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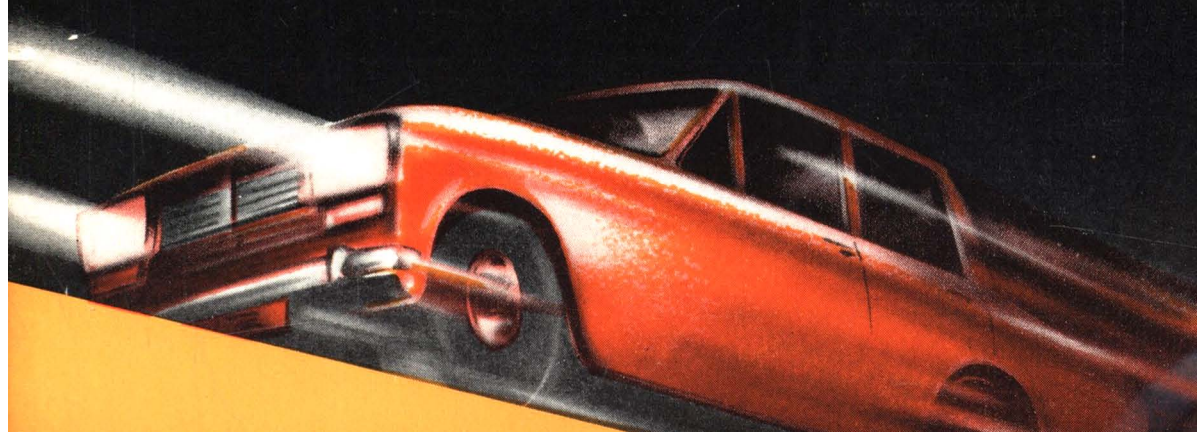
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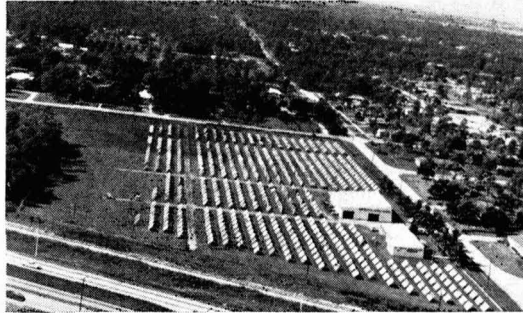
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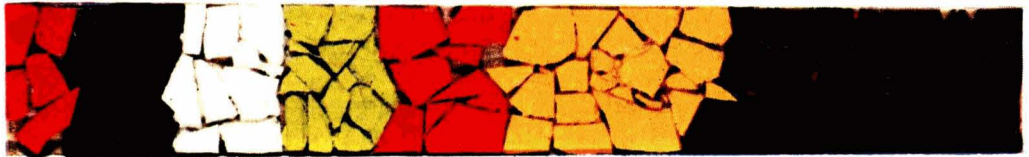


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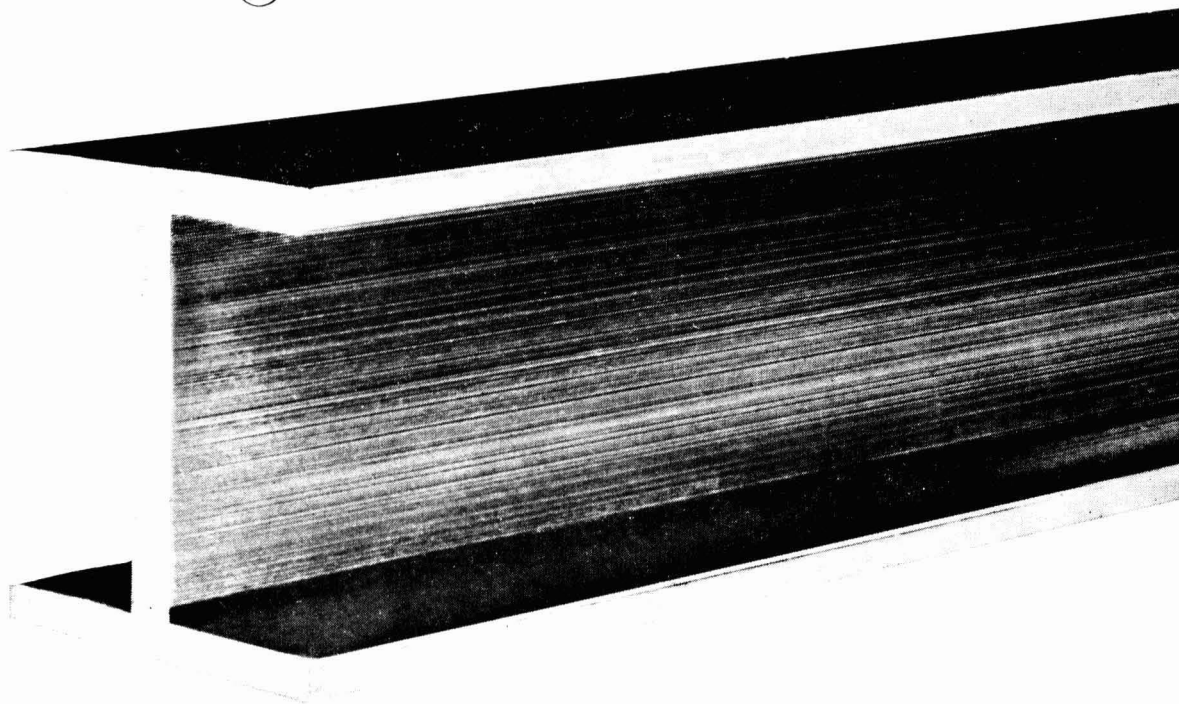
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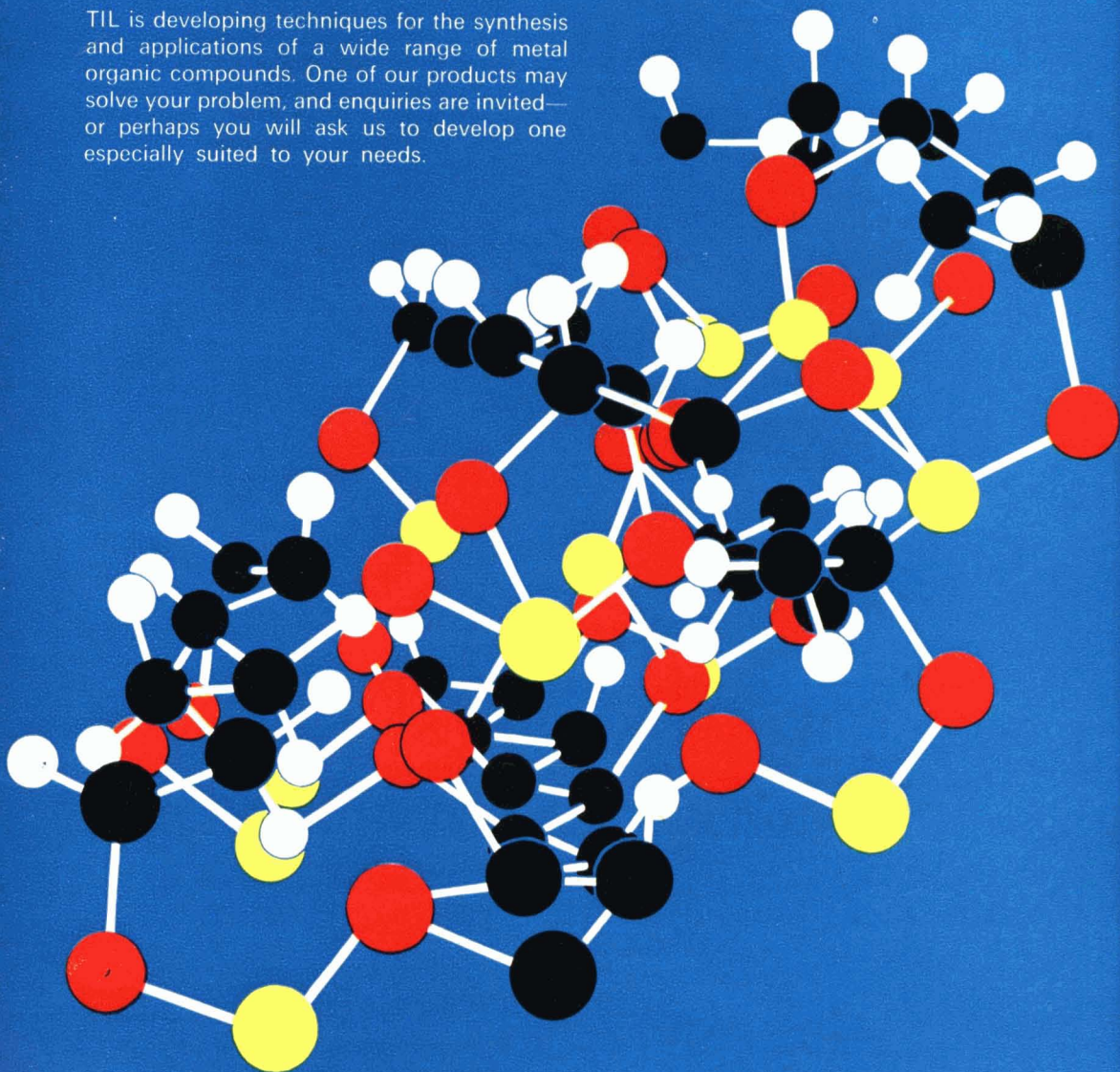
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Transactions and Communications

A critical assessment of the precision of measurement associated with the use of the I.C.I. pneumatic micro-indentor

By R. L. J. Morris

Chemical Inspectorate, Headquarters Building, Royal Arsenal East, S.E.18

Summary

The results obtained by five laboratories using a described method of test and the ICI micro-indentor are presented and discussed. The use of a "3 μm temperature" is suggested as one means of characterising a paint film. The standard deviation in the measurement of micro-indentation is shown to be 0.2 micrometres and in the estimation of the "3 μm temperature" to be 1.8°C.

Key words

Processes and methods primarily associated with service or utility
ageing

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

Processes and methods primarily associated with analysis, measurement and testing
indentation test

Une appréciation critique de la précision de mesure liée à l'utilisation de l'appareil de micro-indentation réalisé par l'I.C.I.

Résumé

On présente et discute les résultats obtenus par cinq laboratoires au moyens soit d'une méthode décrite ensuite, soit du micro-indentateur de l'I.C.I. L'emploi d'une "3 μm température" est proposé comme une possibilité pour caractériser le feuil de peinture. On démontre que l'écart-type du mesure de micro-indentation est de 0.2 micromètres et la valeur prévue pour le "3 μm température" est de 1.8°C.

Eine Kritische Bewertung der Genauigkeit von mit Hilfe des I.C.I. Pneumatischen Mikroindentors Vorgenommenen Messungen

Zusammenfassung

Die von fünf Laboratorien erzielten Resultate, welche alle dieselbe vorgeschriebene Prüfmethode und den I.C.I. Micro-Indentor benutzen, werden vorgelegt und besprochen. Die Anwendung einer "3 μm Temperatur" wird als Mittel vorgeschlagen, um den Charakter eines Anstrichfilms zu kennzeichnen. Es wird aufgezeigt, dass die Standardabweichung bei Messungen mittels Micro-Indentation 0,2 Mikrometer und bei der "3 μm Temperatur" 1,8°C beträgt.

Критическая оценка точности измерений в применении пневматического микро-индентора I.C.I.

Резюме

Иллюстрируются и описываются результаты полученные в пяти лабораториях, применяя описанный метод с использованием микро-индентора I.C.I.

Предлагается применение «3 микрометровой температуры» как одно из средств для характеристики красочной пленки. Показано что среднее стандартное отклонение в измерении микро-вдавливания равно 0.2 мкм а в оценке основанной на «3шт температуры» оно равно 1.8°C.

Introduction

Considerable effort is being given to the problems associated with the measurement of durability of paint systems and the means by which the ageing of paints may best be accelerated in order that a reliable and relatively quick prediction can be made concerning the life of the paint. In order to follow the ageing process of paint films, repeatable methods are required to follow the changes in characteristics of the films. Lawson and Wright¹ examined the change in mechanical properties of detached films, and they related changes in Young's Modulus, tensile strength, and extension at break to checking and cracking of the paint film. These methods were further used² to compare three forms of accelerated weathering cycles. Eley and Peill³, however, criticised the use of tensile strength of a film to follow the ageing process, on the grounds of variability of results owing to adventitious imperfections in the film, such as dust and variation in film thickness. Some doubt was expressed regarding the validity of relating the ageing behaviour and mechanical properties of detached films to those of painted substrates. They used a dynamic method of testing that measured the dissipation factor of paint films at increasing temperature at a frequency of 2,000 Hz, and reported the change in glass transition temperature of five paint systems under various exposure conditions. Monk and Wright⁴ described a pneumatic micro-indentation apparatus and indicated the types of indentation curves that could be obtained from different paint films at different temperatures.

The Prediction of Performance Sub-Committee of the Joint Standing Committee on Paints and Varnishes is concerned with the collection of physical and chemical data of a series of paints and their media, and also with collating changes in the characteristics of these paints under differing weathering conditions. It had been decided to use the micro-indentation technique as one means of characterising the physical state of a paint film, and the ICI pneumatic micro-indentor was chosen as a possibly suitable apparatus.

Before the main programme of testing and exposure could commence, it was considered desirable to examine the data which could be obtained from the instrument. Because of the size of the programme, it was necessary for the work to be done in several laboratories, and consideration had to be given to the possibility of bias existing between instruments and operators. Moreover, since the main programme of investigation was scheduled to last for two to three years, the possibility of changes in operators had to be considered.

This report describes the work which was conducted to correlate different instruments at different laboratories, to provide a statistical analysis of the results in order to quantify the reliability of the data, and also to devise a method of test using the micro-indentor.

Consideration of the experimental variables

The micro-indentor, which has been fully described elsewhere⁴, holds the specimen on a variable temperature stage and measures pneumatically the indentation up to 6 μm under a given load and with a given shaped indenter in the temperature range of -20°C to $+90^{\circ}\text{C}$. The indenter will also follow the recovery of the paint film after the load has been removed. The variables, therefore, that exist in the use of the instrument are:

- load applied,
- size and shape of the indenter,
- length of time for which the load is applied,
- temperature of the test, and
- length of time over which the recovery of the film is measured.

The variables associated with the paint film are:

- the pre-conditioning of the film, and
- the film thickness.

Certain of these variables are interrelated, and a suitable compromise must be sought. It was decided that the film thickness should be 0.0015in and, in order to ensure evenness of application and minimum variation in the film thickness measurement, all the application of paint to the panels should be done by one laboratory. The thinner the film, the greater is the effect of the substrate upon the indentation result for a given indentation with a given tool. If, however, the film thickness is too large, then the drying of the paint is likely to be both adversely affected and atypical. For a given film thickness and indentation depth, the effect of the substrate on the indenting tool is dependent upon the shape of the tool. The greater the width of the contact area between the film and the indenter, the greater is the effect of the substrate⁵. It was decided to use a spherical tool so that the results, if suitable, could be treated mathematically. A suitable tool available with the micro-indentation instrument was an 0.008in radius sapphire tip, and this was used for all the indentation work.

Owing to the size of the main programme, which called for over 800 micro-indentation samples, and the limited time available, it was decided not to measure the recovery characteristics of the paint films. It was realised that this would result in the loss of information, but such measurements would not have been feasible on a programme of this size.

The greater the length of time under a given load, the less is the gradient of the indentation/time curve (Fig. 1) and hence the less the error in the determination of the indentation. An indentation time of 120 seconds was chosen as a compromise between the error in the determination of the indentation under load and the time required to conduct a test. The choice of the load for the

testing of a particular paint was now determined by the range in measurement of the instrument, which was $0.6 \mu\text{m}$.

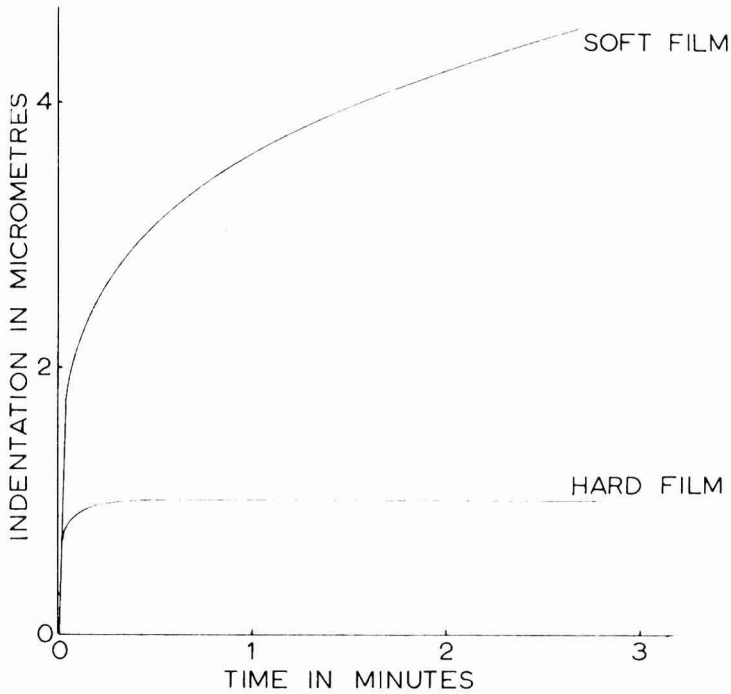


Fig. 1. Indentation/time curve

In order to accommodate as much information as possible within the measuring range of the micro-indentor, it was decided to choose that load for a given paint which would give a one micrometre indentation in two minutes at a temperature of -20°C . With this criterion, it was considered possible to accommodate both the increase in indentation of the paint when examined at higher temperatures and the hardening of the paint which would occur on ageing.

The pre-conditioning of the films before testing was governed by the fact that the paints were to be exposed at outdoor weathering sites. It was expected that these paints, on exposure, would develop a surface layer of dirt together with chalk from the degradation of the pigmented paints. Since the indentation characteristics of such specimens would be adversely affected with regard to repeatability and interpretation, a preliminary washing of the specimens was considered essential. Although such treatment may be considered artificial in that some low molecular weight polymer could be removed in the washing, it was found that washing produced no change in the infra-red spectra of the specimens using the technique of attenuated total reflectance. This fact, and the added advantage of a relatively clean surface on which to make measurements, was considered sufficient reason for washing prior to making measurements.

Elleman and May⁶ had examined the creep modulus of a detached alkyd film after irradiation of the film by ultra-violet light. They showed that the film required at least 100 hours after radiation for the creep modulus to reach an equilibrium value. It was therefore considered necessary for the paint samples that had been exposed in the weatherometer to be left for seven days before testing, in order that the meta-stable products formed during the forcing conditions of an artificial weathering cycle could reach equilibrium.

Since it was envisaged that some testing of the paints would be conducted at -20°C , it was necessary to use the indentation apparatus in dry conditions to prevent the formation of ice on the specimen. This was achieved by the use of phosphorous pentoxide in the glove box containing the micro-indentation apparatus. Drying of the paint samples after washing was required in order that the water in the paint film, which could have a plasticising affect, should not be progressively released during testing in the dry conditions prevailing in the glove box. Therefore, each specimen was placed in a desiccator containing phosphorus pentoxide for 24 hours and then placed in the glove-box overnight. This latter requirement meant that, after a day's use of the instrument, the samples for the next day's work would be placed in the glove box and any moisture entering the glove box during the transfer of the samples would be absorbed overnight by the phosphorus pentoxide in the box.

Although the paints are being examined in an unnaturally dry state, this procedure has the advantage of bringing the paints to a common standard condition prior to testing.

Characterisation of the paint films from the experimental data

Since each of the 800 specimens was to be examined at a series of temperatures, condensation of the data to be obtained was essential for the eventual correlation with other physical and chemical parameters which were simultaneously to be determined. It had previously been established⁷ that the indentation/temperature curve was usually shifted to higher temperatures by weathering of the paint. An example of this for a white oleo-resinous paint is shown in Fig. 2.

The effect of the ageing of the film could be considered to be related to the progressive shift in the indentation/temperature curve. This progressive shift could then be defined in terms of the temperature at which, under the method of test, a given indentation is achieved. From the curves in Fig. 2 it can be seen that, at the $3\ \mu\text{m}$ level, the curves approximate to straight lines and have steep gradients. Thus an error in the determination of the indentation at the $3\ \mu\text{m}$ level will not affect the $3\ \mu\text{m}$ temperature to the same extent. It was, therefore, decided to use the criterion of a " $3\ \mu\text{m}$ temperature" as a parameter defining the indentation characteristics of a paint.

Experimental

Six air-drying media, namely, an alkyd, an oleoresin, an acrylic, a two-pack polyurethane, a chlorinated rubber, a pva emulsion, and a stoving epoxide were each applied to 18 SWG hard aluminium panels to a dry film thickness of $37\ \mu\text{m}$ (0.0015in). The stoving medium was heated at 176°C for 30min and then conditioned with the other panels under laboratory conditions of 65 | 5

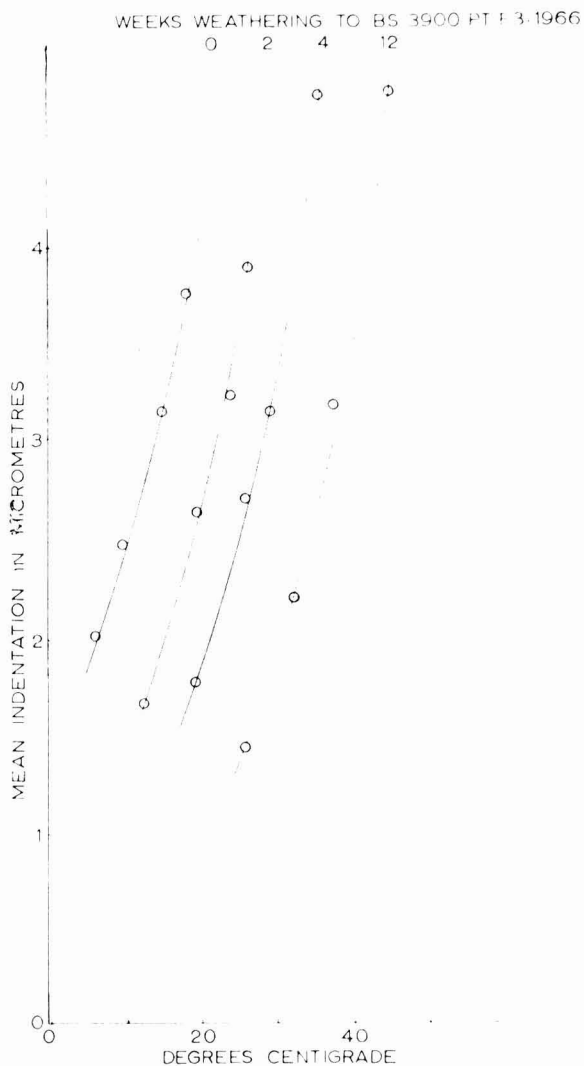


Fig. 2. Shift of indentation/temperature curve on weathering

per cent RH, $18 \pm 3^\circ\text{C}$ for 14 days before testing or placing in the weatherometer to BS3900 Pt. F3. A second similar set of panels, 7 days after application, was force dried at 40°C for 3 days, and conditioned for 3 days at 65 ± 5 per cent RH, $18 \pm 3^\circ\text{C}$. This second set of panels was to be used to examine the effect of removal of most of the solvent from the panels and also to see if such treatment changed the subsequent behaviour of the films in the weatherometer.

The films were to be examined before exposure in the weatherometer and after two and six weeks accelerated weathering using the method of test shown in the Appendix. One-inch diameter discs were cut from the panels, the backs of the discs abraded with "400 wet and dry" paper to ensure flatness of the specimen and the discs distributed to each of the five participating laboratories.

Results

The results reported by four of the participating laboratories for the unexposed and two weeks exposed paints are shown in Table 1, together with the loads chosen for the test by the laboratories, using the criterion defined in Appendix 1.

It was evident that variation in the reported results could be attributed chiefly to the variation of loads chosen for the testing by the different

Table 1

Three micrometre temperatures of initial and two-week aged films in °C (at the shown loading in grammes)

Paint	Pretreatment	Before exposure				After two weeks' exposure			
		Lab 1	Lab 2	Lab 3	Lab 4	Lab 1	Lab 2	Lab 3	Lab 4
Alkyd	Air-dry	17° (1g)	1° (4g)	-5° (4g)	-6° (4g)	34 (1g)		26° (4g)	26° (4g)
	Force-dry	22° (1g)	5° (4g)	3° (4g)	10° (4g)	32° (1g)		27° (4g)	27° (4g)
Acrylic	Air-dry	38° (2g)	27° (8g)	34° (8g)	37° (4g)	41 (2g)		37° C (8g)	44 (4g)
	Force-dry	38° (4g)	32° (8g)	30° (8g)	39° (4g)	42° (4g)		37° (8g)	43° (4g)
Epoxide	Air-dry	48° (4g)	38° (8g)	43° (8g)	46° (8g)	52° (4g)		44° (8g)	47° (8g)
	Force-dry	50° (4g)	44° (8g)	46° (8g)	50° (8g)	51° (4g)		46° (8g)	50° (8g)
Chlorinated rubber	Air-dry	13° (2g)	2° (8g)	8° (4g)	11° (4g)	48° (2g)		46° (4g)	40° (4g)
	Force-dry	26° (4g)	15° (8g)	17° (4g)	14° (4g)	48° (4g)		48° (4g)	45° (4g)
Oleo-resin	Air-dry	13° (2g)	8° (4g)	6° (4g)	8° (4g)	42° (2g)		34° (4g)	36° (4g)
	Force-dry	14° (2g)	12° (4g)	11° (4g)	11° (4g)	38° (2g)		34° (4g)	36° (4g)
Polyurethane	Air-dry	76° (4g)	90° (4g)	60° (16g)	83° (8g)	90° (4g)		74° (16g)	94 (8g)
	Force-dry	92° (5g)	77° (8g)	77° (16g)	82° (15g)	88° (5g)		78° (16g)	86° (15g)
Pva Emulsion	Air-dry	20° (5g)	19° (4g)	17° (8g)	23° (4g)	17° (5g)		21° (8g)	26° (4g)
	Force-dry	23° (4g)	23° (4g)	17° (8g)	23° (8g)	20° (4g)		21° (8g)	22° (8g)

laboratories. Therefore, for the paints aged for six weeks, the participating laboratories were asked to conduct the test using particular loads. The results reported are shown in Table 2.

Table 2
Three micrometre temperatures of films aged for six weeks in °C

Paint	Pretreatment	Load	Lab. 1	Lab. 2	Lab. 3	Lab. 4	Lab. 5
Alkyd	Air-dry	2g	40	35	38	39	44
		4g	38	33	34	35	37
	Force-dry	2g	36	35	40	38	41
		4g	34	30	37	34	34
Epoxide	Air-dry	4g	56	52	58	60	
		8g	48	46	50	51	49
	Force-dry	4g	56	52	60	60	
		8g	50	45	53	52	48
Oleoresin	Air-dry	2g	72		97*		105*
		4g	61		78		96*
	Force-dry	2g	87		100*	90*	112*
		4g	74		88	74	97*
Acrylic	Air-dry	8g		46			
		Force-dry	8g		46		

*These results were extrapolated, since the three micrometre temperature lay outside the working range of the apparatus.

Treatment of results

The results for the alkyd and epoxide films aged for six weeks were examined for variation and bias, since these were the media most extensively tested under specified conditions of loading.

There are three methods available for the comparison of results. First, an analysis of variance of the declared 3 μm temperatures, which results in the value for the standard deviation of the 3 μm temperature determination of 1.8°C. However, the variation in 3 μm temperature will result from bias and random error in the measurement of both indentation and temperature. In order to examine the effect of the variation of these two measurements, one must examine the data used to achieve the 3 μm temperature result. Each laboratory has plotted the mean indentations achieved at particular temperatures and constructed a temperature/indentation curve from which the 3 μm temperature result has been derived. For a given paint and loading, each laboratory will have chosen different temperatures for the indentation testing, so that the indentation temperature curves produced by each laboratory must be examined for variation. This has been conducted in two ways, by examining the relative displacement with respect to temperature and indentation of the experimentally derived curves, and also by the fitting of empirical curves.

Fitting of the experimental curves

For a given paint and pre-conditioning, the data from each laboratory was plotted to the same scale. The curves of four of the five laboratories were superimposed on to the curves of the fifth, laboratory 3, and the displacement of the curves with respect to indentation and temperature relative to those of laboratory 3 noted. An example is given in Fig. 3 where the solid and dashed lines represent the curves produced by the reference and another laboratory respectively. This presupposes that the indentation temperature profile for each paint is independent of the laboratory and will only vary because of bias and random error. The results obtained are shown in Table 3.

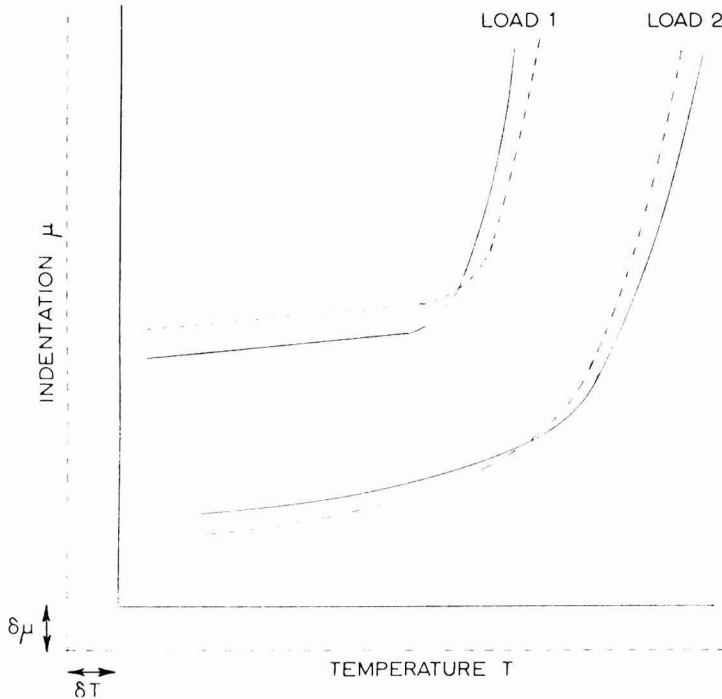


Fig. 3 Comparison of results from laboratory 3 with another laboratory

*Table 3
Comparison of results from different laboratories*

Paint	Conditioning	Variable	Lab. 1	Lab. 2	Lab. 3	Lab. 4	Lab. 5
Alkyd	Air-dried	$\delta \mu$	0.32	0.2	0	-0.1	0.15
		δT	3.2	-1.0	0	1.25	4.25
	Force-dried	$\delta \mu$	0.12	0.2	0	-0.15	0.05
		δT	-3.5	-4.5	0	-2.5	-3.0
Epoxyde	Air-dried	$\delta \mu$	0.32	0.18	0	-0.05	0.12
		δT	-1.0	-5.0	0	1.2	1.5
	Force-dried	$\delta \mu$	0.18	0.25	0	-0.12	0.2
		δT	-3.8	-6.0	0	-2.0	-5.5

The mean deviation in indentation and temperature for each paint and pre-conditioning was then calculated, and the deviation of each laboratory relative to the calculated mean deviation was plotted with respect to indentation and temperature, see Fig. 4. It was considered that the area enclosed by the graph of the results of a laboratory would be a measure of the deviation of results by that laboratory and that the relative location of the area would be a measure of the bias with respect to temperature and indentation measurement.

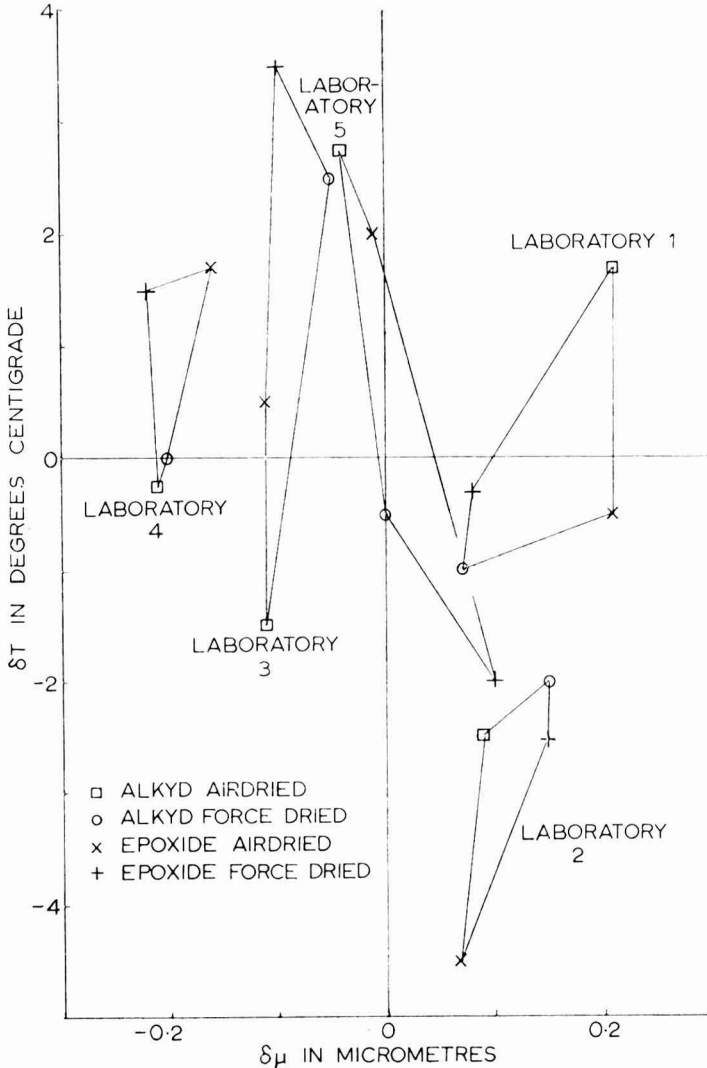


Fig. 4. Deviation of laboratories relative to the calculated mean deviation

Fitting of empirical curves

In order to analyse the differences between the results produced by the laboratories, it was considered desirable to attempt to fit the experimental data to

a family of curves and to derive an arbitrary equation which gave the best fit over the experimental range of results. The deviation of data from the curve could then be calculated together with the deviation in $3 \mu\text{m}$ temperatures interpolated from the derived curves.

It was decided to fit the data to the family of curves defined by the equation,

$$I = A + Be^{CT}$$

Where I = indentation
 T = temperature
 A, B, C = constants.

The computer facility at R.A.E. Farnborough was used to determine the values of the constants A, B , and C which gave the best fit to the data from each laboratory for each paint and pre-conditioning. Using these constants the temperature for $1 \mu\text{m}$, $2 \mu\text{m}$, $3 \mu\text{m}$ and $4 \mu\text{m}$ indentations were calculated. Deviations of the experimental data from the fitted curves had a standard deviation of $0.20 \mu\text{m}$ overall and varied from $0.12 \mu\text{m}$ for laboratory 4 to $0.26 \mu\text{m}$ for laboratory 5. The calculated $3 \mu\text{m}$ temperatures agreed within 1°C with the alkyd and epoxide values shown in Table 2, with two exceptions. The difference between the calculated and plotted values in these two cases was not greater than 2°C . It was found necessary to exclude the data from laboratory 5 for the air-dried alkyd film owing to large and significant deviations from the predicted curve.

By superimposing the fitted curves for the various laboratories, it was evident that above 30°C , laboratory 2 recorded consistently higher values for indentation. Such behaviour can be explained by a small positive bias in indentation measurement and a large negative bias in temperature measurement, as suggested by the graphical treatment above.

Ignoring the results from laboratory 2, the scatter of indentation values predicted by the curves at 40°C was found to be $0.23 \mu\text{m}$. From the inherent scatter of $0.20 \mu\text{m}$ and the fact that at least four points were used to construct the indentation temperature curve, one would have expected the scatter to be smaller by a factor of 2. It is, therefore, clear that there are real curve-to-curve differences for the same paint, and that these can be attributed either to experimental variations or to real differences between nominally similar panels. Apart from laboratory 2, this implies a standard deviation in $3 \mu\text{m}$ values of 1.5°C , which is in general agreement with the residual standard deviation obtained by an analysis of variance of the resulting $3 \mu\text{m}$ values, 1.8°C .

Conclusions

It has been shown that the micro-indentation technique as described can be used to follow changes in physical properties of weathering paint films as characterised by a $3 \mu\text{m}$ temperature. The comparison of results provided by five laboratories has shown that a bias in results does exist in the case of laboratory 2 and, therefore, such results should be corrected. It is proposed that, for the main programme of indentation testing, samples of the force-dried epoxide film be tested by all participating laboratories at regular intervals throughout the programme. This would ensure that any change in bias of results could be followed and allowed for.

Fitting curves of the form $I = A + Be^{CT}$ to the experimental data is shown not to produce significant differences from experimentally drawn curves for the determination of the $3 \mu\text{m}$ temperature. Hence its use has nothing to offer over and above the simpler method for routine use. The uncertainty of the results is 3.6°C at the 95 per cent level.

Acknowledgments

This programme has been conducted for the Prediction of Performance Subcommittee of the Joint Standing Committee on Paints and Varnishes. The participating laboratories in the micro-indentation testing were:

- Atomic Weapons Research Establishment, Aldermaston.
- Building Research Station, Watford.
- Chemical Inspectorate, Woolwich.
- Imperial Chemical Industries, Paints Division, Slough.
- Paint Research Station, Teddington.

The statistical work was conducted by Mr J. H. Cadwell of the Royal Aircraft Establishment, Farnborough.

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Appendix I

Sample preparation

Specimens shall be checked to ensure that the back surface is flat, and shall be abraded as necessary.

Preliminary cleaning

Control samples shall not be cleaned. Samples taken after exposure to natural weathering or the weatherometer shall be cleaned by total immersion in a 2.5 per cent solution of Lissapol N in water and lightly brushed with a camel hair brush, drained, and the procedure repeated with distilled water.

The immersion time of the samples shall be kept to a minimum.

Sample conditioning

Control samples and samples from the natural weathering sites shall be conditioned and tested as soon as possible after receipt. Samples from the weatherometer shall be left for seven days before conditioning and testing, and shall be examined with the minimum of delay. All samples shall be left in a desiccator with phosphoric oxide for 18-24 hours and then be transferred to the glove box of the apparatus, which shall contain phosphoric oxide, to be left overnight before testing.

Test conditions

All measurements shall be conducted with a 0.008in radius needle. For each paint, select by trial the weight that will give a 2 minute indentation value in the range 1-2 micron for the control paint in the glassy state. The following loads and temperatures are given as a guide in making this assessment.

	<i>Medium</i>			<i>Load (g)</i>	<i>Temperature (°C)</i>
Oleo-resin	8	-20
Chlorinated rubber	8	-20
Pva emulsion	8	-20
Alkyd	8	-20
Epoxide	8	0
Acrylic	8	0
Polyurethane	16	20

Procedure

Start at the temperature indicated above and measure 2 minute indentation values at temperature intervals of about 10°C until a temperature is reached at which the indentation exceeds 6 μm .

The exact temperatures at which measurements are made are not important provided that the temperature is steady and recorded accurately. It is essential that the specimen be allowed to reach equilibrium for seven to ten minutes after the temperature has been increased.

Make two separate determinations at each temperature unless the variation between them is more than 5 per cent, in which case make a third determination. If in the latter case one of the determinations differs from the mean of the other two by more than 20 per cent, make a further determination.

Select a fresh point on the sample for each determination. Record the mean of the determinations at each temperature and all individual results.

Plot the mean values of indentation in terms of temperature as the determinations proceed. Investigate immediately the reason for any irregularity in the results, but do not remeasure at lower temperatures after the sample has been taken above the glassy state.

From the graphs obtained, record the temperatures at which the samples show an indentation value of 3 micrometres.

Behaviour of polymeric coatings on steel during deep-drawing

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Summary

Traditional tests of coating fabricability, such as the linear extension and Erichsen indentation tests, fail to predict the behaviour of prefinish coatings on sheet metals during drawing operations. It is shown that a large proportion of any damage to coatings that occurs on drawing is due to the compressive ("hoop") stresses, and not to friction against the punch or die. Bend tests with the coating on the inside cause analogous failures, and can thus be used as a simple check on coating "drawability."

Coating failures during Swift-cupping of typical cross-linked and thermoplastic resins, in the form of one-and two-coat systems on steel, have been related to the coating mechanical properties and shear adhesions to steel, and to the strain distribution induced in the coatings.

To avoid cracking of a fabricated coating in regions of pure extension, the prime requirement appears to be high elongation at break, coupled with adequate initial adhesion. To prevent detachment of coatings in regions of compressive strain, substantial absence of cross-linking seems paramount, while initial adhesion is also of great importance.

In duplex coatings, a topcoat of high elongation at break can eliminate cracking on stretching of a primer of low elongation at break, whether the topcoat be thermoplastic or cross-linked. Furthermore, a thermoplastic primer can reduce loss of adhesion of a cross-linked topcoat in compressively straining regions.

Key words

Types and classes of surface

steel
sheet metal

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

formability

Types and classes of coating

thermoplastic coating
thermosetting coating

Process and methods principally associated with analysis, measurement and testing

bending test
cupping test

Le comportement, pendant l'étirage profond, des revêtements polymères appliqués à l'acier

Résumé

Les essais classiques ayant pour but l'appréciation de l'aptitude d'un revêtement à être manipulé, tels que les essais de l'élongation linéaire et de l'indentation Erichson, ne peuvent pas prédire le comportement des revêtements pour la finition de tôle métallique avant des opérations d'étirage. On démontre que un taux importants des dégâts qui arrivent aux revêtements lors de l'étirage est en raison des efforts de compression ("de frettage"), et non à cause de la friction en provenance des bords du poinçon ou de la matrice. Les essais de pliage, effectués dans le cas où le revêtement se trouve sur le côté interne de l'éprouvette, démontrent des défauts analogues, et ils peuvent donc être utilisés comme un contrôle facile de "l'aptitude à étirage" d'un revêtement.

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Les avortements de revêtements au cours de l'épreuve "Swift cupping" sur des résines réticulées ou thermoplastiques sous forme des systèmes à une ou deux couches sur acier, ont été liés: aux caractéristiques mécaniques; aux adhérences à l'acier devant les efforts de cisaillement, et à la répartition de la déformation entraînée dans les revêtements.

Afin d'éviter, dans les régions de prolongement simple, le fendillement d'un revêtement, le besoin principal semble d'être une elongation à rupture élevée, ainsi qu'un niveau d'adhérence convenable au début. Afin d'empêcher l'enlèvement de revêtements aux régions de déformation due à la compression, il paraît d'une importance cardinale de supprimer aucun risque de reticulation. D'ailleurs, le niveau d'adhérence est également d'une grande importance.

Dans des systèmes de revêtements duplex, une couche supérieure ayant une elongation à rupture élevée peut éliminer le fendillement d'une primaire de faible elongation à rupture, lors de son prolongement, dans le cas où la couche supérieure soit thermoplastique soit réticulée. De plus, une primaire thermoplastique peut diminuer la perte d'adhérence d'une couche supérieure réticulée aux régions de déformation due à la compression.

Verhalten Polymerer Beschichtungsmittel beim Tiefziehen

Zusammenfassung

Die üblichen Prüfmethoden auf Formbarkeit von Lacken wie z.B. lineare Dehnungs- und Erichson Tiefungsproben versagen, wenn das Verhalten vorlackierter Eisenbleche beim Ziehen vorausgesagt werden soll. Es wird gezeigt, dass ein grosser Teil der beim Ziehen auftretenden Schäden auf erhebliche ("Ring") Beanspruchungen und nicht auf das Reiben gegen Stanze oder Prägestempel zurückzuführen sind. Biegeproben an der Innenseite verursachen analoge Fehler und können daher als einfache Kontrollprüfungen auf Ziehbarkeit von Anstrichen angewandt werden.

Beschädigungen von Filmen beim Swift-Tiefziehen typischer vernetzter und thermoplastischer Harze auf Eisenblech in Ein- und Zweischichtensystemen wurden mit den mechanischen Eigenschaften, der Scherhaftung auf Eisen, sowie der in der Beschichtung hervorgerufenen Spannungsverteilung in Beziehung gebracht.

Die wichtigste Anforderung um Reißen der bearbeiteten Lackierung in Regionen purer Ausdehnung zu vermeiden, dürfte hohe Dehnbarkeit am Brechpunkt bei gleichzeitig ausreichender anfänglicher Haftung sein. Um Ablösung von Beschichtungen in Druckspannungsregionen zu verhindern, scheint völlige Abwesenheit von Vernetzung unbedingt erforderlich zu sein; gute Anhaftung ist aber ebenfalls von grosser Wichtigkeit.

Im Zweischichtensystem kann ein Überzugslack von hoher Dehnbarkeit am Brechpunkt das Reißen beim Ausziehen eines Primers von niedriger Dehnbarkeit am Brechpunkt ausschalten, unabhängig davon ob der Überzugslack wärmeformbar oder -vernetzt ist. Weiterhin kann ein wärmeformbarer Primer Haftungsverlust eines vernetzten Überzugslackes in Druckspannungsregionen reduzieren.

Поведение полимерных покрытий на стали в глубокой вытяжке

Резюме

Традиционные испытания производства покрытий, как например линейное растяжение и испытания на давливание Эриксона, не могут предсказать поведение предварительных покрытий на тонких листовых металлах в вытяжных операциях. Показано что большая пропорция повреждений покрытий возникающих при вытяжке, происходит за счет сжимающих («периферийных») усилий, а не благодаря трению штампа или матрицы. Испытания на изгиб с покрытием на внутренней стороне, вызывают аналогичные повреждения и могут таким образом служить проверкой способности покрытий к вытяжке.

Повреждения покрытий при полой вытяжке типичных поперечных и термопластических смол, в виде одиночного и двойного покрытия на стали, отнесены к механическим свойствам покрытия и сдвигу сцепления на стали и также к распределению напряжений вызванных в покрытиях.

Для избежания трещин в фабричных покрытиях в участках чистого растяжения, первым требованием повидимому является высокое разрывное удлинение в сочетании с соответствующим первоначальным сцеплением. Для предотвращения отслоения покрытий в участках сжимающих усилий, должно преобладать отсутствие образования поперечных связей, в то время как первоначальное сцепление также очень важно.

В двойных покрытиях наружный слой с высоким удлинением при разрыве может предотвратить растрескивание при вытяжке грунтовки с низким удлинением при разрыве, как с термопластическим так и с поперечным верхним слоем. К тому же термопластическая грунтовка может уменьшить утерю сцепления в поперечном верхнем покрытии в участках сжимающих напряжений.

Introduction

Sheet metal is increasingly being "prefinished," or coated while still flat with organic stoving coatings, for uses which involve subsequent shaping. The requisite forming operations include folding, roll-forming, stretch forming and drawing. In all of them the metal undergoes major plastic deformation in reaching its final configuration: only slight elastic recovery occurs on release from the forming tools. Drawing differs from stretching of metal, in that in the former the metal around the area being shaped by the impressed tool is not firmly restrained, but is permitted to contract inwards to supply more material around the tool. As a result, thinning is minimised, and more severe deformations can be achieved without causing metal rupture.

During cold-forming, a sheet of metal or precoated metal is subjected in varying degrees to tensile, compressive and/or shear stresses. Organic paint or plastic prefinish coatings are so thin, and of such low yield strength when compared with the substrate metals, that they scarcely affect the plastic flow of the metal during fabrication. Thus, providing that the adhesion of the coating is adequate to cause it to deform with the metal, a strain is induced in the coating by fabrication operations¹. The strain at corresponding points in equivalent fabricated components will be independent of the coating nature, provided only that any lubricating action of the coating does not unduly affect the plastic flow of the substrate metal.

Since thermoplastic coatings can exhibit a viscoelastic response similar to that of a plastically straining metal, they can relieve their resulting internal stresses by themselves deforming plastically. Hence, all current prefinished metal marketed for use in drastic forming operations bears a thermoplastic coating². However, although cross-linked stoving paint coatings generally show flaking, wrinkling or cracking failures when severely formed, they are able to withstand simple bending and roll- or stretch-forming operations without overt failure. Since such cross-linked systems offer many advantages when used as decorative or functional coatings for sheet metals, this study defines the factors causing their failure during severe forming (deep-drawing or inside bending), and assesses the relative behaviour of multi-laminar coating systems built up (as in practical cases) of strata of differing degrees of cross-linking and/or elastic moduli. The latter factor is of interest, since, owing to the lack of dependence of coating strain upon coating nature, coating initial stress after fabrication will be proportional to coating modulus (at the given strain). If this stress exceeds the ultimate extensive or compressive stress of this substance, cohesive coating failure must occur.

Experimental

Role of in-plane compressive strain, rather than shear, in damaging a cross-linked coating

An alkyd paint, which was known to exhibit poor drawing characteristics, was line reverse-roll coated on to Bonderite 901 phosphated 24 gauge cold-

rolled mild steel sheet. The coating was not surface lubricated on line. Its stoved film thickness was 0.00065in.

Round nosed cups were deep-drawn on a Swift cupping press³, starting from various circular blanks of the coated steel of up to 4.5in diameter (that causing metal failure). The cups showed equally severe paint failure by cracking and flaking on the side walls ("skirts") whether the drawing was done in the presence or absence of a (readily sheared) 0.0025in thick polyethylene film between the die and the outside (painted) face of the sample. Furthermore, 2in long samples of the painted steel were pulled out from between smooth mild steel plates clamped together under *ca.* 500 lbf.in⁻² (a force more than ten times that operating on the blankholder in the Swift press), and then showed no flaking of the paint (even when examined under 10x magnification). This was still true even if the painted metal had been subjected to 15 per cent linear extension before the shearing operation. Taken together, these two results indicate that surface shear on the coating alone, in the absence of the compressive ("hoop") strains induced during drawing, cannot alone cause the dramatic failures observed on deep-drawing of steel coated with the cross-linked paint.

Any potential contribution of shear to the observed damage was further reduced in specially conducted Swift cupping trials.

A 4.5in diameter blank was drawn, slightly off-centre and using 1.4in rise. At this stage the outside diameter had been reduced to 3.5in, and flaking of the paint had begun, both on the walls and on the remaining flange areas (see Fig. 1). The asymmetry of draw resulted in approximately 0.1in further reduction of radius at the right of Fig. 1 than at the front left. The difference in shear encountered by the two regions was insignificant, while the difference in the circumferential contractions was about 20 per cent. Paint damage can be seen to be more advanced in the more compressively strained region.



Fig. 1. Partly drawn alkyd-coated steel cup, showing coating failure

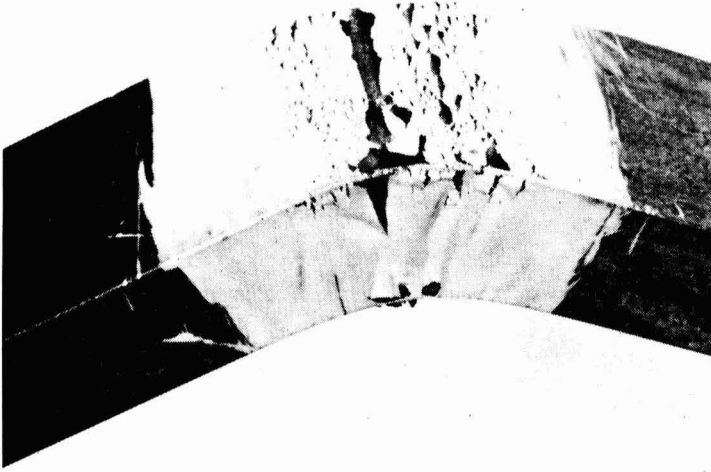


Fig. 3. Paint failure on a bent beam; tensile face



Fig. 4. Paint failure on a bent beam; compressive face

Table 2
Properties of systems used in deep drawing tests

Reference for system†	Composition	Days ambient conditioning before test	Yield strength (lbf/in ²)	UTS (lbf/in ²)	Elongation at break (%)	Initial modulus (10 ⁴ lbf/in ²)	Mean AWRE button shear adhesion (lbf/in ²)
S1H	Araldite 6100: Versamid 115 (5 : 1)	14	4,790	6,100	6	12.7	2,550
S1L	Araldite 6100: Versamid 115 (2 : 1)	14	2,500	3,250	15	1.1	1,600
S2H	Araldite MY750: Versamid 125 (2 : 1)	14	—	2,500	2.5	30.5	1,250
S2L	Araldite MY750: Versamid 125 (1 : 2)	14	125	555	80	5.1	1,000
PH	Versalon 1175	2	600	1,340	28*	15.0	2,100
PI	Versalon 1175 Versalon 1165 (1 : 2)	2	305	625	100	9.7	2,050
PL	Versalon 1,165	2	150	360	180	8.3	1,800

†S = Thermoset systems.
P = Thermoplastic system.
H = High modulus.
I = Intermediate modulus.
L = Low modulus.

*A 1mil thick film of Versalon 1175 coated onto mild steel showed many fine cracks about 0.05 in long when extended 10%.



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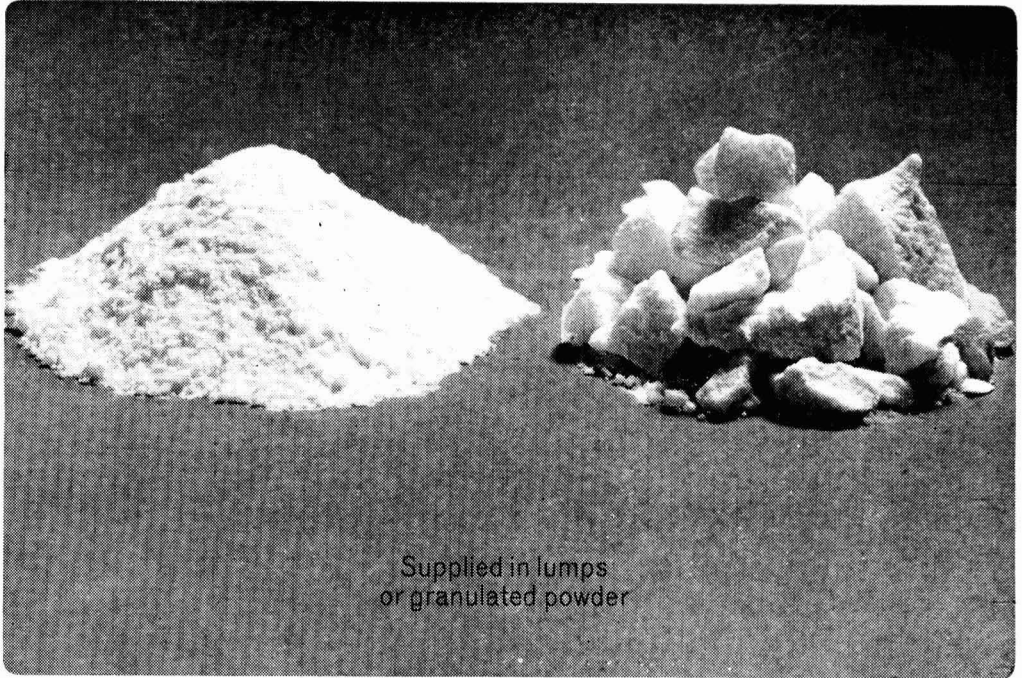
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The behaviour of duplex coating systems

The drawing behaviour of one- and two-coat unpigmented systems was examined. Thermoplastic polyamide and thermosetting epoxy/polyamide coating materials were selected to give as wide a range of mechanical properties as possible, while maintaining chemical similarity and comparable adhesion to mild steel.

Mechanical properties were determined for each system on 0.01in free films, prepared by coating on to tinplate and amalgamation⁶. Standard tensile specimens were cut, and load-extension curves to failure were determined on a Hounsfield Tensometer. Initial moduli were determined from the linear early portions of the load-extension curves. Results are given in Table 2, together with coating system shear adhesions to mild steel determined by the AWRE torque wrench method⁷.

The systems shown in Tables 3 to 5 were coated directly on to 6in × 6in squares of EDD mild steel. The steel was not phosphated, despite the fact that such treatment is used in production of high-quality prefinished sheet, since the intrusion of the relatively rigid phosphate film between metal and polymeric coating would have complicated interpretation of results. The Versalon polyamides were applied by spinning from 30 per cent solutions; the epoxy/polyamides were bar coated, with 24 hour intervals between coats. Discs 4.5in in diameter were cut from the centre of the specimens and drawn into 50mm diameter Swift Cups at 8 ft/min. The results of the drawing tests are described in Tables 3 to 5, and typical failures are illustrated in Figures 5 to 7.

Table 3

Fractions of skirts of cups showing loss of coating adhesion, after drawing of epoxy/polyamide coated steel

Base coat	Top coat				
	Nil	S1H	S1L	S2H	S2L
S1H	0.25	0.6	0.6	—	—
S1L	0.25	0.6	0.6	—	—
S2H	0.5	—	—	0.6	0.7
S2L	1.0	—	—	0.9	1.0

Table 4

Nature of crazing on crowns of cups, after drawing of polyamide-coated steel

Base coat	Top Coat			
	Nil	PH	PI	PL
PH	Moderate	Severe	Nil	Nil
PL	Nil	Micro	Nil	Nil

The coating on the skirt region was in every case undamaged

Table 5

Behaviour of epoxy/polyamide thermoset:polyamide thermoplast two-coat systems on steel, when drawn

Thermoplastic base coat	Thermoset top coat			
	S2H		S2L	
	Crown	Ears of skirt	Crown	Ears of Skirt
PH	Cracking and loss of adhesion (90%)	Circumferential cracking (30%), little detachment	No effect	Break-up and loss of adhesion (30%)
PL	No effect	Break-up and loss of adhesion (30%)	No effect	Circumferential cracking (30%), little detachment

The coating on the upper skirt, remote from the ears, was in every case undamaged.

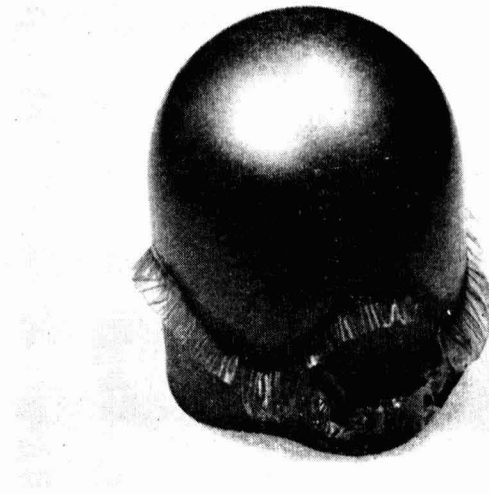
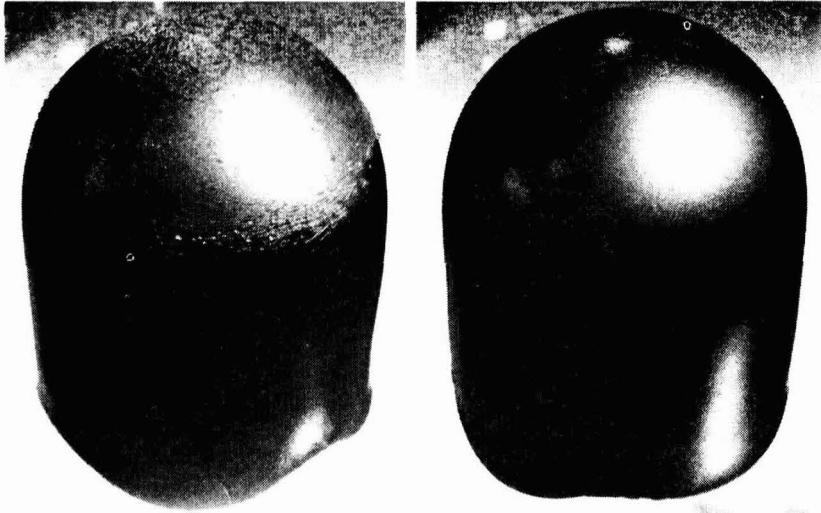


Fig. 5. Representative failure on drawing of epoxy/polyamide coated steel; S1H primer, S1L topcoat

Torque adhesion values⁷ were determined in triplicate on the offcuts around the edge of each specimen. In all cases the intercoat adhesion was greater than the adhesion of the basecoat to the metal.

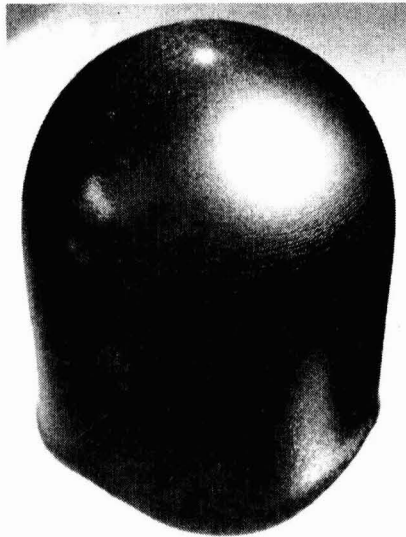
No intercoat rupture or relative movement of strata at cup edges could be detected in the drawn samples having duplex thermoset—thermoplastic coatings, even with the coats dyed different colours.

The strain distribution induced in the coatings was determined from cups drawn from uncoated steel blanks, scribed with a polar grid of concentric circles $\frac{1}{4}$ in apart and radii at 15° intervals. Final compressive hoop strain contours are plotted, as on to the undrawn blank, in Fig. 8; the radial tensile strains are plotted in Fig. 9. A Cartesian grid was not convenient for strain measurements.



(a)

(b)



(c)

Fig. 6. Detail of crown failures of thermoplastic coatings on steel when drawn: (a) PH primer and topcoat; (b) PH primer, PI topcoat; (c) PL primer, PH topcoat

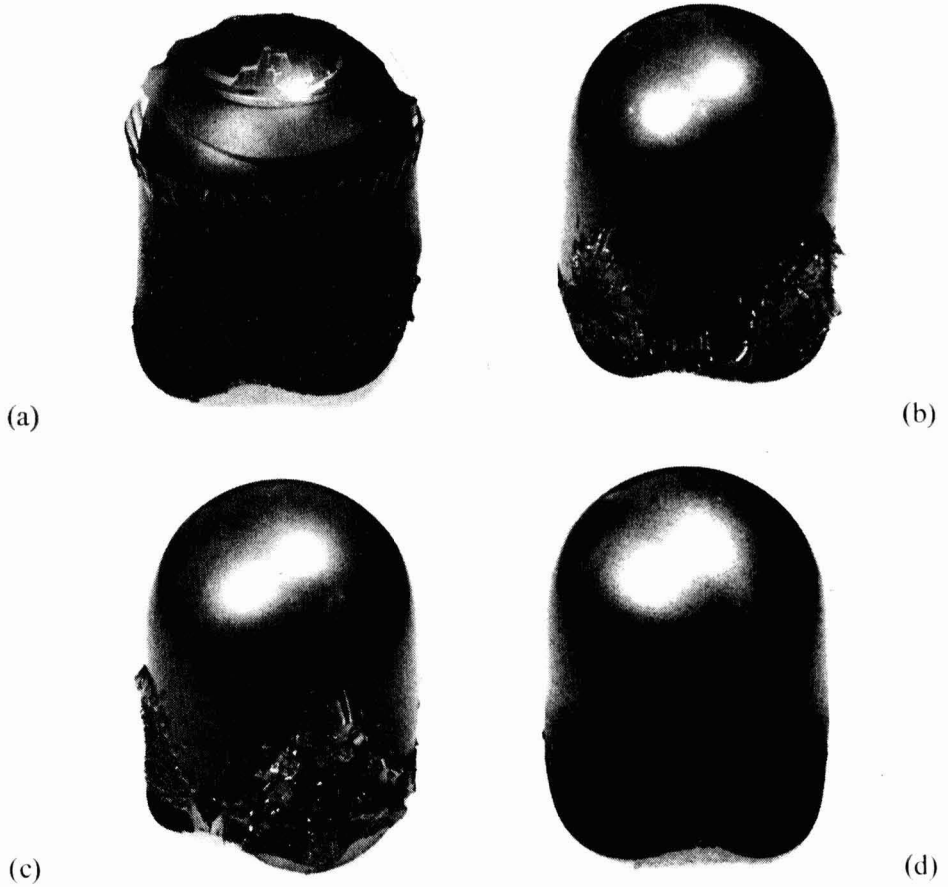


Fig. 7. Failures of thermoset: thermoplast two-coat systems when drawn (a) PH primer, S2H topcoat; (b) PH primer, S2L topcoat; (c) PL primer, S2H topcoat; (d) PL primer, S2L topcoat

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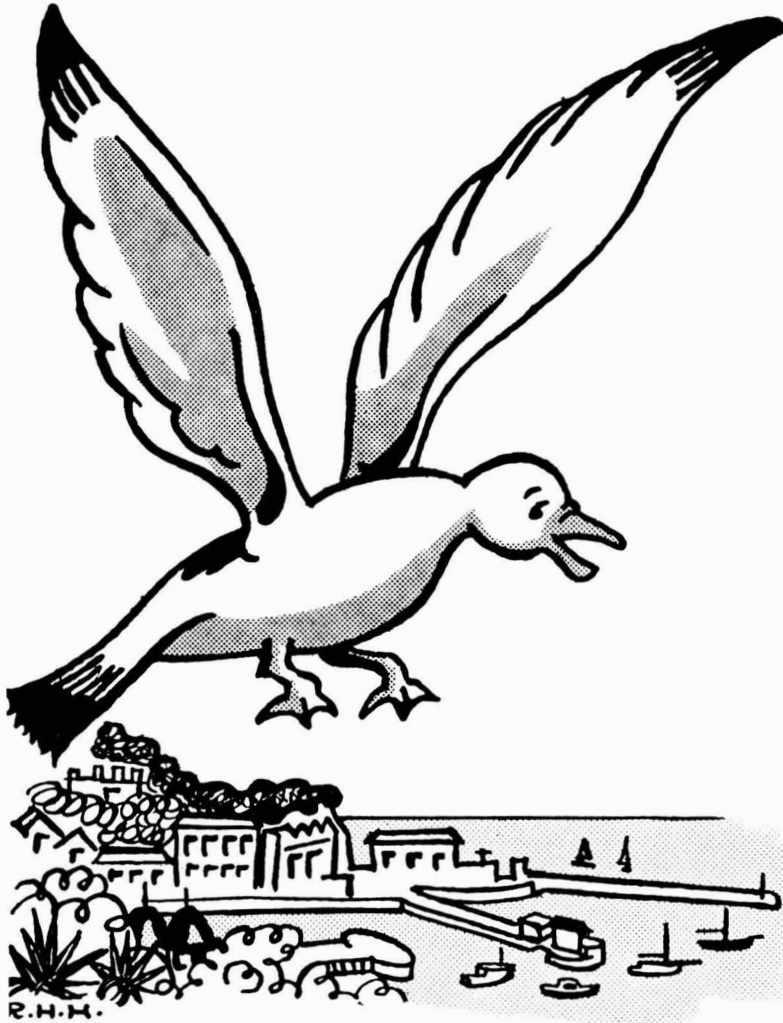
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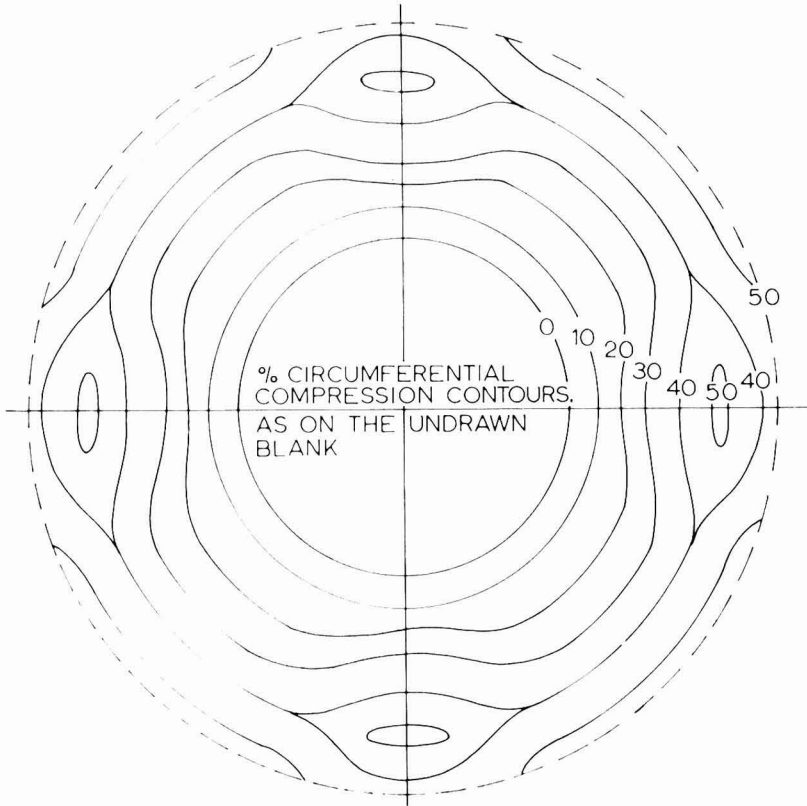


Fig. 8. Distribution of circumferential compressive strain in Swift cups drawn from steel used herein

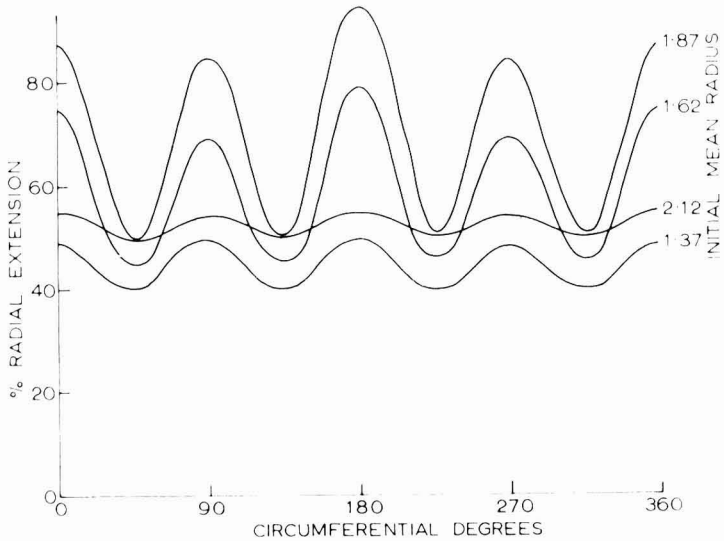


Fig. 9. Distribution of radial extensive strain in Swift cups drawn from steel used herein

Discussion

The relative influences of shear and compressive strain in drawing

It has been thought that shear of the coating, imposed during passage of the coated steel under the blankholder and between die and punch, caused much of the damage done to coatings when drawing prefinished sheet metal. Unquestionably, shearing due to poor lubrication or to rough tool surfaces can scar or buff coating surfaces. However, the severe flaking which occurs on drawing of sheet coated with some cross-linked paints could rather be due to the relative inability of such a paint (as contrasted with thermoplastic coatings) to contract circumferentially with the metal as the latter is pulled in under the hoop stresses. Failure of such a film of a cross-linked polymer on in-plane compression would occur by bulk shear or by buckling (Fig. 10), and, in either case, effectively infinite stresses would thereby be induced at the interface, resulting in loss of adhesion. The various experiments described above uniformly support the latter explanation of the failures. Minimisation of shear in a cupping operation did not affect the extent or character of coating flaking failure. Contrariwise, shear alone did not induce comparable failure in the absence of compressive strain, even when the shear stresses were substantially greater than those imposed during a drawing operation which did cause flaking failure. Flaking only occurred on those regions of the drawn cups which had been subjected to the compressive "hoop" strains (the "skirt" regions). The

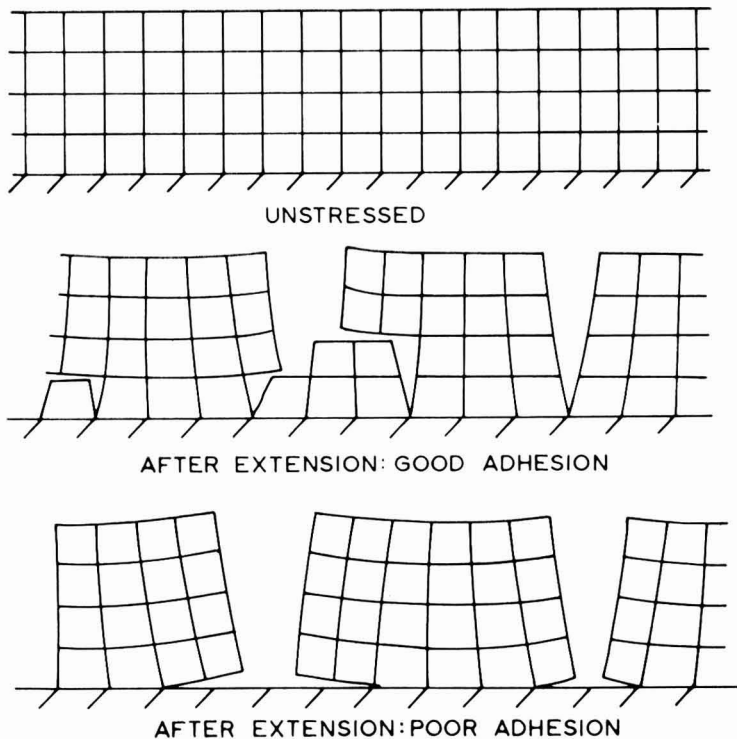


Fig. 10a

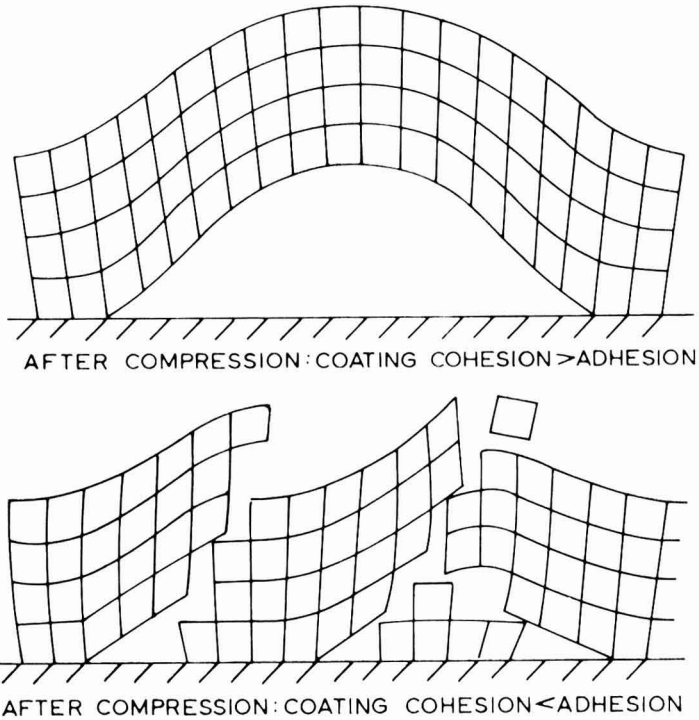


Fig. 10b

Fig. 10. Schematic illustrations of failures of thermoset and thermoplastic coatings, extended or compressed on a plastic substrate

incompletely drawn cupping trials showed that flaking damage develops at a fairly sharply critical degree of compressive strain, before the regions of flexure of metal at the die (Fig. 1), and that completely analogous failures occur even in the total absence of shear, on inside buckled folds (Fig. 2). The damage typically involves detachment of the paint from the metal as folds lying at right angles to the direction of metal contraction, with tearing, generally circumferential, across these folds, and at right angles to the tensile strain. Finally, in the beam bending experiment, the influences of pure compressive and tensile strains were assessed separately. The paint failed on the tensile face of the coated bent beam by forming short cracks normal to the extension. These combined into a tear across the full width of the beam at the point of greatest tensile strain. The extension in this region was much greater than the extension at break of the C.R. steel substrate of the precoated sheet samples, and in the regions of the beam where the surface extension fell within the range tolerated by the sheet metal samples (*ca.* 15 per cent) paint damage was restricted to hair cracking without flaking, as occurs on simple uniaxial tensile testing of specimens of the painted steel; compare Table I with Fig. 3. Failure of paint on the compressive face was by wrinkling detachment of paint along lines normal to the strain, and tearing of the film occurred only near the edges, where some additional tensile strain at right angles to the beam length was introduced by lateral bulging of the specimen (10 per cent expansion).

Micro-mechanics of coating failure in compression

The observed types of coating failures during forming of precoated sheet metal follow rationally from the rheology of the duplex metal/coating system.

In deep-drawing operations, such as Swift cupping, the metal is deformed under a biaxial tension-compression stress field.³ This results in radial elongation of elements of the metal surface with concurrent circumferential contraction⁴, as mapped in Figs. 8 and 9. The presence of the compressive "hoop" stress distinguishes deep-drawing from pure stretch-forming. The hoop contraction is desirable from the standpoint of the metal, since it tends to maintain constant the area of elements of the sheet, thus reducing the thinning which would otherwise occur under the tensile stress component. Such thinning does occur in pure uniaxial or biaxial stretching, as in tensile testing or Erichsen cupping, and limits metal fabricability under such stress modes. The metal thus behaves somewhat like a viscous fluid with a yield stress, showing only a small elastic memory at the end of the deformative process. Thermoplastic coatings, such as pvc homo- or co-polymer types or polyvinyl fluorides, show a substantially similar response. However, a cross-linked paint is unable to respond to stress by such viscous flow. In tension, distributed localised rupture ("hair-cracking") relieves the stress in such paints; many small breaks form, rather than one single crack, because of the anchoring of each microscopic element of paint to the metal surface by the adhesive forces. The mode of failure of a bonded cross-linked paint matrix, in this and other cases, is represented schematically in Fig. 10. Even if adhesion is poor, loss of contact between paint and substrate is limited in extent, since it is not a prerequisite for rupture of bonds in the polymer at extensions (due to metal flow) greater than those tolerated by the cross-linked network. In contrast, in compression, polymer or polymer-metal bond rupture occurs at low strains. In the former case, shearing rupture develops at *ca.* 45° to the direction of stress. Owing to atomic incompressibility, and since movement of atoms normal to the plane of the sheet is restrained by the network structure and ultimately by the adhesive anchoring of polymer to metal, polymer rupture can only occur with concurrent widespread loss of adhesion, since the interface is the line of flow discontinuity (Fig. 10). The consequent massive flaking failures appear only when a significant compressive strain, \gtrsim 10 per cent, has developed in the metal, as evidenced by the interrupted Swift cupping and beam bending tests. Wrinkles of detached paint film are broken into flakes by the concurrent radial extensions in cupping tests.

With less densely cross-linked paint coatings, or those of superior inherent adhesion, the failure may be less evident, being then mainly of the second rather than the first compression type of Fig. 10. However, damage may still be as widespread. Microscopic examination of a cup drawn (without flaking) from a steel coated with an alkyd paint showed hair-cracking, which was, in fact, even denser over the entire walls of the cup than over its biaxially stretched round nose. Such a condition must lead to reduced corrosion resistance and inferior appearance.

A simple test of coating compressive behaviour

From the above, tests of the fabricability of precoated metal which impose only tensile strains, such as uniaxial extension of Erichsen cupping⁵ (a stretch-forming test), will not serve to predict the behaviour of a coating in a drawing operation.

Nor will such tests serve if the coated steel surface is to be otherwise compressively strained, as on tight inside bending. However, a simple bend test on the coated metal, with coating inside and to a non-zero inside diameter which is of the order of the metal thickness, will impose compressive strains of the same order (*ca.* 50 per cent) as those arising in the cupping tests used. Use of simple magnifiers with oblique illumination, and manual probes, can permit detection of any coating rupture and/or loss of adhesion in such simple test pieces, which must not, of course, be unbent before assessment. Such a test has the advantage of being independent of any specific drawn configuration.

A thermoplastic coating can flow into folds or "waves" on compression, and such waves can be seen on stereomicroscopic examination of the extremities of Swift cups drawn from vinyl-coated steels. However, if adhesion is poor, some wrinkling lifting of the coating, as is typical for cross-linked coatings, may be observed. Damage to the thermoplastic coating of pvc/steel laminates is worst between the ears of Swift cups, at which points compression is at a maximum. Such differences of behaviour show up also in the simple "inside bend" test suggested above.

The behaviour of duplex coating systems

More strict model studies were conducted using unpigmented coating systems of controlled mechanical properties, in the absence of phosphate or etch primer pretreatments of the steel, which could only complicate further an already trilaminar system. As expected, the behaviour of all-thermoset and all-thermoplastic systems was in direct contrast.

The thermosets failed by detachment from the compressively strained skirts of the cups (Fig. 5). The regions of coating detachment followed the compressive strain contours. In the S2 series, presence of the lower modulus coat resulted in a worse performance, whether it was the primer or the topcoat (Table 3). The modulus of the primer coat appeared to affect the performance more than did that of the topcoat, but this may have been because the coating of lower modulus had a slightly lower adhesion to metal (Table 2). The S1 series of thermoset systems, which exhibited significantly higher adhesions before drawing, performed better at comparable moduli. (Table 3). Thick coatings from double applications generally showed greater loss of adhesion than did the (thinner) single coatings of the same system, probably because they generate a greater reactive shear thrust at a similar interface. This effect was more marked with the S1 system, with its longer chain length between cross-linkable functions (Table 3).

The thermoplasts, in contrast, showed no damage on the skirt, even when of modulus and initial adhesion similar to those of the thermosets (compare systems PH and S1H, Table 2). However, the high modulus thermoplast system, which has the lowest extension at break in this series, developed cracks on the crown, perpendicular to the radial extension (Table 4 and Fig. 6). Thicker coatings again performed worse than did thinner coatings of the same system.

Cracking occurred on the crown in regions where the radial extension (Fig. 9) was less than that needed to cause rupture in a 0.01in free film (Table 2). On the skirt, however, no cracking was observed in regions of much higher linear extension. Such cracking in regions of low pure extension may occur because the elongation at break of these materials depends on the sample thickness; thin

samples have a higher surface to bulk ratio, and thus a greater statistical chance of failure after crack initiation at low stresses. A 0.001 in coating of thermoplast PH on steel did crack at a low uniaxial extension; thicker free samples of polyamide have been reported as showing considerably greater extensions at break.⁸ The cracking was less severe if a low modulus primer was used under the high modulus top coat, and a lower modulus top coat completely prevented cracking of a high modulus primer (Fig. 6 and Table 4). In this test series, the low modulus coating had a much higher elongation at break (Table 1), suggesting that, as a top coat over a high modulus primer, it may have reduced the statistical chance of crack propagation through or from the stretching primer by filling in incipient surface cracks in the latter. Thermoplastic coatings may have been undamaged in skirt regions because the simultaneous circumferential compression here limited crack propagation or, alternatively, because friction with the die wall raised the temperature of the coating and thus its elongation at break. A 1 per cent change in temperature produces an 8 per cent change in the elongation at break of system PH⁸. This resin showed less cracking on cups drawn at 20°C than on cups drawn at a lower temperature, 7°C, as in the main test series. When a cup was drawn very slowly (0.5 ft.min⁻¹) in an attempt to minimise frictional heating, cracking was still not observed on the skirt. However, cracking on the crown was appreciably less at the slower rate, presumably because the coating has a longer time during which to distribute the induced strain, so this experiment failed to discriminate between the two above explanations for the lack of cracking on the skirts.

Attempts to combine the desirable fabrication properties of the polyamide and epoxy systems, by using the former as a primer for the latter, were informative but did not yield a fully fabricable two-coat system. The thermoplastic primers much reduced the detachment of the epoxies over the skirt region, confining it to the regions of highest compressive strain (Table 5, Figs. 7 and 8). This effect was most marked when the moduli of the two layers were similar (compare the two diagonals of Fig. 7 with its orthogonals). On the crown region, the polyamide, which cracked when used alone, induced cracking in the high modulus epoxy (which had a very low elongation at break), but coating break-up was prevented by the use of a topcoat showing higher elongation at break (Table 5, Fig. 7). Compare the comments made above on purely thermoplastic two-coat systems.

Summary and conclusions

The flaking of cross-linked coatings from coated steels during drawing is not due to shearing of the paint from the metal, but to the inability of the paint to follow the in-plane compression of the metal. Improvement in the initial shear adhesion of the coating can reduce flaking or detachment, but the compressive stresses within the paint film are then relieved by extensive hair cracking. Increase of coating thickness raises the interfacial stresses and thus can reduce fabricability of coatings, other than those having very high extensibilities. Thermoplastic coatings which show a low elongation at break as thin films fail by cracking in extended regions on fabrication, the tendency to such cracking having been observed to decrease with increasing elongation at break, or with decreasing straining rate.

Completely independent variation of the various mechanical properties of

the polymeric strata of one- and two-layer coatings is naturally not possible, both chemical and physical modifications inducing changes in several major properties (Table 2). An overall pattern nevertheless emerges from the authors' data. A coating which is to be subjected to extension, as in outside bending or stretch forming, should possess a high elongation at break together with adequate initial adhesion to the metal, if cracking and consequent detachment of the coating is to be avoided. If the coating is to be compressed, as in the skirt of a Swift cup or in other deep-drawn parts, then the prime requirement to prevent wrinkling, flaking or total detachment of the coating is substantial absence of cross-linking; differences of degree of cross-linking had little influence within the ranges studied. Initial adhesion is also of great importance. The authors have not been able to demonstrate any clear correlations between coating moduli or strength properties, and fabricability in either extension or compression.

The available evidence suggests that multilaminar coatings, including suitably selected strata of both thermoplastic and thermoset natures, may be able to combine the fabrication and other advantages of both coating types. Thus, a top coat of high elongation at break can eliminate cracking on extension of a primer of low breaking elongation, whether the top coat be thermoplastic or cross-linked. A thermoplastic primer can reduce the loss of adhesion of a compressively strained cross-linked top coat. Other such beneficial interactions may remain to be demonstrated.

In such combined thermoplast/thermoset coating systems, there is some indication that matching of moduli of adjacent strata may be desirable for optimum fabricability.

In conclusion, it should be noted that the behaviour patterns herein observed for coatings on plastically deforming metal must also operate in other adhesively-linked multi-laminar systems stressed beyond yield of one stratum. The concepts used herein to account for coating behaviour could therefore aid interpretation of chipping behaviour of multi-laminar coatings⁹. They could also be usefully applied to analysis of the behaviour of bonded structures exposed to high-level shearing stresses, particularly when the latter are of a cyclic nature. Such analyses could also supplement recent studies of the effect of metal plasticity in bonded joints subjected to cleaving stresses^{10,11}, and might lead to design of adhesive primers to enhance joint limit strengths or durabilities.

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Formulation of fungus resistant paints. VII: Addition of metal 8-hydroxyquinolates

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Summary

The hydroxyquinolates of copper, aluminium, barium, calcium, cadmium, strontium, and zinc have been assessed as fungicides in gloss and flat enamel paints. Panels coated with these paints were exposed at Lae, New Guinea, and the mould growth in each case was compared with that on a paint free of fungicide. The loss of the hydroxyquinolate from the coatings was also determined.

Of the compounds investigated only copper 8-hydroxyquinolate (Cu H) imparted fungus resistance to the paint, and then only on the upper side of the panel. The stability of (Cu H) in the paint film is very high.

Key words

Biologically active agents
fungicide
metal 8-hydroxyquinolate

La mise au point des formules de peintures résistante à végétation mycélienne

Résumé

Les hydroxyquinolates de cuivre, aluminium, baryum, calcium, strontium, cadmium et zinc ont été appréciés en tant que fongicides en peintures-émaux brillante ou mate. Eprovettes revêtues de ces peintures ont été exposées à Lae, Nouvelle Guinée, et l'on a en fait comparer la croissance de moisissure auprès de celle d'une peinture exempte de fongicide. La perte de l'hydroxyquinolate à partir des revêtements a été dosée également.

Parmi les composés examinés, seulement le 8-hydroxyquinolate de cuivre (CuH) a remporté une résistance à végétation mycélienne quelconque à la peinture, et quand même sur la face supérieure seulement. La stabilité du (CuH) se démontre très élevée.

Rezeptur für Pilzanwuchsbeständige Anstrichfarben : Zusatz von 8-Hydroxyquinolatverbindungen

Zusammenfassung

Die Hydroxyquinolatverbindungen von Kupfer, Aluminium, Barium, Kalzium, Kadmium, Strontium und Zink wurden auf ihre Eignung als Fungizide für Glanz und Mattlacke geprüft. Mit solchen Farben gestrichene Tafeln wurden in Lae in Neu Guinea exponiert, und der Pilzbewuchs mit je einer kein Fungizid enthaltenden entsprechenden Farbe verglichen. Ebenfalls wurde der Verlust an Hydroxyquinolat vom Film bestimmt.

Von den untersuchten Verbindungen verlieh lediglich Kupfer-8-Hydroxyquinolat (CuH) Widerstandsfähigkeit gegen Pilzbewuchs und auch nur auf der Oberseite der Tafeln. Die Stabilität des (CuH) im Anstrichfilm ist sehr gross.

Формуляция красок устойчивых против плесени Добавление металлических 8-гидроксихинолатов

Резюме

Гидроксихинолаты меди, алюминия, бария, кальция, кадмия, стронция и цинка оцениваются как фунгисиды в глянцевых и матовых эмалевых красках. Панели покрытые этими красками подвергались действию атмосферы в Лае, в Новой Гинее и прирост плесени сравнивался в каждом случае с плесенью в краске свободной от фунгисида. Определялась также потеря гидроксихинолата в покрытиях.

Среди исследованных соединений только 8-гидроксихинолат меди (Cu H) придавал краске устойчивость против плесени, и тогда только на верхней стороне панели. Устойчивость (Cu H) в красочной пленке очень высока.

Introduction

The addition of copper 8-hydroxyquinolate (Cu H) has been proposed as a fungicidal additive to paints, but nothing appears to be known as to its effect on mould resistance in the tropics. For this reason, the compound was included in the current study on fungicides which is being carried out in the Division of Building Research. It was of interest to establish whether other metal 8-hydroxyquinolates showed fungicidal activity, and, therefore, the aluminium, barium, calcium, strontium, cadmium, and zinc compounds have also been tested.

It has been pointed out¹ that, for a rational interpretation of the observations, it is necessary to establish the stability of a fungicide in a paint film. The present paper deals with the loss of the various hydroxyquinolates from the coatings and their fungicidal activity at Lae, New Guinea.

Experimental

Analytical work

The paints containing the fungicides were brushed out on sheets (12in × 6in) of a polyethylene terephthalate polyester film, attached to asbestos cement panels, and exposed under the following conditions.

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

At intervals of approximately six months, a portion of each film was removed and analysed for hydroxyquinolate to determine the loss of the fungicide. (The method of analysis has been described elsewhere².) The panels at Highett were mounted on racks at an angle of 45° facing north, those at Lae had the painted film attached to both sides and were mounted at 45° facing 31° east of true north.

Exposure at Lae, New Guinea

A separate set of hardboard panels painted with gloss and flat enamel paints, and the corresponding blanks, were exposed at Lae, New Guinea. The intensity and extent of mould growth was assessed at intervals of about three months, and the results are summarised in Tables 1 and 2.

Table
Assessment of mould growth on paint

Paint	Replicate	4 months		8 months		10 months		14 months		17 months	
		I	C	I	C	I	C	I	C	I	C
G	1, 2, 3	1	100	2	70	3	100	4	Tr	2	100
G Cu	1, 2, 3	0	100	0	100	0	100	0	100	0	100
F	1, 3	3	100	2	100	0	100	9	30	9	30
	2	2	100	2	100	0	100	1	100	1	100
F Cu	1, 2, 3	0	100	0	100	0	100	0	100	0	100

G, Gloss enamel paint without copper 8-hydroxyquinolate; G Cu, gloss enamel paint with flat enamel paint with copper 8-hydroxyquinolate.

C = Percentage area covered by colour intensity I

I = Intensity of colour according to scale 9 (black) - 0 (white)

I = 0 and C = 100 means that the panel is free of mould

Tr = Trace

Table
Assessment of mould growth on paint

Paint	Replicate	4 months		8 months		10 months		14 months		17 months	
		I	C	I	C	I	C	I	C	I	C
G	1, 2, 3	3	Tr	3	100	2-3	90	4	60	4	50
G Cu	1, 2, 3	2-3	10	3	100	4	100	2-4	100	2-3	100
F	1, 2, 3	5	100	4	100	5	100	3-5	100	3-9	100
F Cu	1, 2, 3	2	100	8	50	4-5	100	9	100	3-5	100

G, Gloss enamel paint without copper 8-hydroxyquinolate; G Cu, gloss enamel paint with flat enamel paint with copper 8-hydroxyquinolate.

C = Percentage area covered by colour intensity I

I = Intensity of colour according to scale 9 (black) - 0 (white)

I = 0 and C = 100 means that the panel is free of mould

Tr = trace

Preparation of hydroxyquinolates

8-hydroxyquinoline was dissolved in ethyl alcohol and the equivalent amount of the metal nitrate or chloride in water was added. The pH of the slurry was adjusted to 7, and the hydroxyquinolate was filtered off, dried, and ground.

1

films exposed at Lae—upper side of panels

Exposure

21 months		24 months		27 months		30 months		33 months		36 months	
I	C	I	C	I	C	I	C	I	C	I	C
0	100	0	100	0	100	1	100	1-2	100	1-3	100
0	100	1-2	100	1-2	100	1-3	100	1-4	100		

copper 8-hydroxyquinolate; F, flat enamel paint without copper 8-hydroxyquinolate; F Cu,

2

films exposed at Lae—under side of panels

Exposure

21 months		24 months		27 months		30 months		33 months		36 months	
I	C	I	C	I	C	I	C	I	C	I	C
2-3	100	2-3	100	2-3	100	2-4	100	2-4	100	2-4	100
3-5	100	4-6	100	4-6	100	2-6	100	2-6	100	2-6	100

copper 8-hydroxyquinolate; F, flat enamel paint without copper 8-hydroxyquinolate; F Cu,

Paints

A gloss enamel paint containing 1.8 per cent, and a flat enamel paint containing 2.5 per cent, of the copper 8-hydroxyquinolate were used. The aluminium, barium, calcium, cadmium, strontium, and zinc hydroxyquinolates were tested

in a flat enamel at about 2 per cent 8-hydroxyquinolate in the form of the metal salt.

Discussion

As can be seen from Figs. 1 and 2, (Cu H) is very stable in both gloss and flat enamel paint films. Only 24 per cent was lost from the upper side of the gloss film in 32 months at Lae (Fig. 1, curve 1) and nothing on the under side (Fig. 1, curve 2). On the upper side, the surface stayed free of mould (Table 1) for 27 months, but appreciable mould growth occurred after 36 months. It is possible that the appearance of fungus after this time was due to its adaptation to the conditions on the surface. A wash with hypochlorite solution, by killing off all the spore population, may have restored the original fungus resistance of the surface. Alternatively, the diffusibility of (Cu H) from the body of the film to the surface may be so slow that its concentration becomes too low to be effective. Only further experiments could decide between these possibilities.

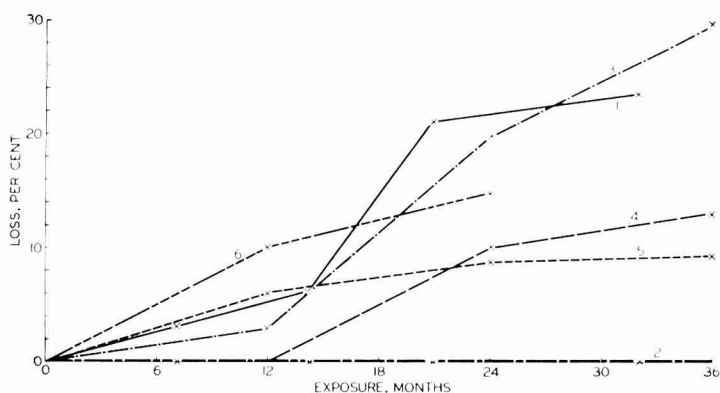


Fig. 1. Loss of copper 8-hydroxyquinolate from gloss alkyd enamel paint

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

In spite of the great stability of (Cu H) on the under side, there was no fungicidal effect at all. A similar observation has been made with paints formulated with zinc oxide³. Certain types of zinc oxide render the paint fungus-resistant on the upper side but not on the under side.

The reason for this difference in behaviour is a matter of speculation. Possibly the metabolism of the mould is somewhat different on surfaces exposed to strong light, compared with surfaces which receive only comparatively weak light.

The loss of (Cu H) from flat enamel paint film was somewhat greater than from gloss paint films, amounting to 38 per cent in 32 months on both upper

and lower sides, (Fig. 2, curves 1 and 2). There was no improvement in fungus resistance on the under side (Tables 1 and 2).

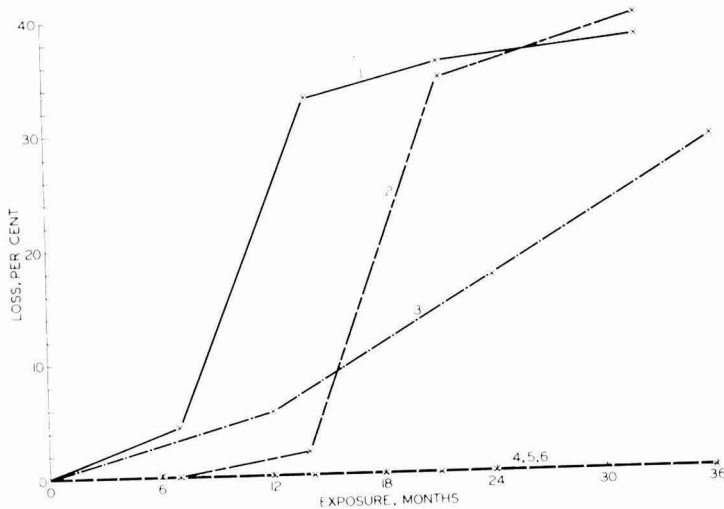


Fig. 2. Loss of copper 8-hydroxyquinolate from flat enamel paint

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

Hydroxyquinolates of aluminium, barium, calcium, cadmium, strontium, and zinc and their mixtures showed no fungicidal activity on the upper or under sides (Table 3).

It is interesting to note that, in contrast with (Cu H), all these compounds were quickly lost from the paint film. On the upper side, the loss in 9 months varied from 68 to 90 per cent, and on the under side it was as high as 67 per cent for the calcium hydroxyquinolate (Table 4).

The fungicidal activity of the various compounds was also tested by the Vicklund-Manowitz procedure⁴, and only (Cu H) was found to have any activity (Fig. 3). Two points should be noted: first, the absence of any zone of inhibition; secondly, according to this test the material is active, but in fact, it has been shown to be so under special conditions, that is, at sites in sunlight. This behaviour certainly could not have been derived from the laboratory test.

Table 3

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

Paint	Replicate	Exposure									
		4 months		8 months		11 months		15 months		18 months	
		I	C	I	C	I	C	I	C	I	C
F	1, 2, 3	1-2	100	2-3	100	3	100	3	100	2-9	100
F Al	1, 2, 3	1	100	2	100	3-4	100	3-4	100	3-9	100
F Ba	1, 2, 3	1-2	100	2	100	3-4	100	3	100	3-9	100
F Ca	1, 2, 3	1-2	100	2	100	3-4	100	3	100	3-9	100
F Cd	1, 2, 3	1	100	2	100	2	100	2-3	100	2-9	100
F Cu	1, 2, 3	0	100	0	100	0	100	0	100	1	100
F Sr	1, 2, 3	1-2	100	2	100	4-5	100	4	100	2-9	100
F Zn	1, 2, 3	1-2	100	3	100	2-3	100	2-4	100	3-9	100
F Al, Ba, Sr ..	1, 2, 3	1	100	2-3	100	2	100	2-4	100	2-9	100
F Al, Ba, Cd	1, 2, 3	1	100	2-3	100	2	100	2-3	100	2-9	100

F, flat enamel paint without quinolate; F Al, etc., flat enamel paint with the indicated quinolate added; F Al, Ba, Sr and F Al, Ba, Cd mixture of quinolate added

C = percentage area covered by colour intensity I

I = Intensity of colour according to scale 9 (black) > 0 (white)

I = 0 and C = 100 means that the panel is free of mould

Table 4

Loss of some metal 8-hydroxyquinolates from a flat enamel paint film exposed for 9 months at Lae

Cation	Initial 8-hydroxyquinoline in the form of quinolate	Loss in 9 months, %	
		Upper side	Under side
Al ..	2.15	85	37
Ba ..	2.03	87	62
Ca ..	1.60	83	67
Cd ..	2.36	68	21
Sr ..	1.81	90	65
Zn ..	2.31	71	26

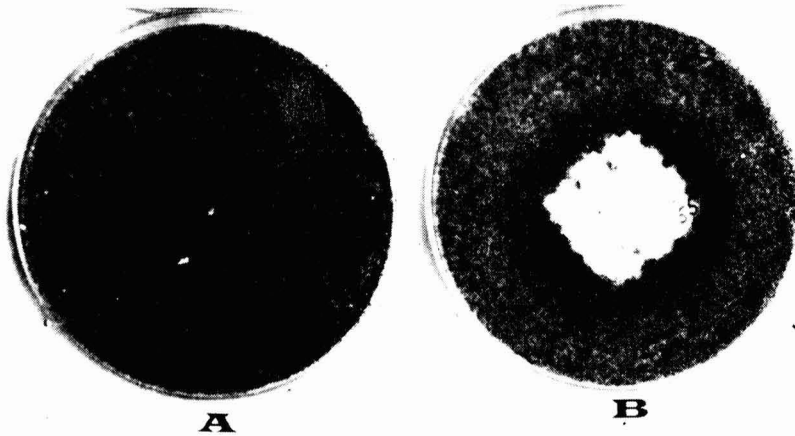


Fig. 3. Vicklund-Manowitz test

"A" gloss enamel paint without fungicide

"B" gloss enamel paint with copper 8-hydroxyquinolate added

Conclusions

Of the metal 8-hydroxyquinolates investigated, only the copper 8-hydroxyquinolate increased the fungus resistance of paint in the humid tropics, and then only on the upper side of the test panels.

Acknowledgment

Thanks are extended to Mr J. R. Barned of the Division of Building Research, CSIRO, for his assessment of the paints at Lae.

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Instrumental measurement of colour

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Summary

Colorimetry and spectrophotometry are briefly introduced with particular reference to the newer CIE data. A few of the problems encountered in colour measurement are highlighted. The assessment of colour strength is of major importance and two methods of doing this are investigated.

- (a) The Kubelka-Munk equation and
- (b) The International Standard Depths method.

Small patterns present measurement problems, and methods of getting round this are given for use with G. E. Hardy and Large Sphere Color Eye Spectrophotometers.

Colour match prediction is mentioned only briefly.

The effect of surface characteristics on colorimetric results is demonstrated.

Key words

Process and methods primarily associated with analysis, measurement testing
colorimetry
spectrophotometry

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

Colorimétrie Instrumentale

Résumé

On présente brièvement la colorimétrie et la spectrophotométrie, au point de vue de récentes données de la C.I.E. On souligne certains problèmes que l'on rencontre sur le plan de colorimétrie. L'appréciation du pouvoir colorant est d'une grande importance, et l'on examine deux méthodes pour l'effectuer:—

- (a) L'équation de Kubelka-Munk.
- (b) La méthode "International Standard Depths."

Les échantillons-types de petite taille présentent des problèmes en ce qui concerne leur colorimétrie et l'on donne certaines méthodes pour les éviter en utilisant soit le spectrophotomètre G. E.-Hardy, soit celui appelé "Large Sphere Color Eye."

On ne mentionne que brièvement la prédiction du contretypage de couleur.

On démontre l'effet qu'exercent des caractéristiques de surface sur les résultats colorimétriques.

Farbmessung mit Instrumenten

Zusammenfassung

Kolorimetrie und Spektrophotometrie werden eingangs kurz erwähnt, insbesondere unter Bezugnahme auf die neueren CIA Merkmale. Auf einige wenige beim Farbmessen begegnete Probleme wird hingewiesen. Die Bewertung der Farbkraft ist von besonderer Wichtigkeit. Diesbezüglich wurden zwei Methoden geprüft

- (a) die Kubelka-Munk Gleichung und
- (b) die International Standard Depths Methode.

Das Messen kleiner Muster bietet Probleme, und Methoden, diese zu überwinden, werden für die Anwendung mit dem G. E. Hardy und dem Large Sphere Colour Eye Spectrophotometer angeführt. Voraussagen für die Farbeinstellung werden nur kurz erwähnt.

Der Einfluss von Oberflächencharakteristika auf kolorimetrische Ergebnisse wird dargelegt.

Приборное измерение цвета

Резюме

Дается краткое введение в колориметрию и спектрофотометрию, ссылаясь особо на новейшие данные С.И.Е. Уделено особое внимание некоторым проблемам возникающим при измерении цвета. Анализируется оценка прочности цвета как вопроса первой важности и дается два метода осуществления такой оценки.

- а) Уравнение Кубельки – Мунка и
- б) Международный метод стандартных глубин.

Малогабаритные образцы предъявляют трудности в проблемах измерения и прилагаются методы обойти эту трудность, применяя спектрофотометр Г. Е. Гарди и сферический, визуальный, цветной спектрофотометр. Прогноз подбора цветов упоминается лишь кратко.

Иллюстрируется влияние поверхностных характеристик на результаты колориметрических измерений.

Introduction

Colour measurements fall into two fairly distinct groups; colorimetry and spectrophotometry. Colorimetry is a direct method of attempting to simulate instrumentally the mechanism of the eye. One has an illuminating light source, the pattern and a detector system (usually three filters: red, green, and blue; and a photocell). The detector system is really meant to represent the eye, and instruments will vary in the closeness with which they approximate to the eye, but which eye? This was one question raised by the introduction of colorimetry; another was, which illuminant? In 1931, the International Committee on Illuminants, the CIE¹, attempted to answer these questions by setting standards for the artificial representation of naturally occurring lighting and by describing a standard observer representing observers with normal colour vision. Since then, most colorimeters have tried to fit these standards and all methods of converting spectrophotometric information to colorimetric have used the mathematics. This statement is not completely true, as in 1963 the CIE published the "10° observer" data² and recently committee E-1, 3.1³ recommended an additional illuminant, D₆₅₀₀.

To explain the "10° observer" data, it is necessary to consider briefly the mechanism of colour vision. In the retina of the human eye there are two types of light sensitive cell, called the rods and the cones. The rods are sensitive to intensity only and have an upper intensity threshold above which they will not function. The cones sub-divide into red, green and blue sensitive cells, and have a lower threshold below which they are not activated. Hence, at low levels of illumination man possesses no colour vision. Another important factor is the distribution of the cells across the retina. The cones have their highest population density at the fovea, the centre of the retina, and fall off in density towards the periphery. There are no rods in the foveal area, which is approximately 0.5mm across and subtends an angle of about 2° at the eye lens.

Beyond the fovea the rod population relative to the cone increases. Consequently, detailed colour vision is restricted to the centre of the field of view whereas motion, without colour sensitivity, can be observed right out on the periphery.

When Wright⁴ and Guild⁵ made their measurements of the sensitivity of the eye to mixtures of three stimuli, they chose viewing conditions that meant the patterns viewed only activated this foveal region (that is, an area subtending an angle of 2°). For some time, people had agreed that such viewing conditions did not represent normal industrial practice for inspection of coloured patterns. Stiles⁶ and Speranskaya⁷ made similar experiments to those of Wright and Guild except that their viewing conditions created a 10° subtention on the retina. The important difference between the two sets of data is that in the first set only cone vision is involved whereas in the later work both cone and rod vision are used. The differences between the distribution coefficients \bar{x} , \bar{y} , \bar{z} , can be seen in Fig. 1. In 1963, the CIE recommended the adoption of this additional set of colour matching functions whenever more accurate correlation with visual colour matching of fields of large angular subtense was required.

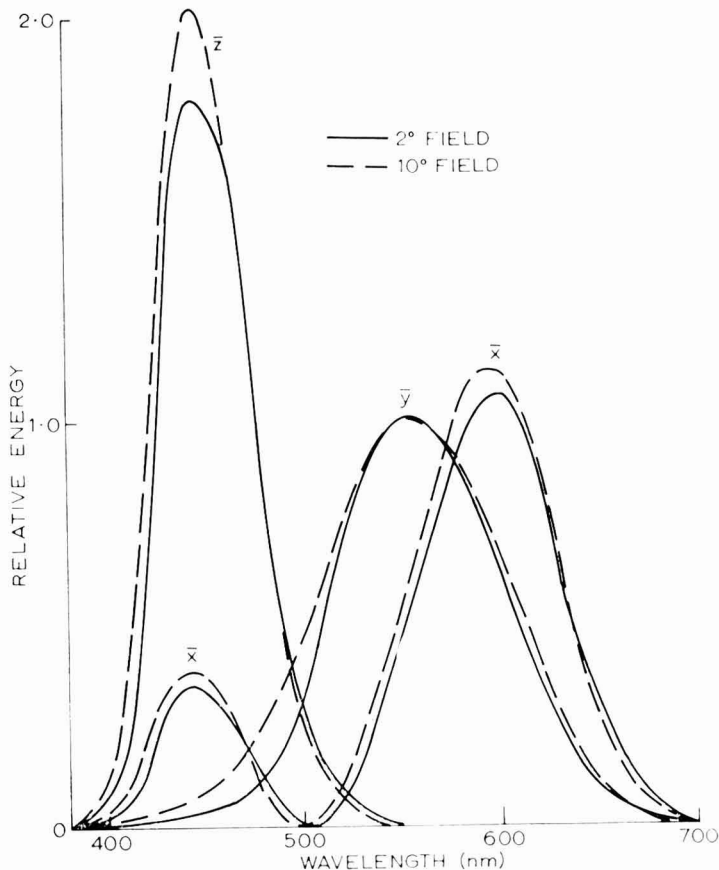


Fig. 1. CIE distribution coefficients

The 1931 CIE committee also made recommendations of the light sources to be used in colorimetry by specifying illuminants *A*, *B*, *C*, of correlated colour temperatures 2854°K, 4870°K and 6740°K respectively, as approximations to an incandescent lamp, mean noon sunlight and average north sky light. The definitive curves are given in Fig. 2, in which one can see that *A* is predominantly

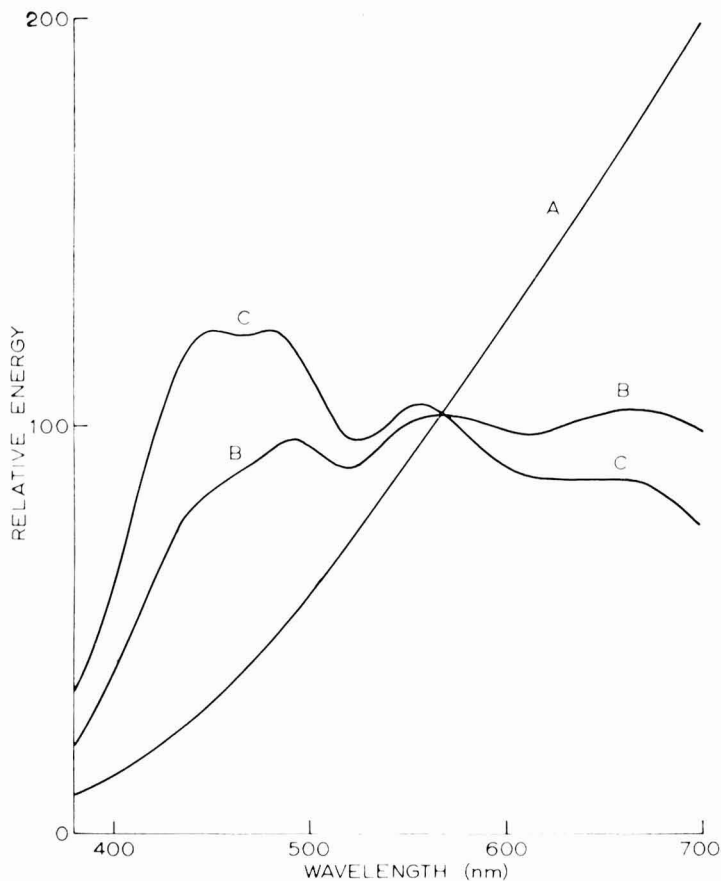


Fig. 2. 1931 standard illuminants

orange, *B* is nearly neutral, and *C* is mainly blue. These have been used as standards for many years, with reasonable success in the visible range but with only poor correlation to natural radiation in the ultra-violet. Historically, there are good reasons for not considering the UV in the original specification. At the time, lamp manufacturers were restricted to incandescent lamps whose UV content was very low; the use of fluorescent colours and optical brightening agents was not of commercial magnitude, if they were being used at all; and, finally, the importance of the role played by ultra-violet radiation in photo-chemical degradation processes was not fully appreciated.

These factors are better appreciated now, and are the reasons for the recommendation mentioned earlier (Fig. 3). D_{6500} has been defined between 300

and 830nm, and is a representation of daylight. The committee also gives methods for calculating relative spectral energy distributions for any correlated colour temperature between 4,000°K and 25,000°K. Its recommendation was: "in the interests of standardisation D_{6500} be used whenever possible; when D_{6500} cannot be used it is recommended that one of the two relative spectral energy distributions having correlated colour temperatures of 5,500°K and 7,500°K be used, whenever possible." This recommendation has been adopted by the BSI.

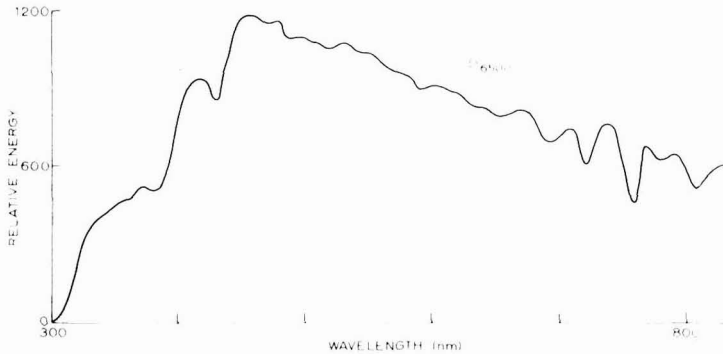


Fig. 3. D_{6500} standard illuminant

Colorimetry

Colorimetry is a method of describing any colour in terms of relative amounts of three primary stimuli. Any three additive primaries will suffice in theory, although it has become conventional to take red, green and blue. It cannot be stressed too often that the primaries are red, *green* and blue. These must be the primaries of any colour description system because the eye is stimulated by light, without any reference to the way in which that light was produced, be it by light sources, filters, paints or dyes, and the additive laws of colour mixing govern the visual effect, interpreted by the brain, from the stimulation of the receptors. The principle of additivity was tested by König at the end of the last century and has been checked recently by Stiles for the 10° field. Stiles suggests that additivity does not hold completely under these circumstances and that occasionally some disagreement between visual and instrumental results might arise.

The derivation of the laws and equations of colorimetry is well established, and the reader is referred to the several textbooks on the subject, in particular to Wright "The measurement of colour"⁸.

The CIE chose its three primaries such that X , Z lie on the alychne, and as a consequence the Y stimulus was related to the photopic curve, i.e. the light adapted visual sensitivity curve.

Spectrophotometry

A particularly important application of the colour mixture relations is to the derivation of the specification of a colour when its spectral composition is known (E_λ). Before this can be done, the amounts of X , Y , Z that would be

required to match each wavelength in turn in the equal energy spectrum must be known. These were obtained by the colour matching experiments of Wright and Guild referred to above. They have been given the symbols \bar{x} , \bar{y} , and \bar{z} , and are known as the distribution coefficients. Therefore a colour made up of two wavelengths λ_1 and λ_2 is given by

$$\begin{aligned} X &= (E_\lambda \bar{x})_1 + (E_\lambda \bar{x})_2 \\ Y &= (E_\lambda \bar{y})_1 + (E_\lambda \bar{y})_2 \dots\dots\dots(1) \\ Z &= (E_\lambda \bar{z})_1 + (E_\lambda \bar{z})_2 \end{aligned}$$

which, when extended to all wavelengths of the equal energy spectrum, gives

$$\begin{aligned} X &= \Sigma E_\lambda \bar{x} \\ Y &= \Sigma E_\lambda \bar{y} \dots\dots\dots(2) \\ Z &= \Sigma E_\lambda \bar{z} \end{aligned}$$

So far, this only applies to a light source. Extending this to a reflecting surface such as a paint or a piece of cloth, one must include the effect of this surface on the equal energy spectrum, that is its reflection curve giving:

$$\begin{aligned} X &= \Sigma E_\lambda \bar{x} R \\ Y &= \Sigma E_\lambda \bar{y} R \dots\dots\dots(3) \\ Z &= \Sigma E_\lambda \bar{z} R \end{aligned}$$

Because of the specification of the *Y* stimulus, it is usual to rationalise these values, so that the *Y* for magnesium oxide = 100.00 where MgO is the accepted primary standard for 100 per cent reflectance at all visible wavelengths.

The full specification of the tristimulus values is given by equation 4

$$\begin{aligned} X &= \Sigma E \bar{x} R / \Sigma E \bar{y} \\ Y &= \Sigma E \bar{y} R / \Sigma E \bar{y} \dots\dots\dots(4) \\ Z &= \Sigma E \bar{z} R / \Sigma E \bar{y} \end{aligned}$$

Whilst thinking of these equations as (the light source) × (the pattern) × (the eye), it must be realised that \bar{x} , \bar{y} , \bar{z} , only represent the eye, they are in no way a description of the physiological behaviour of the individual receptors. (The light source) × (the pattern) × (the eye): change any one of these three and the stimulus to the brain is changed, although by examination of the last set of equations it is obvious that *R* can be changed to give other combinations with the same *E* and \bar{x} , etc. such that *X*, *Y*, *Z* are equal. Thus, two different patterns appear the same under one light source, but they will not combine with a different set of *E* values to equate. This is the well known phenomenon of metamerism. If two patterns have the same *R* values at all wavelengths, they will always match independent of light source and eye so long as the same ones are used to view both patterns. This is known as a spectral match.

The major differences between colorimetry and spectrophotometry are thus highlighted. With spectrophotometry, one can mathematically employ any illuminant, including the standards specified by the CIE, in colorimetry one is restricted to the light sources available in any particular instrument and to the accuracy with which they match, or otherwise, the CIE specification. With spectrophotometry, metamerism is immediately obvious, with colorimetry, at least two sets of measurements must be used to detect it.

Strength assessment

One of the more important demands upon colourists is the assessment of the relative strengths of two colourants. If a relationship between reflectance and colourant concentration exists, then spectrophotometry provides a method. In 1931, Kubelka and Munk⁹ presented an approximate solution for this relationship for reflecting films of known thickness. Duncan¹⁰ simplified this for optically infinite films in 1940 to give the well established Kubelka–Munk relationship

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \propto \text{concentration} \dots\dots\dots (5)$$

where K = the coefficient of absorption
 S = the coefficient of scatter
 R = the reflectance measured against standard = 1.0

Certain very important assumptions were made in the derivation of this equation:

- the colourant absorbs without scattering,
- the base white scatters without absorbing,
- the scattering material is embedded in a medium of the same refractive index as that in which the measuring radiation is incident.

These conditions are most closely met in dyed *natural* fibres. One must specify natural fibres because the opacity, i.e. the scattering of many synthetic fibres, is created by the inclusion of titanium dioxide within the fibre, in which case the third assumption is no longer valid. In many respects this assumption is the least worry, as corrections have been made to overcome the effects of an extra optical boundary by Saunderson,¹¹ Duncan¹² and others¹³. If the function K/S is plotted against dyestuff concentration, where the reflectance used is that of minimum deviation the relation should be linear. Such practical plots for a dye and a pigment are shown in Fig. 4. In neither case are they linear over the full range of concentrations shown. The non-linearity is only slight until relatively high concentrations are reached and it can be ignored in strength assessment of medium depths. This non-linearity will be discussed later.

Thus, an almost linear relation exists between a function of reflectance and concentration in an analogous way to the Lambert-Beer law for solution concentration. This gives a method of assessing the relative strengths of two patterns, especially as tables of R against $(1 - R)^2/2R$ are available for both the original function and the surface reflectance corrected function. How reliable is this method? The following are some results obtained in attempting to answer this question.

Three paints, a yellow, a red, and a blue were made up as standards, using single pigments. From each standard paint, twelve further paints were made as one repeat standard, five small increments in the amount of the original pigment, four small introductions of pigments of slightly different shade, and two very small additions of carbon black. In this way variations in strength alone and brightness alone were created; the attempts to produce simple shade differences unfortunately also affected the other parameters. Each of the twelve patterns, as 6in × 4in panels, was compared against the standard by twenty observers, under a colour matching lamp. The observers were allowed to adjust

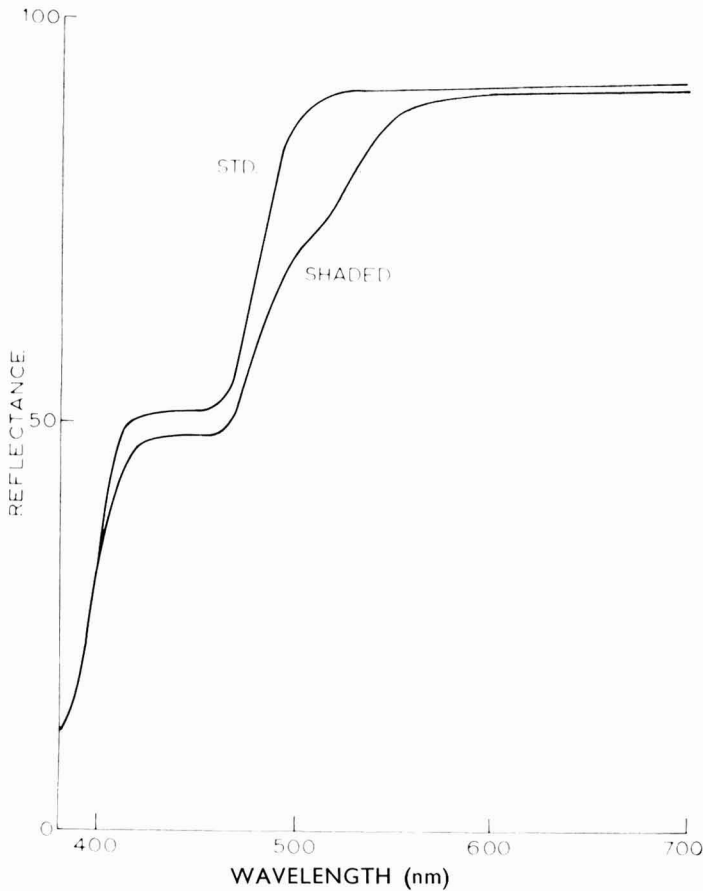


Fig. 4. Effect of shading on yellow

viewing angle, distance and position at will, but were asked to compare each panel only against the standard and to stipulate a numerical strength difference. The panels were measured spectrophotometrically and strength assessments relative to the standard made using four methods.

$$(1) \frac{(1-R)^2}{2R} \propto \text{concentration}$$

$$(2) \frac{(1-X)^2}{2X} \propto \text{concentration}$$

(3) Method (1) with the surface reflection correction

(4) Method (2) with the surface reflection correction

The results obtained are summarised in Tables 1, 2, and 3. After averaging, any visual result different from the visual mean by twice the standard deviation was ignored and a new mean was established. Several observations can be made. If only strength differences are present, the instrumental methods do not

Table 1
Results of strength assessment tests

Yellow		10	4	8	5	9	2	7	6	3	11	12	13
visual	Panel												
	mean	97.9	99	100.9	103.4	102.8	106.5	105.1	109.8	103.5	105.1	89.0	84.0
	standard deviation	3.24	3.18	2.52	4.11	4.05	4.71	3.14	4.70	6.00	13.00	6.91	7.64
	2σ	6.48	6.36	5.04	8.22	8.10	9.42	6.28	9.40	12.00	26.00	13.82	15.28
inst.	new mean	98.8	99.0	101.3	102.8	103.5	105.8	104.5	108.9	102.6	102.7	90.6	84.0
	new σ	1.90	3.18	2.16	3.15	2.76	3.57	2.15	3.04	4.69	7.76	5.26	7.64
	method 1	97	101	102	104	108	111	111	129	116	126	98	102
	2	96	104	102	106	110	114	117	136	136	158	101	107
Variation to paint	3	98	101	102	104	107	109	109	124	113	122	98	102
	4	97	103	102	105	109	112	114	129	129	148	101	106
	strength				6	8	10	5	10	5	10	0.1	0.2
	shade	None	2	4	6	8	10	5	10	5	10	0.1	black

Table 2
Results of strength assessment tests

Reds		3	13	7	9	6	5	10	4	11	2	8	12
visual	Panel												
	mean	96.4	98.7	96.8	100.8	101.0	103.5	103.2	105.6	95.8	104.6	92.5	89.4
	standard deviation	3.79	4.04	3.11	3.76	2.87	2.91	3.82	4.44	4.96	7.37	4.51	5.05
	2 σ	7.58	8.08	6.22	7.52	5.74	5.82	7.64	8.88	9.92	14.74	9.02	11.10
	new mean	96.4	98.6	97.5	100.1	101.3	102.8	103.6	106.2	95.8	103.8	92.5	89.4
	new σ	3.79	2.50	2.17	1.78	2.56	1.99	3.38	3.78	4.96	6.59	4.51	5.05
inst.	method 1	97	98	96	99	101	106	102	108.5	98	103.5	96	96
	2	97	97	97	97	101	105	99	103	107	122	97	102
	3	97	98	97	99	101	105	102	108	98	103	96	96
	4	98	98	98	98	100	104	100	103	106	118	98	102
Variation to paint		None	2%	4	6	8	10	5	10	5	10	0.1	0.2
		strength											
		shade											
		black											

Table 3
Results of strength assessment tests

Blues		7	11	4	8	2	1	5	3	13	10	12	9
visual	Panel												
	mean	99.5	100	101.7	102.6	104.7	105	96.8	101.1	102.8	104.8	97.4	97.8
	standard deviation	3.97	3.21	3.11	5.63	3.89	5.25	4.79	6.69	6.73	7.34	4.15	3.95
	2 σ	7.94	6.42	6.22	11.26	7.78	10.50	9.58	13.38	13.46	14.68	8.30	7.90
	new mean	99.4	99.5	101.6	101.9	104.7	107.4	96.8	99.6	102.8	103	97.4	97.1
	new σ	2.40	2.25	2.00	2.83	3.89	4.54	4.79	4.97	6.73	5.46	4.15	2.77
inst.	method 1	100	101	103	104	106	112	102	107	96	101	102	100
	2	100	101	103	104	114	109	105	109	110	117	102	101
	3	100	101	103	104	105	109	102	105.5	97	101	102	100
	4	100	101	102	103	111	107	104	108	108	114	102	101
Variation to paint		None	2%	4	6	8	10	5	10	5	10	0.1	0.2
		strength											
		shade											
		black											

differ between themselves or from the visual observation, i.e. good agreement is obtained all round, up to about 5 per cent strength differences. Above this, there is slight overestimation instrumentally and underestimation visually. When shade differences are present, methods 1 and 3 agree and 2 and 4 agree, but there is only poor visual correlation for yellow, although the red and blue are not too far away. Brightness differences had poor correlation. In Table 4 the results are summarised by showing for each observer how many times the opinion was less than 5 per cent different from the instrumental results (methods 1 and 3). The agreement was best for red, next blue and finally yellow at only 50 per cent within 5 per cent. The overall performance is about 2/3 agreement, with the yellow creating greatest difficulty, as one would expect from experience. These results are encouraging, especially when one considers that in the region of greatest visual confusion, yellow, there is the minimum of instrumental confusion. Whether differences between two patterns are strength, shade or brightness can often be detected very easily spectrophotometrically. For example, in Fig. 5 are shown the standard and one of the shaded yellows. The difference is obviously in shade and strength, but could be confused visually.

Recently Gall and Riedel¹⁴ published an article describing a range of colours at "international standard depths." With this range, it was their intention, with the aid of colorimetry, to provide a relatively simple method of obtaining patterns which, although different in hue, were the same visual depth as each other and an international hue standard. These equal depth patterns would provide useful comparisons of hue, brightness, light fastness and many application

Table 4
Strength assessment tests—summary of results
Frequency of "within 3 per cent"

Observers	Yellow	Blue	Red	Total
13	8	12	12	32
3	7	11	11	29
7	7	11	9	27
11	7	9	10	26
5	6	8	10	26
12	5	10	10	25
17	7	9	9	25
14	5	7	12	24
16	6	8	10	24
6	7	9	7	23
9	4	12	7	23
2	5	8	9	22
10	9	6	7	22
18	7	6	8	21
19	6	7	8	21
1	3	6	11	20
8	5	8	7	20
4	6	7	6	19
15	5	7	6	18
20	5	2	6	13
Total	120	157	176	459
Maximum	240	240	240	720
Percentage	50	65	75	64

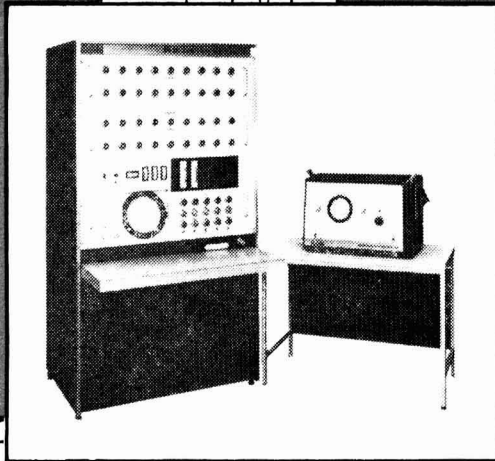
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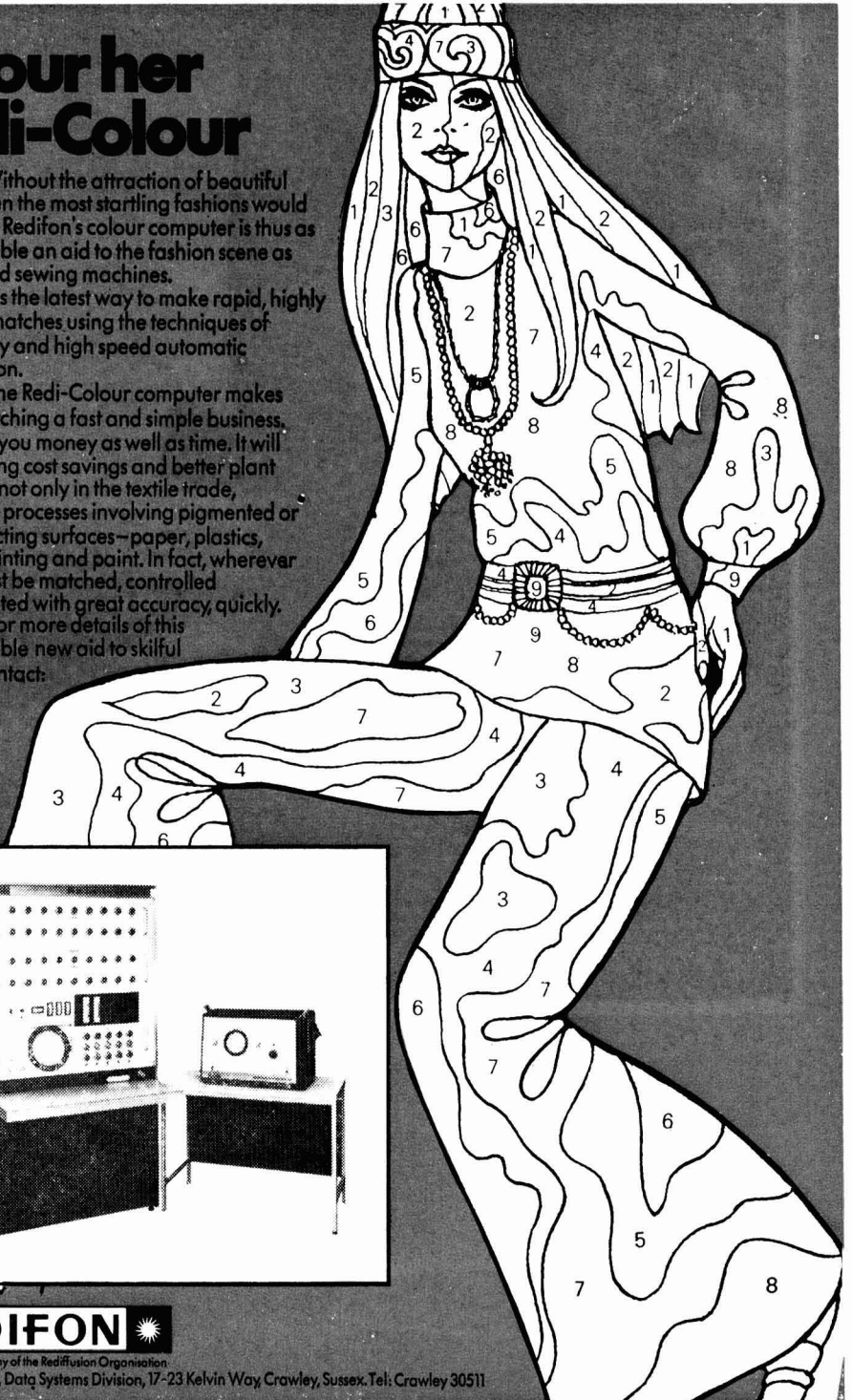
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FW 2 V *	63	0,78	700	13	460	for all types of high quality deep black finishes
FW 200 *	63	0,73	650	13	460	for all types of high quality deep black coatings, particularly acrylic stoving finishes
S 170	71	0,98	650	17	200	for all types of black finishes
Special Black 5 *	75	0,83	430	20	240	for all types of black finishes
Special Black 15	84	0,96	250	25	100	for highest quality offset and letterpress inks
Special Black 4 *	80	0,86	300	25	180	in finishes applied by dipping or electrophoresis, high-grade flexo and special gravure inks and duplicating inks
Special Black 4 A	80	0,86	230	25	180	for high-grade printing inks, carbon paper and typewriter ribbons
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Carbon Black LTD	81	0,66	360	35	80	for industrial and decorative paints, gravure, flexo and rotary news inks
Printex® V **	83	0,95	400	25	110	for decorative paints, carbon paper, gravure, flexo and rotary news inks
Printex® 140 V *	84	0,91	360	29	96	for decorative paints, carbon paper, gravure, flexo and rotary news inks
Printex® 400	84	1,01	330	25	95	for letterpress and offset inks of good colour
Printex® 30 *	90	0,91	400	27	78	for rotary news inks
Printex® 300 ***	90	1,00	360	27	78	for gravure and inexpensive letterpress and offset inks
Printex® A *	94	0,73	300	41	46	for gravure inks
Printex® G *	98	0,64	250	51	31	for tinting paints, and in gravure inks and one-time carbon papers
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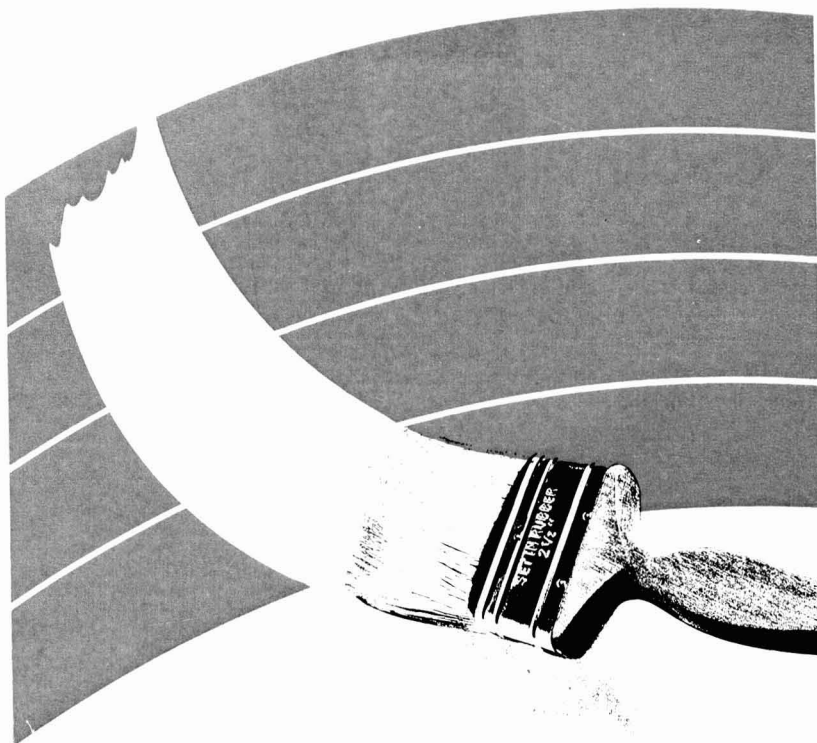
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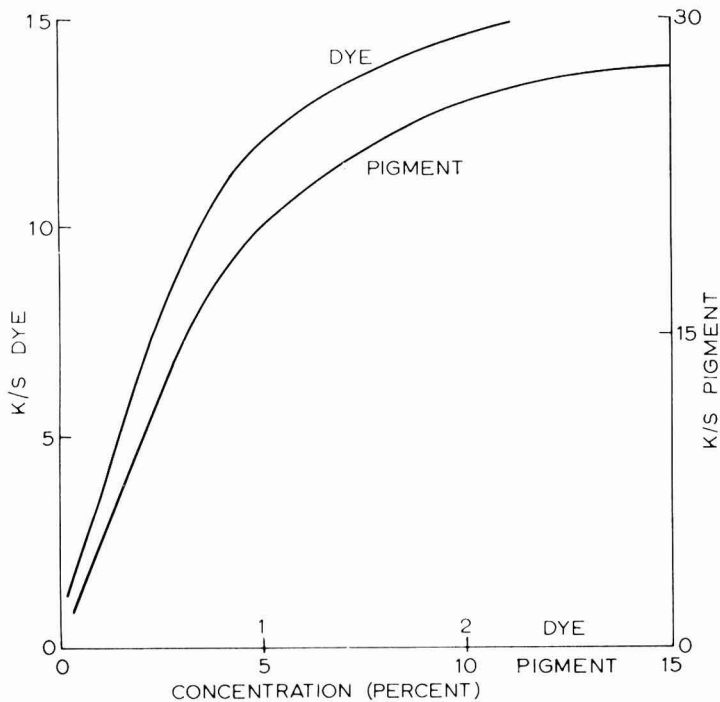


Fig. 5. Kubelka-Munk plots

properties of pigmented systems, as, for example, it has long been argued that the light fastness of pigmented systems is only of interest at equal depth, not at equal pigment content. Alternatively, if from this method one obtains the concentrations of two pigments necessary to create the same international depth, their relative tinting strengths are immediately available.

The authors defined two equations for two international standard depths, which they called 1/3 and 1/25. The equations are

$$\begin{aligned}
 &\text{For } 1/3 \\
 &B = S a(\lambda_f) + \frac{100 - 10\sqrt{Y}}{1.4 + 0.8 S^2} = 52 \pm 0.2 \\
 &\text{and for } 1/25 \\
 &B = S a'(\lambda_f) + \frac{100 - 10\sqrt{Y}}{1.6 + 2 S} = 27
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} B = S a(\lambda_f) + \frac{100 - 10\sqrt{Y}}{1.4 + 0.8 S^2} = 52 \pm 0.2 \\ B = S a'(\lambda_f) + \frac{100 - 10\sqrt{Y}}{1.6 + 2 S} = 27 \end{aligned}} \right\} \dots\dots\dots(6)$$

where B = the depth of tone

S = the linear distance of the colour from the white point on the chromaticity diagram.

$a(\lambda_f)$ = an empirical factor dependent on tone.

Y = the luminance.

From these equations and the "international standard depth" patterns which are available, it is possible to calculate values for $a(\lambda_f)$ and plot its relationship with dominant wavelength, say, to describe hue. Knowing $a(\lambda_f)$ for any dominant wavelength it is possible, by measuring patterns of the colour under examination at known concentrations, to calculate their B values and from a plot of B versus concentration to estimate the pigment concentration necessary to give $B = 52$ or $B = 27$.

The work carried out on this system indicates the same problem as in the previous method, that is, so long as shade differences are very small the method is good, if somewhat longwinded, but for large shade differences the method breaks down.

Colour match prediction

If strengths of individual dyes can be assessed instrumentally, why not assess each dye in a mixture dyeing? Well one can, and such an analysis forms the basis of one method of colour match prediction. The Pretema computer solves four simultaneous equations at four wavelengths to determine the amounts of four dyes present.

$$\left. \begin{array}{l} \text{at } \lambda_1: \\ \lambda_2: \\ \lambda_3: \\ \lambda_4: \end{array} \right\} \begin{array}{l} F(R_1) - F(R_1)_s = a_{11}C_1 + a_{21}C_2 + a_{31}C_3 + a_{41}C_4 \\ F(R_2) - F(R_2)_s = a_{12}C_1 + a_{22}C_2 + a_{32}C_3 + a_{42}C_4 \\ F(R_3) - F(R_3)_s = a_{13}C_1 + a_{23}C_2 + a_{33}C_3 + a_{43}C_4 \\ F(R_4) - F(R_4)_s = a_{14}C_1 + a_{24}C_2 + a_{34}C_3 + a_{44}C_4 \end{array} \quad (7)$$

$$\text{where } F(R) = \frac{(1-R)^2}{2R}$$

$F(R)_s$ = this function for the undyed substrate.

C_1 C_2 etc. are the concentrations of the four dyes present. a_{11} , a_{12} , etc. are the values of $F(R)$ for unit concentration of the individual dyes at each wavelength.

The Pretema uses these rough concentrations to calculate the reflectance curve of a mixture and hence X , Y , Z . This is compared with the measured X , Y , Z , of the pattern to be matched and manual alterations made to the dye concentration until reasonable agreement between XYZ 's is obtained.

There are other methods of match prediction; the Davidson and Hemendinger computer COMIC and digital computer methods such as published by Atherton¹⁵, Duncan¹⁶ and several others. The majority of prediction methods assume

$$\frac{K}{S} = \frac{(1-R)^2}{2R} = 1 + xC$$

However, Fig. 4 showed that K/S versus concentration was not linear. The assumptions made to derive this equation adequately cover the dyed fabric situation at all concentrations, but the practical dyer knows there is a limit to

how much dyestuff can be put on to a given weight of fibre. There is a saturation limit. This limit means that beyond a certain concentration the concentration axis is in error, as the amount of dye in the bath does not represent the amount of dye on the fibre.

The non-linearity is a function of the dyeing technology, not the optics. With pigmentation one knows exactly how much pigment is in the paint or fibre, so that the concentration axis cannot be wrong. Since all pigments scatter light at low pigmentation levels, the assumption that they do not do so significantly compared to the high scatter of the white is reasonable, but at high pigmentation this does not hold. The non-linearity is a function of the optics, not the technology.

How important is this non-linearity? In practice it is important, as Orchard¹⁷ has indicated in a recent article, but it does not limit the applicability of prediction methods, as each method has its own way of getting round the problem. The COMIC has its correction dials, the Pretema its manual adjustment, and digital computers use the correction matrix.

Small patterns

No matter how good the prediction system, and most seem very successful, at some stage a pattern must be measured. All instruments, spectrophotometers and colorimeters, have a physical limit to the smallness of pattern that can be measured, simply owing to the size of the aperture and beam in the instrument. This varies from instrument to instrument. Unfortunately, there are occasions when the only pattern size available is too small and one must consider methods of getting round it. In 1963, Graham¹⁸ suggested a method at the Lucerne International Colour Conference. He developed an equation that gave the reflectance for a small pattern of one colour on a background of different colour. This equation was

$$\frac{A_B}{a} R_S - \frac{A_B - a}{a} R_K = R_L \quad \text{.....(8)}$$

where R_S = reflectance of the small pattern on the background

R_K = reflectance of the background alone

R_L = reflectance of the small pattern alone, that is, as if it were a large pattern

A_B = the area of the incident beam

a = the area of the small pattern

This equation can be rearranged as

$$\frac{A_B - a}{A_B} R_K + \frac{a}{A_B} R_L = R_C \quad \text{.....(9)}$$

where R_C = the calculated value for R_S , which was compared with R_S as an indication of the effectiveness of the method. Small squares of accurately known areas were cut from four paper coatings whose R_L values were known. These were mounted over emulsion paint panels on coated card. The paper coatings were yellow, red, green, and blue, the paints were yellow, red, green,

Table 5
Measurement of small patterns—analysis of variance

Source of variation	Sums of squares	Degrees of freedom	Mean squares	F factor	significance (%)
A	0.00591	2	0.00295	(1) 1.15686	≥ 10.0
B	0.04703	3	0.01568	(2) 6.14902	≤ 1.0
AB	0.02135	6	0.00356	(3) 1.39608	≥ 10.0
C	0.04264	5	0.00853	(4) 3.345098	≤ 1.0
AC	0.03486	10	0.00349	(5) 1.36863	≥ 10.0
BC	0.09003	15	0.00600	(6) 2.35294	bet. 1.0 & 5.0
ABC	0.07648	30	0.00255	(7) 9.65909	≤ 1.0
R	0.01100	15	0.00073		
AR	0.01080	30	0.00036		
BR	0.01013	45	0.00023		
ABR	0.02228	90	0.00025		
CR	0.06299	75	0.00034		
AC	0.04203	150	0.00028		
BCR	0.05595	225	0.00025		
ABCR	0.06993	450	0.00016		
Total	0.60343	1151			
Residual (N)	0.03564	135	0.000264		

A 3 pattern size
 B 4 pattern colour
 C 6 background colour
 R 16 repeat
 Grand mean = 0.99644

1 = (A)/(ABC) 2 = (B)/(ABC) 3 = (AB)/(ABC)
 4 = (C)/(ABC) 5 = (AC)/(ABC) 6 = (BC)/(ABC)
 7 = (ABC)/(N)

blue, white, and grey, the small pattern sizes were approximately $\frac{1}{8}$ in, $\frac{1}{4}$ in, $\frac{1}{2}$ in squares, giving a total of $4 \times 6 \times 3 = 72$ patterns. These were measured at 16 wavelengths using the standard beam of the G. E. Hardy spectrophotometer. The analysis of variance (Table 5) was obtained, showing that pattern colour and background colour were significantly affecting the results, whereas pattern size had no significant effect. Another experiment was carried out in which deep, medium, and light yellow patterns, $\frac{1}{4}$ in square, were measured on three grey backgrounds and black and white, as it was felt that the brightness of the background should be matched to that of the pattern for best results. The analysis of variance of R_C/R_S shown in Table 6 gave a significant effect of the background depth, but no significance of the pattern depth. In Table 7 the mean values of R_C/R_S are given. As can be seen, R_C/R_S approaches one, its theoretical value, at higher background brightness for increasing pattern brightness.

Table 6

Measurement of small patterns—variance at R_C/R_S

C = sample depth

B = background depth

Source of variation	Sums of squares	Degrees of freedom	Mean S.S. = $\frac{(SS)}{df}$	Variance (F factor)	Significance
C	0.0218	2	0.0109	1.0583	$\geq 10\%$
B	0.2009	4	0.0502	4.8738	$< 1.0\%$
C \times B	0.0823	8	0.0103	2.0600	$\sim 4\%$
residual	1.1349	227	0.0050		
Total	0.8299	239			

Table 7

Measurement of small patterns—mean values at R_C/R_S

Pattern	Y	Background									
		Black (1)		2		3		4		White (5)	
		R_C/R_S	Y	R_C/R_S	Y	R_C/R_S	Y	R_C/R_S	Y	R_C/R_S	Y
Dark	82.11	0.9700	5.00	1.0217	12.80	1.0055	32.10	1.0088	73.10	0.9401	93.40
Yellow											
Medium	86.45	0.9588	5.06	1.0289	12.84	1.0309	32.13	1.0126	73.3	0.9970	93.40
Yellow											
Light	90.27	0.8956	5.05	0.9966	12.85	1.0134	32.15	1.0077	73.27	1.0019	93.27
Yellow											

One other effect was considered, that of gloss. Should the gloss of pattern and background be matched? Patterns were measured such that pattern/background pairs gave gloss/gloss, gloss/matt and matt/gloss combinations. The mean values of R_C/R_S shown in Table 8 indicate that the surface structures should be similar.

Table 8

Effect of gloss—mean values of Rc/Rs

Combination	Rc/Rs	Standard deviation
gloss/gloss	1.0065	0.009
gloss/matt	1.0295	0.014
matt/gloss	1.0284	0.013

From the above experiments it can be concluded that this method should work if three conditions are satisfied.

The sample must be small enough to be covered easily by the spectrophotometer beam.

The surface state of the background should be similar to that of the pattern.

The brightness of the background must be similar to that of the pattern.

These results justified using the method to attempt a prediction of a small pattern. A light grey, a dark green, and a medium lilac on 4 ounce nylon were chosen. These particular patterns had already been matched and were available as large patterns. The actual concentrations used were compared against one prediction using the large patterns and one using small patterns. The concentrations are given in Tables 9 and 10.

Table 9

Comparison of large and small patterns—dye concentrations

Dye	Lilac		
	actual	large	small
Rubine	0.014	0.016	0.009
Violet	0.09	0.065	0.107
Brown	0.014	0.017	0.034

Table 10

Comparison of large and small patterns—dye concentrations

Dye	Light Grey			Green		
	actual	large pattern	small pattern	actual	large pattern	small pattern
Rubine	0.02	0.025	0.034	0.05	0.044	0.068
Blue	0.09	0.071	0.11	0.35	0.270	0.290
Brown	0.30	0.264	0.38	2.00	1.51	1.57

At first sight, some of these correlations do not appear very good, but in fact all these recipes corrected within two corrections or less. It must be realised that the dyes used in the original patterns have been used in the predictions.

Another technique was developed for measuring small patterns on the Large Sphere Color-Eye. It was found that Graham's method could not be used with this instrument because a reliable estimate of beam size was not available. Consequently, black masks were placed over both the standard and sample apertures so that circular holes of known equal areas were central in each aperture. Measurements were made of reflectances at 16 wavelengths of large patterns, both with and without the masks present. R_L , the reflectance without the mask, was plotted against R_S , the reflectance with the mask, and the results for 1in, $\frac{3}{4}$ in and $\frac{1}{2}$ in diameter apertures are shown in Fig. 6. The regression coefficients of all these lines were better than 0.999. By knowing the equations of these straight lines, conversion tables could be produced very easily on a computer. These results were used to make predictions of the same three patterns used for the small patterns exercise on the GE instrument. The results of these predictions are given in Table 11.

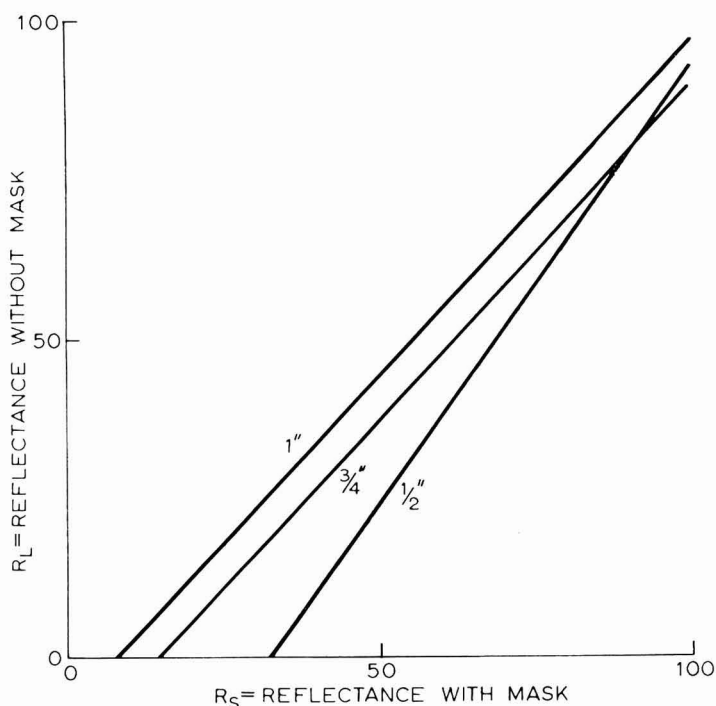


Fig. 6. Small pattern regression lines (CE)

Gloss

Whilst discussing small patterns, mention was made of the effect of the nature of the surface. Gloss, or lustre, does not usually cause problems in textile systems but can be very important in certain circumstances, such as weathering of paints

Table 11
Prediction of concentration using Color-Eye and Hardy instruments

Pattern descriptions	actual concentrations	Color-Eye predictions			Hardy predictions
		1 in.	$\frac{3}{4}$ in.	$\frac{1}{2}$ in.	
DARK GREEN:					
Erionyl Rubine E-3GS	0.05	0.056	0.060	0.054	0.068
Erionyl Blue E-FGL	0.35	0.298	0.293	0.264	0.290
Erionyl Brown E-5GL	2.0	1.578	1.516	1.769	1.57
LIGHT GREY:					
Erionyl Rubine E-3GS	0.02	0.024	0.025	0.024	0.034
Erionyl Blue E-FGL	0.09	0.084	0.085	0.077	0.11
Erionyl Brown E-5GL	0.30	0.267	0.262	0.270	0.38
LILAC:					
Erionyl Rubine E-2BFL	0.014	0.008	0.010	0.011	0.009
Erio Fast Violet RL	0.09	0.094	0.093	0.087	0.107
Erionyl Brown E-5GL	0.014	0.022	0.020	0.019	0.034

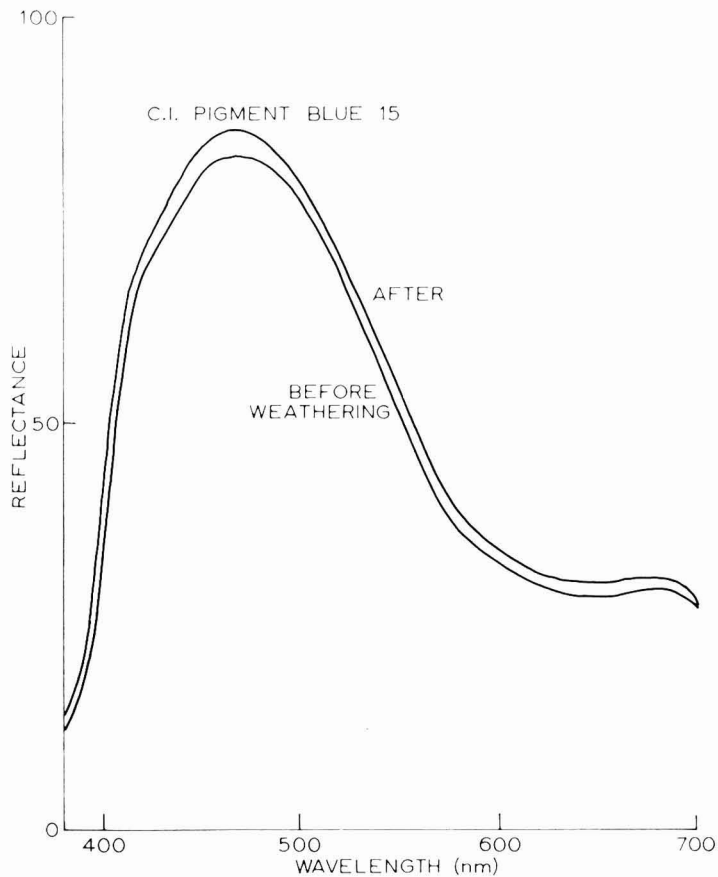


Fig. 7. Anomalous weathering effect

or plastics. Normally, colorimeters and spectrophotometers are set to exclude surface reflected light from measurements, as this is unaffected by the pattern. If a film surface is roughened, the surface reflectance still occurs but is no longer directional and, therefore, cannot be excluded from the measurements. At the worst possible change, from perfect gloss to perfect matt on weathering of an alkyd paint film, about 4½ per cent reflectance can be added at each wavelength. If one is following the effect of weathering on the organic pigment present, this change means an apparent large fading of the pigment. (Fig. 7). This *false* result can be avoided by including the surface reflected light in both the initial and final measurements when the change in colour is recorded, but not when the change in appearance is noted. These comments are in no way meant to suggest the spectrophotometer can be used as a glossmeter. It cannot, but this is an example of asking the instrument the wrong question and therefore getting the wrong answer. In any study of exposure, or weathering, both the colour change and the appearance change should be measured where high gloss samples are involved.

Fluorescence

Another problem which besets the colour physicist is fluorescence. There are two aspects of the problem. It is necessary to arrange that the light is monochromated after striking the pattern, otherwise energy which should be recorded at the fluoresced wavelengths is recorded at the excitation wavelengths; the colour recorded is not in error, it is totally wrong. The other problem arises if fluorescent colours are used in colour match prediction. Dyed textile systems are applications of subtractive colour mixing. Fluorescent dyes create their effects by a combination of additive and subtractive colour mixing. The existing prediction mathematics are unlikely to work. For example,

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

assume $R = 1.4$ i.e. fluorescence

$$\text{then } \frac{(-0.4)^2}{2.8} = \frac{K}{S} = 0.0571$$

$$1 - 2R + R^2 = 2R \times 0.0571$$

$$R^2 - 2.114R + 1 = 0$$

$$\text{i.e. } R = 0.816$$

This solution is the one a computer would give for such a value of K/S . In other words, the starting value of 1.4 cannot be obtained, which must lead to ambiguity in the mathematics.

Conclusion

The intention was to highlight a few of the problems associated with colour measurement and attempts to get round them. The author ended with a problem without offering any solution to it. This was intentional, because as each difficulty is overcome, another arises to challenge us.

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14. Gall and Riedel, *Farbe und Lack* 1965, **71**, 894.
15. Alderson, Atherton, and Derbyshire, *JSDC* 1961, **77**, 657.
16. Duncan, D. R., *JOCCA*, 1962, **45**, 300.
17. Orchard, S. E., *JOCCA*, 1968, **51**, 44.
18. Graham, "Report of Int. Colour Conf. Lucerne," 1965, p. 529.

Next month's issue

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

"Colour difference measurement," by *J. S. Mudd and M. Woods.*

"Sand grinding versus ball milling in relation to pigment particle size," by *W. Carr.*

"The measurement of resin viscosity during manufacture: a high temperature cone and plate viscometer," by *P. S. Pond and C. J. H. Monk.*

"Formulation of fungus resistant paints: Part VIII Addition of n-trichloromethylthiophthalimide," by *E. Hoffmann and A. Saracz.*

Correspondence

The surface area and porosity of titanium dioxide pigments

SIR,—We note the letter from Professor Hamann (*JOCCA* 1969, 52, 1170) and would add the following observations.

Rechmann (*Farbe und Lack* 1969, 75, 51) discussed changes in the surface area of titanium dioxide pigments which arise from variations in processing operations, and concluded that the BET area was of little value in predicting pigmentary properties. Variations of this type have been known to pigment manufacturers for many years—we have made similar observations. However, recent work at the BTP research laboratories has also shown that both the BET surface area and certain technological properties of treated pigments are directly affected by processing conditions: the BET area can therefore be used to indicate relative changes in pigmentary performance.

For instance, whilst Rechmann and ourselves both agree that, within limits, there is a linear relationship between the surface area and the coating level for a particular type of treatment, we also find that the pH to which the coating process is taken directly controls the surface area, with associated effects on pigmentary properties, e.g. adsorption of driers on to the pigment surface causes depletion in the bulk of the film and consequent increase in drying times. We have found that a series of pigments coated with varying amounts of hydrated silica and alumina adsorb driers as a linear function of surface area. The paint drying times for these pigments were found to be directly proportional to the drier adsorptions, so that, for a constant amount of drier, drying times increased with surface area.

Similar relationships (not necessarily linear) also exist between surface area and properties such as durability characteristics, hiding power, tint reduction and oleoreactivity for a given coating type. It must be emphasised that we do not consider the surface area to be the independent variable in these relationships: processing conditions which cause property changes also cause the related changes in surface area.

Further investigations of these phenomena are being pursued in our laboratories and will be communicated in due course.

Yours faithfully,

D. Urwin
T. J. Wiseman
8 July 1970

*British Titan Products Company Limited,
Central Laboratories, Stockton,
Teesside TS18 2NQ.*

Review

ORGANIC PHOTOCHEMISTRY VOL. 2

BY: ORVILLE L. CHAPMAN (Editor). New York: Marcel Dekker Inc. 1969. Pp. xi + 230. Price: £6 11s 0d.

Many specialised branches of chemistry are advancing at such a rate that even the specialist has difficulty in keeping abreast of developments. Organic photochemistry is prominent among them, and this series is intended to provide critical summaries of various areas with the object of systematising the vast accumulation of factual knowledge, summarising progress, and clarifying problems. Judging by this volume that object is admirably achieved by the series.

This volume contains four substantial reviews. The first, by Turro, Dalton & Weiss, of Columbia University, comprises 62 pages devoted to photosensitisation by energy transfer. Theoretical considerations are followed by descriptive matter on some nine classes of organic compounds, ranging from various types of hydrocarbons through carboxyl and sulphur compounds to nitrogenous chromophores.

There follow 54 pages by D. J. Trecker of Union Carbide Corp. on photodimerisations, where the point is made that the phenomenal upswing of interest since the 1950's was largely due to the discovery that many photochemical reactions can be brought about by the use of additives which absorb light and efficiently transfer energy to an appropriate level of the reacting substrate. This is an important aspect of industrial photochemistry but neither here nor elsewhere in the book are industrial applications mentioned. The treatment throughout is essentially mechanistic.

Photochemistry of heteroaromatic nitrogen compounds is treated in 51 pages by Beak and Messer of the University of Illinois. These authors, too, teach a useful lesson in warning against attempting correlations too early. In this field, superficial similarities are often misleading and tempt one into oversimplification. Nevertheless, the use of formal analogy, though often of fleeting validity, does at least stimulate further experimental enquiry. This chapter is logically divided into sections which deal with the formation of bonds to nitrogen, the cleavage of bonds to nitrogen and the various types of reaction involving ring carbon atoms.

The final review, of photochemical additions to multiple bonds, occupies 45 pages and is written by Dov Elad of the Weizman Institute of Science. Just about every possible class of adding species is discussed, from the simple halogens to alkyl polyhalides, thiols, amines, silanes and peptides.

The emphasis throughout the book is on reaction mechanism and, whilst many rationalisations are speculative, they are always frankly so.

References are numerous and production is first class, but the index adds little to what is provided by the table of contents. If you want to read about a particular compound you will have to scan most of the book to find it.

A. R. H. TAWN

Student Review

Courses 1970-71

Information on courses relevant to students in the paint, printing ink and allied industries has been received from two colleges and this is given below for the information of Student Members.

Manchester Polytechnic, John Dalton Faculty of Technology

It is expected that the following courses will be available.

The City and Guilds Paint Technicians Certificate Parts I and II.

The Higher National Certificate Endorsement Subject, (for LRIC purposes) "Chemical technology with special reference to polymers and surface coatings."

The Associateship of the Society of Dyers and Colourists, (including Branch 5 relevant to paints, lacquers and printing inks).

Enrolment for the above courses will take place at the College on 14, 15 and 16 September, during the periods 10.00 a.m.—12.00 p.m., 2.00—4.00 p.m. and 6.00—8.00 p.m. It is also intended that a short course will be held in the department during Easter 1971. It is envisaged that this course will be of a general nature most suited to representatives or older members of the industry.

Any person requiring further information on any of the above courses should contact the Head of Department, Dr V. G. Bashford, at John Dalton Faculty of Technology, Manchester Polytechnic, Department of Polymer Technology, Chester Street, Manchester M1 5GD or discuss the matter with members of staff during enrolment week.

London College of Printing

Five courses leading to formal qualifications are to be organised:

Printing ink technology (Advanced)—leading to the City & Guilds Printing Ink Technicians Advanced Certificate.

City & Guilds Printing Ink Ordinary Certificate.

City & Guilds Printing Ink Technicians Certificate.

Ordinary National Certificate in printing.

Higher National Certificate in printing.

Several other short courses are offered, mainly for scientists and technologists in the printing and printing ink industries. Titles of most interest to ink men are:

Modern aspects of ink technology.

Rheology in printing.

Appreciation of printing techniques and materials.

Full details of these courses may be obtained from Mr B. W. Hodder, Science Department, London College of Printing, Elephant & Castle, London SE1.

West Riding Section

Works visit

Members of the Student Group of the West Riding Section visited Joseph Crosfield & Sons Ltd., of Warrington, on Thursday 25 June 1970.

The visit commenced in the training centre, where Mr R. R. Bowman, aided by Mr S. Maskery and Mr K. Elliot, gave an introductory talk outlining the history and development of the company from its formation in 1814 as a small family concern, producing soap and candles in a factory covering one third of an acre, to the complex it is today, covering well over 30 acres and producing a very wide range of raw materials for the paint, ink, plastics and other industries and being the largest manufacturer of silicates in the United Kingdom. This was followed by lunch in the recently opened senior staff dining room. After an excellent lunch, the students were shown the continuous production of sodium and potassium silicate glasses by the high temperature fusion of sand and sodium or potassium carbonate, and the subsequent preparation of their aqueous solutions. They were also able to walk into and inspect the inside of a fusion furnace which was shut down for maintenance.

The precipitated silicates plant was then toured. Students were able to see the production of Microcal ET from the initial precipitation, washing and drying through to grinding, classification and packing. As there was not enough time to cover the whole of the factory, the final part of the afternoon was spent in the technical centre, where the students were taken through the quality control department and were shown the various techniques used for particle size measurement and quantitative analysis. In the technical service department, the application of Crosfield's products in the paint, rubber and allied industries was demonstrated.

At the end of the visit all agreed that they had had a very interesting and enjoyable day—even the weather was kind!

Information Received

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

English China Clays Limited has recently announced that **Golden Valley Colours Limited**, the company which was taken over by ECCS towards the end of 1968, is to cease trading in the near future. It is stated that the Golden Valley Colours factory is "intrinsically uneconomic and, even if a very large price increase were to be imposed, a considerable loss would be shown."

In order to assist customers in changing to an alternative source of supply, limited production is to continue at Golden Valley's Wick factory until the end of August, and orders can be accepted provided they can be completed by this date.

It has recently been announced that, as a result of a licence agreement between **Dufay Plastics Ltd.**, and **Societe Industrielle de Voisons**, of Paris, *Polydrox* epoxy powder coatings will be available in the UK through the former company.

The agreement allows for initial marketing of the product, followed after one year by UK production. Fast, standard, and low bake powders are available in a full range of colours, including black, white, and metallics, in both gloss and matt finishes.

Atlas Copco (Great Britain) Ltd. has recently issued a 43-page handbook entitled "Paints and their sprayability." The handbook gives brief details of paint types, their spraying characteristics, and testing, manufacture, and safety.

It has recently been announced that **Titania A/S**, the Norwegian associate of **Kronos Titanium Pigments Ltd.**, is to extend the mining plant at Tellnes, Norway, to an annual capacity of a million tons of ilmenite concentrate. By-products will include 55,000 tons of magnetite, and 15,000 tons of nickel and zinc concentrates. It is estimated that, at this rate of production, the Tellnes deposit will not be exhausted for 100 years.

Cassella Farbwerke Mainkur AG has introduced a new acrylic resin system capable of cross-linking with polyisocyanates. The system, based on *Macrynal 5408* and *Macrynal 5481*, is said to offer all the properties of a stoving enamel finish, while air-drying rapidly. Long pot life and good adhesion to old paint are also claimed.

Cassella has also introduced *Cassopal 5439*, a non-modified non-yellowing urea/formaldehyde resin, claimed to be superior to most etherified u/f resins in curing properties and ageing resistance, and to have a relatively high white spirit tolerance and relatively low viscosity.

A UK sales organisation has recently been formed by **Sachtleben AG**. Based in Edenbridge, Kent, the new organisation is aimed at improving the service to British customers by importing in bulk, and delivering from a central storage centre in Isleworth, Middlesex.

Two new products from **Harmon Colours Inc.** have been announced by **Allied Chemical SA**, the company's European associate.

Gold Paste EF-9131 is a flushed iron oxide type gold paste for use in thermosetting acrylic systems. A high degree of transparency is claimed for cured films over bare metal or polished aluminium, together with good intercoat adhesion and humidity resistance. Use with aluminium pigment for "metal flake" finishes is recommended.

Indofast Orange EO-8024, and the lake form, *Indofast Orange Lake EOL-8778*, are new halogenated anthanthrone pigments to Pigment Red 168. Use for transparent or "metal-flake" finishes is recommended.

It has recently been announced that the four companies in the **Unilever** group that handle synthetic resins, namely **Chas. Lowe & Company (Manchester) Limited**, **Beck Koller Limited**, **James Beadel & Company Limited**, and **Styrene Co-polymers Limited**, have been merged. The new company, which commenced operations on 1 July, is called **Synthetic Resins Limited**, and will combine the marketing, research and development experience of the four component units. It will be based at Speke, with two main divisions, surface coating resins, based at Cheadle Hulme in the former premises of Styrene Co-polymers, and industrial resins, based at Speke.

It is stated that the new company will be able to offer a more comprehensive service in product development and technical service to customers of the four former companies, and will be the largest company in England manufacturing surface coating resins, polyesters, and other industrial thermosetting resins.

A new pre-determining counter control unit has been developed by **Berk Limited**. The unit, which operates using pneumatic signals only, is intended primarily for use with the *Graco Adjusta-Stroke Metering System*, but has been designed for easy integration into any pneumatic control system. By using the unit in place of electrically operated counter control units, all controls can now be mounted in areas where electrical equipment is prohibited because of fire risks.

Cinquasia Blue GF BT 465D is a new green shade phthalocyanine blue pigment introduced by **E. I. du Pont de Nemours & Co. Inc.**, and available in the UK from **Hardman & Holden Ltd**. Improved flocculation resistance, easier dispersion, greater transparency, better humidity resistance, and higher strength are claimed for the pigment.

Anwill Instrument Company has developed a new moisture meter for the building and construction industries. The instrument, the *AIC Wetcheck Moisture Meter*, is approximately four inches by two inches by one inch deep, and has scales to give direct readings of moisture in timber, plaster and concrete. Needle probes and an extension lead are supplied, and the retail price is 10 guineas.

In order to increase even further the steady progress it has made in direct exports, **Ault & Wiborg** is to increase the size of its export company. The first step in this direction has been to rename the export company **Ault & Wiborg International Ltd.**, which will be a wholly owned subsidiary of Ault & Wiborg Ltd.

Badische Anilin—& Soda-Fabrik AG has added two pigments to the *Heliogen* range. *Heliogen Blue 7081D* and *Heliogen Blue 7082TD* are β -form copper phthalocyanines, and are surface treated for easy dispersion. *7081D* is recommended for lithographic varnishes and toluene gravure inks, and, it is claimed, gives excellent dispersion in high-grade industrial paints. *7082TD* is recommended mainly for nitrocellulose gravure inks for packaging.

"Protecting steel with zinc dust paints" is the latest publication from the **Zinc Development Association**. The book, which contains papers from the ZDA symposium last year, is available free of charge from the ZDA'S London office.

ICI Limited has prepared a handbook on catalysts, which has been published by **Wolfe Scientific Books**, it was recently announced. Said to be a unique contribution in its field, the "ICI Catalyst Handbook" records the store of knowledge accumulated by ICI Agricultural Division in the commercial use on a large scale of its catalysts, both in its own and its customers plants. The general editor is Mr P. W. Young of ICI's Catalytic Processes Research Group.

Two lacquer systems for heat sealing aluminium foil, paper and board to polypropylene and polyethylene have been developed by **Swale Chemicals Ltd.** One system, *FT 2681*, is designed to resist sterilisation after sealing, and requires high sealing temperatures, while the other, *FT 2952*, can be sealed at lower temperatures, and is designed for use with composite substrates, such as polypropylene/pvc, where higher temperatures cause curling or marring of the composite.

Both systems are claimed to give a strong, easily peelable seal, and are suitable for use on traditional coating plant.

Farbwerke Hoechst AG has recently issued "Technical Information sheet, Pigment No. 24," dealing with benzidene yellow pigments.

Association Honorary Treasurer

Mr F. Cooper, who succeeded Mr A. W. Blenkinsop as Hon. Treasurer at the AGM in June, was born in Widnes, Lancashire, and educated at Wade Deacon Grammar School. His athletic prowess, as captain of both rugby and cricket, was evidently equalled by his academic achievement, as he became school captain. At Liverpool University, however, he claims to have been better known as producer of Chemical Society christmas concerts and treasurer of the Guild of Undergraduates than as a budding chemist; nevertheless, he emerged with a BSc (Hons) in chemistry.

He joined the Orr's Zinc White works of Imperial Smelting in 1931 and is now in his 40th year with the same company,

which is, of course, now part of the RTZ organisation. He is currently Sales Manager (Surface Coatings) of Imperial Smelting Corporation (Alloys) Ltd.

Since joining the Association in 1950, Mr Cooper has been a Committee Member, Hon. Treasurer and Vice-Chairman of the Midlands Section, and was Chairman 1958-60. He has also served on Council, as a Vice-President 1961-63 and Elective Member 1967-69.

When asked about hobbies, Mr Cooper says regretfully that he has had to abandon active participation in his old loves of rugby and cricket for the role of spectator. His main hobbies are now his family, the theatre, and golf.

Jordan Award

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

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

The rules of the Award are appended below.

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

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

3. The selection of the recipient of the Award will be made by a Committee under the Chairmanship of the Associa-

tion's Hon. Research and Development officer.

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

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

Foundation Lecture

Human relationships and communications in industry

As previously announced in the *Journal*, the 1970 Foundation Lecture is to take place on Thursday 8 October at the Painter-Stainers Hall, Little Trinity Lane, London, EC4, at 7.00 p.m. The speaker will be Sir Paul Chambers, KBE, CB, CIE (Chairman of ICI Ltd. 1960-68, Past President of the Institute of Directors, President of the Advertising Association and Chairman of the Royal Insurance Co. Ltd.). The title of his lecture is to be "Human relationships and communications in industry."

Admittance to the Lecture will be by ticket only. It will be followed by a short Informal Reception, and Dinner will be taken in the Dining Hall of the Painter-Stainers Company at 8.00 p.m. Informal dress will be worn, but it is particularly requested that Past Presidents', Section

Chairmen's and Past Chairmen's badges, where applicable, are worn.

The inclusive charge for dinner, together with wines with the meal and drinks at the reception, is £3 15s 0d per head; details of the menu are set out below. Application forms are included in this issue, and application should be made as soon as possible, and in any case not later than 18 September, to the Director & Secretary, at the Association's offices.

Application for the inclusive tickets (Lecture, Reception and Dinner) is **restricted to Members**. Members wishing to attend the Lecture only, should write to the Director & Secretary, who will inform them after 18 September if accommodation is still available. This will naturally depend upon the demand for the inclusive tickets for the Lecture, Reception and Dinner.

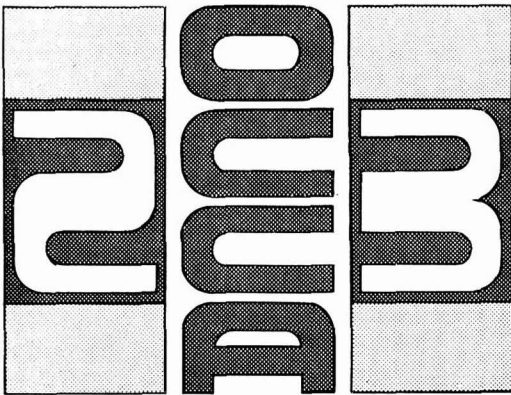
Menu

Alsatian Sylvaner 1966

Bordeaux: Chateau Latour
Camblanes 1964

Port: Quinta do Noval LBV
Brandy: Hine VSOP

Consomme Madrilene
River Trout Amandine
Roast Saddle of English Lamb
Brussels Sprouts, Parisienne Potatoes
Fruit Melba
Coffee



Technical Exhibition

21-25 June 1971

As announced in the August issue of the *Journal*, the Twenty-third Technical Exhibition will be held in the Empire Hall, Olympia, from 21-25 June 1971.

Many companies, both from the UK and overseas, have already applied for space, thus emphasising the success of the exhibition at Olympia last year. Any

company, therefore, wishing to exhibit is urged to apply to the Director & Secretary immediately at the address shown on the front cover.

Olympia is easily accessible from hotels in the West End. The special extension underground service from Earls Court to Olympia will be operating at 10-15 minute intervals throughout the period of the Exhibition. The hours when the Exhibition will be open are given below:

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

As usual, information leaflets in six languages are available free of charge

and these will be distributed to paint companies overseas well before the Exhibition. Any company or individual requiring copies to send to colleagues overseas should apply to the Association's office.

Interpreters for French, German, Italian and Spanish visitors will be in attendance throughout the period of the Exhibition, and all overseas visitors are asked to sign the Visitors' Book at the Information Centre.

The Association has made arrangements with several hotel groups for hotel accommodation for visitors to the Exhibition. Full information will be given in the *Official Guide* being sent overseas in the New Year, but any person wishing to take advantage of this service should write to the Association's offices.

Association Conference, 4-8 May 1971

Surface properties and appearance

As previously announced, the Association's Conference in 1971 will be held at the Palace Hotel, Torquay, from 4-8 May. Four technical sessions are planned, on the three mornings of the Conference and one afternoon, having the title "Surface properties and appearance." Also, in response to increasing interest in the industry to the application of management sciences, a session of papers on the theme "The management of innovation" will be held, running parallel with the afternoon technical session. Three workshop sessions will be held, and the final afternoon of the Conference will be taken up with the Association's Annual General Meeting.

So far ten papers have provisionally been arranged, and these are: "Relationship between measured gloss and dispersion in acrylic paint films," by Dr J. Dunderdale, of Laporte Industries Limited, "Effect of pigment dispersion on the appearance and properties of paint films" by Dr W. Carr, of Geigy UK Ltd., "Influence of surface reflectances on the capacity of roller coatings" by Mr D. G. Dowling and Mr D. R.

Tunstall of British Titan Products Co. Ltd., "Colour specification by visual means," by Mr K. McLaren, of ICI Ltd., Dyestuffs Division, "Gas chromatographic investigation of interaction forces between binder and solvent in paint films" by Dr K. H. Reichert, of the Forschungsinstitut für Pigmente und Lacke, "Film appearance and its dependence on solvent formulation" by Mr L. A. Tysall, of Shell Research Ltd., "Appearance and performance factors in coatings for buildings" by Mr P. Whiteley, of the Building Research Station, and papers for which the titles have not been decided, by Mr J. R. Taylor, of BP Chemicals (UK) Ltd., and Mr Bates, of National Lead Company, together with the Keynote Address.

Further offers of papers are in hand, and a full list will be published in due course.

Full details concerning the registration fees, and forms of application, will be sent to all Members before the end of the year; non-members wishing to receive these details, when available, should apply in writing to the Director & Secretary at the Association's offices.

OCCA Australia



We are indebted to Mr L. A. Hill (Editor of Proceedings & News of the Oil & Colour Chemists' Association Australia) who recently visited the Association's offices, for the interesting photograph reproduced above showing Mr M. Pack,

the present chairman of the Victorian Section of OCCA Australia (left), in conversation with the Duke of Edinburgh on his recent visit to the Clunies Ross House in Melbourne.

OCCA West Riding Golf Trophy

The OCCA West Riding Golf Trophy competition is to be held on Friday 11 September at Sandmoor Golf Club, Alwoodley, Leeds, when Members from all Sections will take part in a Stableford competition. Members of the West Riding Section entering this competition will also be competing for the West Riding Chair-

man's Trophy.

Buffet lunch will be available at Sandmoor Golf Club at 12.30 pm, and play will commence at 2.00 pm. High tea will be served in the clubhouse at 6.30 pm.

Entries for this event close on 5 September; all members received entry forms with the August issue of the Journal.

Irish Section

Annual Golf Outing and Treasure Hunt

Two successful functions were held by the Irish Section during June.

On Tuesday 16, the Annual Golf Outing was held at the Edmonstown Golf Club. Twenty-seven members and friends took part in the competition, and the John Kershaw Trophy was won for the second year running by Mr D. Godden. Mr M. O'Hanlon was runner up. The Visitor's Prize was won by Mr G. Day, and Mr P. Holmes was runner up.

The Annual Treasure Hunt was held on Saturday 27 June. The route this year covered 28 miles through pleasant countryside to the south of Dublin, and ended at the Shangri La Hotel, Dalkey, where a buffet supper was provided. Forty-one members and friends took part in this event, and the prizes were distributed by the Vice-Chairman, Mr D. Sharpe. This event was ably organised by Mr J. Corrigan, and the winner was Mr D. Walsh.

Newcastle Section



The joint winners with the British Titan Cup; Mr R. Lamb (left) and Mr J. G. Bell

The British Titan Cup

The ninth annual tournament for the British Titan Cup was played for over the Hexham golf course on Saturday 27 June 1970. The competition, a four ball, better ball, against bogey, was won jointly by

Messrs J. G. Bell and R. Lamb—seven up.

During the afternoon, which was unfortunately marred by a thunder storm, a Stapleford competition was held and was won by Mr D. Ansbro who scored 36 points.

News of Members

Following the formation of Synthetic Resins Ltd., the new Unilever company, details of which are given in this issue, three Members have received board appointments.

Mr T. Gerard, an Associate Member attached to the Manchester Section, has been appointed marketing director. Mr Gerard was previously managing director of James Beadel & Co. Limited.

Dr G. Swann, an Ordinary Member attached to the Manchester Section, has been appointed technical development director. A member of the council of the Paint Research Station, Dr Swann was previously a director of Beck Koller Limited.

Mr R. S. Robinson, an Ordinary Member attached to the Manchester Section, has been appointed co-ordinating director, Cheadle Hulme. Mr Robinson was previously managing director of Styrene Co-polymers Limited.

Mr G. W. Fowkes, an Ordinary Member attached to the Midlands Section, has recently been appointed area representative for BASF United Kingdom Limited, based on the company's new Bristol office, and responsible for products for the paint, printing ink, adhesives and metal finishing industries, and colours for the plastics industry.

Mr I. K. D. Cameron, an Ordinary Member attached to the London Section, is transferring to the technical staff of BASF United Kingdom Limited, and will be responsible for technical service for products for the paint, printing ink and plastics industries.

Mr A. M. Crouch, an Ordinary Member attached to the London Section, will take Mr Cameron's place as representative in London and the Home Counties for products for the paint and printing ink industries, and colours for the plastics industry.

Joint Conference

The third of the conferences on "Advances in polymer science and technology"—organised by the five Societies with polymer interests, namely the Institution of the Rubber Industry, The Plastics Institute, the Plastics and Polymer Group of the Society of Chemical Industry, supported by the Society of Dyers and Colourists and this Association, takes place on 29 September-1 October. A programme has been organised around the essential chemistry of new polymeric materials and will open and close with invited plenary lectures by Professor C. E. H. Bawn, and Dr W. Cooper, respectively. Dr Cooper's lecture, as well as being the closing lecture of the conference, has been declared an open lecture to all members of the participating societies, whether they have joined the conference or not. Bona fide students studying polymer science at recognised centres are also welcome. It will take place at 3.35 pm on Thursday 1 October.

The conference will be noteworthy for introducing into the chemistry of polymers, papers on their interaction with dyestuff and other smaller molecules.

A Conference Dinner has been arranged with Sir Harry Melville, FRS, as a principal speaker.

The Conference will be held at the University of London (William Beveridge Hall), London WC1, and all inquiries should be made to R. H. Craven, Institution of the Rubber Industry, 4 Kensington Palace Gardens, London W8.

Urethanes group of the IRI

As a result of the rapid expansion that is taking place in the British urethane industry, a new urethanes group has been formed by the Institution of the Rubber Industry. The group will operate on a national basis, working in close collaboration with existing sectional committees of the IRI.

German Chemical Society Conference

The 36th Conference of the Working Party on Paints and Pigments of the German Chemical Society is to be held at the Kurhaus, or Spa Hotel, at Bad Nauheim, a health resort north of Frankfurt, from 29 September to 2 October 1970. A full technical and social programme has been organised, as well as a special programme for the wives of delegates. Full details and application forms are available from Dr H. Rechmann, Titangesellschaft mbH, 509 Leverkusen, Postfach 80/90, W. Germany.

"Plastics technology for scientists" course at Brunel University

A five day course for science graduates wishing to orientate or reorientate themselves to manufacturing and processing techniques in the plastics industry is being organised by Brunel University. The course, which will run from 21 to 25 September, will include lectures, demonstrations, practicals and seminars; Brunel has available most polymer manufacturing and processing apparatus, and almost all commercial operations can be demonstrated and practised.

Full details are available from Professor W. A. Holmes-Walker, at Brunel.

FSPT Semiannual Index

The Federation of Societies for Paint

Technology has recently published the third "Semiannual Index to Coatings Literature." These indexes contain references to articles in more than 100 periodicals, including this *Journal*, and the key wording system used permits rapid scanning for articles on specific topics. The third edition is a compilation of the Monthly Indexes published in the *Journal of Paint Technology* from July to December 1969, and can be obtained from the FSPT at \$25.00 per copy.

FSPT Annual Meeting and Paint Show

Arrangements for the 48th Annual Meeting and 35th Paint Industries' Show, to be held in Boston, Mass., from 28-31 October 1970, are now well in hand. A special "Afternoon of colour" has been arranged for the meeting, the theme of which is "Coatings technology production '70." Also, Mr A. G. North, an Ordinary Member attached to the London Section, will give a paper, during which he will convey the greetings of the Association to the meeting.

During the meeting, the FSPT elections will be confirmed: Mr J. P. Teas has been nominated as President-Elect, and Mr A. G. Rook as Treasurer.

Interest in the Paint Industries' Show has been great, and about 125 companies are expected to show.

Section programmes for 1970-71 session

London Section

All meetings will be held in the new extension building of the Borough Polytechnic, Borough Road, London SE1, at 7.00 p.m., unless otherwise stated.

1970

Wednesday 14 October

European Liaison Lecture: "Rheology and processibility of printing inks" by Mr C. O. Rosted, of Sadolin and Holmblad A/S, Copenhagen.

Wednesday 11 November

"The significance of glass transition temperatures of paint films" by Mr

J. L. Prosser, of the Paint Research Station.

Wednesday 25 November

Joint symposium with the Colloid and Surface Chemistry Group, Society of Chemical Industry: "Characterisation of pigment surfaces." To be held at Brunel University, at 10.00 a.m.

Thursday 10 December

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

Friday 20 November

"Ladies' Night," to be held at the Criterion-in-Piccadilly, London W1, at 7.30 p.m.

West Riding Section

All lectures will be held at the Griffin Hotel, Boar Lane, Leeds, at 7.30 p.m. unless otherwise stated.

1970**Thursday 3 and Friday 4 September**

Seminar—"Future trends in surface coatings," to be held at Bodington Hall, University of Leeds.

Friday 11 September

OCCA and West Riding Golf Match, to be held at Sand Moor Golf Club.

Tuesday 6 October

"Manufacture of wallpaper," by Mr A. O. Sutherland, of ICI Wallpapers Limited.

Joint meeting with the Society of Dyers and Colourists.

Tuesday 10 November

"Zinc rich paints," by Mr B. Jones, of Amalgamated Oxides Limited.

Friday 27 November

Annual Dinner and Dance, to be held at the Crown Hotel, Harrogate.

Tuesday 8 December

"Milling—a variable in ink performance," by Mr J. Groom, of Sandoz Products Limited.

1971**January**

Joint half-day Symposium: "Surface coatings: their use and abuse."

Wednesday 17 February

"Techniques of electrographic reproduction" by Mr D. P. Maple, of Ozalid Ltd.

Wednesday 17 March

"Applications of the scanning electron microscope to the examination of paint systems," by Mr H. Wells.

April

Annual General Meeting. (Details to be arranged).

Joint meeting with the Institute of Printing.

1971**Tuesday 12 January**

"Two-pack epoxy coatings," by Mr A. McKay, of CIBA-ARL Limited.

Tuesday 9 February

"Compositional changes of solvent mixtures during the film formation process," by Mr L. A. Tysall and Dr D. H. Shearer, of Shell Research Limited.

Tuesday 9 March

"Carbon black in coating applications: dispersion and formulation techniques," by a speaker from Columbian International Limited.

Tuesday 6 April

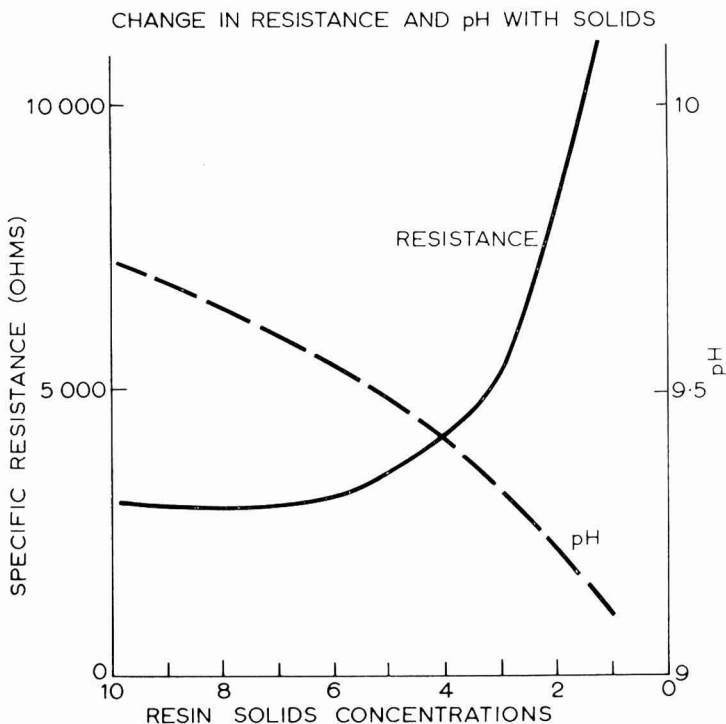
AGM, and Buffet Supper.

May

Luncheon Lecture.

Addendum

We regret that, in the paper by A. G. North from *JOCCA* May, the figure referred to as being in the Appendix was omitted. This figure has now been obtained and is reproduced below.



Errata

We regret that two errors occurred in the Association programme for 1970/71, published in the *August* issue.

The date of the Foundation Lecture, 10 October 1970, is a Thursday, and not a Tuesday, as printed.

The Association AGM is to be held on Friday 7 May 1971, and not on Thursday 6 May.

Register of Members

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

Ordinary Members

- CHESWORTH, ALAN GEOFFREY, BSc, PhD, Reliance Universal of Canada Ltd., PO Box 100, Daveluyville, Quebec, Canada. (*Overseas*)
 GARDNER, JOSEPH, 61 Eastfield Crescent, Oulton, Nr. Leeds, Yorks. (*West Riding*)
 HAWKER, RAYMOND DAVID, 244 Sheringham Avenue, Manor Park, London, E12. (*London*)
 MADHAVAN, KRISHNAMURTHI, BSc, "Lalit Mahal," C-2/13, Safdarjung Development Area, New Delhi, 16, India. (*Overseas*)

Associate Members

- CHEETHAM, RICHARD ANDREW, 111 Dockfield Road, Shipley, Yorks. (*West Riding*)
 COLGAN, WILLIAM HARVEY, R. W. Greff & Co. Ltd., 65 West Regent Street, Glasgow, C2, Scotland. (*Scottish*)
 STIRLING, GEORGE DOUGLAS, 33 Wellshot Drive, Cambuslang, Glasgow, Scotland. (*Scottish*)

Forthcoming Events

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

Thursday and Friday 3 and 4 September

West Riding Section: Seminar—"Future trends in surface coatings," to be held at Bodington Hall, University of Leeds.

Friday 11 September

West Riding Section: OCCA and West Riding Golf Match, to be held at Sand Moor Golf Club.

Wednesday 16 September

Manchester Section—Student Group: "Modern machinery for the manufacture of paint and printing inks" by Mr D. P. Sullivan of D.H. Industries Limited, to be held at the Manchester Literary and Philosophical Society at 4.30 p.m.

Friday 18 September

Irish Section: "Solvents" by Mr L. A. Tysall of Shell Research Limited, to be held at the International Hotel, Belfast—preceded by a Works Visit if it can be arranged.

Thursday 24 September

Thames Valley Section: "Management principles, and can a small firm survive" by Mr J. R. Webster of Business Operations Research Services Limited, to be held at "The Beech Tree," Maxwell Road, Beaconsfield, at 7 p.m.

Friday 25 September

Bristol Section: "Colour measurement" by Mr R. P. Best of Instrumental Colour Systems Limited, to be held at 7.15 p.m. at the Royal Hotel, Bristol.

Midlands Section: "Wood protection" by Mr G. L. Holbrow of the Paint Research Station, to be held at the Chamber of Commerce House, 76 Harbourne Road, Birmingham 15, at 6.30 p.m.

Tuesday 29 September

Auckland Section: A lecture by Mr J. Smallfield of Flexible Abrasives Limited, to be held at the "C.T. Club" at 12.15 p.m.

Thursday 1 October

Midlands Section—Trent Valley Branch: "Metrication and paint packaging in the future" by Mr R. B. Beazley of the Metal Box Co. Limited, to be held at British Rail School of Transport at 7 p.m.

Newcastle Section: "Painting of timber" by Mr R. Hill of TRADA, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle, at 6.30 p.m.

Monday 5 October

Hull Section: A panel discussion evening. Three short lectures will be followed by questions and a discussion; to be held at the Queen's Hotel, George Street, Hull, at 7 p.m.

Tuesday 6 October

West Riding Section: "Manufacture of wallpaper" by Mr A. O. Sutherland of ICI Wallpapers Limited. Joint meeting with the Society of Dyers and Colourists, to be held at the Griffin Hotel, Boar Lane, Leeds, at 7.30 p.m.

Wednesday 7 October

Newcastle Section—Student Group: Works visit to Dufay Paints, Shildon, Co. Durham.

Friday 9 October

Hull Section: Annual Dinner Dance at the Hotel Eden, Willerby.

Manchester Section: "Industrial espionage" by Major R. B. Matthews of Management Investigations Limited, to be held at the Manchester Literary and Philosophical Society at 6.30 p.m.

Tuesday 13 October

London Section—Southern Branch: "Driers" by Mr J. Turner of Hardman and Holden Limited, to be held at the Pendragon Hotel, Clarence Parade, Southsea, at 7 p.m.

Wednesday 14 October

Manchester Section—Student Group: "Some aspects of paint formulation" by Mr T. W. Wilkinson of Laporte

Industries Limited, to be held at the Manchester Literary and Philosophical Society at 4.30 p.m.

Thursday 15 October

Scottish Section: "Some aspects of coil coating" by Mr J. Hortensius of Synres International NV, and Mr L. Tasker of Laporte-Synres Limited, to be held at the St. Enoch Hotel, Glasgow, at 6 p.m.

Friday 16 October

Irish Section: "The role of chlorinated rubber in modern anticorrosive systems, including its use in printing inks" by Mr P. A. Herbert of ICI Limited, to be held at the Clarence Hotel, Wellington Quay, Dublin at 8 p.m.

Midlands Section: "Polymer developments—the seventies and beyond" by Mr A. R. H. Tawn of Cray Valley Products Limited, to be held at the Chamber of Commerce House, 75 Harbourne Road, Birmingham 15, at 6.30 p.m.

Wednesday 21 October

Scottish Section—Eastern Branch: "Analysis of materials for paint and ink," by a speaker from ICI Limited, to be held at the Carlton Hotel, North Bridge, Edinburgh, at 7.30 p.m.

Thursday 22 October

Thames Valley Section: "Corrosion" by Dr T. P. Hoar of the University of Cambridge, to be held at "The Beech Tree," Maxwell Road, Beaconsfield, at 7 p.m.

Friday 23 October

Manchester Section: Annual Dinner Dance, to be held at the Piccadilly Hotel, Piccadilly Plaza, Manchester 1.

Tuesday 27 October

Auckland Section: "High speed dispersion techniques" by Mr W. Blane of Morrison Pim Limited, to be held at "Shell House" at 7.30 p.m.

Friday 30 October

Bristol Section: "Powder coatings" by Mr G. T. Bassett of Berger J & N Paints Limited. Joint meeting with Birmingham Paint, Varnish and Lacquer Club, to be held at the Hawthorne Hotel, Bristol, at 6.30 p.m.

Monday 23 November

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

Oil and Colour Chemists' Association

President: A. S. FRASER

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

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

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

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

PUBLICATIONS

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

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

Paint Technology Manuals

Part 1 : " Non-convertible Coatings," Second Edition, Pp. 343, 36s.

Part 2 : " Solvents, Oils, Resins and Driers," Second Edition, Pp. 268, 36s.

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

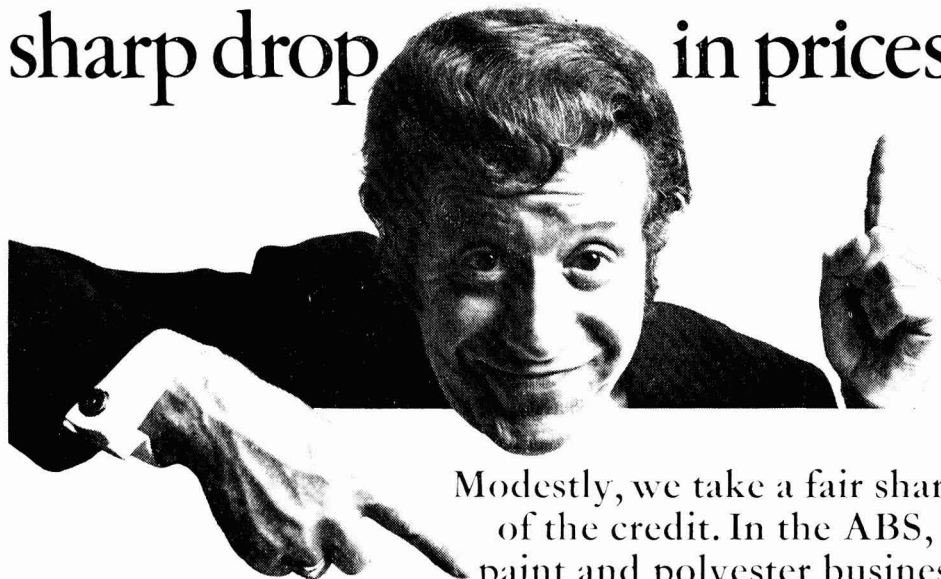
Part 4 : " The Application of Surface Coatings," Pp. 345, 35s.

Part 5 : " The Testing of Paints," Pp. 196, 35s.

Part 6 : " Pigments, Dyestuffs and Lakes," Pp. 340, 35s.

Director & Secretary : R. H. Hamblin, M.A., F.C.I.S., Wax Chandlers' Hall, Gresham Street, London, EC2V 7AB.

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

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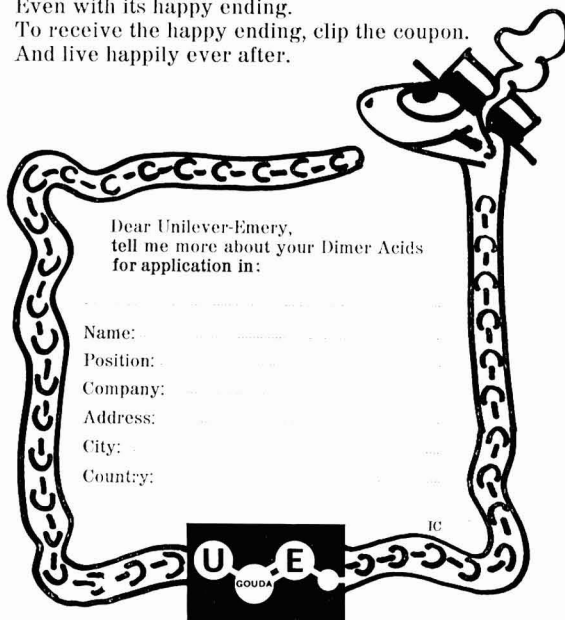
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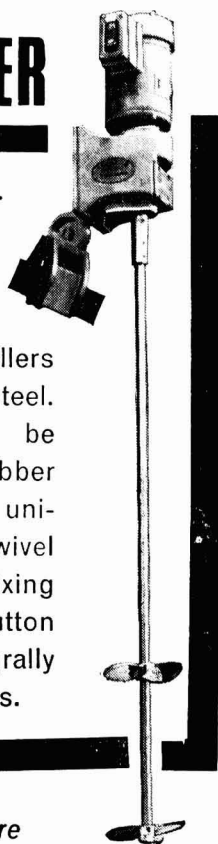
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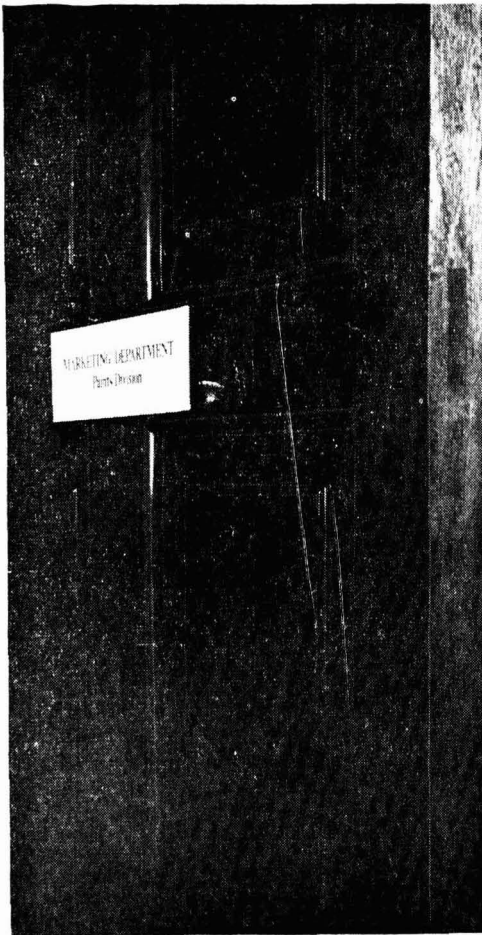
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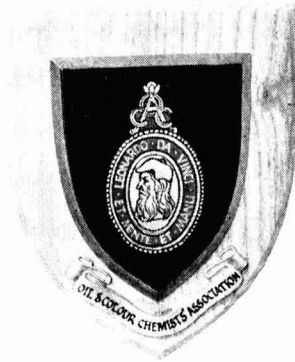
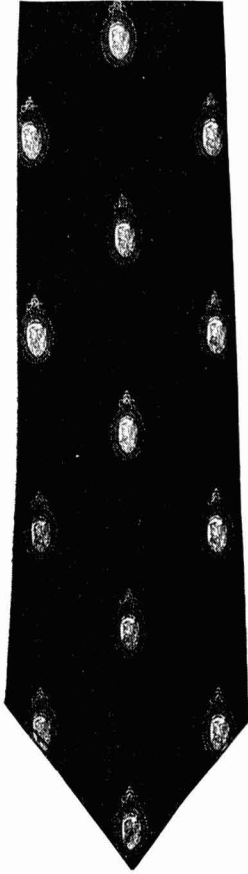
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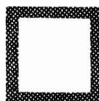
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