | 68 | 56 | 58 | 79 | 73 | 66 | 49 |
| Brushing time (sec) 25/3/74 | 44 | 53 | 52 | 51 | 57 | 59 | 41 | 49 |
| Brushing ranking 21/3/74 | 2 | 6 | 3 | 4 | 8 | 7 | 5 | 1 |
| Brushing ranking 25/3/74 | 2 | 6 | 5 | 4 | 7 | 8 | 1 | 3 |
| Average brushing time (sec) | 49 | 60 | 54 | 55 | 68 | 66 | 54 | 49 |
| Average brushing ranking | 2 | 6 | 4 | 4 | 7.5 | 7.5 | 3 | 2 |
| Rank of average brushing time | 1.5 | 6 | 3.5 | 5 | 8 | 7 | 3.5 | 1.5 |
| Pigment grade | Ι | I | I | I | п | II | II | п |

1976 (4) HIGH SHEAR RHEOLOGY OF ARCHITECTURAL PAINTS

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| | | | able 12 | | | | | |
|---|------------------|-------------------|-------------------|-------------------|------------------------|-------------------|-------------------|-------------------|
| Scale of manufacture Formulation number: | Small 30/21/1 | Large 24/119/1 | Small 30/24/12 | Large 24/119/2 | Small 30/21/17 | Large 24/119/3 | Small 30/24/18 | Large 24/119/4 |
| Shear rate (sec ⁻¹) | | | | Viscosity | (N m s ⁻²) | | | |
| 8.97 | 1.583 | 1.652 | 1.828 | 1.825 | 1.520 | 1.550 | 1.612 | 1.390 |
| 11.3 | 1.434 | 1.603 | 1.649 | 1.602 | 1.300 | 1.422 | 1.403 | 1.345 |
| 14.2 | 1.275 | 1.232 | 1.449 | 1.420 | 1.170 | 1.222 | 1.233 | 1.168 |
| 17.9 | 1.106 | 1.072 | 1.274 | 1.240 | 1.050 | 1.072 | 1.103 | 1.008 |
| 22.5 | 0.991 | 0.952 | 1.124 | 1.090 | 0.950 | 0.930 | 0.964 | 0.903 |
| 28.3 | 0.876 | 0.817 | 0.992 | 0.943 | 0.855 | 0.802 | 0.855 | 0.784 |
| 35.7 | 0.773 | 0.717 | 0.880 | 0.796 | 0.748 | 0.714 | 0.755 | 0.700 |
| 44.9 | 0.682 | 0.633 | 0.792 | 0.712 | 0.663 | 0.628 | 0.669 | 0.620 |
| 56.6 | 0.594 | 0.566 | 0.698 | 0.634 | 0.594 | 0.566 | 0.599 | 0.538 |
| 71.2 | 0.548 | 0.508 | 0.633 | 0.567 | 0.527 | 0.498 | 0.535 | 0.482 |
| 89.7 | 0.491 | 0.447 | 0.567 | 0.502 | 0.471 | 0.436 | 0.484 | 0.418 |
| 113 | 0.444 | 0.398 | 0.536 | 0.443 | 0.423 | 0.396 | 0.431 | 0.372 |
| 142 | 0.435 | 0.358 | 0.480 | 0.422 | 0.382 | 0.352 | 0.397 | 0.331 |
| 179 | 0.384 | 0.342 | 0.432 | 0.372 | 0.365 | 0.336 | 0.365 | 0.296 |
| 225 | 0.348 | 0.278 | 0.393 | 0.334 | 0.327 | 0.297 | 0.327 | 0.277 |
| 283 | 0.315 | 0.275 | 0.358 | 0.300 | 0.290 | 0.265 | 0.290 | 0.244 |
| 357 | 0.287 | 0.249 | 0.322 | 0.268 | 0.261 | 0.238 | 0.261 | 0.218 |
| 449 | 0.261 | 0.223 | 0.294 | 0.244 | 0.237 | 0.210 | 0.235 | 0.193 |
| 566 | 0.261 | 0.208 | 0.285 | 0.221 | 0.216 | 0.178 | 0.211 | 0.171 |
| 712 | 0.239 | 0.186 | 0.262 | 0.223 | 0.207 | 0.172 | 0.192 | 0.156 |
| 897 | 0.217 | 0.185 | 0.240 | 0.195 | 0.192 | 0.167 | 0.186 | 0.143 |
| 1130 | 0.200 | 0.170 | 0.219 | 0.177 | 0.175 | 0.150 | 0.167 | 0.140 |
| 1420 | 0.186 | 0.158 | 0.278 | 0.167 | 0.162 | 0.140 | 0.155 | 0.121 |
| 1790 | 0.173 | 0.143 | 0.179 | 0.155 | 0.152 | 0.127 | 0.143 | 0.112 |
| 2250 | 0.162 | 0.134 | 0.159 | 0.148 | 0.136 | 0.113 | 0.133 | 0.107 |
| Pseudoplasticity factor (n) | 0.648 | | | | | | | |
| Recovery (%) | +15.4 | +3.8 | +6.78 | +22.0 | +8.17 | +4.0 | 0.0 | +6.7 |
| Viscosity at 104sec-1 (N m s-2) | 0.094 | | | | | | | |
| Viscosity at 10 ³ sec ⁻¹ (N m s ⁻²) | 0.222 | 0.175 | +0.225 | 0.185 | +0.182 | 0.155 | 0.181 | 0.138 |

Table 12

Appendix D

Formulations

Flat latex (Series A and C)

| | Weight per cent |
|--|-----------------|
| Titanium dioxide | 18.75 |
| Talc | 10.18 |
| Whiting | 17.41 |
| Water | 10.31 |
| Naphthalene sulfonic acid salt | 0.80 |
| Mercurial fungicide | 0.07 |
| Antifoam agent | 0.27 |
| Ethylene glycol | 1.34 |
| Butyl carbitol acetate | 0.54 |
| Protective colloid (cellulosic) | 8.57 |
| Poly-vinyl acetate/acrylate emulsion | 20.76 |
| Ammonia | 0.27 |
| Thickener and water (to give a viscosity of $0.4 \text{ N} \text{ s} \text{ m}^{-2}$ using an ICI Rotothinner) | 10.27 |
| Total (PVC 60%) | 99.54 |
| | |

In series A and C the formulations were varied using 18 separate proprietary protective colloids.

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| Alkyd undercoat (Series B) | Weight per cent |
|-------------------------------|-----------------|
| Titanium dioxide | 28.43 |
| Whiting | 14.86 |
| Talc | 11.40 |
| Long oil rosin modified alkyd | 25.40 |
| White spirit | 8.98 |
| Power kerosine | 7.50 |
| Safflower oil | 2.73 |
| Cobalt naphthenate (6%) | 0.15 |
| Lead naphthenate (24%) | 0.20 |
| Manganese naphthenate (6%) | 0.15 |
| Methyl ethyl ketoxime | 0.20 |
| Total | 100.00 |
| | |

These ingredients were modified with the following combinations of an amine-modified montmorillonite clay and soya lecithin:

| Formulation number: 19/91/ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|-----|------|-----|---|-----|-------------|-----|-----|------|------|
| Amine-modified clay (% wt. on total) | 0.0 | 0.45 | 1.4 | _ | - | . <u></u> , | 1.3 | | _ | 0.14 |
| Sova lecithin (% wt. on total) | | _ | | | 0.9 | 0.14 | | 1.3 | 0.45 | |

(PVC 55%)

Appendix E

Spearman Rank difference correlation coefficient

Correlation coefficients were calculated according to the following algorithm:

$$r = 1 - \frac{6 \Sigma D^2}{x (x^2 - 1)}$$

where r = Spearman Rank difference correlation coefficient

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D = The difference between ranked pairs

x = The number of pairs

Interfacial phenomena in inks*

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Summary

Some of the problems which arise when formulating inks for printing on polymer foils are discussed; furthermore, some of the very special problems concerning inks for the lithographic process

Keywords

Properties, characteristics and conditions primarily associated with: materials in general

> interfacial tension surface tension wettability

structures or surfaces being coated

printability

Les phénomènes interfaciaux aux encres d'imprimerie

Résumé

Dans cet exposé on discute certains problèmes qui se produisent lors de la mise au point des formules d'encres destinés à être imprimés sur les feuilles polymères; d'ailleurs on décrit certains problèmes très particuliers à l'égard des encres pour les procédés

Grenzflächenphänomene bei Druckfarben

Zusammenfassung

In dieser Abhandlung werden die Probleme diskutiert, welche beider Rezeptierung von Farben zum Bedrucken von Polymerfolien auftreten; weiterhin wird, gemeinsam mit einigen Prüfmethoden eine Anzahl der ganz speciellen, sich auf Druckfarben für das

Introduction

During this century, printing has developed to such a degree that it is possible for a printer to print on practically any substrate which may be presented to him. By the use, in principle, of one of four different printing processes, it is possible to present prints on paper, cardboard, polymer foils, metals, and even medical capsules and footballs. Although printing on these substrates is based on a very limited number of printing processes, very different properties are required of the printing system, including the printing forme (or "plate") and the printing inks.

No matter which method is chosen, the printing process is always based on the bringing together of different surfaces: ink on to roller system, ink on to printing plate, and ink on to substrate. In the lithographic process, the interfacial relationship is further complicated by the presence of a rubber blanket and a dampening unit, which introduce thin layers of water into the system.

One of the greatest problems within the printing ink industry is to include in the formulation of inks, materials which make printing possible, taking into consideration the different interfacial phenomena which occur during the printing process, whilst still providing a final print of the required quality. are described, together with some test methods. Finally, a method for measuring ink setting on paper is described.

lithographiques et l'on mentionne quelques méthodes d'essai. Enfin on décrit une méthode pour déterminer le temps de prise de l'encre appliqué sur papier.

lithographische Verfahren beziehenden Probleme beschrieben. Schliesslich wird auf eine Methode zur Messung des Antrocknens auf Papier eingegangen.

Printability of polymer foils

Refs. 1-10

Printing on polymer foils is normally carried out using the gravure process or flexography. Each of these printing methods demands inks with relatively high solvent content and relatively low viscosity. The printing processes themselves are not to be discussed in this paper, and they are, compared with other printing methods, rather simple in principle.

Many of the problems when printing on polymer foils are related to the demands for immediate adhesion of the wet ink to the foil, relatively rapid solvent release, and good adhesion of the dried ink to the foil. All of these properties are controlled by the formulation of the ink, its surface tension, and the solubility of the solid components making up the ink, and also by the solubility characteristics and surface tension of the foil.

The surface tension of the liquid ink is determined mainly by the choice of solvent; in other words, it is a "free" parameter, which can be changed within certain limits. One of these limits arises from the second demand, that the binder in the ink must be soluble in the solvent chosen.

The solubility of the binder in a given solvent may be predicted by introducing the "solubility parameter" concept whereby the limitations of solubility for a particular polymer

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127

are given by defining a space in a three-dimensional system of parameters (Fig. 1): the total solubility parameter δ of a solvent can be divided into three single parameters, and referring to the forces of dispersion δ_d , polar forces δ_p and those of hydrogen bonding δ_h ; thereby, a solvent is classified in the three-dimensional solubility parameter system by three more or less exact figures.

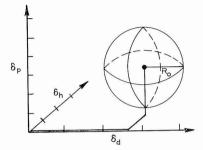


Fig. 1. Sketch of a typical volume of solubility for a polymer

A resin may be classified by the same type of system, so that the parameters δ_d , δ_p and δ_h will define a volume within which the resin will be soluble ^{2, 3}.

The space is normally reproduced on three two-dimensional planes, referring to pairs of parameters; in Fig. 2, an example of the solubility space for polymethylmethacrylate is given.

Since it becomes somewhat complicated to work with a three-dimensional system, or to use three diagrams, as in Fig. 2, it has been found practical in many cases to use only two parameters, for example, the hydrogen bonding parameter plotted against the total solubility parameter; examples are given in Figs. 3 and 4.

The highest degree of solubility is to be expected in the centre of the space, the solubility decreasing, the further the distance from the centre. Outside the limits, no solubility can be expected, although it is possible to use solvents outside their individual limits, if solvent mixtures are employed. The solubility of the resin gives well known limitations in the choice of solvents for inks, but there are often several solvents, which theoretically can be used. In practice, however, this relatively free choice of solvent in the ink formulation is restricted by the nature of the foil substrate.

Some properties of the foil are dominating factors with regard to printability: the surface tension of the foil determines ink spreadability; the solubility of the surface of the foil determines spreadability and to some degree the adhesion of the ink film and the interactive forces between ink and foil.

Several attempts have been made to explain the surface phenomena which occur between ink and foil, with the purpose of predicting the printability of the foils.

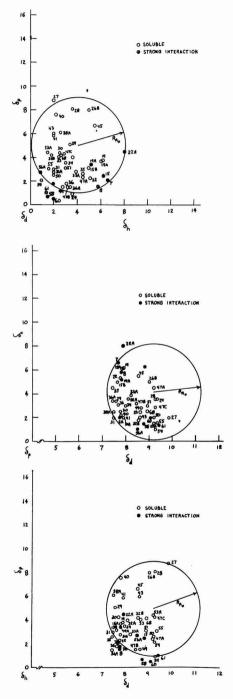


Fig. 2. The solubility of polymethylmethacrylate

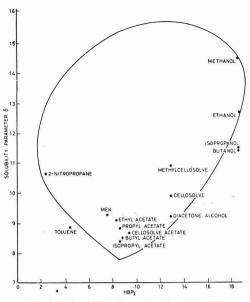


Fig. 3. Resin solubility diagram for nitrocellulose SS

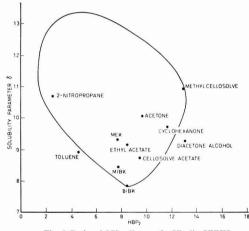


Fig. 4. Resin solubility diagram for Vinylite VYHH

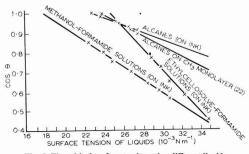


Fig. 5. The critical surface tension using different liquids

Fox and Zisman⁵ introduced in 1950 the concept of "critical surface tension" (CST) of a substrate, defined as the surface tension of a liquid which, on contact with the substrate, has a zero contact angle θ (i.e. $\cos \theta = 1$. Fig. 5).

In practice, measurements of contact angles of a print or a foil are carried out using an homologous series of solvents, such as mixtures of methanol-formamide, or different alcanes^{6,7} (Table 1).

Table 1 Various liquids for determination of ye

| Liquid | Surface tension $(10^{-3} \text{ N m}^{-1})$ |
|-----------------------------------|--|
| Water | 72.6 |
| Glycerol | 63.4 |
| Formamide | 58.2 |
| Thioglycol | 54.0 |
| Methylene iodide | 50.8 · |
| Trichlorobiphenyl (Arochlor 1242) | 45.3 |
| 1-Bromonaphthalene | 44.6 |
| Tricresylphosphate | 40.9 |
| Hexachloropropylene | 38.1 |
| 1.1-diphenylethane | 37.7 |
| TertButylnaphthalene | 33.7 |
| Dicyclohexyl | 32.8 |
| Bis (2-ethylhexylorthophthalate) | 31.3 |
| Squalene | 29.5 |
| Hexadecane | 27.6 |
| Tetradecane | 26.7 |
| | |

The values of contact angle, that is the $\cos \theta$ values, are plotted in a diagram against the surface tension of the liquids used (Fig. 5). For an homologous series of solvents or solvent mixtures, a straight line can often be drawn through the points so obtained and then extrapolated to the line $\cos \theta = 1$, where the value of surface tension is defined as the critical surface tension γ_c . However, as the diagram shows, the γ_c -value so measured depends upon the series of solvents used, and differences are found not only in the values of surface tension at the intercept with $\cos \theta = 1$, but also in the gradient of the line plotted from the experimental results.

As Zisman⁶ mentions in his publications, the critical surface tension is an empirical value, which is very useful in the characterisation of the surface properties of foils or other surfaces to be printed. It is questionable, however, whether the different values of γ_c found by this method can be used to give a more detailed explanation of the surface properties of foils.

When carrying out measurements of contact angles of foils, Zisman⁶ mentions that the measurements are valid for the surface of the foil (Table 2), which consists of chemical groups not identical with those of the foil taken as a whole.

The end groups of polymers will orientate themselves towards the surface of the polymer, thereby forming a high concentration at the surface of, for example, $-CH_3$ groups, -COOH groups, -CHO groups, or other groups characteristic of the foil in question. This concentration of "active" groups at the surface of the foil or print⁸ normally increases the surface tension of the polymer surface, and is deliberately formed during the treatment of polyethylene, for example, to improve the printability of the foil.

| Surface constitution | γc | Examples | | | |
|--|-------|--|--|--|--|
| –CF ₃ | 6 | Monolayer of perfluorolauric acid | | | |
| -CF ₂ H | 15 | | | | |
| -CF ₂ - and CF ₃ | 17 | | | | |
| -CF2 - | 18 | Polytetrafluoroethylene (Teflon) | | | |
| -CH ₂ - CF ₃ | 20 | | | | |
| -CF ₂ - CFH - | 22 | Polytrifluoroethylene | | | |
| -CF ₂ - CH ₂ - | 25 | Polyvinylidene fluoride | | | |
| -CFH - CH ₂ - | 28 | Polyvinylfluoride | | | |
| CH3 | 22–24 | Monolayer of stearic acid, paraffin etc. | | | |
| CH2 | 31 | Polyethylene | | | |
| $-CH_2 - and -CH_{\infty}$ | 33 | Polystyrene | | | |
| -C CIH - CH ₂ - | 39 | Polyvinylchloride | | | |
| -C CI ₂ - CH ₂ - | 40 | Polyvinylidenchloride | | | |
| | 43 | Polyethyleneterephthalate | | | |
| | 46 | Polyhexamethyleneadipamide | | | |

It seems reasonable to assume that wetting of a polymer surface by solvent is dependent not only upon the surface tensions of liquid and foil, but also on other forces of interaction between solvent and polymer⁹. Some explanation of the differences concerning intercept and slope of the CST-curves can be obtained when the solubility properties of the polymer surface are taken into consideration. In this connection, it is important to underline that determination of the solubility of the foil as a whole is not of any great value, since the composition of the interior of the foil may differ considerably from that of the surface.

The "solubility parameter" concept may be a great help in an investigation of the solubility properties of the polymer surface. As mentioned previously, the solubility parameter of a solvent is calculated on the basis of three single parameters, representing dispersion forces, polar forces, and hydrogen bonding forces.

A determination of the solubility parameter of the polymer surface, makes it possible to calculate the surface energy (Table 3). Rabel¹⁰ has given calculations of the surface energy of polymer foils, and, furthermore, has given the calculated values for the energy of dispersion and the energy of the polar forces; each of these parameters may be calculated separately.

The hydrogen bonding forces are included in the polar forces parameter to simplify calculation, which appears reasonable since, in addition to the dispersion forces, either polar forces or hydrogen bonding forces will be present, but very rarely both.

In comparison with the critical surface tension of the polymer, a rather good agreement has been found between surface energy and critical surface tension. Furthermore, it is seen from the values obtained for treated polyethylene that the critical surface tension and the surface energy increase during the treating process (in air), dependent upon the time taken for the treatment. The value of the dispersion forces decreases to a small degree, whilst the value of the polar forces increases rapidly during the treating process, due to the formation of polar groups on the surface of the polyethylene (-COOH, -CHO and other oxygen containing groups). The results of treating the polyethylene surface in a nitrogen atmosphere show that the surface energy and the critical surface tension do not increase significantly, indicating that the presence of oxygen is necessary if a good result is to be obtained from the treatment process.

The empirically determined critical surface tension seems, according to Rabel¹⁰, to provide a relatively good measure of the energy of the surface, and moreover, this is a quantity

| Table 3 Surface energy of polymers | | | | | | | | | |
|--|---|-----------------------------------|--------------------------------------|--|--|--|--|--|--|
| Surface energy (10 ⁻³ N m ⁻¹) | | | | | | | | | |
| Polymer | Dispersion forces | Polar forces | Total | CST (10 ⁻³ N m ⁻¹) | | | | | |
| | d YS | $\gamma_{\rm S}^{\rm p}$ | $\gamma_{\rm S}$ | γ _c | | | | | |
| "Teflon" | 18.5 | 0 | 18.5 | 18.5 | | | | | |
| Paraffin | 25.1 | 0 | 25.1 | 25.5 | | | | | |
| Polyethylene | 31.6 | 0.2 | 31.8 | 30.5 | | | | | |
| Polypropylene | 30.5 | 0.7 | 31.2 | 30.0 | | | | | |
| Polyethyleneterephthalate | 32.9 | 4.5 | 37.4 | 38.5 | | | | | |
| Polystyrene | 36.5 | 1.5 | 38.0 | 37.7 | | | | | |
| Polycarbonate | 37.0 | 1.8 | 38.8 | 38.5 | | | | | |
| Polyvinylchloride | 36.5 | 1.6 | 38.1 | 37.5 | | | | | |
| Polyethylene treated in air for: | | | | | | | | | |
| 0 s 5 s 10 s 20 s 30 s | 31.6 30.8 30.2 27.3 25.5 | 0.2 3.2 5.7 10.6 13.3 | 31.8 34.0 35.9 37.9 38.8 | 30.5 34.0 36.0 39.0 40.0 | | | | | |
| Polyethylene treated in nitrogen for 0 s 5 s 10 s 20 s 30 s | : 31.6 28.6 29.3 29.0 28.4 | 0.2 1.2 1.8 2.4 2.9 | 31.8 29.8 31.1 31.4 31.3 | 30.5 30.0 31.0 31.0 31.5 | | | | | |

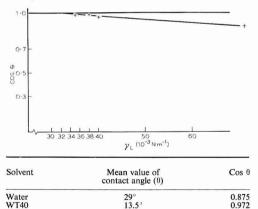
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which is easier to determine experimentally than the surface energy.

An examination of the critical surface tension determination shows that different results are found, depending on the solvents used for the measurements, and that two parameters seem to determine the wetting properties or the printability of the foils. The explanation of these differences could be that the total surface energy, which corresponds with the critical surface tension, is divided into two components: dispersion forces, and polar or hydrogen bonding forces.

Thus, different results will be obtained, depending upon the value of the polar forces (or hydrogen bonding forces) of the liquids (or mixture of liquids) used, according to the value of the polar forces (or hydrogen bonding forces) of the foil. This theory introduces two parameters which determine the printability of the foil: the critical surface tension of the polymer foil, and the slope of the curve running through the values obtained for homologous series of solvents or mixtures of solvents.

Fig. 6 gives the determination of CST for a PT cellophane. The CST value is calculated to be 34×10^{-3} N m⁻¹, which is a relatively high value. Furthermore, the slope of the curve is very flat, indicating that an increase in the surface tension of the solvent changes the contact angle only to a small degree. The measurements were carried out using the "wetting tension" solvents recommended by ASTM⁴, that is, mixtures of formamide and ethylcellosolve. Printing on cellophane is known to be relatively easy and to give good adhesion of the print. Since the CST of the cellophane is relatively high and the slope of the curve relatively flat, these two parameters seem to be the quantities of interest and the ones to optimise for any foil.



8 7.5 Fig. 6. Critical surface tension, PT cellophane

5

0.989

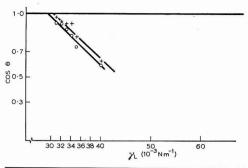
0.991

WT38

WT35

Fig. 7 shows the determination of CST for a polyethylene foil, which has been treated on one side. In the determination, the same homologous series of solvents (mixtures of formamide and ethylcellosolve) was used. The measurements carried out on the treated side of the foil gave a higher CST and a less steep curve than did the corresponding measurements on the untreated side of the foil. The increase in the CST from untreated to treated polyethylene, however, is quite small compared with the values given in Table 3, which may be an indication of a decrease in the printability properties caused by ageing of the foil. In other words, the effect obtained by the

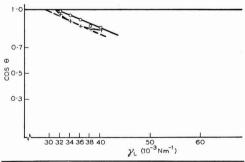
treatment is lost after a period of time; however, a change of the CST-value from untreated to treated foil has been found.



| <i>a</i> . | Solvent | Mean value of contact angle (θ) | Cos θ |
|--|---------|--|-------|
| Treated | WT40 | 51° | 0.629 |
| $\gamma_{c} = 3 \times 10^{-2} \text{ N m}^{-1}$ | WT35 | 35° | 0.819 |
| | WT34 | 22° | 0.927 |
| | WT33 | 22° | 0.927 |
| | WT32 | 20° | 0.940 |
| | WT31 | 13° | 0.974 |
| Untreated | WT40 | 52° | 0.616 |
| $\gamma_{\rm c} = 2.9 \times 10^{-2} { m N} { m m}^{-1}$ | WT35 | 42° | 0.743 |
| • | WT34 | 34° | 0.829 |
| | WT33 | 29° | 0.875 |
| | WT32 | 22° | 0.927 |
| | WT31 | $\overline{20}^{\circ}$ | 0.940 |

Fig. 7. Critical surface tension, treated and untreated polyethylene

The curves for two polyester foils (Fig. 8) show a CST value of approximately 30×10⁻³ N m⁻¹-a value which does not differ very much from the CST-value found for polyethylene. However, the slope of the curve is flatter for the polyester, indicating better printability properties.



| | Solvent | Mean value of contact angle (θ) | Cos θ |
|--|---------|--|-------|
| Mylar | WT40 | 33° | 0.839 |
| $\gamma_{\rm c} = 2.9 \times 10^{-2} \rm N m^{-1}$ | WT48 | 32° | 0.848 |
| | WT36 | 30° | 0.866 |
| | WT34 | 25° | 0.906 |
| | WT32 | 16° | 0.961 |
| Terphan | WT40 | 32° | 0.848 |
| $\gamma_{\rm c} = 3.1 \times 10^{-2} \rm \ N \ m^{-1}$ | WT38 | 30° | 0.866 |
| | WT36 | 23° | 0.920 |
| | WT34 | 18° | 0.951 |
| | WT32 | 12° | 0.978 |

Fig. 8. Critical surface tension: polyesterfoils, mylar and terphan

Table 4Formulations of varnishes and inks

| Binder A | Binder B | | | Binder C | | |
|--|---|--------------|-------------|---|-------------|------------|
| 50% Pentalyn 255, flaked 50% ethanol (99.9%) Viscosity, DIN No. 4: 21.5s | 40% polyamide 40% 2-propanol 10% 1-propanol 10% ethylcellosolve Viscosity, DIN No. 4: 40s | | | 30% nitrocellulose, AF 0 54% ethanol (99.9%) 10% ethylacetate 6% ethylcellosolve Viscosity, DIN No. 4: 97 | | |
| Inks for cellophane: | ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,, | | | | , 2 | |
| mus jor cenophane. | 101 white | 102 white | 103 blue | 104 blue | '105 red | 106 red |
| Ti0 ₂ (RN 45) | 60 | 60 | | | | |
| Phthalocyanine blue (LBGN) | | | 20 | 20 | | - |
| Rubine toner (BOX, Ca) | | | | _ | 24 | 24 |
| Binder A Binder C | 60 60 | 40 80 | 80 80 | 60 | 76 | 56 |
| Ethylcellosolve | 10 | 10 | 10 | 100 10 | 80 10 | 100 10 |
| Total | 190 | 190 | 190 | 190 | 190 | 190 |
| Inks for polyethylene: | | | | | | |
| | | 1 white | | 2 nite | 3 blue | 4 red |
| Ti0 ₂ (RN 45) | | 60 | | 60 | | e |
| Phthalocyanine blue (LBGN) | | | | _ | 20 | _ |
| Rubine toner (BOS, Ca) | | | | | | 24 |
| Binder B Binder C | | 90 30 | | 90 30 | 120 30 | 120 28 |
| 1-propanol | | 30 | | 8 | 10 | 28 |
| Polyethylene wax (12%) | | | | 6 | | _ |
| Amide wax | | _ | | 6 1 | | - |
| Dioctylphathalate | | | | 5 | - | _ |
| Total | | 180 | 2 | 00 | 180 | 180 |
| | | | | | | |

Corresponding measurements of surface tension and the construction of CST-curves can be performed for dry films of printing ink or varnish.

In Fig. 9, the curves for three varnish films are shown, which were determined by the use of the above-mentioned wetting-tension solvents. The varnish based on nitrocellulose (Fig. 9c) shows a rather flat curve, whilst the varnish based on polyamide (Fig. 9b) shows a very steep curve, and the varnish based on a maleic resin (Fig. 9a) is intermediate between these two.

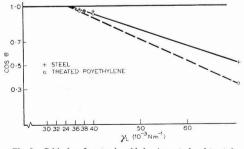


Fig. 9a. Critical surface tension; binder A on steel and treated polyethylene

According to the theories given by other workers, a requirement for good printing properties on foils is that the ink should have a surface tension lower than the CST of the foil. In theory, this would mean that the varnish based on nitro-

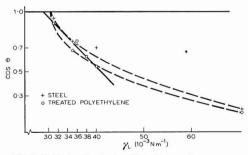


Fig. 9b. Critical surface tension; binder B on steel and treated polyethylene

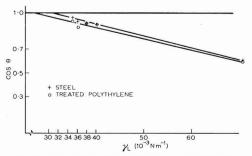


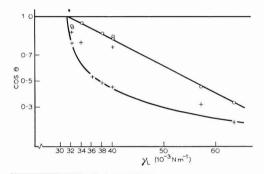
Fig. 9c. Critical surface tension; binder C on steel and treated

1976 (4) INTERFACIAL PHENOMENA IN INKS

cellulose, having a CST for the dry varnish film of approximately 28×10^{-3} N m⁻¹, should be useful for printing on polyethylene. In practice, however, poor results are obtained when printing on polyethylene foils with a nitrocellulose-based ink. The reason is probably that the surface tension curve for the nitrocellulose film is flatter than the curve for polyethylene, indicating that two requirements must be fulfilled: not only should the CST of the ink be smaller than that of the foil, but the curve of the surface tension values for the ink should be lower than the corresponding curve for the foil. Because of this, a better printing result is obtained on polyethylene when a varnish based on a polyamide resin, in preference to a nitrocellulose-based ink.

The introduction of pigments into the varnish complicates the prediction of the slope of the CST-curve, and uormally additives of different kinds are introduced into inks, which further complicates determination of the CST and plotting of the CST-curve.

As an example, the CST-curve for two white inks is given (Fig. 10), based on the same pigment and binder, but with a different additive in the ink marked *B*. The print of ink *A* was found to have a very poor adhesion according to the tape test, but the addition of polyethylene wax and amide wax improved adhesion.



| | Solvent | Surface tension of (N m ⁻¹) | Mean value of contact angle θ | Cos 0 |
|--|------------------------|---|-------------------------------------|-------|
| White ink A | Water | 0.0720 | 69° | 0.250 |
| $\gamma_{c} = 3.1 \times 10^{-2} \text{ N m}^{-1}$ | WT40 | 0.0720 | 33° | 0.358 |
| $r_{c} = 3.1 \times 10^{-2}$ N III - | WT38 | 0.0400 | 30° | 0.839 |
| | WT34 | | 19° | 0.866 |
| | WT32 | 0.0340 | | 0.946 |
| | | 0.0320 | 24° | 0.914 |
| | Formamide | 0.0568 | 63° | 0.454 |
| | Glycerin Tricresyl- | 0.0634 | 70° | 0.342 |
| | phosphate Dioctyl- | 0.0396 | 34° | 0.829 |
| | phthalate | 0.0320 | 24° | 0.914 |
| White ink B | WT40 | 0.0400 | 63° | 0.454 |
| $\gamma_{c} = 3.1 \times 10^{-2} \text{ N m}^{-2}$ | WT38 | 0.0380 | 61° | 0.485 |
| | WT36 | 0.0360 | 58° | 0.530 |
| | WT34 | 0.0340 | 37° | 0.799 |
| | WT32 | 0.0320 | 29° | 0.875 |
| | Formamide | 0.0568 | 71° | 0.326 |
| | Glycerin Tricresyl- | 0.0634 | 79° | 0.191 |
| | phosphate Dioctyl- | 0.0396 | 40° | 0.766 |
| | phthalate | 0.0320 | 38° | 0.788 |

Fig. 10. Critical surface tension; two white inks on treated polyethylene

The CST-curves in Fig. 10 show that the introduction of wax into the ink increases the surface tension of the ink film to a small degree, and the CST-curve of ink *B* is lower than that of ink *A*; furthermore, the curve is no longer rectilinear. In other words, by lowering the CST-curve, a surface is obtained which is more difficult to wet by solvents and, for example, the glue on the tape in the tape test. The true adhesion of the ink film to the polyethylene foil, however, is determined by the varnish, and it may be established simply by carrying out a scratch resistance test that the true adhesion has not been improved.

The introduction of wax into the ink changes the surface properties, so that the print seems smoother and, thereby, not only the adhesion according to the tape test seems to be improved, but also the scratch resistance seems to be increased, because a needle will slide over the surface more easily. Unfortunately, the existing methods of test used for determining the adhesion of paint films are not useful for prints, because the film of ink is so thin (a few micrometres) compared with the film thickness of paints (more than 20 micrometres).

A "drawing" method for measuring the adhesion of printing ink films has been attempted, but because of printing irregularities, the adhesive will often penetrate through the ink film, and the adhesion of the glue to the substrate, rather than to that of the ink film will be measured.

Interfacial phenomena in lithographic printing

The interfacial phenomena in lithographic printing present rather different problems from those discussed above concerning the printing on foils, metals, and other non-absorbent substrates.

In lithographic printing, the substrate is normally paper or cardboard (disregarding metal decorating). Here, the relationship between ink and substrate is dominated by the absorptive properties of the latter. Although the properties of the paper can cause trouble in lithographic printing, they are not problems of a type pertinent to this paper and will not be discussed here.

The dominating interfacial phenomena in lithographic printing are due to the introduction of water or alcohol into the printing process by the dampening system. In principle, the water prevents the non-image areas from accepting ink during the inking process, whilst the image areas will accept ink but more or less refuse water. Some of the most common problems in lithography are related to unwanted mixtures of water and ink, and to acceptance of ink by the non-image areas, which leads to printing faults.

These printing defects can, in many cases, be attributed to the properties of the ink such as the interfacial tension between ink and water, the affinity between ink and metal plate (or rather the dampened printing plate) and the rheological properties of the ink, and will also vary according to other variables, such as the pH-value of the dampening liquid. All these properties might give the impression that the process is impossible, but in practice, of course, the process works. In this paper, two of the above mentioned ink properties will be discussed: the interfacial tension between ink and water; and the affinity of inks for the printing plates.

Interfacial tension

An important factor concerning the capability of an offset ink to mix with the dampening liquid (water or alcohol) is the interfacial tension between the two. This interfacial tension is Interfacial tensions can be determined by, for example, the use of a de Noüy tensiometer, which measures the force needed to draw a platinum ring through the interface. Unfortunately, the viscosity of the liquid has a rather great influence on the measurement of IT and, therefore, the measurement cannot be carried out directly at the water/ink interface. In addition, the method obviously cannot be used directly to determine the IT between a dry pigment and water. Measurements can be carried out, however, for solutions or suspensions of ink, binder or pigment in xylene, at a suitable concentration.

Before a determination is made of the IT for pigment suspensions, it is necessary to carry out a filtration in order to eliminate the pigment particles. Fig. 11 shows some examples of IT-curves for pigment suspensions at different concentrations interfaced with water. Similar curves have been found for measurements carried out on suspensions or solution of printing ink.

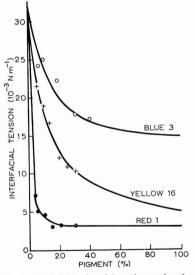


Fig. 11. Interfacial tension of three pigments in xylene

The IT of a pigment or an ink interfaced with water is given by the extrapolation to 100% pigment or ink concentration on the curves found for solutions or suspensions in xylene. Comparison of the IT-values of pigments with those of inks based on these pigments (Table 5) (the same binder being used in all these inks) shows that pigments with extremely low IT (Red 1 and Red 59) give inks with very low IT-values.

It may seem surprising that these pigments, which are normally considered to be relatively non-active towards water, show such low IT-values. It has been established, however, that impurities from the manufacture of the pigments are often present on the surface of pigment particles, leading in some cases to these low IT-values. By repeated washing with xylene of pigments having very low IV-values, it has been found that the IT-values increases approximately tenfold after two washings.

Good printing properties for an ink depend on a number of factors, but normally the IT-value should not be too low, since this can cause scumming and "toning" during printing. On the other hand, the IT-value should not be too high, since the ink should be able to emulsify a small quantity of water; in fact, the print areas of the printing plate will always be wetted by a thin water layer. The IT-value of an offset ink should normally be between approximately 15×10^{-3} and 25×10^{-3} N m⁻¹ according to practical printing experiments.

Affinity

The thin layer of water on the image areas of the printing plate, which need be only a monomolecular layer, is very important to the ink transfer process, but other factors also influence the process and these can be summarised by the single concept of "affinity between ink and metal plate". No attempts have been made to calculate this "affinity" thermodynamically, since so great a number of properties of metal, water and ink would make such calculations impossibly complicated. Instead, an attempt has been made to estimate the affinity, or rather the transfer properties of ink on to a dampened metal plate, by a practical test carried out using simple instruments.

The equipment used for test consists of a metal block carrying metal plates of different materials. The total height of the block and plates is the same as the normal height of printing materials (types or clichées) used in letterpress printing, and the total system can be placed in a vessel with a suitable dampening liquid. When carrying out the affinity measurements, the metal plates are inked by the use of the roller from an IGT inking unit, so that the amount of ink offered is known. The metal plates are inked firstly in dry condition and a print is drawn on a normal proofing press (in the case of the author's experiments, using a Littlejohn

 Table 5

 Interfacial tension (IT) between inks (40% in xylene) and water, and between pigments used in the inks (same pigment concentration in xylene as in ink) and water

| Pigment | Pigment concentration in ink (%) | IT of pigment (10 ⁻³ N m ⁻¹) | IT of ink (10 ⁻³ N m ⁻¹) |
|-----------|--|--|--|
| Yellow 2 | 24 | 16 | 12 |
| Yellow 3 | 24 | 21 | 17 |
| Yellow 16 | 12 | 22 | 22 |
| Yellow 23 | 12 | 27 | 18 |
| Orange 2 | 24 | 20 | 9 |
| Orange 1 | 24 | 16 | 16 |
| Red 1 | 24 | 5 | 4 |
| Red 56 | 24 | 0.5 | 2 |

1976 (4) INTERFACIAL PHENOMENA IN INKS

proofing press). Thereafter, the metal plates are cleaned and placed in a vessel which contains the dampening liquid; the metal plates are inked with the same amount of ink, but a new print is then made on the proofing press using damp plates. A direct comparison of the two prints gives an immediate impression of the degree to which the wetted plate accepts ink compared with the dry one.

To obtain a more quantitative expression, however, colour measurements or density measurements must be carried out. Some of the results obtained so far have been based on experiments using aluminium, stainless steel and copper, and nine different inks; some of the ink properties are given in Table 6. As may be seen from these data, the inks have very dissimilar properties and it is difficult to make direct comparisons of affinities between the inks, although the data are useful in an assessment of ink transfer or affinity of the inks to different metal surfaces. Figs. 12-14 illustrate the results of the affinity measurements.

In Fig. 12, the transfer curves calculated from colour measurements of prints on aluminium are given. The relative ink transfer is determined by the value of S_w/S_d , the ratio between transfer on a wet metal surface to that on a dry metal surface. The smaller this value, the better is the transfer from the wet surface compared with the transfer from the dry surface, since the reflection values will increase when inking is decreased. From the Fig., it can be seen that the inks based on varnish I, in general, show relatively good transfer from the wet metal surface, meaning that the inking of the surface is disturbed only to a small degree by the water layer. The inking (or the affinity) decreases, however, from the blue to the red, to the yellow ink.

The inks based on varnish II show similar transfer curves for all three inks. It is observed, however, that beyond a certain limit of inking, given by an S_d value, the gradient curves increases rapidly, indicating that a reasonable amount of ink only is transferred, when the amount of ink offered exceeds a certain quantity.

Blue and red inks based on varnish III demonstrate an excellent transfer from wet plates with S_w/S_d -values between

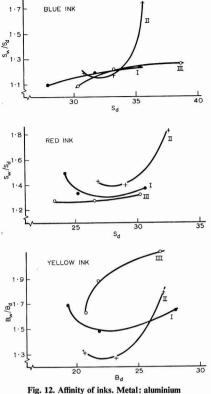
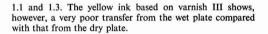


Fig. 12. Annuty of mks. Metal. aluminum



| Table 6 Ink properties for "affinity" measurements | | | | | | | | | |
|--|--------------------|------|-----|------|------|------|--------|------|------|
| Ink | | Blue | | Red | | | Yellow | | |
| Varnish number* | I | п | ш | I | п | ш | Ι | п | ш |
| Interfacial tension of varnish (10 ⁻³ N m ⁻¹) | 7 | 13 | 17 | 7 | 13 | 17 | 7 | 13 | 17 |
| Interfacial tension of pigment $(10^{-3} N m^{-1})$ | 23 | 23 | 23 | 12 | 12 | 12 | 0.1 | 0.1 | 0.1 |
| Interfacial tension of ink $(10^{-3} N m^{-1})$ | 13 | (38) | 18 | 18 | 32 | (39) | 3 | 4 | 4 |
| Viscosity of ink at 25° Pa s† | 4170 | | | 4270 | 5460 | 2710 | 2650 | 6450 | 1950 |
| Yield value of ink at 25° (N m- | ²) 930 | | | 2200 | 230 | 1000 | 1600 | . 0 | 320 |
| Viscosity of varnish at 25° Pa s | † 600 | 2200 | 800 | 600 | 2200 | 800 | 600 | 2200 | 800 |

T-11- 6

*Varnish I: Phenolic resin + linseed oil + alkyd

Varnish II: Parco resin + mineral oil

Varnish III: Linseed stand oil

Blue pigment: phthalocyanine

Red pigment: lithol rubine

Yellow pigment: benzidine yellow

†One pascal-second equals one-tenth of a poise.

The same phenomenon may be observed on the corresponding curves for the other two metals, steel and copper (Fig. 13 and 14), that is, good transfer to wet plates for blue and red inks based on varnish III, but poor transfer to wet metal surfaces for the yellow ink. The reason is probably that all yellow inks show a very low interfacial tension with water (approximately 3×10^{-3} N m⁻¹), caused by the extremely low interfacial tension of the pigment, so that the ink will immediately absorb any water coming into contact with its outer layer, and this outer layer will then slip over the metal plate, almost as if the inking were being carried out using water instead of ink.

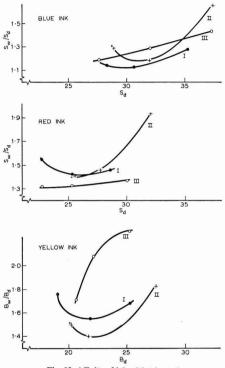
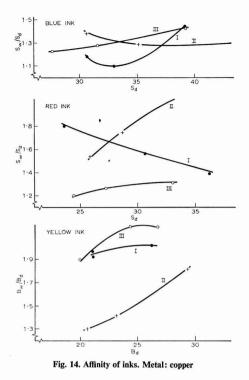


Fig. 13. Affinity of inks. Metal: steel

The following results are found for affinity of the inks to different wet metal surfaces: blue ink I (Figs. 12-14) shows a good transfer to all three metals; Ink II shows, at relatively high inking levels, a poorer transfer to aluminium and steel than to copper; ink III shows on all three metals a relatively good transfer. The question arises why ink II transfers better to a wet copper surface than to a wet aluminium or steel surface. The answer is probably concerned with contact angles of water on the three metals; these have been found to be approximately 83° for steel, 85-86° for aluminium, and 89° for copper. The contact angles of paraffin are, according to the literature, 110° for steel, 140° for aluminium, and 77° for copper. This means that copper, which shows the highest contact angle for water and the lowest contact angle for oily substances, does not bind the water layer very well, so that when ink II is applied, the water is easily pressed away from the surface and replaced by ink.

Steel and aluminium, which give lower contact angles for water and higher contact angles for paraffin, do not give up the



water layer so easily, and the ink is more difficult to transfer from roller to metal.

For the red inks (Fig. 12-14), the affinity curves measured on steel and aluminium are very much alike, meaning relatively good transfer to wet plates for inks I and III, and poor transfer for ink II at low inking levels. Unlike the blue ink II, red ink II shows a poor affinity to copper at low inking levels. Red ink III shows a good transfer to all metals.

It has already been stated that the yellow inks show poor transfer of ink III. The yellow ink I also shows a relatively poor affinity to all metals, whilst ink II shows a relatively high affinity at high inking levels. This is the only case where the ink based on varnish II demonstrates the best ink transfer or the highest affinity. The reason is probably that varnish II ("Parco" resin in mineral oil) cannot take up much water even at low IT, since the resin and the mineral oil are not capable of rapidly forming an emulsion with water. The low interfacial tensions of inks I and III, which facilitate the formation of a water layer on the surface of the ink on the roller, do not, therefore, affect the water uptake of ink II as long as contact with the water is only for a very short period. Consequently, ink II shows a poor affinity to wet metal plates and this is independent of both the pigment used and the interfacial tension of either ink or pigment. The other varnishes lead to poor results because of a very low interfacial tension between water and pigment.

The inks based on varnish II, whilst having a poor affinity for the wet metal plate, nevertheless appear to be the best choice, because the ink properties are not influenced by the interfacial tension of the pigment.

1976 (4) INTERFACIAL PHENOMENA IN INKS

The measurements discussed above are only the preliminary results of this investigation, and even if the results can explain many effects, they are not conclusive, since the influence of other factors, such as the properties of the dampening liquid, still remain to be investigated.

Ink setting

So far, this paper has been concerned with relationships between inks and non-absorbent surfaces. One of the most important surfaces within the field of graphic arts is paper. The properties of this material can vary to a great extent and introduce factors such as absorbency and strength of the paper to the printing operation. Some of the problems connected with ink setting on paper (which arise from a combination of ink properties and paper absorbency) are, therefore, briefly discussed below.

The "setting" of an ink is defined as the time from the moment of transfer of ink to paper until the ink is sufficiently dry to be handled mechanically—the ink will still not be completely dry at this stage.

Normally, ink setting is measured by a determination of the time interval between printing and the moment when no "set-off" is found on a clean sheet of paper pressed against the print. The ink setting or set-off depends on the properties of both paper and ink, on the ink film thickness, on the pressure of the rollers when making the impression, etc.

A test method being investigated includes the measurement of set-off at different ink film thicknesses, thereby making it possible to calculate the ink setting properties at different predetermined ink film thicknesses. In principle, the method works as follows:

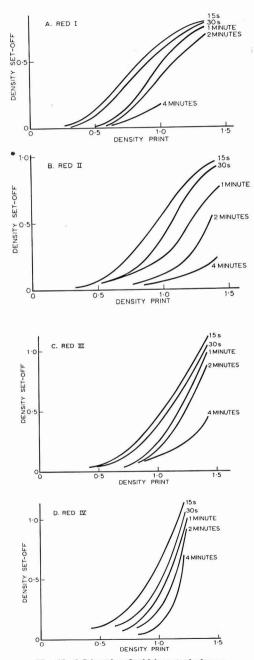
Five strips of paper, each of a size suitable for taking an impression on an IGT tester, are taped to a larger sheet of paper. An iris print is produced on these five strips using an ordinary proofing press. At various times each one of the strips is mounted on an IGT printability tester, and a set-off printing is carried out using an ordinary round IGT cliché, on which a paper strip is mounted. The print is placed in such a way that only half the print is pressed against the clean paper strip.

Finally, the density of that part of the print which has not been used for set-off is measured at different places of the print, and the densities at the corresponding positions on the set-off strip are measured.

The densities of the set-off strip are plotted against the densities of the print at each time interval used. From these curves, the densities of the set-off strips are read at different predetermined densities of the print, and from the curves showing density of the set-off print as a function of the time interval at a predetermined density of the print, the ink setting is evaluated.

Fig. 15a-d shows examples of the relationship between density of set-off and density of print for four red inks. Ink I is based on a mixture of phenolic resin, linseed stand oil and alkyd, and ink III is based on pure linseed stand oil. Inks II and IV correspond to inks I and III, the only difference being that 5 per cent of the linseed oil is replaced by mineral oil in inks I and III in order to improve ink setting. Each of the Figs. represents five curves showing measurements of density of set-off at six different ink film thicknesses, that is six print densities. The five curves represent these measurements carried out at time intervals between printing and set-off printing of

0.25, 0.5, 1, 2 and 4 minutes. In Fig. 15a, the five curves for ink I are relatively close to one another, indicating that the amount of drying of the ink which takes place between 15 seconds and 4 minutes after the printing is very small.



Figs. 15a-d. Ink setting of red ink on standard paper (Density measurements: green filter)

In Fig. 15b, representing the same ink with the addition of five per cent mineral oil, the curves show a greater scattering, indicating accelerated drying or setting compared with ink I.

In Fig. 15c and d, the same type of curves are given for inks III and IV. When it is considered that the only difference between ink III and ink IV is the content of five per cent mineral oil in ink IV, it is apparent that the change of the curves from Fig. 15c to d shows the opposite effect compared with the results from Fig. 15a to b.

Reading from these curves the density of the set off-print at three different densities of the print, the values given in Table 7 are found. From these values, it can be seen that the density values for ink red II, in general, are lower than for ink red I, indicating a faster setting of ink red II. For ink red IV the densities for the set-off prints have increased considerably compared with ink red III.

In Fig. 16 the set-off densities are plotted against the time interval between printing and set-off. In all three sets of curves, it is seen that ink red I shows higher values than ink red II. In this case, the addition of mineral oil has improved the setting of ink red I. If red inks III and IV are compared, a small improvement of the setting seems to be indicated at densities 0.8 and 1.0, but at density 1.2 ink red IV shows very poor setting; in other words, the addition of the mineral oil has reduced the ink setting. The reason is probably that the mineral oil is absorbed by the linseed stand oil and this softens it. Thus, instead of a rapid absorption of thinned mineral oil into the paper, the ink as a whole becomes stickier, and the result is to increase set-off.

The set-off of four commercial inks has been determined: the inks were delivered as two batches, each representing a quick setting and a slow setting ink.

The set-off values for one batch of inks are given in Table 8, and show no great difference between the values for the two inks. The curves for set-off (Fig. 17) show no significant difference between the set-off of the quick setting ink and the slow setting one. In both cases, the set-off values increase with increasing density of print, and no difference can be established between the setting properties of these two inks.

| Table 7a |
|---|
| Density of set-off print as a function of density of print and time interval between printing and set-off |

| Ink | Time interval (seconds) | Density of print = 0.8 | | | Density of print = 1.2 |
|------------------------|-------------------------------|------------------------------|------|--------|------------------------------|
| Red I | 15 | 0.42 | 0.63 | 0.80 | 0.75 |
| | 30 | 0.39 | 0.58 | 0.77 | 0.77 |
| (Phenolic resin $+$ | 60 | 0.22 | 0.45 | 0.74 | 0.67 |
| linseed oil $+$ alkyd) | 120 | 0.15 | 0.37 | 0.68 | 0.55 |
| 3 | 240 | 0.09 | 0.18 | - | _ |
| Red II | 15 | 0.31 | 0.53 | 0.92 | 0.80 |
| 100 11 | 30 | 0.24 | 0.42 | 0.85 | 0.73 |
| (Red I $+ 5\%$ | 60 | 0.14 | 0.24 | 0.65 | 0.48 |
| mineral oil) | 120 | 0.07 | 0.12 | 0.43 | 0.27 |
| mineral ony | 240 | 0.03 | 0.06 | 0.15 | 0.10 |
| Red III | 15 | 0.22 | 0.42 | 0.84 | 0.75 |
| Ked III | 30 | 0.22 | 0.42 | 0.84 | 0.75 |
| (Linseed stand oil) | 60 | 0.14 | 0.38 | 0.84 | 0.74 |
| (Linseed stand on) | 120 | 0.14 | 0.28 | 0.62 | 0.44 |
| | 240 | 0.09 | 0.20 | 0.82 | 0.44 |
| | 240 | 0.09 | 0.11 | 0.27 | 0.22 |
| Red IV | 15 | 0.35 | 0.60 | (1.20) | 1.10 |
| | 30 | 0.20 | 0.39 | (1.05) | 0.95 |
| (Red III $+ 5\%$ | 60 | 0.15 | 0.21 | (1.05) | 0.93 |
| mineral oil) | 120 | 0.08 | 0.10 | (1.15) | 0.89 |
| 2 | 240 | 0 | 0.07 | (1.15) | 0.65 |
| | | | | | |

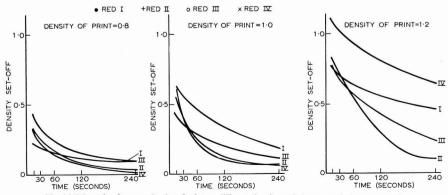


Fig. 16. Ink setting for same density of prints at different time intervals between printing and set-off

| Ink | Time interval (seconds) | Density of print = 1.0 | Density of print = 1.3 | Density of print = 1.6 |
|---------------------------------------|-------------------------------|------------------------------|------------------------------|------------------------------|
| Blue AH | 15 | 0.49 | 0.80 | 1.09 |
| (Commercial ink, quick setting) | 30 | 0.31 | 0.56 | 0.94 |
| | 60 | 0.11 | 0.18 | 0.43 |
| | 120 | 0.13 | 0.22 | 0.45 |
| | 240 | 0.04 | 0.05 | 0.09 |
| Blue BL | 15 | 0.38 | 0.55 | 0.98 |
| (Commercial ink, slow setting) | 30 | 0.28 | 0.40 | 0.70 |
| · · · · · · · · · · · · · · · · · · · | 60 | 0.22 | 0.33 | 0.45 |
| | 120 | 0.12 | 0.12 | 0.19 |
| | 240 | 0.06 | 0.06 | 0.07 |

Table 8
 Density of set-off as a function of density of print, and time interval between printing and set-off

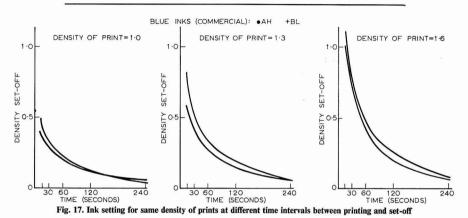


Table 9
 Density of set-off as a function of density of print, and time interval between printing and set-off

| Time interval (seconds) | Density of print = 1.0 | Density of print = 1.3 | Density of print = 1.6 |
|-------------------------------|--|--|---|
| 15 | 0.48 | 0.65 | 0.85 |
| 30 | 0.36 | 0.47 | 0.60 |
| 60 | 0.21 | 0.27 | 0.50 |
| 120 | 0.09 | 0.12 | 0.16 |
| 240 | 0 | 0.04 | 0.07 |
| 15 | 0.42 | 0.80 | 1.25 |
| 30 | 0.26 | 0.50 | 0.95 |
| 60 | 0.19 | 0.45 | 0.82 |
| 120 | 0.16 | 0.23 | 0.55 |
| 240 | 0.05 | 0.08 | 0.20 |
| | interval (seconds) 15 30 60 120 240 15 30 60 120 | $\begin{array}{c c} \text{interval} \\ (\text{seconds}) \end{array} & \begin{array}{c} \text{of print} \\ = 1.0 \end{array} \\ \hline \\ 15 \\ 30 \\ 0.36 \\ 60 \\ 0.21 \\ 120 \\ 0.09 \\ 240 \\ 0 \end{array} \\ \hline \\ 15 \\ 30 \\ 0.26 \\ 60 \\ 0.19 \\ 120 \\ 0.16 \end{array}$ | $ \begin{array}{c cccc} \text{interval} & \text{of print} & \text{of print} \\ \text{(seconds)} & = 1.0 & = 1.3 \\ \hline \end{array} \\ \hline \\ 15 & 0.48 & 0.65 \\ 30 & 0.36 & 0.47 \\ 60 & 0.21 & 0.27 \\ 120 & 0.09 & 0.12 \\ 240 & 0 & 0.04 \\ \hline \\ 15 & 0.42 & 0.80 \\ 30 & 0.26 & 0.50 \\ 60 & 0.19 & 0.45 \\ 120 & 0.16 & 0.23 \\ \hline \end{array} $ |

The set-off values for the other set of inks are given in Table 9, from which it can be seen that the slow setting ink has higher set-off values than the quick setting ink at the same density.

The corresponding curves are given in Fig. 18, showing no significant difference in set-off at the density 1.0. At the density 1.3, the difference between the curves is distinct, and at the density 1.6, a large difference can be observed. For the quick setting ink, it can be seen that the set-off does not increase very much when the density of the print (i.e. the ink film thickness) is increased, whilst the set-off of the slow drying ink increases considerably with increasing ink film thickness.

The test method described above is not really a new method of measuring ink setting, but rather an improvement on the existing methods. It has the advantage, however, of enabling measurements to be carried out on the basis of automatic printing, instead of using hand-driven rollers for measuring set-off at different times. Furthermore, the ink setting is determined at different ink film thicknesses (or densities), thereby, giving a more exact picture of the ink setting properties.

In this paper, some test methods relating to printability properties have been described. These methods, however, deal with only a small proportion of the problems arising daily in

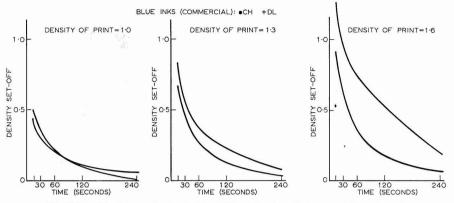


Fig. 18. Ink setting for same density of prints at different time intervals between printing and set-off

the printing industries. Many efforts are being made to evaluate and improve the relevant test methods, not only to facilitate the formulation of the best inks for different printing purposes, but also to give an end product of the best possible quality. It is the hope of the author that the methods described in this paper will contribute to these endeavours.

[Received 9 April 1975

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The application of UV-curing materials and technology to packaging*

By A. D. Lott

Metal Box Ltd, Corporate R & D Dept, Acton, London W3

Summary

The current usage is outlined of ultraviolet curing for inks and other decorative materials used for packaging, including metal sheets and containers, labels and cartons, plastics containers and closures, fiexible laminates and films. The advantages that have already been experienced and some of the remaining problems, such as

Keywords

Types and classes of coatings and allied products metal decorating finish printing ink

Types and classes of structures or surfaces to be coated

aluminium metal plastic tinplate inadequate adhesion on some metals and incomplete conversion, are discussed. Ultraviolet lamps and driers and their installation on printing machines are briefly surveyed and the need is suggested for certain developments in equipment and materials.

Processes and methods primarily associated with drying or curing of coatings

ultraviolet curing

L'utilisation de la technologie et des produits durcissables par rayons ultra-violets dans l'industrie d'emballage

Résumé

On trace les grandes lignes de la technologie de durcissement par rayons ultra-violets d'encres et d'autres produits utilisés dans l'industrie d'emballage, y compris les plaques et les récipients en métaux, les etiquettes et les cartouches, les récipients et les fermetures en plastique, les feuilles et les lamifiés en plastique fexible. On discute les avantages qui ont été déjà mis en évidence et d'ailleurs certains des problèmes qui restent encore à résoudre, tels que l'adhérence insatisfaisante à certains métaux et la durcissement inachevé. On considère brièvement les lampes et les séchoirs ultra-violets et aussi leur installation sur les machines d'imprimerie. On suggère la nécessité de certains développements dans les domaines du matériel et des produits.

Die Anwendung von UV-härtbaren Materialien und der Technologie auf Verpackungen

Zusammenfassung

Die gegenwärtig gebräuchliche Verwendung von Ultravioletthärtung auf Druckfarben und andere für Verpackungszwecke verwendente, dekorative Materialien, einschliesslich Bleche und Behälter, Etiquetten und Schachteln, Kungststoffbehälter und Verschlüsse, flexible Laminate und Filme wird skizziert. Die bereits gewonnenen Vorteile, sowie einige der noch offenen Probleme, wie

Introduction

Ref. 1

Inks that could be cured rapidly by ultraviolet radiation were first introduced for printing packaging materials in the USA in 1970 and in Europe, including this country, in the following year. The initial applications were in metal decorating and in carton and label printing. During the following few years, there has been a slow but steady growth in the number of installations, with a significant increase within the last year. At the same time, there has been an appreciable expansion in the choice of UV drying equipment available.

The use of UV-curing inks is not confined to packaging: they are also being employed in publication printing by web offset, particularly in the USA, and to a lesser extent in Europe. Developments in materials and equipment for this ungenügende Haftung auf einigen Metallen und unzureichende Härtung, werden besprochen. Eine kurze Übersicht von ultravioletten Lampen und Trockenapparaten, sowie deren Installation an Druckpressen, sowie Anregungen für gewisse notwendige Verbesserungen in Ausrüstung und Materialien werden gegeben.

field have brought benefits to packaging printing, and vice versa, as the requirements and technologies have much in common.

In packaging, the use of UV-curing materials is now sufficiently well established for certain patterns to emerge and for some of the required further developments to be clearly identifiable. The ranges of both actual and potential applications are widening, and there now seems little doubt that the number of installations will increase quite rapidly in the next few years.

Nevertheless, the use of these new materials must be viewed in the context of printing as a whole. At present, they represent barely 1 per cent of the ink consumption in the USA, but it has been forecast¹ that this may grow to about 26 per cent by the end of this century.

*Paper presented at the Newcastle Section's symposium on "Ultraviolet polymerisation" held at Durham University on 10 and 11 April 1975.

Applications in packaging

The various possible applications for UV-curing materials are summarised in Table 1.

Potential outlets for UV-curing materials in packaging

| Product | Substrate | Application process |
|--|---|--|
| Metal containers and closures | Tinplate, aluminium, tin-free steel | Lithography, dry offset, roller coating |
| Labels and cartons | Papers and boards | Lithography, dry offset, letterpress, roller coating |
| Plastics containers and closures | Polyethylene, polystyrene, ABS, PVCl, polypropylene | Dry offset, screen process |
| Bags, film, pouches and other flexible packaging | Plastic films, aluminium foil, paper | Gravure, flexography, adhesive laminating |

Metal decorating

Metal sheets and formed containers are decorated by two processes, firstly roller coating for the application of protective and decorative lacquers, pigmented coatings and varnishes, and secondly printing.

Sheet printing

An early use for UV-curing inks was in inter-deck setting on multicolour tin-printing lines. Unlike paper and board printing, where up to six colours could be printed in a single pass (due to the substrate usually possessing some absorbency), sheet metal printing had been limited to two or three impressions per pass followed by stoving and then the printing of any further colours. UV-curing has enabled four colours to be printed in one pass, the first two inks being set by radiation and then overprinted with conventional oxidation drving inks prior to varnishing and stoving. In this application, the inks are sufficiently set only to enable them to be overprinted, and they are finally cured and hardened in the oven. The amount of UV radiation and the formulation of the inks have to be adjusted to ensure the print has sufficient adhesion to plain metal so that it is not picked off by the following printing blanket, whilst at the same time the film must develop sufficient inter-film adhesion with the overlying conventional inks and varnish.

The main advantage of inter-deck setting is to reduce the number of passes required to print multicolour designs. So far it has been applied on two, three and four colour printing lines, but there is no technical reason why the number of printing units should not be increased if there is sufficient commercial demand. Other advantages are also gained from the use of UV inks, such as their high press stability, which **results in less** time spent in wash-ups.

Inter-deck setting enables existing printing lines to be extended or used more efficiently, but it does not lead directly to the replacement of ovens. Metal decorating ovens are expensive, costing up to £40 000 or more according to length: they occupy much factory space and are very wasteful in energy consumption.

The next stage of development, therefore, will be inter-pass setting, where the oven on the end of a tin-printing line will be replaced by a UV drier, which should be cheaper, will occupy much less space and require less energy. The print will have to be cured sufficiently to avoid scratching and more particularly set-off when the sheets are stacked in the unloader. More radiation than for interdeck setting, for example a larger number of lamps, is likely to be required.

Inter-pass setting would enable only a limited number of printing ovens to be replaced, because the final printing pass, which often includes a varnish applied in-line, would still have to be undertaken on a standard line with conventional inks and a varnish. The wholesale elimination of printing ovens, therefore, awaits the development of UV-curing varnishes.

Sheet coating

The development of pigmented coatings and clear varnishes has not yet advanced as far as printing inks. In the first instance, the formulation of suitable low viscosity vehicles has proved to be more difficult, the amount of reactive diluent which can be incorporated being strictly limited. Furthermore, pigmented coatings, which are usually white, are applied in heavier films (up to 15 g m⁻²) than are inks, and complete curing throughout a pigmented film is more difficult to achieve due to its higher opacity.

Roller coating materials must possess satisfactory application properties, one of the most important of which is flowout, to eliminate any ribbiness arising from the application by a roller. With conventional materials, flow-out is often completed in the oven, where initially there may be a sharp reduction in their viscosity. UV materials will be required to flow out without this assistance. In addition, the distance the sheets travel, and hence the time between application and curing, should not be too long, otherwise one of the advantages in eliminating the oven (*viz*. the reduction in space), will be diminished.

All materials for metal decorating have to possess a certain functional performance, as well as a satisfactory appearance: the functions might include withstanding a variety of manufacturing and handling conditions of differing severity, pasteurising, steam processing, resistance to contents of the pack, etc. The most stringent demands fall on the varnish, which usually needs to have good gloss, adhesion, scratch resistance and colour, and possibly in addition good mobility and freedom from blushing.

Considerable progress has been made in the past year or so in the development of suitable white roller coatings and varnishes for UV curing, and in the near future these are likely to be introduced for certain limited uses.

Can decorating

In the can-making industry, the growing interest in the drawn and wall-ironed or "two-piece" tinplate or aluminium can has naturally focused attention on the possibility of using UVcuring materials for its decoration. These "two-piece" cans are usually coated and printed on special machines at speeds of up to 800 cans per minute.

Many of the same demands on material performance apply in this area as in sheet decorating. One significant difference is that, particularly in the USA, usually no varnish is applied over the print, so that the inks must possess a good finish and good resistance to scratching. It is quite likely that a complete UV-curing decorative system will be used on cans before one is available for sheets.

A further application for UV-curing materials is on extruded rigid or collapsible tubes and containers, which are decorated at slower speeds. In the case of aerosol containers, an important requirement is that the varnish should have good resistance to a variety of solvents and essential oils used in perfumes and toiletries.

Materials development

In spite of the considerable progress made, there are still certain overall limitations to the performance of UV-curing materials.

In the first place, their adhesion to metal surfaces varies appreciably, depending on the particular metal: on plain tinplate, adhesion is usually rather poor, due mainly to the presence of a lubricant; it can also vary to some extent according to the passivation given to the metal, which alters the amount and nature of the tin and chromium oxides on the surface.

There is some evidence that the rapid curing initiated by UV radiation sets up internal stresses in the printed or coated film, which tepds to shrink it and weaken the bond. Subsequent stoving appears to relax the stresses and adhesion is then considerably improved. On coated metal surfaces, a satisfactory bond can often by achieved by UV irradiation alone.

Another limitation is the amount of unreacted material which can remain after curing. For varnishes and coatings, this can be as much as 5 to 10 per cent by weight, according to the degree of irradiation. Unreacted material is often associated with an odour and can cause contamination of the inside of decorated sheets when they are stacked. For many purposes this would not matter, but where foodstuffs or beverages are concerned it is essential to avoid any possibility of tainting and in these cases a post-stoving operation would be necessary. This requirement may well limit the full exploitation and potential benefit of UV-curing materials in metal decorating, and it is very desirable that materials be developed which, as nearly as possible, attain complete conversion. Until these materials are available, it is unlikely that UV-curing will be seriously considered for internal lacquers on food and beverage cans.

Labels and cartons

UV-curing lithographic inks are beginning to be used in significant quantities for printing cartons, and to a lesser extent for labels. They are usually introduced to print on "difficult" surfaces, such as aluminium foil or other nonabsorbent materials, where set-off can cause severe problems, or to achieve a significant improvement in print quality. Among the advantages that have been found are a reduction in machine wash-ups due to the inks" high press stability, reduction in factory space occupied by stacks of printed board when drying, and a quicker turn round of work.

Unlike metal decorating, where the potential advantages, such as the elimination of ovens, are fairly obvious, it is less easy to justify the appreciably higher cost of the inks and the additional capital cost of drying equipment where none exists already. It has been the general experience, however, that the improvements in efficiency and the savings, which are difficult to forecast and quantify, have invariably justified the installation.

The drying of UV-curing inks is much less dependent on the substrate than that of conventional inks, whilst their appearance on the poorer and more absorbent materials is usually significantly better due to the very short time interval between printing and curing. This is true, even though they still have a slightly inferior gloss compared with conventional inks and varnishes.

The performance of the print from UV-curing inks can often be superior in some respects to that of conventional inks. Thus their odour and taint characteristics are usually judged to be better, so that they are particularly suitable for some food cartons. In addition, their scuff and rub resistance, as well as their resistance to softening and bleeding, can also be higher.

A further improvement in print quality can be achieved by inter-deck setting on multicolour machines. This eliminates dot doubling as well as inter-deck trapping and effectively substitutes wet-on-dry for wet-on-wet printing. At present, most of the sheet-fed machines so equipped are in the USA, whilst in Europe mainly final drying has been installed.

There is a specialist interest in using UV-curing varnishes applied by roller coating to produce a high gloss finish, sometimes as an alternative to film lamination. This exploits the ability of quite thick unpigmented films to be cured without incurring any set-off or sticking.

A further development that is likely to arise from the adoption of UV curing is the extension of both sheet and web-fed machines to include follow-on operations, such as the cutting and creasing of printed board for cartons. For the most part, its realisation depends on bringing into harmony the running speeds and "make-ready" times of all the operations in a line.

Plastics containers and closures

At present, the use of UV-curing dry offset inks for printing plastics containers and closures (cups, tapered pots, tubes, lids, etc) is confined almost entirely to the USA and there it is growing fairly rapidly. One of the main advantages, compared with the use of conventional inks, is much better press stability, which makes for easier running, better print quality and less wastage. The more reliable method of curing should also ensure freedom from set-off when tapered pots and lids are nested—an important consideration as they are mostly used for foodstuffs and any contamination on the inside is very undesirable.

There has been difficulty in achieving satisfactory adhesion and product resistance on some plastics and this has somewhat restricted the use of these inks. With improved formulations, the limitations are being overcome and their wider use seems certain to occur.

In the western world, the screen printing of plastics containers with UV-curing inks has yet to be realised. By this process, comparatively thick films $(20-30\mu m)$ are printed. Sufficient penetration of the radiation to ensure adequate curing is not easy to achieve and can depend very much on pigmentation. Not only is it necessary to obtain good adhesion, but resistance to softening or loosening of the printed film by various products may also be required.

Nevertheless, the growing success of UV-curing screen printed resists for printed circuit boards-together with the

144 UV 12

keen interest of screen printers of flat sheets in eliminating some of their existing cumbersome drying equipment—is bound to stimulate interest in the development of satisfactory inks for various purposes.

Flexible packaging

Limited progress has been made in developing inks for gravure and flexographic printing and as yet there are no production installations. Some of the technical problems are similar to those encountered with roller coating materials, for example, the development of suitable low viscosity vehicles.

The commercial interest in inks for these processes has so far been very limited due mainly to their appreciably higher cost, but demand for them may start to rise as some of their potential advantages are better appreciated. Thus the elimination of volatile, low flash solvents from press rooms would lead to safer working conditions and hence produce some cost saving. The substitution of existing highly unstable inks by press stable varieties should also provide some benefits (particularly in flexographic printing), such as easier running and better print quality.

The development of UV laminating adhesives is also receiving some attention. These new products might enable some of the difficulties which occur with existing materials, due to retained solvent, to be avoided. Their use would, of course, be restricted to combinations where at least one of the plies was transparent to radiation.

UV-curing equipment

Ref. 2

Lamps

From its inception, the medium pressure mercury vapour lamp, usually operated at 80 watt per cm, has been the mainstay of UV-curing. It provides a broad selection of available radiation extending from about 230 to 406 nm (Table 2).

| | | | | 2 | Table 2 | 10 | |
|-------------|----------|----|---|---|---------|----------|---------|
| Ultraviolet | emission | of | a | | watt/cm | pressure | mercury |

| Wavelength | | Intensity |
|------------|-------|-----------|
| (nm) | | (watt/cm) |
| 235 | | 0.094 |
| 238 | | 0.181 |
| 240 | | 0.165 |
| 246 | | 0.071 |
| 248 | | 0.417 |
| 254 | | 0.535 |
| 258 | | 0.063 |
| 260 | | 0.087 |
| 264 | | 0.110 |
| 265 | | 0.772 |
| 270 | | 0.181 |
| 275 | | 0.134 |
| 280 | | 0.433 |
| 289 | | 0.205 |
| 292 | | 0.087 |
| 297 | | 0.583 |
| 302 | | 1.111 |
| 313 | | 2.140 |
| 334 | | 0.292 |
| 366 | | 3.385 |
| 391 | | 0.047 |
| 405 | | 0.898 |
| 406 | | 0.189 |
| | Total | 12.180 |

The lamp's wide range has made it suitable for a wide variety of pigmented and unpigmented systems. Much remains to be learned about the interaction of UV radiation and systems consisting of various resins, photo-initiators and pigments, all of which may have very different UV absorption characteristics. It may well be that a selection of wavelengths is necessary to initiate these different systems and, if so, there will probably always be a place for a wide spectrum general purpose lamp.

It has to be recognised, however, that a large amount of the radiated energy will be dissipated as unwanted heat and, in addition, that only a small proportion of the available UV energy is likely to be utiljsed effectively in any particular instance. In order to obtain improved efficiency, there may arise a need for special purpose lamps whose outputs would be concentrated at certain wavelengths, and which would be used with specific types of material, such as clear varnishes or white pigmented coatings.

Such special purpose lamps may be no more than modified versions of the existing "standard" lamp with suitable additives to enhance emission at certain wavelengths. On the other hand, they may emerge as one or more of the alternative lamps, or combination of lamps, that have recently become available. These include a metal-halide lamp, a radio frequency driven lamp and a combination of low and high power lamps. It may well be that for any of these sources to become established on a wide scale, it will be necessary to develop special formulations (tailored to the lamp's emission characteristics), which would be significantly cheaper or give enhanced performance.

Lamp units and driers

There is an appreciable range of lamp units and drying installations now available. Most of the equipment is designed around the "standard" lamp, which is usually housed in an elliptical reflector giving a sharply focused beam, although some parabolic reflectors are now being used. At one time it was believed that the most intense concentration of radiation was required for maximum efficiency, but for most applications there seems to be little to choose between the two systems.

To remove the heat produced and to prevent the lamp deteriorating, some form of cooling is essential. A variety of means are used, including extracting air over the lamp, blowing air over the lamp and extracting it, water cooled reflectors, water cooled shutters, water cooled or air cooled sheet transfer systems, enclosing the lamp in a water jacket, etc. Since the "standard" lamp produces ozone, some form of extraction to the atmosphere is necessary. However, an ozonefree version, which is claimed to have comparable efficiency, is now available; it will be interesting to observe whether this will have any influence on the design of driers.

During short stoppages, it is undesirable to switch off a "standard" lamp due to its fairly lengthy re-striking time. Instead, its power loading is usually reduced to 50 per cent and it is shielded either by rotating the housing to a closed position, or by some form of shuttering. Some of the alternative lamps are not restricted by this re-switching limitation and their housings are correspondingly simpler.

The complete drier has to be so designed that the radiation is adequately screened and cannot be either deliberately or accidentally viewed. This involves the use of interlocks on any movable sections so that the equipment is made virtually fool-proof.

Installation on printing machinery

Both interdeck and final drying units have now been developed to fit many sheet and web offset printing machines², although limitations of available space have prevented some designs being realised in practice. There are also separate conveyor driers to fit on the end of sheet fed machines and special purpose driers for metal and plastics containers.

Recently, one of the first machines to be designed specifically for running UV-curing inks has been introduced. In addition to providing space for inter-deck setting, use is made of the high press stability of the inks by varying their temperature in order to control their rheological properties and hence the print quality. It seems certain that this will be followed by other machines with compact UV driers built in, rather than added on: it is here that an appreciable reduction in the heat produced by the lamp would provide the designer with greater flexibility.

General observations

One of the main factors which stimulated the development and introduction of UV-curing materials in the USA was the need to reduce atmospheric pollution by solvent emission from printing and decorating lines. In Europe, so far, this has been a lesser incentive, but it seems likely that similar pressures may well arise here that will encourage, if not require, the use of low solvent or solventless decorative systems. To this extent UV curing will be competing with water based and powder materials. The rising cost of solvents and the need to conserve energy and raw material resources are further reasons for stimulating the use of radiation convertible systems.

The higher cost of UV-curing materials has certainly discouraged their widespread introduction and led to their selective use. At the start, this was probably fortunate as the wholesale adoption of this new technology could have had very undesirable results, such as the use of poorly designed or hastily manufactured equipment, which might have presented safety hazards. Initially, the cost of UV-curing inks was on average about 80 per cent higher than for the corresponding conventional inks. This differential has narrowed slightly (due mainly to the relatively greater increase in the cost of conventional materials), but not yet to the extent originally forecast. With the successful establishment of the technology in many areas, it is now clearly desirable to reduce the dissuasive cost factor by the development of more efficient lamps and of cheaper vehicles which will reduce both energy costs and the comparatively high concentration of expensive photo-initiators in current formulations.

Not surprisingly, the novelty of UV-curing systems has resulted in a cautious approach to their use. They are based on a variety of components not hitherto used in inks and surface coatings, some of which are potentially very reactive. Their safe handling, both during manufacture and before and after curing, is a matter of concern and it is encouraging to know that a number of suppliers have undertaken extensive testing for possible skin irritation and other hazards. It is clearly essential that if these materials are to retain their present high reputation, they should be based only on components which have been screened as carefully as possible.

Conclusion

The use of UV-curing materials for the printing and decorating of packaging is becoming firmly established, after a fairly slow start, and is likely to grow in the foreseeable future. The extent of the growth depends partly on economic factors, particularly the relative cost of the materials, and partly on the solution of certain technical problems. The development of more efficient lamps and their integration into printing machines designed for the purpose are further requirements.

[Received 7 July 1975

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Photochemical excitation

By R. B. Cundall

Since the publication of his paper in the March issue (page 95; "Ultraviolet polymerisation" book, page UV I), Prof. Cundall has been appointed Professor of Chemistry in the Department of Chemistry and Applied Chemistry at the University of Salford, Salford M5 4WT, Lancs.

Next month's issue

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

Photoinitiation by aromatic carbonyl compounds by A. Ledwith

The technological literature relating to polymerisation photoinitiators by A. Pryce

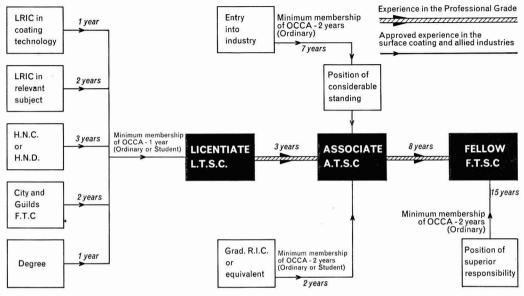
Photopolymerisation: the kinetics of a-type photopolymerisation by F. C. de Schryver and N. Boens



Optional Professional Grade for Ordinary Members

The innovation of the Professional Grade has proved to be most successful, as evidenced by the impressive list of names in the December 1975 issue of the *Journal*. For the convenience of potential applicants, a chart indicating different routes to the various grades is shown below.

Routes to the Professional Grades



Note: At present there is no restriction on Students up to 21; between 21 and 25 a certificate from the employer or college confirming the course being taken is required.

Application

A leaflet has been prepared by the Association showing the diagram above and giving the full regulations for admission to all three of the Professional Grades. Copies of this leaflet and application forms for admission are available from the Association's offices (at the address on the Contents page). It is felt that some overseas Members, in particular, might encounter difficulties contacting the required number of sponsors and applicants who find themselves in this position are advised to write to the Director & Secretary of the Association in the first instance.

Completed application forms should be returned, together with the appropriate remittance, to the Director & Secretary at the Association's offices (except in the case of those Members attached to the Auckland, South African and Wellington Sections who should address their forms to their Section Hon. Secretaries).

The Committee wishes it to be known that Members rejoining the Association after a period in other industries may include length of service as an Ordinary Member before their resignation as part of the qualifying periods for entry into the Grade.

Students wishing to apply for entry into the Professional Grade must first make application in writing for upgrading to Ordinary Membership, giving the reasons for their eligibility for such regrading. Applications, together with the appropriate remittance, should be addressed as for application for admission to the Professional Grade.

Potential applicants are recommended to give the fullest possible details of their appointments, including the number and type of staff under their control, and indicating to whom the applicant is responsible, as this aids the committee considerably in its deliberations.

It is felt that applicants for admission to the Licentiate grade might wish to have further information on the pattern which it is suggested should be followed for dissertations, the subjects of which have first to be approved by the Professional Grade Committee.

The dissertation should be preceded by a short summary and commence with a brief introduction and some account of the current state of knowledge. Where practicable it should follow the general format of a paper in the Journal.

The dissertation may be a review of a subject, a theoretical treatment, descriptive of practical work or a combination of these. It must indicate that the candidate has a reasonably wide and up-to-date knowledge of his chosen subject and understands the basic scientific principles underlying it, and that he is able to think critically and constructively.

Where practical work is described, some attempts should be made to draw theoretical conclusions or to form some provisional hypothesis, together with an outline of what further work would be required to confirm the views put forward or further to advance the knowledge of the subject.

Where the dissertation is a review or a theoretical treatment, there should be an attempt to contrast and compare any opposing views expressed in earlier works, to examine the views critically, to suggest any compromise interpretation, to account for all the known facts and to outline any further work by which the opposing views could be tested.

Where applicable, references should be given to published work, graphs, diagrams etc. to be appended.

Length: Text should be approximately 5000 words.

Applicants should refer to the paper by Moss which appeared in the January 1973 issue; the Professional Grade Committee feels that candidates for the Licentiate grade could with advantage use this paper as a model for their dissertations.

Admissions

For details of the latest admissions to the Professional Grade, see page 155 of this *issue*.

Information Received

ATIPEC President

Mr G. H. Clinkemalie has recently been re-elected President of ATIPEC.

BASF to increase ethylene diamine capacity

BASF is to increase its ethylene diamine capacity at Antwerp to 25 000 tonnes by the end of next year. Capital investment for the project will run to some DM 50 million.

The production process, based on monoethanolamine, has been substantially improved and permits flexible production of controlled quantities of diethylene triamine, aminoethyl ethanolamine and piperazine products.

British corrosion consultancy in USA

The British corrosion engineering consul-tancy, R. J. P. Nicklin & Co. Ltd of Sheffield, is opening a branch in Houston, Texas. The company at present has 80 resident engineers based throughout western Europe, the Middle East, Africa and serving the North Sea oil industry, and provides a the North Sea of industry, and provides a range of consultancy services embracing corrosion surveys, specification preparation and inspection and supervision. The move to Houston follows a long appraisal of the American oil industry by a Nicklin execu-tive team. Mr. R. J. P. Nicklin is an Ordinary Member attached to the London Section.

Chemical resistant sheet laminate

Loyne (Manchester) Ltd of Dukinfield, Cheshire, has been appointed sole British licensee for "Kynar" multiple ply laminate, a stress free fluoroplastic lining material.

Compounding Ingredients in Czechoslovakia

large potential business in Czechoslovakia is predicted by the Manchester based chemical company, Compounding Ingredients Ltd. The new eastern Europe

business is the result of the joint agreement with Exico, the sales organisation representing CIL in Czechoslovakia.

Du Pont sells Swedish paint plant

Du Pont de Nemours Nordiska AB and AB Wilhelm Becker, a Swedish paint company, have reached a preliminary agreement for the sale of Du Pont's finishes plant at Märsta, Sweden, to Beckers.

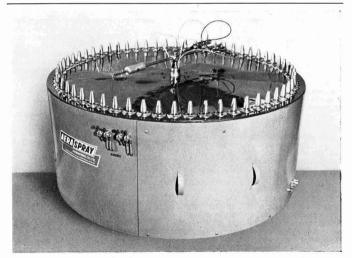
Du Pont's sales of industrial finishes in Sweden and neighbouring Scandinavian markets have not developed as expected in relation to the plant's capacity. Following transfer of the plant, Du Pont Nordiska will make imported paint products available to its customers.

Expansion by Unilever-Emery in the Netherlands

Unilever-Emery NV of Gouda, the Netherlands, will spend 40 million guilders on a new production unit for chemical intermediates. The products to be manufactured are azelaic and pelargonic acids and their derivatives. They are used as basic or auxiliary materials in many industries: synthetic lubricants for jet aircraft engines, high quality paints for automobiles, fibres and nylon engineering plastics, oil-free resins for artificial leather covering materials are a few examples from a wide range of applications.

Completion of the new project will require about three years. This new plant not only trebles the production capacity in this sector, but its advanced design enables the manufacture of a highly purified azealic acid, not previously manufactured in Europe. Hitherto this speciality has only been manufactured by Emery Industries, Inc. of Cincinnati.

The new unit will eventually provide employment for 35 people. In the meantime, some 400 people will be involved during



The new AT60 sixty-spindle indexing turntable, introduced by Aeraspray Engineering Co. Ltd 148



new "Digitherm Universal" electronic thermometer recently announced by Kane-May Ltd. The pocket-size instrument gives an instant reading to $\pm 0.1^\circ C$ over various temperature ranges from -50 to $1100^\circ C$ and has built in compensation for ambient temperature and loss of battery power

construction. The plant will be built adjacent to the present manufacturing complex on the Hollandse IJssel river.

Fluxa agents in Italy for AES

Albany Engineering Systems Europe Ltd, Industrial Filtration Division, have appointed Fluxa, via Pier Capponi 13, Milan, to represent them throughout Italy for the supply of AES permanent media liquid filters.

Garrick Equipment agents for Horst Geppert

Garrick Equipment & Co. Ltd, Garrick Street, London, has been appointed UK agent for Horst Geppert of West Germany to market its drum mixer.

New PRI Section

The Plastics and Rubber Institute has The Plastics and Rubber Institute has formed its eleventh overseas section, the Netherlands Section. The first Chairman is Dr Ir P. J. Bakker, FPRI, the Director of the Plastics and Rubber Institute, TNO, Delft, and the Honorary Treasurer is Mr T. C. N. Belgraver, c/o Stichting Opleiding Rubber en Kunststoffen, Balistraat 97 (PO Box 1806), The Hague.

Surface treatment and finishing show

The Surface Treatment & Finishing Show, organised by the British Metal Finishing Suppliers' Association and the Institute of Metal Finishing, will be held at the National Exhibition Centre, Birmingham, from 18 to 21 May 1976.

Swale Chemicals moves to new research centre

Swales Chemicals Ltd, manufacturer of specialised coatings and inks, has moved its laboratories to new custom built premises near Croydon. The address is Swale House, 164 Thornton Road, Thornton Heath, Surrey CR4 6BB. From this unit, research and development will be carried out for the whole of Swales' international operations, serving its export markets and associated manufacturing companies in Australia, Ireland, South Africa and Switzerland.

New products

Indexing turntable

Aeraspray Engineering Co. Ltd, Birmingham, manufacturers of a complete range of equipment for the application of industrial finishes, have announced the introduction of the AT60-Spindle Indexing Turntable.

Designed for the automatic application of sprayed finishes to small components, the Aeraspray AT60 can handle 600 items per hour. As operation of the AT60 is continuous, all that is required of the operator is for him to fit articles to the spindles and to remove finished ones whilst the machine is running. A spray gun or guns are mounted on the central spindle, where vertical motion and dwell time are pre-set to suit the product being finished, adjustment being achieved by variation of the controlling cam mechanism. Indexing is controlled by a geneva-wheel mechanism under the work surface.

The main advantage claimed for the AT60 over previous models is that the increased number of spindles results in more time being required for the turntable to complete a cycle, and this allows better drying times without slowing either the spraying time for individual items.

Infrared spectrophotometers

Two new, low cost infrared spectrophotometers have been announced by Perkin-Elmer Ltd, the Models 197 and 297. These spectrophotometers have been designed specifically to meet the growing need for higher performance routine instrumentation which can provide reliability, accuracy, versatility and simplicity of operation.

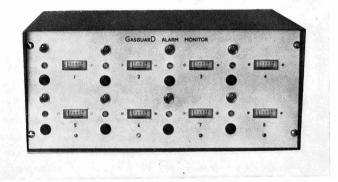
Both the Models 197 and 297 are double beam optical null spectrophotometers covering the range 4000 to 600 cm⁻¹, using the well established Perkin-Elmer Flowchart recording system. The latest solidstate electronics and stepper motor drive incorporated into both instruments contribute to their high reliability and range of scan speeds. They also allow the charge and monochromator to be driven at high speed to any wavenumber, with a slow "inching forward" facility taking over to reach the exact wavenumber required.

Laboratory UV-curing system

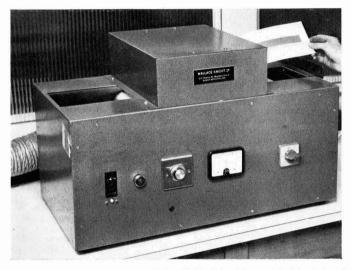
One of the leading British manufacturers of ultraviolet-curing equipment, Wallace Knight Ltd, has recently introduced a new scaled-down version of its UV-curing system, which has been designed specifically for laboratory or colour matching purposes. Based on the company's standard production equipment, the new system known as "Labcure" is a compact unit, which can be either bench or trolley mounted. It operates from a standard mains (220/250 volts) outlet.

Pigmented gel coats

A new range of "URA" pigmented isophthalic gel coats has been introduced by Synthetic Resins Ltd, Speke. Eleven standard colours with improved chemical resistance and weathering properties are now available for GRP products and components.



The new "Gasguard" alarm monitor, recently introduced by Analytical Equipment Co. Ltd, which the company particularly recommends for the detection of explosive gases. The control console allows a number of locations to be monitored from one surveilance point



The new "Labcure" unit developed by Wallace Knight Ltd and in use at the laboratories of Lorilleux & Bolton Ltd

Water-based finishing system for wood

A Swedish firm, Acroma Lack AB, has recently announced the introduction of a new "Lacroma" range of water-based surface finishing systems for wooden furniture.

Literature

About polymers

"Know more about your polymer", a new publication from Waters Associates, describes the importance of molecular weight distribution as a fundamental polymer property. The document then gives step-by-step directions how to obtain and use the molecular weight distribution to solve polymer-related problems, and describes the mechanism by which the distribution is obtained.

The 28-page document is complete in itself, but can also be used to amplify an earlier Waters' publication, "How to tell good from bad". Copies of "Know more about your polymer" are available free of charge from Waters Associates Inc., Maple St, Milford, Mass. 01757 USA.

Gas and liquid chromatography

A volume "Gas and liquid chromatography abstracts—Cumulative Indexes 1969-73", edited by C. E. H. Knapman, has been published recently by Applied Science Publishers Ltd, 22 Rippleside Commercial Estate, Barking, Essex. The book comprises 381 pages, and includes complete author and subject indexes. It is bound in hardback version and copies are available at £16.00 each. (Since 1973, "Gas and liquid chromography abstracts" has appeared as a quarterly journal, details of which are available from the publishers.)

Industrial amines

Garrick Equipment & Chemical Co. Ltd has announced that new literature is available on three new industrial amines available from Abbot Laboratories:

- 1. N-Methylcyclohexylamine
- 2. N-Phenylcyclohexylamine
- 3. Dimethylamino propylamine

New Tioxide publications

"Dispersion of Tioxide pigments in nonaqueous media" (BTP: 162) is the latest addition to Tioxide's range of "industry" publications that help manufacturers make

Reviews-

High-speed liquid chromatography

By P. M. Rajcsanyi and E. Rajcsanyi

New York and Basel: Marcel Dekker Inc, 1975

Pp. VIII + 203. Price \$15.50

The first problem with this new technique is to agree on its name. It is conventional liquid column chromatography with the feature that the material to be separated is forced through the column under pressure. High-pressure, high-performance and high-speed liquid chromatography are all synonymously used in the literature but the authors have chosen the lastnamed, that is HSLC. Although this term also includes high-speed ion-exchange chromatography and gel-permeation chromatography, these are dealt with only briefly, the main emphasis being on liquid-liquid and liquid-solid chromatography. The position is very much the same as in the early days of gas chromatography when vapour phase chromatography competed with gas-liquid chromatography (GLC) for the title. The authors, in fact, consider that HSLC is in much the same position as GLC in the early 1960s and that spectacular advances in the field will follow in the next few years. At present, analysts in the coatings and polymer fields are somewhat disappointed at the rate of advance of the new technique. Certainly, problems of separation of mixtures of components not sufficiently volatile for GLC rather than identification of separated components is the outstanding problem, but there have been few successes so far in this field.

The book deals firstly with theory and secondly instrumentation, particularly detectors and columns. The "gradient elution" technique, where the composition of the eluting solvent changes throughout the run, is also described, but commercial equipment for this is rather expensive.

The third section of the book on applications confirms that there have been few separations effected so far, with the exception of phthalate plasticisers, phenols and non-ionic surfactants of value to the coatings industry. A short section on polymer resins refers mainly to gel permeation chromatography.

This work forms a useful first book in a new field for those who believe in the future of the technique for their requirements. Although the authors are from Hungary, there are no language difficulties in the presentation.

L. A. O'NEILL

INFORMATION RECEIVED JOCCA

Tioxide Group Ltd has also issued two new product booklets—Tioxide R-FC5 (BTP: 187) and Tioxide R-TC2 (BTP: 188) —which will be of interest to plastics manufacturers.

Road markings

The British Standards Institution has announced the availability of BS 3262: 1976 "Hot-applied thermoplastic road marking materials".

Unsaturated polyester resins

Cray Valley Products Ltd has issued a technical data sheet as a requirement of the 1974 Health & Safety At Work Act entitled "The safe handling and use of CVP unsaturated polyester resins".

Farbenlehre und Farbenmessung

By W. Schultze

the best use of titanium pigments in their

products. Complementary to the booklets that recommend specific Tioxide grades for individual applications, BTP: 162 gives a

detailed account in Section A of the process

of dispersion, its measurement, and the nature of the different classes of titanium

dioxide pigment which are available. It goes on to discuss millbase composition and gives full practical details of millbase formulation with the different classes of

medium used in modern solvent-borne airdrying plants, industrial finishes, printing inks, and special products.

Section B contains a comprehensive review of the various types of dispersion

equipment which are available, with critical notes as to their suitability for different

products.

Third revised edition

New York: Springer Verlag, Berlin: Heidelberg, 1975

Pp. 97. Price \$13.20, DM 32.00

This is the third updated edition of a brief introduction to colour and colour measurement. The text comprises 86 pages divided into nine chapters, of which the last one on the aesthetic valuation of colours occupies only one page. The book appears to be designed for students needing an appreciation of colour, colour systems and colour measurement. It opens with a chapter on the nature of colour and colour vision. This is followed by a clear description of the spectral evaluation of colours and of the CIE tristimulus system of colorimetry, with very brief references to a number of well known instruments. The Ostwald, Munsell and DIN systems of colour classification and the various methods of colour difference measurement are presented and there are short chapters on some further aspects of colour vision and on fluorescent colours.

The author manages to restrict the use of mathematics to a minimum. During the discussion of colour difference measurement, which is admittedly one of the most complex problems in the whole field of colour measurement, he resorts to mathematical formulae. In chapter eight, devoted to the practical applications of colour measurement, the reader will encounter some relatively simple formulae describing the Kubelka-Munk relationship as applied to the prediction of colour matches.

It is hoped that any future edition will give a little more space to the instrumental aspects of colour measurement, particularly as it appears that there is no major textbook on colour available in the German language. Nevertheless, this work is a useful introduction to the fascinating world of colour.

The book is clearly printed on excellent paper. It is well indexed and contains a comprehensive bibliography.

H. R. HAMBURG

Section Proceedings-

Hull

Water-based gloss paints

The fifth ordinary meeting of the 1975/76 session was held at the George Hotel, Land of Green Ginger, Hull, on Monday 2 February 1976. Dr K. Sellars of Harlow Chemical Company Limited gave a lecture entitled "Water-based gloss paints".

The speaker discussed the design of water-borne gloss paints with particular reference to systems containing alkalisoluble polymers. The effect of these polymers on such factors as rheology, opacity, re-coatability, colour stability, gloss, cleansability, durability, and wet and dry adhesion was examined.

This short meeting, which was attended by some 30 Members and visitors, was brought to a close with a vote of thanks from Mr J. Hasnip.

D.M.W.

The use of microvoids as pigments

The sixth ordinary meeting of the current session was held at the George Hotel, Land of Green Ginger, Hull, on Monday 16 February 1976. Mr E. Armstrong, the Section Chairman, introduced Mr J. Clark of Tioxide International, who gave a lecture entitled "The use of microvoids as pigments".

Mr Clark began by demonstrating how it was possible to obliterate a black and white Morest chart with a foam shaving cream. Bubble coatings, manufactured by emulsifying a volatile solvent in a binder, had been known for a long time. Whilst they dried to give good opacity, they were pressure sensitive. Later, it had been found that the inclusion of glass beads also resulted in good opacity; this technique had been subsequently patented by the Japanese. Microvoid-based coatings were similar, but instead of minute glass spheres, vesiculated polymer beads were used.

A marked improvement in optical performance might be expected if titanium dioxide could be trapped in the vesicles. A technique was outlined by which this result could be achieved: an aqueous dispersion of titanium dioxide is emulsified into a reactive resin and this emulsion is itself emulsified. The resin is cured by addition of initiators, yielding a product consisting of a slurry of vesiculated polymer beads containing titanium dioxide and air in the vesicles.

The present microvoid products were designed for use in semi-gloss and matt emulsion paints. Simple paints of high performance could be manufactured by blending the microvoid slurry in with an emulsion resin by mechanical means. Alternatively, a conventional emulsion paint could be modified simply by stirring the slurry into the mill-base and then letting down with an emulsion resin.

The inclusion of microvoids into a matt emulsion paint gave improved film integrity at the same opacity, and gave better stain and burnishing resistance. High quality emulsion paints based on microvoids would exhibit minimal change in opacity on drying and give improved durability in terms of chalk resistance as measured in a carbon arc weatherometer to BS 3900. The microvoid slurry would withstand ballmilling and sandmilling. Paints based on microvoids had exceptionally good flow and brushing characteristics and were also resistant to flooding and floating.

The lecture was followed by a prolonged discussion during which Mr Clark and Dr Reeves ably answered questions put by the audience. The meeting was attended by 26 Members and visitors and was closed with a vote of thanks from Mr P. Adamson; the audience expressed their appreciation in the usual manner.

D.M.W.

London

The coatings industry in a changing world

An afternoon meeting of the Section was held on Thursday 16 October 1975 at the Imperial College of Science and Technology, London SW7, where Dr H. Wittcoff, of General Mills Inc., gave a lecture on "The coatings industry in a changing world".

Dr Wittcoff began his lecture by discussing the changes that were occurring today and indicated how many of them contributed to the crises that were an inescapable part of the modern world. He then went on to discuss the effect of these changes on the coatings industry and talked in depth about the implications of automation, pollution and population growth on the future of the industry.

Using as examples the changes occurring in America, Dr Wittcoff showed how demands for greater productivity from those in the manufacturing industries had increased in recent years as the numbers involved in production had decreased and the service industries had expanded. Increased automation had created greater amounts of leisure time and this changed the demands for various types of surface coatings. Coatings manufacturers had to be aware of the way potential markets were opening to them in areas where they had not necessarily been involved before.

The speaker indicated how the recent legislation in the USA controlling emission of pollutants into the atmosphere and waterways had created interest in alternative technologies to the organic solvent borne coatings. It was only by being fully aware of the changes that suppliers were able to meet the challenge and produce the coatings required.

The increasing growth of the world's population also produced a challenge to the coatings industry as depletion of energy and raw materials necessitated the need to look for alternatives to both. Lower energy curing techniques, such as ultraviolet and electron beam curing, were being actively evaluated and more and more development was taking place with materials not previously considered for surface coatings.

Dr Wittcoff ended by giving his forecast of the uses of various types of coatings in the future. He foresaw water borne coatings having the greatest increased growth and radiation cure obtaining a significant share of the market.

After the lecturer had answered a number of pertinent questions, a vote of thanks was proposed by Mr R. H. E. Munn.

A.J.N.

Decoration of plastics

A one-day symposium entitled "Decoration of plastics" was held at Thames Polytechnic, Woolwich, London SE18 on 19 November 1975 in conjunction with the Plastics and Rubber Institute and covered the decoration of flexible and rigid plastics.

The symposium was opened by Mr D. A. Fagg, of Bowater Flexible Packaging Ltd, on the theme of "Printing on flexible packaging" with a presentation of flexographic and gravure techniques. Visual aids were used with effect by the speaker and enabled the intricacies of both these forms of printing to be made clear even to those with no previous experience of liquid ink processes.

Mr K. Kohlkepp of Hoechst (UK) Ltd then enlightened the delegates on "Printing on rigid plastics". Mr Kohlkepp discussed the different pretreatment and printing techniques for thermoplastics; the use of non-polar solvents might result in stress cracking. There followed a guide to solvent and printing techniques recommended for a range of rigid plastics.

An area new to most Members was "vacuum metallising" as presented by a representative from Edwards High Vacuum Ltd. Attention was drawn to the many uses to which this technology was applied; the embellishments which it provided were taken for granted by many.

Mr P. J. Lyon of Marley Tile Co., gave a paper on "The decoration of floor coverings". Delegates were soon made aware of the early history of floor coverings from asphalt through thermoplastics to the PVCI foam cushion floors. The process of applying PVCI foam to asbestos paper (inert and heat stable) and covering with a thin film of PVCI was expertly explained, as was the method of chemical embossing, for which there were many patents. By the incorporation of inhibitors into the printing ink to prevent foaming of certain areas, a two-dimensional effect was achieved.

Problems common to all types of decoration were covered by Mr D. M. Varley of CIBA-GEIGY Ltd. Although the talk was entitled "Problems in the pigmentation of plastics", the areas which Mr Varley covered were familiar ground to the surface coatings fraternity present. It was obvious that although heat and light fastness were critical factors affecting pigment choice, the parameters which workers in the plastics industry would emphasise would be the nature of the polymer's heat fastness and migration resistance.

Dr S. Kut of E. Wood Ltd wound up the symposium with his lecture "Decoration of plastics with surface coatings". With a talk well illustrated with samples and slides, Dr Kut showed the decorative and protective qualities of paint in the plastics field. The automotive and distillery trades were those most aware of the benefits to be derived from this technology, but from Dr Kut's confidence, it could be assumed that many examples of new applications would soon be seen in other industries.

K.W.

Cellulose ethers

A meeting was held on Monday 19 January 1976 at East Ham College of Technology, London E6 when Dr V. Knittel of Kalle, Wiesbaden, West Germany, presented a paper entitled "Applications of cellulose ethers in the paint industry".

Dr Knittel opened his lecture by outlining the chemical structure of cellulose and the derivation of the ethers from its reaction with various etherifying agents. He discussed in depth the differences in properties between the cellulose ethers most commonly used in the paint industry and showed how these could be used to modify coatings so that a particular set of physical characteristics, such as flow, viscosity and substrate wetting for a particular application, could be obtained. The addition of the cellulose ethers to various paint systems was discussed and the level of ether added was shown to be dependent on the number of tasks it had to do in the paint.

The speaker indicated how the viscosity, flow and wet bulk stability of paints could be affected by using different molecular weight cellulose ethers. Dr Knittel concluded his lecture by stating that theoretical considerations of the effect of cellulose ethers in a system were impossible due to the complex interactions between pigments, resins, other surfactants and solvents in the paint. Practical evaluation was the only way to determine the type and level of cellulose ether required.

A vote of thanks was proposed by Dr H. Hamburg after Dr Knittel had answered a number of questions.

A.J.N.

Midlands

The outworker

The November meeting held on Friday 21 November 1975 was the Annual Student Lecture and was given by the Chairman of the Section, Mr D. E. Hopper. His talk was entitled "The outworker".

An "outworker" was defined as a company carrying out finishing processes to protect and/or decorate components manufactured and sold by a second party. The advantages of sub-contracting the surface finishing process were enumerated, and the speaker went on to use his own company's experience to illustrate the various functions of the average outworker. Progress was measured in terms of turnover, and results over the 13 years of the company's trading were illustrated with slides.

Initial equipment requirements were modest, but expansion had necessitated the acquisition of a compressor of high efficiency, together with wide spray booths and large box ovens. Conventional hand guns remained in use, as simplicity was considered most important. Airless spraying had been largely abandoned because of lack of flexibility of the process when dealing with a variety of articles. The vital importance of cleanliness and efficient maintenance in what was inherently a dirty process was stressed.

Next followed a list showing the great variety of components handled. One common factor was the need for efficient pretreatment before painting, and treatment in addition to the conventional trichlorethylene degreasing bath was often required. The wide variety of components handled tended to be matched by the number of finishes required. Sample production and approval by the customer prior to commencing full-scale production was considered essential, as standards could be fixed and accurate costs calculated at an early stage.

The use of suitable jigs maximised throughput, but many other problems arose, ranging from the problems caused by poor pretreatment to dust on the articles prior to curing. To rectify these was costly, and rejects were kept down to about two per cent. The hazards of using prefinished components on building sites were well-illustrated with a series of slides.

The speaker concluded with reference to customer specifications and the principles of costing, the latter obviously being no easy matter. Future trends were expected to embrace powder coatings and various water-based systems, giving wider scope with regard to the industries to whom a service could be offered.

An extended question time was finally brought to a close by the acting chairman, and a vote of thanks proposed by Mr R. Tennant was applauded by all.

West Riding

The role of pigment preparations in the surface coatings industry

A meeting was held on 10 February 1976 at the Griffin Hotel, Leeds. Mr M. Cotton, of Sandoz Products Ltd, presented a paper dealing with pigment preparations.

Mr Cotton outlined the benefits from using pigment preparations and the properties required of them. In particular, they should possess easy dispersibility, be stable to storage, show no rub-up or flotation, have no adverse effect on system properties and possess a high tinting strength. Most pigment preparations were actually being produced by the paint or printing ink manufacturers themselves.

Correspondence

Membership subscriptions

SIR—The subscription I paid in 1973 was ± 5.00 per annum. This was increased to ± 8.00 in 1974—an increase of 60 per cent. This year the payment is ± 12.00 —an increase of 50 per cent over 1974, when the subscription was still ± 8.00 . The increase between 1973 and 1976 is, in fact, 47 per cent per annum.

If there is a similar increase between 1976 and 1980 as there has been between 1973 and 1976, the members of OCCA can expect to pay a subscription of $\pounds 56.00$ per annum in 1980. Should not the Prices and Incomes Board have power to vet such increases? What steps are the Association taking to decrease costs? Is the 50 per cent increase justifiable?

I would also like to draw attention to the fact that in 1975 an entrance fee was charged for non-members to go to the Exhibition which should have given a healthy increase in revenue.

Perhaps the Journal could carry the views of other members?

Yours truly,

A. K. UNSWORTH

1 Court Downs Road, Beckenham, Kent BR3 2LL 6 January 1976

If Mr Unsworth had studied the increase in cost during recent years of some of the major items of the Association's expenditure, such as postage, printing and paper, it would have become obvious why the increase in subscriptions for membership became necessary.

Should he be able to estimate accurately the extent to which these items are likely to increase in future, he might be able to predict what the subscription is likely to be in 1980.

At the Scarborough Conference, a member mentioned that when he first joined the Association the annual subscription amounted to one per cent of his salary. If the concessional rates for retired members and students are taken into account, there can be very few members who currently pay one per cent of their salaries on the subscription, even at £12.00 per annum. Hon. Editor

Theories—laboratory investigations—practical performance

SIR—Mr Lindberg's paper (*JOCCA*, 1975, **58**, 399) is regrettably incomplete in that he has not recognised the work of Hoffmann and Saracz (*JOCCA*, 1969, **52**, 113; 1969, **52**, 1130; 1971, **54**, 450; 1972, **55**, 100). Their observations clearly The most common types of preparation available were pigment press cakes, flushed pigments, chipped pigments, easily dispersible pigments, aqueous tinting pastes and universal tinting pastes. Mr Cotton briefly outlined the method of manufacture of each type of preparation and discussed their advantages and disadvantages. The biggest growth area was in the production of universal tinting pastes, in which the pigment was usually dispersed in a glycol-type carrier plus dispersing agents. This type of product was simple to handle and would blend easily into most paints.

A lively discussion followed Mr Cotton's lecture and the vote of thanks was proposed by Mr A. Heywood.

R.A.C.C.

delineate the folly of expecting to obtain "correlation" between exterior exposures (at *three* different sites) and laboratory testing when different vehicle systems are involved and when no effort has been made to match the exposure conditions in the weatherometer to those of at least one of the "natural" environments.

The statement quoted from my 1966 paper on the dew cycle certainly makes me appear far more confident of the "correlation" to be expected than I ever intended. I wished simply to convey my belief that the results of the method would be reproducible "anywhere in the world"—something which of course can not be said for exterior exposures. On re-reading the published paper, however, I must admit that the statement is easily misinterpreted due to its location in the same paragraph as a reference to correlation with Florida exposures. It appeared in a separate, concluding paragraph in the original manuscript. The text, in any event, clearly disclaims good correlation when different vehicle systems are compared.

My recent paper, "The Dew-Cycle Weatherometer Reevaluated", which appears in the December 1975 issue of *Journal of Paint* (now *Coatings*) *Technology*, was written about one year before Mr Lindberg's contribution, but I believe that it adequately explains the difficulties reported in the latter.

"Correlation" is the Philosopher's Stone of accelerated weathering; it does not exist, but we may unavoidably learn something while searching for it. Nevertheless, it is to be hoped that the resources available to Mr Lindberg will some day be applied to a study of the relative responses of coating resins (and pigments) to the several exposure factors that combine to produce the destructive effects of natural weathering. The weatherometer offers an opportunity to vary the intensity of these factors independently and to observe their effects. Statistical design of experiments and statistical analysis of the results may be expected to provide far more enlightenment than the endless repetition of arbitrary exposure cycles.

Yours faithfully,

F. B. STIEG

Titanium Pigments Division, NL Industries, USA 16 December 1975

Present address: Pigmentech Consulting, 226-C Marchester Lane, Jamesburg, NJ 08831, USA

Notes and News-

Scottish Section

Annual Ladies' night

The annual Ladies' Night and Dinner & Dance was held at the Albany Hotel, Glasgow on Friday 9 January 1976. As in former years, this was a function well supported by Members and friends from far and wide.

After a most enjoyable meal, the Chairman, Mr A. McLean, welcomed the top table guests and their ladies in his own inimitable fashion, making full use of "broad Scots' verse", and proposed a toast to the ladies and guests.

Replying on behalf of the ladies and guests, the President, Mr A. Rudram spoke of his long and close association with the Scottish Section, making particular reference to the Student Section. In conclusion, he asked all present to join him in a toast to the Scottish Section.

Dancing followed until 1.00 am, by which time all present were in a mood to agree wholeheartedly with the Chairman's earlier

London Section

Kekwick Prize 1975 and 1976

The London Section Committee has made Awards to students who have taken an approved course of study in London, as follows:

1975 Mr D. P. Sawyerr, LTSC (East Ham College of Technology)

1976 Miss J. Mathews (London College of Printing) Mr P. Trew (East Ham College of Technology) Mr I. W. Hardie (Polytechnic of the South Bank)

Awards will be presented at the Section's AGM on 22 April 1976, to the students listed above, with the exception of Mr Sawyerr, who is now living in Nigeria.

Ladies' night

The annual Ladies' Night was held on Friday 24 October 1975 at the Piccadilly Hotel, London W1. The chairman, Mr J. Tooke-Kirby, and his wife welcomed the 200 Members and guests, who included Mr M. Farid of the Society of Dyers and Colourists and Lady Ursula Glynn. Following the dinner the chairman made a speech of welcome and Lady Ursula Glynn replied on behalf of the guests. Dancing continued until midnight.

remarks about the enjoyable nature of this annual event and to echo his thanks to the Vice-Chairman Mr Davidson, and Social Secretary, Mr Morrow, for their endeavours in arranging the evening, which was once again up to the high standard of previous Ladies' Nights.



Top-table guests at the Scottish Section Ladies' Night: (from left to right) Mr D. E. Hopper (Midlands Section Chairman), Mr A. McLean (Scottish Section Chairman), Mr A. McKendrick (Chairman, Eastern Branch), Mr A. T. S. Rudram (President), Mr H. G. Clayton (Manchester Section Chairman), Mr J. D. W. Davidson (Scottish Section Vice-Chairman and representative on Council); (from left to right) Mrs Hopper, Mrs McLean, Mrs Rudram, Mrs McKendrick, Mrs Davidson, Mrs Clayton

Report of Council Meeting

A meeting of Council took place at the Great Northern Hotel on 24 February 1976 with the President, Mr Rudram, in the chair. There were 25 members of Council present.

It was reported that Dr R. C. Denney had been appointed the Association's representative on the British National Committee for Chemistry with effect from 1 January 1976.

The Council discussed its Annual Report for 1975 and agreed this for presentation to the Members at the Annual General Meeting to be held on 25 June 1976 at 3.00 pm at the Crown Hotel, Harrogate, immediately after the termination of the West Riding Section's two-day symposium on "Exports". The agenda for the AGM was discussed and finalised.

Details were given of the organisation of the Association's Dinner Dance to be held on 14 May 1976 at the Savoy Hotel. It was noted that the 1978 Dinner Dance would coincide with the sixtieth anniversary of the foundation of the Association. Council gave further thought to the celebration of this important milestone in the Association's affairs and full details will be communicated to Members in due course.

Consideration was given to the venue for the 1979 Conference, and it was reported that topics for some of the papers had already been submitted for the 1977 Conference, which would take place at Eastborne from 17 to 19 June 1977 under the title "The conservation of energy, materials and other resources in the surface coatings industry".

Details of the 1976 Exhibition were reported to Council, together with the arrangements for the 1977 Exhibition, which would again take place at Alexandra Palace. It was unanimously agreed, in accordance with article 14, that any Member whose current subscription was three months or more in abeyance would not be sent the April issue of the *Journal* until payment of the subscription due had been received.

Progress reports were made on the Association publications, including the revision of the Introduction to Paint Technology, of which a new edition would be appearing later in the year, and the second edition of Part IV of the Paint Technology Manuals, and it was agreed to publish the Decennial Index of the Journal covering the period 1966-1975. The Index would be charged at £5.00, but Members of the Association would be entitled to apply for one copy each at the preferential rate of £2.00. A form would be enclosed in a copy of the Journal as soon as the publication was available.

It was agreed to confer Commendation Awards upon two Members of the Association for their active support of the Association over a long period: Mr G. F. Jones (Irish Section) and Dr W. Carr (Manchester Section).

Council had before them a report from the Honorary Secretary of the London Section, Mr H. C. Worsdall, on his recent visit to the Ontario Branch of the London Section, and the desire amongst Members of the Branch that it achieve Section status. The Chairman of the London Section, Mr J. Tooke-Kirby, reported that he hoped everything would be in hand, in accordance with article 70, for the petition by the Members to be given final approval by the Council at its meeting on 1 April 1976, so that Section status could be granted with effect from the AGM of the Branch to be held on 23 April.

Reports from the various Sections and items arising these from were then discussed by the Council in detail.

1976 (4) NOTES AND NEWS

It was reported that a request had been received from the Federations of Societies for Coatings Technology for an Association paper to be presented at the Convention of the Federation, 27-29 October 1976 at Washington DC, and any Member who is planning to offer a paper to the Convention is asked to contact the Director & Secretary as quickly as possible.

There being no other business, the President thanked members for their attendance and declared the meeting closed at 3.50 pm.

Professional Grade

Admissions

At a meeting of the Professional Grade Committee held on 24 February 1976, the following admissions to the Professional Grade were authorised:

Fellows

Peter Birrell (London Section—Ontario Branch) John Theodore Tooke-Kirby (London Section)

Associates

Michael Denis Thomas Clark (Wellington Section) Basil Ray Green (General Overseas Section—West Indies) Svend Johnsen (General Overseas Section—Denmark) Reginald Claude Pobjoy (General Overseas Section—Zambia) Michael Melvyn Nolan (Irish Section) Allan Whatting (Manchester Section)

Transferred from Licentiate to Associate

Garth Anthony Cox (West Riding Section)

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 1947-49 and an Honorary Member, and who died in December 1964. The Committee invites applications for the fourth award of £100.

The rules of the Award are:

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.

 The final date for submission of applications will on this occasion be 31 December 1976 and it is hoped to present the award at the 1977 Association Conference.

 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 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.

News of Members

Mr D. G. Addenbrook, an Ordinary Member attached to the Manchester Section, has been appointed Head of Marketing (UK) for the Pigments Division of CIBA-GEIGY (UK) Ltd. Mr Addenbrook was formerly Marketing Manager of the Division's Paint Industry Group.

Mr D. L. Austin, an Ordinary Member attached to the Bristol Section and a Fellow in the Professional Grade, who has been deputy chief chemist of Pearl Paints for twenty-one years has been appointed chief chemist in succession to Dr Katz.

Mr E. Greenfield, an Ordinary Member attached to the Midlands Section and an Associate in the Professional Grade, has been awarded the C.G.I.A. for his thesis entitled "An investigation into powder coating formulations and the evaluation of the resulting coatines".

Dr S. Katz, an Ordinary Member attached to the Bristol Section, retired as chief chemist of Pearl Paints Ltd at the end of January after 38 years' service with the company. He will be continuing his association with the company as consultant.

Mr R. C. Knight, an Ordinary Member attached to the London Section and an Associate in the Professional Grade, has been awarded the degree of Doctor of Philosophy by the North East London Polytechnic. Mr R. W. M. McEwan, an Ordinary Member attached to the Scottish Section, has received an upgrading in professional status with the Royal Institute of Chemistry from Grad RIC to MRIC, C.Chem.

Mr R. H. E. Munn, an Ordinary Member attached to the London Section and a Fellow in the Professional Grade, has taken up an appointment as General Manager of Cray Valley SA, 65 Rue des Cités, Ambervilliers, France, a newly formed subsidiary of Cray Valley Products Ltd, with whom Mr Munn was formerly Technical Manager.

Mr F. E. Ruddick, an Ordinary Member and past Chairman of the Bristol Section, who retired recently from BP Chemicals International Ltd at Barry, has taken up an appointment with Dyno Industrier AS at its factory in Norway. He is assisting Dyno with the thermosetting acrylic and amino resins, which were transferred when BPCI withdrew from the manufacture and sale of surface coating resins. He reports that he has settled down and is enjoying his stay in Norway.

The President, Mr A. T. S. Rudram, has accepted an invitation to join the editorial board of the journal "Progress in Organic Coatings".

Mr E. A. Watson, an Ordinary Member of the Newcastle Section, presented a paper entitled "Modern paint coatings in theory and practice" to a joint meeting of the Malmo Section of the Swedish Paint and Varnish Technologists Association and the Danish Varnish and Paint Chemists' Association in Copenhagen on 17 March.

Obituary

Rowland Alfred Brett

The sudden death of Roy Brett on 28 January 1976 at the early age of 54 came as a great shock to his many friends. His studies at Birkbeck College (University of London) were interrupted by the war when he had service in the RAF, demobilised with rank of Flight Lieutenant. He joined the Paint Research Association in 1946. completing his BSc, in chemistry with honours in 1948. Roy was well known and respected in scientific circles of the paint industry, particularly for his work on alkyd resin chemistry. He was elected an Ordinary Member of the London Section in 1958. After 27 years' service, he retired from the PRA in September 1973.

Roy Brett was a modest man with great charm, and many who worked with him in the laboratory will remember with gratitude his advice and guidance that were always readily available. Everything he did was done well as those who have read his many papers (he published at least 40) and attended his lectures will testify. He was master of his subject and, altogether too rare with lecturers, had a first rate way of communicating his ideas.

He was a keen sportsman and excelled in many activities, notably cricket, tennis, snooker and, a great favourite in later years, golf—he was runner-up in the tournament at the 1969 Eastbourne conference.

Roy leaves a wife and two grown-up sons, to whom his many friends extend their deepest sympathy.

G. L. Holbrow

Register of Members

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

Ordinary Members

TERRENCE MICHAEL, BSc, Sissons Paints Ltd, Princess AWAI. Margaret Highway, Chaguanas, Trinidad, West Indies.

(General Overseas) BERNARDI, JOSEPH, 7250 Cambrett Drive, Mississauga, Ontario L4T 2R5, Canada. (London Section—Ontario Branch)

BOYER, KEITH GRAEME, MSc, PGH Industries NZ Ltd, PO Box 13-231, Auckland, New Zealand. (Auckland)

CARSON, JOHN, Defense Research Establishment Pacific, FMO, Victoria BC, Canada. (London Section-Ontario Branch)

COOPER, PAUL DOMINIC FRANCIS, 1070A Avenue Road, Toronto, (London Section-Ontario Branch) Ontario, Canada.

CURME, GEOFFREY CHARLES, BSc, MRIC, Revertex Ltd, Lithenes Division, Temple Fields, Harlow, Essex. (London) DANIELS, NIGEL ALAN, 8 Barwick Place, Sale, Cheshire.

- (Manchester) DENNIS, REGINALD HERBERT, LRIC, 13 Bramleys, Stanford-le-Hope, Essex. (London)
- GIGANTE, LUCIANO, 15 Ellis Street, Bellevue, Johannesburg, South Africa. (South African)

HAGEDORN, HAL, 39 Richview Road, Apt 104, Toronto, Canada, (London Section-Ontario Branch)

HARE, CLIVE, 179 Walnut Street, Stoughton, Massachusetts 02070, (London Section-Ontario Branch) ÚSA.

Forthcoming Events

Details are given of meetings in the United Kingdom up to the end of the month following publication.

Friday 23 April

April

Thursday 1 April

Newcastle Section: Annual General Meeting.

Friday 2 April

Bristol Section: Annual Dinner Dance at Mayfair Suite, New Bristol Centre.

Tuesday 6 and Wednesday 7 April

Manchester Section: Symposium at UMIST. "Films—formation and be-haviour." Further information available from Mr A. C. Jolly, Synthetic Resins Ltd, Edwards Lane, Speke, Liverpool.

Wednesday 7 April

Thames Valley Section: Annual General Meeting, followed by a Supper for Members and guests, and an illustrated talk on "Heraldry" by Mr E. F. Redknap of the Paint Research Association.

Friday 9 April

Manchester Section: Annual General Machester Section. Allina General Meeting, at the New Albion Restaurant, 34 High St, Manchester, at 6.30 pm (to be followed by supper).

Midlands Section—Trent Valley Branch: Midlands Section—Irent valley branch. Annual General Meeting, followed by Buffet Dance at Cross Keys Inn, Turnditch at 7.30 pm.

Tuesday 13 April

West Riding Section: Annual General Meeting. Venue and time to be announced.

Thursday 22 April

London Section: Annual General Meeting, to be followed by a talk on "The restoration of Elizabethan buildings" by Dr R. J. Cereasa. To be held at the Piccadilly Hotel, Piccadilly, London W1. Please note change of venue.

Irish Section: Annual General Meeting

to be held at Clarence Hotel, Dublin at

8.00 pm.

Midlands Section: Annual General Meeting. Venue and time to be announced.

Friday 30 April

Bristol Section: Annual General Meeting, to be held at the Royal Hotel, Bristol at 7.15 pm.

Association Dinner and Dance 1976

The Association's Biennial Dinner and Dance will be held on Friday 14 May 1976 at the Savoy Hotel, London WC2R 0EU. The Reception will take place at 7.00 pm for Dinner at 7.30 pm and on this sociation there will be two short speeches only—a Welcome by the President and a Reply on behalf of the guests—so that dancing, to the Jerome Orchestra, can commence as soon as possible and continue until 1.00 am.

The price of single tickets is £10.00 plus 80p VAT each and applications should be made by Members as soon as possible. Tables will be arranged to accommodate 12 or 10 persons each, although it may be possible to arrange a few tables for eight persons. Non-members wishing to receive forms should contact the Association's offices at the address on the contents page of this issue.

West Riding Section Symposium

Exporting paints and similar products

The Section will hold a symposium at Harrogate on 24 and 25 June 1976 on the subject "Exporting paints and similar products".

Papers will be presented on both the technical and practical aspects of exporting, Whilst the meeting is intended primarily

for paint manufacturers, it is expected that allied industries and suppliers to the surface coatings industry will also find the subject matter to be of interest.

Application forms may be obtained from Mr M. J. Cochrane, 49 Almsford Drive, Harrogate, Yorks.

HARRISON, ROGER, 7 Newport Road, North Cave, Brough, East Yorkshire. (Hull)

HEALY, DAVID FRANCIS, 72 Hampden Avenue, Wahroonga, NSW

2076, Australia. (General Overseas) INACIO, PLACIDO DE JESUS FERREIRA, BOX 1139 GPO, Sydney, NSW 2001, Australia. (General Overseas) JOHNSON, Derek, LRIC, 44 Rydal Mount, Belthorn, Blackburn,

(Manchester) Lancs. Kartos, Kartos (West Riding)

- REETZ, STANLEY CUMMING, Usher Walker Ltd, 16 Marshgate Lane, Stratford, London E15. (London)
- ROPER, THOMAS, 182 Ralph Road, Shirley, Solihull, West Midlands B90 3LB. (Midlands)
- (Midlands) RowBoTHAM, CLIFFORD, 10 Richmond Walk, Radcliffe, Manchester M26 0JN. (Manchester)
- MILO UJIN. (Manchester) SILSBY, PETER KARL JAMES, AIRI, ANCRT, 22 Forest View, Buckshaft, Cinderford, Glos. (Bristol) SINGLETON, ALAN, American Hoechst Corp, 129 Quidnick Street,
- Coventry, RI 02818, USA. (London Section-Ontario Branch)
- TAYLOR, DERYCK, BSc, Stoney Brae, 13 Thornhill Road, Edgerton, Huddersfield. (Manchester)
- WARD, LAWRENCE JOSEPH, 4607 Todd Street, Vancouver, BC (London Section-Ontario Branch) Canada.

Associate Members

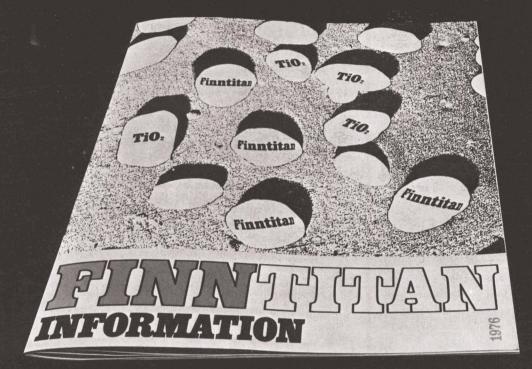
- FREDERICK, 39 Lugard Road, Aigburth, EDWARDS, Liverpool L17 0BA. (Manchester)
- PATERSON, Ross, 19 Sifton Court, Willowdale, Ontario, Canada (London Section—Ontario Branch) TRAILL. THOMAS WARNEFORD, PO BOX 78509, Sandton 2146, South

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JOCCA is published every month and Classified Advertisements can be acceptional circumstances the 20th of the month preceding publication. Advertisers who wish to arrange for an extension of the copy deadline should contact the Assistant Editor, C. A. Tayler, at the address given above (telephone 01-908 1086, telex 922670 OCCA Wembley).

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