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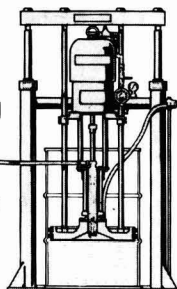
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The effect of bleed on particle size measurement

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Summary

The authors have, in the past, demonstrated the importance of the pigment particle size of organic pigments in paints and inks.

The particle size measurements in the wet state were carried out by a centrifugal sedimentation technique and the work was restricted to non-bleeding organic pigments.

Many organic pigments do bleed even in weak solvents, and it

was therefore decided to see whether the particle size measurement of certain well known mono-azo pigments was affected by this bleed.

A six pronged experimental approach was made on this problem. The results showed that for these pigments sedimenting in weak solvents, the bleed does not significantly affect the particle size measurements.

Keywords

Types and classes of coatings and allied products

non aqueous dispersion
water base dispersion

*Processes and methods primarily associated with
manufacturing or synthesis*

dispersion

*Properties, characteristics and conditions primarily
associated with*

raw materials for coatings and allied products

particle size
bleeding

L'effet du saignement des pigments sur leur granulométrie

Résumé

Dans le passé les auteurs ont déjà démontré, dans le domaine de peintures et encres d'imprimerie, l'importance de la grandeur particulaire des pigments.

Les mesures de la grandeur particulaire ont été effectuées en phase liquide exclusivement sur des pigments organiques non saignants par une technique de sédimentation centrifuge.

Plusieurs pigments organiques sont susceptibles à saigner même

en présence de faibles solvants, et par conséquent on a décidé de déterminer où la granulométrie de certains pigments bien connus du type monoazo fût influencée par cette tendance à saigner.

Un essai expérimental à six dents était effectué à ce problème. Les résultats montrent que, dans le cas de ces pigments en train de sédimenter en faibles solvants, la tendance à saigner n'exerce pas d'influence importante sur la granulométrie

Der Einfluss des Pigmentausblutens auf die Teilchengrößenmessung

Zusammenfassung

Die Autoren haben die Wichtigkeit für Beschichtungen und Druckfarben der Teilchengröße von organischen Pigmenten schon demonstriert.

Die Teilchengrößenmessungen wurden bei Nasszustand und mittels einer zentrifugalen Absetztechnik durchgeführt und der Versuch auf nichtausblutende organische Pigment eingeschränkt.

Manche organischen Pigmente bluten sogar in schwachen

Lösungsmitteln aus, und deshalb wurde es entschlossen zu entdecken ob diese Ausblutentendenz einen Einfluss auf die Teilchengrößenmessung gewisser wohlbekannten Monoazopigmente hätte.

Ein sechsfache Experimentalversuch wurde auf dieses Problem durchgeführt. Die Resultate zeigen dass im Falle dieser in schwachen Lösungsmitteln sedimentierenden Pigment, die Ausblutentendenz keinen bedeutsamen Einfluss auf die Teilchengrößenmessung hat.

Introduction

Most of the common inorganic pigments, whether white or coloured, are essentially insoluble in both aqueous and non-aqueous media of the types likely to be found in surface coatings.

With organic pigments however, the position is different. A number are indeed completely insoluble in the usual aqueous and non-aqueous media, but the majority "bleed" slightly in solvents and some in water. This bleed is usually considered to be a very slight solubility in the vehicle giving rise to a coloured filtrate after separation. It could conceivably be due to the solution of impurities, or the dissolving of surface treatments applied to the pigment, or even to a small degree of spontaneous dispersion, rather than to slight solubility of the pigment itself. Not much has been published on this subject, and it is the authors' belief that, in most cases, it is the pigment itself that is dissolved. This paper is not concerned with the cause of the bleed, but with its possible effect on particle size measurement.

This subject is of considerable scientific and commercial interest, which is based on the growing appreciation by both users and suppliers of pigments that dispersibility and the degree of dispersion are important pigmentary and application properties. It is now known, and generally accepted, that the degree of dispersion of a pigment in a paint controls its optical properties such as colour strength, gloss, gloss retention and the so-called flocculation effect of phthalocyanine blue. Pigments, to be used efficiently, must be dispersed to a fairly fine level.

The dispersion measurements on which these findings have been made were carried out by a centrifugal technique, which separates the particles into different sizes by their different sedimenting rates. It is well known that if Stokes Law is to be applied to sedimenting particles, the sedimentation must be free and unhindered, and there must be no crowding effect whereby the fall of one particle interferes with the fall of another. In practice, using an instrument such as the Joyce-Loebl Disc-Centrifuge, the paint (or ink) has to be diluted to a pigmentation level of approximately 0.5 per cent by weight with a suitable diluent (often white spirit), and 1ml of this diluted paint is injected into a spin fluid (usually a mixture of white spirit and carbon tetrachloride). The spin fluid volume is 20ml, which gives a final concentration of pigment particles in the spin fluid of the order of 0.025 per cent by weight/volume.

If the pigment has any bleeding tendency, it will certainly show up at these low concentrations and the spin fluid will certainly be coloured.

This poses the question as to whether this bleed will significantly affect particle size measurements carried out by centrifugal sedimentation in the normal manner. Errors could arise due to the colour of the spin fluid as a consequence of the bleed, or from the reduction in particle size of the particles due to their partial solution.

The problem can be related to the prospect of attempting to measure the size of a cube of sugar as it falls through a long column of water. This example may appear to be extreme, but in the case of pigments, very small particles are being examined, ranging from 1µm down to 0.02µm, which can be present in a liquid for up to two hours. Such particles will have high surface areas in

contact with the fluid and hence every opportunity for the bleed to have a maximum effect.

Even if newer methods of particle size analysis emerge (and a number based on the use of laser beams in conjunction with minicomputers have been recently described), the problems associated with bleeding pigments may get worse, the pigment content required for these measurements being much lower. In using the Coulter Nano-Sizer, a commercial example of such a development, the theory requires, and the manufacturers recommend, that the concentration of pigment particles in the sample presented to the instrument should not be greater than 0.005 per cent by weight.

The problem is further complicated by the fact that the degree of pigment bleed in water and solvents can vary for pigment type and solvent type.

Most of the pigments exhibiting this bleeding effect are the mono-azo pigments and the number and volume of them in regular use in surface coatings is still very considerable. There is, therefore, considerable scientific and commercial interest to ascertain whether their dispersion characteristics can be determined by the normal methods of particle size analysis, or whether such methods are ruled out by the effect of the bleed. This is the justification for the experimental work described in this paper.

Experimental approach

Refs. 1, 2

How to tackle the problem experimentally was not particularly obvious at first sight. Suspensions can be measured of a bleeding pigment prepared from dispersions at varying ballmilling times using the centrifugal technique, and if the results were completely nonsensical in character, then it could be assumed the bleed was causing major problems. However, if the results were, in fact, more or less reasonable, it might not be possible to ascertain whether they were in error due to the bleed. The experimental approach used was consequently many pronged.

Initially, a bleeding pigment was used. It was dispersed in water and its particle size distribution determined on a Joyce-Loebl Disc-Centrifuge, using both the absolute method and a photo-sedimentometer (PS) method. A calibration curve for the pigment was then determined using the results from both methods.

Secondly, as pigments bleed much less in water than in solvents, a solution of dyestuff was added to the aqueous spin fluid so that the "artificial bleed" was similar to that of the same pigment in a solvent. The particle size distribution could then be measured by both methods, i.e. the absolute and PS methods. A calibration curve could then be determined and compared with the one obtained without using an artificial bleed.

Thirdly, the same pigment was dispersed in a non-aqueous system and its particle size distribution determined by both absolute and PS methods. A calibration curve was again determined. This was compared with the calibration curve from the experiments carried out on the aqueous systems.

Fourthly, if the results from the above experiments were encouraging, then the last experiment would be repeated

using a spin fluid that was saturated with the bleed from the pigment.

Fifthly, if all these experiments gave promising results, then a series of experiments would be carried out to determine the relationship between the colour strengths of the dispersion and their particle size distributions. This experimentally determined relationship would then be compared with the theoretical relationships calculated for the same pigment using the Mie theory.

Sixthly, if all the results were reasonable, the experiments would be repeated using other bleeding pigments.

It was felt that after such a series of experiments on a number of bleeding pigments, some positive conclusions could be drawn on the effect of pigment bleed on particle size determinations.

Before going on to describe the experimental procedure and results in some detail, some explanatory notes on the previously described experimental approaches may be of help.

In the absolute method of operating the Joyce-Loebl Disc-Centrifuge, a separate spinning is made for each size fraction and a sample is automatically withdrawn by a probe from a fixed depth after a pre-set time. In this way, a number of samples are obtained representing different size fractions, and then the pigment content of each of these fractions is determined by analysis.

The analysis is relatively easy for organic pigments, much more difficult for inorganic pigments and virtually impossible for carbon blacks.

In the photo-sedimentometer (PS) technique, a narrow beam of light shines through the disc and falls onto a photocell. The resulting voltage is amplified and fed to a pen recorder which plots a curve of turbidity versus time. The light passes through the disc at the same depth from the surface that the probe reaches in the absolute method.

From one spinning, a curve is obtained of turbidity versus time. From the speed of the disc, the instrument constants, the density of the pigment and the spin fluid, the time axis can be converted to particle size and the graph can be redrawn to give a curve of turbidity versus particle size.

This curve can then be normalised to give a curve of weight per cent undersize versus particle size and this can then be compared with the corresponding curve obtained by using the absolute method. The advantages of the PS method in time and applicability are real and positive and are described in detail by Carr¹.

However, one major problem is that the results obtained with the PS method differ considerably from those obtained by the absolute method. An indication of the sort of differences obtained is given in Table 1, where the results for a paint stainer based on dioxazine violet (a non-bleeding pigment) in an alkyd resin system are given.

The authors believe that the absolute method gives correct results whilst the PS method gives values which are in error because of the uncertainty concerning the relationship between concentration and turbidity at low particle sizes. This deviation in results between the PS method and the absolute method is a major drawback to

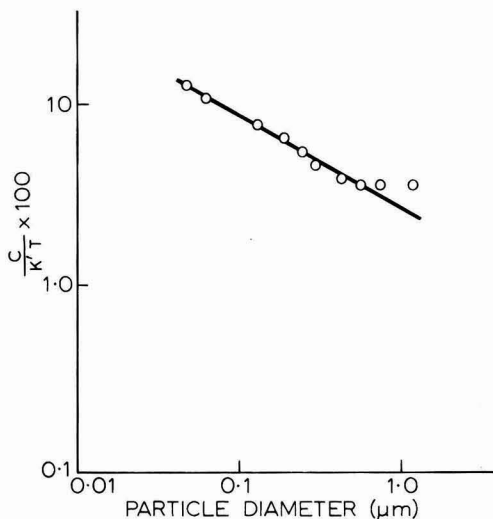


Figure 1. Calibration curve for dioxazine violet

the use of the former method. It can, however, be largely overcome by the use of calibration curves. For any one specific pigment, a suitable pigmented system is made up and its particle size distribution is determined by both the absolute and the PS methods. To obtain the calibration graph for this pigment, $\log(c/k'T)$ is plotted against $\log d$ on log-log paper. The values of c and the weight of pigment particles in the spinning disc for sizes below $2\mu\text{m}$ in diameter are derived from the weight percentage undersize results obtained using the absolute method. The term $k'T$ is the arbitrary turbidity or optical density reading obtained on the vertical axis of the chart in the PS method, and d , the pigment particle diameter, is calculated from the instrument constants, the time and speed of spinning. The calibration curve for this pigment is shown in Figure 1 and it will be seen that the graph is linear between sizes 0.1 and $1.0\mu\text{m}$.

Other organic pigments give straight-line graphs by this method although the lines differ markedly in slope. The pronounced deviation from linearity for sizes above $1\mu\text{m}$ may be due to the single spinning of the PS method being too rapid for them.

The straight lines can be better defined by plotting $c/k'T$ against d on linear graph paper, drawing the best curve through the points, and using this curve to obtain the log-log plot.

Table 1

Comparison of sizes from absolute and PS measurements, dioxazine violet in alkyd-based decorative paint stainer

Ball milling time (hours)	6	12	24	96
50% diameter (PS method) (μm)	0.56	0.42	0.26	0.21
50% diameter (absolute method) (μm)	0.35	0.26	0.21	0.18

This calibration curve can be readily used with the PS method, where the single spinning gives a plot of $k'T$ against time. The graph is redrawn with the time axis converted to particle diameter d , and for each selected value of d , the corresponding $k'T$ reading is multiplied by the value of $c/k'T$ read off from the calibration graph for that size. This gives a term c which is a function of pigment concentration. The graph of c against d on linear graph paper is normalised as before to give a weight per cent undersize versus particle diameter.

This size distribution is now an absolute one and this can be checked by repeating the experiments using the absolute method without the photosensing device.

It is believed that the gradient of the calibration curve obtained in this manner is a constant, characteristic of the particular pigment used, since it is believed to be based on the optical constants of the pigment. In addition, it is believed that the gradient is also independent of the liquid medium in which the pigment is dispersed. It must be kept in mind that the calibration graph is only linear in the region between $d = 0.1\mu\text{m}$ and $d = 1.0\mu\text{m}$.

Dinitraniline red (CI Pigment Red 5)

This was one of the first pigments examined as it is a typical example of a bleeding azo pigment which, nevertheless, is fairly widely used both in inks and paints. It certainly gives a slight but definite bleed in a mixture of 30 per cent carbon tetrachloride/70 per cent white spirit (wt/wt), which is used as the medium through which the pigment particles sediment in the Joyce-Loebl Disc-Centrifuge when non-aqueous dispersions of the pigment are examined.

When aqueous dispersions are examined, the sedimenting medium (spin fluid) is usually a 15 per cent solution of glycerol (wt/wt) in a 0.01 per cent solution of Triton X-100 in water. Triton X-100 is a non-ionic surfactant. The pigment does not bleed in this spin fluid.

Aqueous systems – colourless spin fluid

Dispersions were prepared using this pigment, an anionic surfactant and water by ball milling. The actual pigment used was IRGALITE Red 2GW, and the dispersing agent was Belloid SFD, both of Ciba-Geigy. Dispersions of medium fineness were prepared as previous experience had shown that the PS technique, and hence the linear calibration graph, did not apply to either very fine or very coarse dispersions.

Dispersions were prepared by ball milling at 15 per cent pigment and 5 per cent surfactant on weight of pigment for the following times:

- (i) 3 hours
- (ii) 5 hours
- (iii) 7 hours 30 minutes
- (iv) 48 hours

The dispersions were sieved through nylon muslin cloth. Particle size distribution measurements were carried out on the disc-centrifuge using both the absolute and the light transmission (PS) techniques. Using the weight per cent undersize values from the absolute method and the $k'T$ turbidity values from the PS technique, calibration curves were plotted for each of the dispersions. These curves were

all linear between 0.1 and $1.0\mu\text{m}$ and the gradients of the lines were calculated. The results are shown in Table 2.

The four separate experiments were in very good agreement with respect to the gradients of the calibration graphs. This is a fairly strong indication that both absolute and PS techniques for particle size distributions of aqueous dispersions of Red 2GW on the disc centrifuge are sound.

Aqueous dispersions – coloured spin fluid

An artificial bleed was introduced into the standard colourless spin fluid for aqueous dispersions (15 per cent glycerol in a 0.1 per cent solution of Triton X-100 in water). This was done by dissolving a small quantity of an acid dyestuff, Erio Orange AS 150 (CI Acid Orange 10), in the spin fluid to produce a colour comparable to that caused by the bleeding of the pigment in the standard non-aqueous spin fluid of carbon tetrachloride and white spirit (30:70).

Table 2
Gradients of calibration graphs of aqueous dispersions of Red 2GW

Dispersion reference	50% diameter from absolute technique (μm)	Gradient of calibration graph
(i)	0.86	1.54
(ii)	0.82	1.47
(iii)	0.72	1.53
(iv)	0.50	1.55

The particle size distribution curves of the two dispersions, reference (ii) and (iv), were re-determined using the coloured spin fluid and the absolute technique.

The corresponding size distribution curves were virtually identical and the mean diameters obtained are shown in Table 3.

Table 3

Dispersion Red 2GW in water + 5% surfactant	50% diameters in μm	
	Colourless spin fluid	Coloured spin fluid
(iii) 7.5 hours B/M	0.72	0.70
(iv) 48 hours B/M	0.50	0.50

These results were encouraging as they show that the presence of colour in solution in the spin fluid has little significance in aqueous systems.

Non-aqueous systems

The non-aqueous dispersions were paint stainers made by ball milling Red 2GW into URALAC P470 and white spirit. (URALAC P470 is the trade name for an air-drying long oil soya penta alkyd resin supplied as a 70 per cent solution in white spirit.)

Dispersions of the dinitraniline red (Red 2GW) were prepared by ball milling the pigment into a vehicle based on P470 and white spirit for different lengths of time.

The pigmentation level in the mill was 20 per cent and the medium solids was 30 per cent. After milling, the system was reduced to a 10 per cent pigmentation level. Millings were carried out for 2, 5 and 16 hours and the particle size distribution curves were determined by both the absolute and PS techniques. From the results, three calibration graphs were obtained. Each was linear between 0.1 and 1.0 μ m and their gradients were measured. The results are given in Table 4.

Table 4
Red 2GW in P470/white spirit

Ball milling time (h)	50% diameter from absolute technique	Gradient of calibration graph
2	0.45	1.55
5	0.41	1.43
16	0.28	1.61

Mean gradient = 1.53

It will be seen that the mean values of the gradient of the calibration graphs are virtually identical for both aqueous and non-aqueous systems. The above experiments were carried out using the standard spin fluid of (30:70 w/w) carbon tetrachloride/white spirit mixture. This was colourless to start with but became coloured during the sedimentation because of the bleed of the pigment particles into it.

To check the effect of the bleed in more detail, a coloured spin fluid was made by preparing a saturated solution of the pigment in the carbon tetrachloride/white spirit mix by shaking the pigment and the spin fluid vigorously for 2 hours and removing the undissolved pigment by centrifuging in a Janetski centrifuge for 1 hour at 15,000 rpm.

Using this spin fluid, which was already saturated with dissolved pigment, particle size distributions were determined by the absolute method for two of the Red 2GW/P470 stainers already prepared (2 hours and 5 hours ball milling). It was hoped that the particles of pigment would not bleed or dissolve into the spin fluid as they sedimented through it because the spin fluid was already saturated with dissolved pigment. The particle sizes actually measured should therefore be true particle sizes. The results are given in Table 5.

Table 5
Red 2GW in P470/white spirit using saturated spin fluid

Ball milling time of stainer (h)	50% diameter from absolute technique (μ m)	Gradient of calibration graph
2	0.45	1.55
5	0.41	1.43

The corresponding size distribution curves were virtually identical as were the corresponding mean diameters.

These results show that the effect of bleed on particle size analysis has negligible effects for dinitraniline red (Red 2GW) where the solvent in the stainer is white spirit

and the spin fluid is the usual mixture of carbon tetrachloride and white spirit. The latter restriction must not be overlooked. If a spin fluid had to be used consisting of more powerful solvents producing a greater bleed, there is no guarantee that the effect of the bleed would still be negligible. Such conditions could apply if the Red 2GW were to be used, for example, in a gravure ink.

Determination of the effect of dispersion on colour strength of dinitraniline red

Because the results so far seemed to indicate that the bleed of the dinitraniline red pigment in a white spirit/carbon tetrachloride mix, although apparent visually, was not enough to vitiate particle size measurements on the disc-centrifuge, it was decided to attempt the experimental determination of the colour strength of this pigment as a function of particle size. If this could be done, the resulting curve could be compared with that obtained for other non-bleeding organic pigments, to see if they followed a similar pattern. The experimental curve could also be compared with the theoretical curve of colour strength versus particle size for this pigment by measuring its optical constants n , the refractive index, and k , the absorption coefficient, and applying the Mie theory.

The experimental approach was to make paint stainers by grinding the Red 2GW into the P470 resin/white spirit solution by ball milling. The times of ball milling were varied progressively so that a series of dispersion levels of the pigment were achieved ranging from poor to very fine. Apart from this variation in dispersion level, the paint stainers were identical in formulation. The actual dispersion levels were determined on the disc-centrifuge using a straight white spirit/carbon tetrachloride spin fluid. The colour strengths were determined by making reductions of each stainer with a standard white paint based on titanium dioxide in P470/white spirit, the reduction in each case being 1 part of Red 2GW to 25 parts of TiO₂. Films were drawn down from each of these reductions and after drying were measured on a reflectance spectrophotometer (GEC:Hardy Recording Instrument). Their k/s values were calculated, and since the films were completely opaque, they were directly proportional to their colour strengths.

This technique has been used many times by the authors before and is described in more detail elsewhere².

The results obtained are given in Table 6 and shown graphically in Figure 2.

Table 6
 k/s values and particle sizes of Red 2GW stainers

Ball milling times (h)	50% diameters (μ m)	k/s values
1	0.62	0.225
2	0.52	0.257
4	0.45	0.292
16	0.34	0.410
24	0.295	0.439
36	0.26	0.501
48	0.26	0.531
72	0.225	0.640

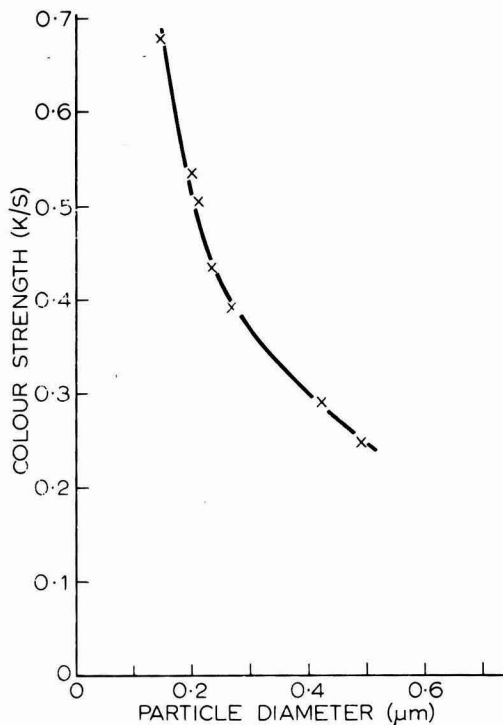


Figure 2. Master curve for dinitraniline red 2GW

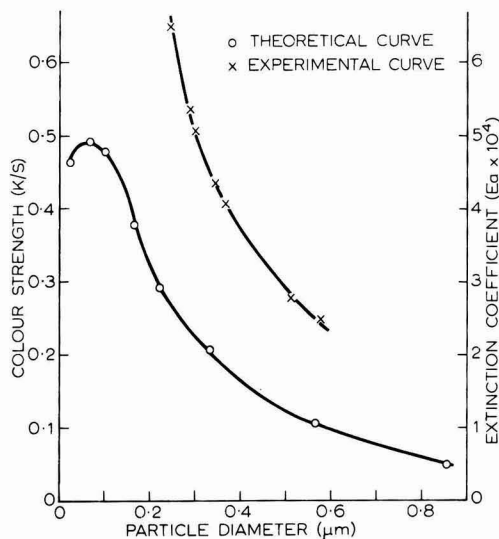


Figure 3. Comparison of the experimentally determined curve with the theoretical curve for dinitraniline red 2GW

The graph shows clearly the relationship between colour strength and particle size for this pigment, and the shape of the graph is clearly similar in pattern to that obtained for non-bleeding pigments using the same technique². This pattern shows a steady but slow increase in colour strength as the mean diameter is reduced from 0.62 to 0.5 μm. As the mean diameter is reduced further, the increase in colour strength quickens and once the mean diameter is below about 0.35 μm, the rate of increase in colour strength with further dispersion becomes very rapid.

The theoretical curve of colour strength versus particle size for this pigment was determined by a colleague (Dr G. F. Bradley) using the Mie theory, the optical constants and a computer program. His results were obtained in the form: $E_a \times 10^4$ versus mean particle diameter, where E_a is the extinction coefficient of the pigment dispersion and again is proportional to the colour strength of the pigment stainer. The two curves are shown in Figure 3. It will be seen that the curves are widely separated but reasonably parallel.

The curves are separate and not close to each other for several reasons. Firstly, in the experimental curve of k/s versus particle size, the exact value of S , the scattering function, is not known as this is determined both by the concentration of titanium dioxide and its level of dispersion. This is not known as it was not measured. However, as the same batch was used to reduce all the Red 2GW stainers, the denominator S in the ratio k/s was a constant throughout the experiment. The variations in the value of k/s were due solely to variations in the absorption power of the organic pigment and hence in the colour strength.

Furthermore, the units in which k/s was measured are different from those in which the extinction coefficient was measured. It is therefore parallelism of the two curves, experimental and theoretical, that is being looked for as a criterion of the soundness of the experimental technique.

That the curves are not exactly parallel is evident, but it is equally clear that they are very similar in shape over a range of particle sizes from 0.2 to 0.6 μm.

This is regarded as strong evidence that there is no major error introduced into the particle size measurements of the Red 2GW stainers using the disc-centrifuge measuring technique by the fact that this is a pigment that bleeds into the stainer vehicle and the spin fluid.

Combined with the earlier experimental evidence, it reinforces the conclusion that the bleed of dinitraniline red in simpler paint systems does not seriously affect the dispersion measurements carried out on this pigment.

Other pigments

Similar projects have been carried out on a number of other bleeding pigments. The same end was in view, namely, to establish whether the bleed seriously affected the particle size measurements. The other pigments examined were arylamide yellow G (CI Pigment Yellow 1), arylamide yellow 10G (CI Pigment Yellow 3) and a Research Yellow (CI Pigment Yellow 74).

The results were in broad agreement with those found for the dinitraniline red, namely:

1. The effect of the bleed was found to be negligible

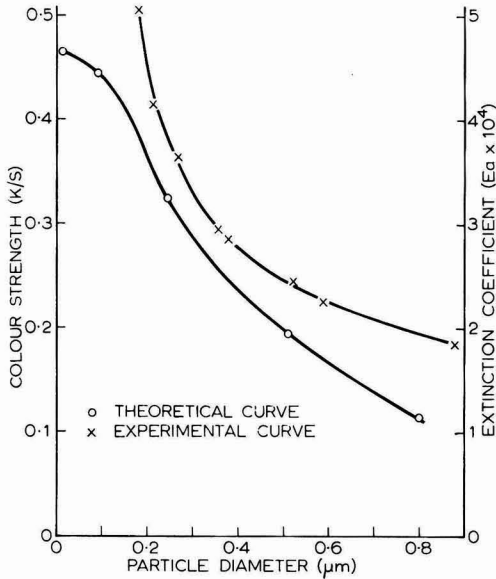


Figure 4. Comparison of the experimentally determined curve with the theoretical curve for arylamide yellow G

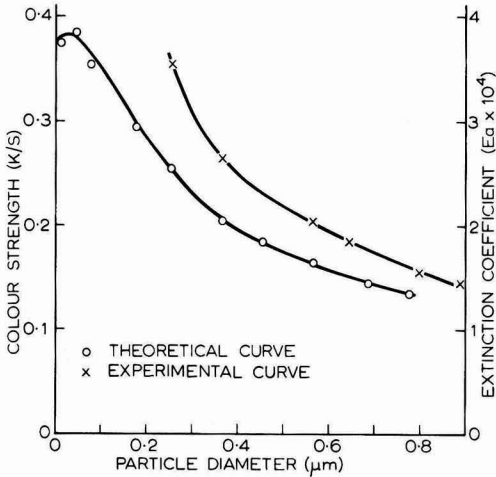


Figure 5. Comparison of the experimentally determined curve with the theoretical curve for arylamide yellow 10G

- using a model aqueous system with an artificial bleed.
2. The effect of the bleed was found to be negligible using a saturated solution of the particular pigment in a non-aqueous spin fluid.
3. The experimentally determined curves of k/s versus colour strength for reduced paints based on P470 stainers of each pigment were found to be very similar in pattern and shape to the theoretical Mie curves for each pigment.

The experimental and theoretical curves for the

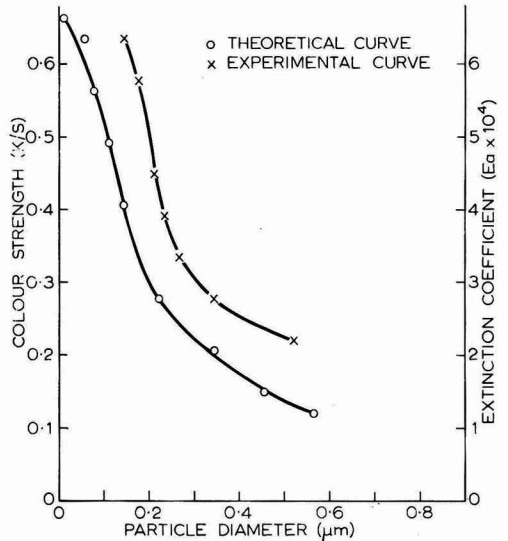


Figure 6. Comparison of the experimentally determined curve with the theoretical curve for Research Yellow 74

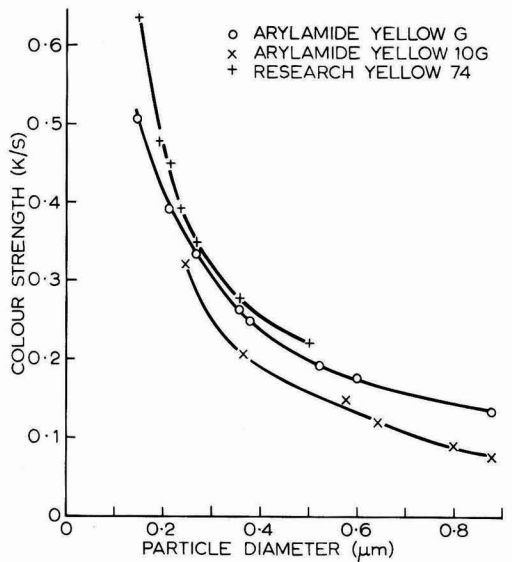


Figure 7. Comparison of experimentally determined curves for the three yellows

arylamide yellow G are shown in Figure 4, for the arylamide yellow 10G in Figure 5 and for Research Yellow 74 in Figure 6.

An interesting set of curves for the three yellows is shown in Figure 7, where the k/s versus particle size curves for each of these pigments are shown. The closeness

of these curves to each other would seem to indicate that there are no considerable differences in intrinsic colour strength between these three pigments. It must therefore be concluded that the apparent strength differences found between them in practice are basically due to differences in dispersibility.

Conclusion

The authors feel that the evidence put forward in this paper shows that the bleed of dinitraniline red, arylamide yellows G and 10G, and Research Yellow 74 in systems based on white spirit or mixtures of white spirit and

carbon tetrachloride, does not affect particle size measurements using centrifugal sedimentation as the size measuring technique. It must be stressed again, however, that this may not necessarily be the position when the pigments are used in more powerful solvents.

[Received 26 May 1981

References

1. Carr, W., *Progr. Org. Coat.*, 1976, 4, 161.
2. Carr, W., *JOCCA*, 1971, 54, 155.

A review of the relationship between visual and instrumental assessment of colour difference, part 2*

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12. Attempts to derive improved colour-matching formulae 1970-79

Refs, 70, 82-96

12.1 Multiple linear regression techniques

In 1971, McLaren⁸³ used multiple linear regression techniques on the Davidson and Friede data to determine the pattern of non-uniformity existing in ANLAB space. He derived a multiple regression equation in terms of lightness (L), metric chroma (C) and hue angle (T), and used this to correct the ΔE values. He obtained the following improvement in performance:

	r	Disagreements
Visual assessment 1 observer ANLAB (42)	0.565	49 (17.1%)
Multiple regression correction	0.648	46 (16.0%)

The equation used was:

$$\Delta E_{30} = 1.792 + 0.193 \left(\frac{L-42}{14} \right) + 0.316 \left(\frac{C-26}{19} \right) - 0.155 \left(\frac{C-26}{19} \right)^2 + 0.202 \left(\frac{T-154}{109} \right)^2$$

Sample/standard pairs with $\Delta E < \Delta E_{30}$ are formula passes and samples with $\Delta E > \Delta E_{30}$ are formula rejects. McLaren's work therefore showed that the numerical ΔE values of pairs of samples with perceptually equal colour differences increased as the metric chroma and lightness of the pairs increased.

12.2 Tolerance ellipsoid fitting techniques

Kuehni⁸⁴ quoted a comprehensive study by Strocka⁸⁵ which showed that scarcely any statistically significant differences in correlation were obtained from the Davidson and Friede, and the Thurner and Walther data with eight of the most commonly used formulae including ANLAB. Strocka showed that a simple formula based on circles of equal size in the chromaticity diagram and a simple lightness scale results in correlations equal to or better than those obtained with the other eight formulae. Mudd and Woods⁷⁰ proposed a similar formula. The Strocka formula was called the CIRCLE formula. Kuehni concluded that the relative success of the CIRCLE

formula was due to differences in the relative sizes of the tolerance ellipses in different areas of the chromaticity diagram which were not matched by the existing formulae, including ANLAB. The relationship of lightness differences to chromaticity differences might also be different. It was unlikely that the tolerances were, in fact, circles, otherwise the correlations for the CIRCLE formula would have been much greater.

Kuehni fitted tolerance ellipses by eye to the following data and plotted these on the CIE xy chromaticity diagram: Davidson and Friede, Thurner and Walther, Robinson, and Kuehni data (Kuehni data consisting of standards with 113 samples on polyester-cotton fabric and 10 observers). He found that (a) in the majority of ellipses the major axis pointed in the direction of the spectrum locus of higher wavelengths compared to the MacAdam ellipses, 20-30 degrees in most cases; (b) there was a tendency for colours of greater saturation to have increasingly larger tolerance ellipses. These differences explained the relatively low degree of correlation for formulae based on MacAdam ellipses. He suggested that similar discrepancies probably existed for other formulae. Kuehni found that in most cases, formulae based on the Adams Chromatic Value System (ANLAB) matched the directions of his acceptability ellipses quite closely. He suggested that the low degree of correlation found for the Davidson and Friede data obtained with the ANLAB type formulae must be due to lack of matching the relative sizes of the ellipses as well as to unsuitable weighting of lightness differences as reported by Schultze and by Gall⁸⁶. No justification for the FMC-2 K1 factor or Simon Goodwin chart alterations for different lightness values was detected in the ellipses, i.e. there was apparently no change in chromaticity tolerance with lightness change. There was an apparent absence of any fundamental difference between perceptibility and acceptability data ellipses. Kuehni asked MacAdam to fit the parameters of his xi-eta equation for a good fit to the Davidson and Friede, and Robinson ellipses and, together with a cube-root lightness scale, these formed a Kuehni SPECIAL formula. The following correlations were found for the total data set:

Equation	D and F	T/W	Robinson	Kuehni
FMC-2	0.62	0.40	0.84	0.64
Cube Root	0.57	0.39	0.78	0.75
CIRCLE	0.65	0.42	0.64	0.68
SPECIAL	0.75	0.38	0.87	0.76

Kuehni⁸⁷ later extended his data to include that of the

Metropolitan Section⁸⁸. Kuehni used the MacAdam ellipse equation:

$$(\delta s)^2 = g_{11}(\delta x)^2 + 2g_{12}(\delta x\delta y) + g_{22}(\delta y)^2$$

and calculated the g_{ik} values for his graphically determined tolerance ellipses using the above equation and combined it with the cube-root lightness scale. Colour differences were calculated and correlation coefficients determined. The ellipse semi-axes and angles were then systematically varied until the correlation coefficient reached a maximum. The resulting optimised ellipses are listed. Further improvement in correlation necessitated adjustment of the lightness equation: it was found that the simple relationship, $\Delta L = 10\Delta Y/Y$ Std., gave optimum correlations for all the data. On applying this combination of ellipses and lightness function to the test data, he obtained a correlation of 0.77 for the total data set and a correlation of 0.87 as the average of individual correlations. Further investigation showed that the slopes of percentage acceptability versus ΔE values were different for each region of colour space. No correlation between hue, saturation or lightness and the angle of the regression lines could be found. On the other hand, the angle of the regression line appeared to be systematically influenced by the number of observers taking part in the experiment. The Robinson line from 131 observers was especially flat.

Kuehni's acceptability ellipses differ from the perceptibility ellipses of MacAdam and Brown in a clockwise rotation of most ellipses. In general, the ellipses point in the direction of one of four hypothetical primaries – red, green, blue or yellow. There is a tendency for larger ellipses in colours of greater saturation. The size of the individual ellipse is very much affected by the severity of the observers. Kuehni quoted evidence from his earlier paper⁸⁷ and of Billmeyer⁸⁹ and Driebergen which did not support a variation in ellipse size with lightness. Kuehni stated that Schultze⁹⁰, Steen and Tonquist⁹¹ had reported that several colour-difference formulae produced a tilt of the vertical axis of the ellipsoid in the direction of lower saturation. This was especially so in the CIE 1964 formula, but also in formulae based on the Munsell systems and others. Schultze and Gall⁹² showed that their visual data for a saturated red and blue was best described by formulae which did not produce a tilt of the ellipsoid. MacAdam's investigation at threshold level using luminous colours revealed no, or only an insignificant and unsystematic, tilt of ellipsoids⁹³. From this, Kuehni concluded that the ellipsoids are not tilted.

Kuehni showed that many variables affect the exact shape of the determined acceptability ellipsoids. Some of these variables, such as the number of observers taking part in the acceptability experiment and the severities of the observers, make it quite unlikely that a colour-difference formula optimised for one set of data will be near optimal for another set of data. On the other hand, it was made clear that relatively minor differences in ellipse semi-axes and ellipse angles can reduce the absolute value of the correlation coefficients considerably. Therefore, Kuehni concluded that it is unlikely that any colour-difference formula will describe, near optimally, the different published sets of acceptability data. According to Kuehni, the optimum formula should:

(a) represent the ellipsoid orientations closely,

- (b) have ellipses gradually increasing in size with increasing saturation,
- (c) not change ellipse size with changing lightness,
- (d) have the optimal lightness scale
- (e) have the correct relationship between chromatic difference and lightness difference.

Kuehni suggested such a formula, which is a modification of the Cube Root formula⁹⁴ with a factor which increased the chromaticity difference linearly as the saturation of the standard increased, combined with the lightness function derived above. This formula fits the combined Davidson and Friede, Robinson, Kuehni Metropolitan data better than FMC-2 or the standard cube root equation.

33 standards, 439 sample/standard pairs			
	Total	Average	Disagreements (%)
Cube Root	-0.60	-0.68	21
FMC-2	-0.63	-0.69	22
Kuehni	-0.64	-0.77	16

Padgham and Rowe⁹⁵ described a colour scaling experiment in which observers at the Physics Exhibition in London in 1971, were asked to place 10 colours in position on a chromaticity chart and grey scale. The results from 323 observers showed that the spread in position of hue estimates decreased as the saturation of the colours increased, and that scatter in the saturation estimates increased as the saturation of the colours increased. The lightness estimates agreed well with the Munsell value scale. The experiment confirmed results from other investigations that saturation scaling is less precise than for hue.

Billmeyer, Howe and Rich⁹⁶ utilised a computer algorithm developed by Powell in a direct search procedure to determine the dimensions of tolerance ellipses in the CIE xy diagram, the ellipses being optimised to fit visual perceptibility matchings of gloss lacquers by a panel of 15 observers. Four colour sets were chosen – blue, orange, grey and green. The chromaticity differences were defined by the MacAdam ellipse equation and the criterion for optimisation was to maximise the "maximum likelihood function" based on the probability of acceptance by the visual observer of a pair of samples identical colorimetrically. The probability of such a pair of samples not being seen as a match was called the "false alarm rate" and this was built into the likelihood function.

The ellipses constructed gave contours for which the probability of samples lying thereon being seen as a match was about 60 per cent.

The colours were matched against a grey background, but the green colour was also matched against a black and against a white background. The grey surround gave larger ellipses than either the black or white surround. The grey was also matched against a black background but in this case no significant difference in size was found from the matches made against the standard grey background.

Billmeyer *et al.*⁹⁶ were surprised at the magnitude of the false alarm rates. For example, a sample that was colorimetrically identical to the reference colour was seen as not matching that reference in at least 20 per cent of the judgements.

12.3 McDonald ΔE_a equation

McDonald⁸², following up the multiple linear regression approach of McLaren⁸³, utilised experimental data obtained in J. & P. Coats Ltd. He carried out a matching experiment in which eight observers were given a grey scale consisting of four pairs of grey patterns, each pair representing a different commercial matching tolerance. The observers were asked to assess, in relation to the grey scale categories, the colour differences perceived between 135 pairs, including 16 colours and 11 greys, evenly distributed throughout colour space. The results were separated into groups according to the grey scale categories. When multiple linear regression was applied to each of the groups of data, it was found that the ANLAB ΔE value increased linearly as the metric chroma of the colours increased. It was found that effects of lightness and hue, when incorporated into the multiple regression equations, were insignificant after the correction for metric chroma had been applied. It was found that the set of four linear equations, one for each grey scale category, formed a family of equations which could be combined into the following simple relationship for ANLAB (50) space:

$$\Delta E_a = \frac{\Delta E}{1 + 0.022C} -$$

Where:

C is the mean metric chroma of sample and standard in ANLAB (50) units

ΔE is the measured colour difference

ΔE_a is the equivalent colour difference at the neutral grey (achromatic) point

The equation thus enabled any measured colour difference to be converted to its equivalent at the neutral grey point. The improvement in correlation with visual decisions was significant, not only with the J. & P. Coats experimental data, but also with the Davidson and Friede data. (See table below.)

On both criteria of correlation coefficient and of disagreements with visual observer, the ΔE_a modification is significantly better than the formula previously tested by McLaren and listed in section 12.1.

13. The Morley perceptibility data

Refs, 73,97,98

Kuehni⁹⁷ commented on the fit of the CIELAB equation to the Morley data. The Morley data consisted of 19 standards in various regions of colour space. Approximately 30 samples were arranged around each standard. The observers were asked to place the perceived colour differences into four visual categories of increasing leniency. The scores were treated statistically and converted to a continuous psychological scale which was directly related to perceived colour difference. Kuehni fitted ellipsoids to 17 of the 19 colour sets. The ellipsoids consisted of a combination of MacAdam ellipses and a lightness function $\Delta Y/Y$, and were fitted individually to each cluster of data grouped around each colour standard. The correlation coefficient obtained with these optimised ellipsoids for the total data set of 17 colours was 0.843, compared to a value of 0.723 for the CIELAB equation. Kuehni showed that the chromaticity ellipses became smaller for desaturated colours, particularly evident for grey colour SG, and an absence of a detectable influence of lightness level on ellipse size. Ellipses were generally oriented with their major axes towards the neutral grey point. When chromaticity ellipses were constructed by calculation from the CIELAB formula, certain disturbing features were revealed: ellipse directions deviated by as much as 90 degrees in the saturated yellow-orange region; relative weighting of the lightness to chromaticity difference in the total colour difference was approximately twice that required by the optimisation; the dependence of ellipse size on lightness level was, if required at all, much smaller in the data than predicted by the CIELAB formula.

McLaren⁹⁸, however, pointed out that the Morley data had provided conclusive evidence that there was no better formula available than the CIELAB for quantifying small colour differences. McLaren⁷³ showed that the CIELAB equation gave the highest correlation coefficients for the combined Davidson and Friede, and HATRA 589 data, and that CIELAB also gave the highest correlation with the Morley data. This evidence justified the decision of the CIE to recommend CIELAB for international use, but the Kuehni evidence simply further illustrated the residual systematic discrepancies between data and formula.

14. The HATRA acceptability data

Refs, 87,97,99-101

Jaekel and Ward⁹⁹ listed correlation coefficients for the HATRA 589 and the Davidson and Friede data, including modifications made to ANLAB and other formulae

Matching grade	No. of samples	Correlation		Disagreements with visual observer		ΔE		ΔE_a	
		ΔE	ΔE_a	No.	%	No.	%	No.	%
J. & P. Coats data									
1	72	0.36	0.48	11	15.3	4	5.5	4	5.5
2	194	0.42	0.53	42	21.6	33	17.0	31	16.0
3	167	0.44	0.58	72	43.1	93	55.6	80	47.9
4	309	0.41	0.61	68	22.0	72	23.3	51	16.5
Davidson and Friede data									
	287	0.58	0.68	49	33.6	59	20.6	45	15.7

produced after adoption of ANLAB by the Society of Dyers and Colourists in 1970. The results were:

Formula	r
Coates, Provost and Rigg	0.71
HATRA/ANLAB optimisation	0.71
Coates, Day, Provost, Rigg	0.70
CIELAB	0.67
Glasser, Morton Cube Root	0.67
Reilly, Glasser Cube Root	0.67
ANLAB	0.66
McConnell modified CIELAB	0.63
McDonald ANLAB ΔE_a	0.62
FMC-2	0.61
MacAdam xi-eta	0.61
Hunter	0.60

The formula of Coates, Provost and Rigg, and the formula of Coates, Day, Provost and Rigg are not given in the Jaeckel⁹⁹ paper, but he commented that although good formulae, these did not provide ΔE s readily separable into useful practical components. The optimisations of McConnell and McDonald were each better for different restricted groups of patterns than for the combined HATRA/Davidson and Friede data. The Morton cube root equation was chosen by HATRA for the colour control system developed by them in 1976, but the use of CIELAB was also recommended.

Jaeckel found that even with the best formula, Morton cube root, the pass tolerance for relatively bright light fuschias was twice as great as for dull dark browns. This conclusion again indicated an expansion in tolerance as the saturation of the colours was increased.

In addition to the ΔE value, Jaeckel found it useful to have a print-out of the ΔL , Δa , Δb , Δ hue angle and Δ chromaticity. Alternative print-outs used were ΔL , Δ hue and Δ chroma. Jaeckel stated that in practice the dyer can set up tolerance limits by inspection of a few completed batches. Tolerance can be specified in either ΔE terms or in one to three parameters, e.g. ΔE and ΔL , or ΔL , ΔC and ΔH .

Graphs to facilitate dyehouse control were given by Jaeckel and allowed for bias in visual preference, e.g. preference for shades heavy to standard or, say, green to standard. Jaeckel plotted the ratios of largest acceptable ΔE values for a selection of colours to the smallest ΔE values, and found a trend indicating higher tolerance for colours further removed from black, especially if both lighter and more saturated.

Keuhni¹⁰⁰ further analysed the HATRA 589 data by separating it into 10 groups involving 17 sets of the HATRA data with a total of 400 samples, in some cases combining results from different sets with similar standards. Ellipsoids were fitted to the data.

Correlation coefficients were calculated between the fitted ellipsoids and visual acceptability, and also for the ANLAB(40) colour-difference formula. (The performance data obtained are shown in the table below.)

The correlation for the total data set based on fitted ellipsoids was 0.75. From a plot of the ellipsoid contours

Group	Fitted ellipsoids	ANLAB (40)
11, 12	0.87	0.86
17, 18	0.88	0.87
23, 24	0.80	0.80
25, 29	0.79	0.56
33, 35	0.72	0.66
3, 4	0.83	0.80
6, 7	0.86	0.65
0	0.75	0.70
300	0.90	0.89
900	0.77	0.45
Average	0.79	0.72

in the CIE xy diagram, it was evident that the substantial dependence of ellipse size on saturation found in other acceptability and perceptibility data^{87,97,101} was not so clearly apparent in the HATRA data. In this it differs from other comparable data. The ellipse directions were in good agreement with those of the ellipsoids fitted to comparable data. The ellipsoids were on average somewhat less elongated than those of comparable data. Change of ellipse size with lightness of standard was noticed in group 900 ($Y=2.13$) compared with group 11, 12 ($Y=19.25$). On the other hand, groups 0 ($Y=63.89$) and 33, 35 ($Y=13.93$) did not show expansion with increasing lightness. Kuehni noted that group 900 was the darkest group of shades and had the lowest level of correlation of any of the groups, a correlation that could not be markedly improved by ellipsoid fitting, indicating a low level of consistency of data within the group. Among the possible reasons suggested for this were the decreased ability of the observers to make accurate judgements at this low level of lightness or difficulties in the accurate measurement of these samples. As with other similar sets of data, Kuehni noted that the ellipsoid fitting indicated that the optimal weight of the lightness difference in the total colour difference for the data should be approximately one half of the weight that was assigned to the lightness difference in formulae such as ANLAB. Kuehni concluded that the data appeared to be, in general, comparable to other acceptability data published. There were internal discrepancies apparent in the direction of fitted ellipsoids in the blue and purple areas as well as with respect to ellipse expansion with lightness.

15. Perceptibility and acceptability judgements

Refs. 77, 79, 97, 102-104

Visual colour-matching data fall into two categories: acceptability data, such as the Davidson and Friede, and HATRA data, and perceptibility data, such as the Morley data. It was uncertain whether the CIELAB formula, which had been developed as a result of its tested superiority with acceptability data, would work equally successfully with perceptibility data. McLaren¹⁰² compared correlation coefficients for several formulae on both types of data. (See table below.)

The close similarity of the two ranking orders suggested that any differences between acceptability and perceptibility assessments, other than that of size, were insignificant, a view which Kuehni had also reached from his comparison of acceptability and perceptibility ellipsoids⁹⁷.

From experience in 16 dyehouses using instrumental

Formula	Perceptibility (MMB)	Acceptability (D and F, HATRA)
	555 Paris r	775 pairs r
CIELAB	0.721	0.672
ANLAB	0.721	0.664
Saunderson-Milner	0.721	0.650
CIE1976 LUV	0.706	
Glasser Cube Root	0.684	0.671
Hunter	0.684	0.605
FMC-2	0.677	0.610
MacAdam xi-eta		0.608
FMC-1	0.669	0.445
NBS	0.631	0.640
CIE1964 UVW	0.610	0.588

measurement, McLaren¹⁰² found that in most cases the tolerance for hue difference was significantly less than for any other type of difference. This meant that either

1. the colourists were biased against hue differences, or
2. the ANLAB formula underestimated the perceptibility of hue differences.

Using an iterative optimisation technique, McLaren determined the optimum weighting factors to be applied to the three components of colour difference: hue, lightness and metric chroma, in order to maximise the correlation coefficient. The factors determined are l, c, h in the following ΔE equation:

$$\Delta E = [(l \Delta L)^2 + (c \Delta C)^2 + (h \Delta H)^2]^{\frac{1}{2}}$$

Four sets of data were optimised using the ANLAB equations. (See table below.)

Significant increases in correlation can, therefore, be achieved by optimised weighting. The perceptibility data of Morley⁷⁷ were further analysed to determine if size of colour difference affected the weighting ratios but little difference in weighting was obtained. These results, therefore, indicated that there was a difference between perceptibility (MMB) assessments and acceptability (D and F, HATRA, JPC) assessments.

The data also showed that, in ANLAB space, the surface containing all colours which are equally perceptually different from a given colour, was not a sphere but an ellipsoid whose metric chroma axis is approximately 1.5 times as long as the lightness axis.

To quantify any absolute bias on the part of the textile shade passers, the optimised weighting factors for the acceptability data were divided by the Morley per-

ceptibility factors. This gave, for the acceptability data, an indication of the bias relative to the Morley observers:

Data	Bias		
	l	c	h
D and F	1	2.0	2.9
HATRA	1	1.8	1.9
JPC	1	2.2	7.6

Thus, the other observers were much more sensitive to hue/metric chroma differences than the Morley observers, the JPC observers being particularly sensitive to hue differences.

To explain why the ANLAB formula works equally well with both the perceptibility data of Morley and the acceptability data above, compared to other colour-matching formulae, McLaren suggested that the colourist first assessed a colour difference for perceptibility and, if the difference was very small, his decision was "pass", if the difference was very obvious, his decision was "fail"; equations of the ANLAB type are best for providing a numerical scale of perceptibility. However, if the perceived difference is near the permitted tolerance limit, then the observer was influenced by the nature of the difference. McLaren suggested that it was unlikely that any equation which was less reliable for scaling perceptibility could more than compensate for this deficiency by correctly scaling acceptability.

Robertson⁷⁹ referred to the standardisation in Europe on ANLAB which appeared in the "best group" in many of the studies of visual assessment against calculated colour difference. Robertson, therefore, plotted the contours of Munsell loci of constant hue and chroma in the CIELAB and CIELUV ab and uv diagrams. In neither case was a perfect uniform spacing obtained, but the ANLAB ab diagram was slightly better in uniformity. A similar exercise was carried out with the MacAdam ellipses. Neither diagram was successful in transforming the ellipses into circles, which would be indicative of a uniform diagram. Both were equally unsuccessful. Robertson pointed out that the Munsell colour differences were larger than those encountered in near threshold colour matching and that the MacAdam ellipses were, on the other hand, based mainly on sub-threshold colour differences, whereas colour-difference formulae were intended for colour differences slightly greater than threshold.

Lozano¹⁰³ applied ten colour-difference formulae including ANLAB and CIELAB to a set of 193 samples used on colour scaling investigations by Mattiello. In a subset of 97 samples, only the lightness of the samples was

Data	Type	No. of samples	No. of colours	Weighting factors			Correlation	
				l	c	h	1:1:1 weighting	Optimum weight
MMB	perc.	518	18	1	0.5	0.7	0.715	0.743
D and F	perc.	286	19	1	1.0	2.0	0.570	0.628
HATRA	acce.	589	12	1	0.9	1.3	0.699	0.715
JPC	acce.	169	169	1	1.1	5.3	0.326	0.533

D and F = Davidson and Friede, perc. = perceptibility, acce. = acceptability

varied, in the second subset of 96 samples, only the chroma was varied. From these investigations, psychological scale values for 196 possible pairs in the first group and 264 possible pairs in the second group were obtained, giving a total of 460 pairs. Regression analysis between the psychological scale values and the ΔE from each formula was carried out. The correlation coefficients obtained are as follows:

Group 1 (Lightness differences)		Group 2 (Saturation differences)	
Reilly Cube Root	0.913	Judd Hunter	0.772
CIELAB	0.911	Hunter-Scofield	0.776
ANLAB	0.908	Reilly cube-root	0.761
FMC-2	0.906	CIELAB	0.760
Hunter-Scofield	0.906	ANLAB	0.759
Saunderson-Milner	0.897	Saunderson-Milner	0.734
FMC-1	0.883	CIELUV	0.729
Judd Hunter	0.882	MacAdam Geodesic	
CIELUV	0.851	space	0.704
		FMC-2	0.682
		FMC-1	0.621

The results showed that the Reilly cube-root and the CIELAB formulae were those which gave the best overall fit to the two sets of data. ANLAB and Hunter-Scofield formulae were also correct for large colour-difference evaluations. Lozano considered that the result established a relation between the observer-behaviour for threshold experiments and those in which the differences were much larger than threshold differences. As far as the above work was concerned, it could be said that in both cases the observer-behaviour was similar. The paper contains a list of all formulae in detail.

Kuehni and Marcus¹⁰⁴ with the ISCC data found no fundamental difference between ellipses fitted to perceptibility judgement scales and to acceptability judgements.

16. The ISCC data

Refs, 38, 102, 104

Kuehni and Marcus¹⁰⁴ reported on an experiment carried out under the auspices of the ISCC committee on colour-difference problems, which involved visual scaling of small colour differences for six colour centres. The colour differences were evaluated by ranking, by estimation and by acceptability judgements. Visual scales were calculated and correlations between the scales and CIELAB, CIELUV, FMC-2 and Friele's Fine Color Metric (FCM) formulae were determined³⁸. Optimised ellipsoids were also fitted to the data. No fundamental differences were found between the results of the perceptibility judgements and the acceptability judgements. Higher correlations than reported for earlier comparable experiments were obtained between visual and calculated colour differences.

Two of the data sets involved dyeings on textiles, the other four consisted of matt paints on cardboard. There were approximately 30 samples distributed around the standard of each of the six sets. Two sets were observed by 37 observers, and 4 sets by 26 observers. Observations were by:

1. Ranking

- Subjective estimates of colour difference in a scale 1 to 10 (10 being the largest perceived colour difference in a set).
- Acceptability as a commercial match – no specification of the matching tolerance being given.

Correlation coefficients were calculated between each of the visual scales and the following formulae: CIELAB, CIELUV, FMC-2 and FCM. Correlations are listed for each colour centre, together with the averaged correlation. The following were the average of the individual correlation coefficients:

	vs. scale 1	vs. scale 2	vs. %A (4-96%)
CIELAB	0.847	0.842	0.722
CIELUV	0.784	0.786	0.712
FMC-2	0.662	0.663	0.655
FCM	0.871	0.865	0.723

Significance testing of the correlation coefficients showed that there was overlap of the confidence limits for all four formulae in the case of the yellow, purple and blue sets, which indicated that the differences were not significant. For the orange set, the coefficients were significantly lower for the CIELUV and FMC-2 formulae, whilst for the green and grey sets only the FMC-2 formula resulted in a significantly lower correlation.

Kuehni observed that for these experiments there was no apparent fundamental difference between the perceptibility judgement scales and the acceptability judgements. This was substantiated when the fitted optimised ellipsoids were compared. No hue bias of acceptability judgements as postulated by McLaren¹⁰² was observed. There was, however, expansion of ellipse size as the saturation of the standards increased. The optimised ellipses were substantially more elongated than those resulting from the CIELAB formula. It appeared that perceptibility judgements were somewhat more consistent and, therefore, provided a more efficient technique for establishing visual data with object samples. Each of the four formulae produced a highest correlation for at least one of the six sets. Two formulae of significantly different structure, CIELAB and FCM, led to average correlations of comparable magnitude. However, each was substantially better or substantially worse than the other for some of the sets.

17. Friele FCM line element

Refs, 38, 96

Friele in 1978 published a new line element³⁸ in which he optimised the parameters to fit ellipsoids which he had calculated for the Davidson and Friede, Robinson, Thurner and Walther, Kuehni, Morley, Metropolitan, and Vos and Walraven data (coded the VVVR data). Friele indicated that the VVVR data consisted of 10 standard colours in gloss paint, with 20 sample/standard pairs in each set; 14 observers made paired comparisons, 14-25 observers gave pass/fail judgements. Friele called his new line element the FCM metric. (It should be noted that there is an error in the FCM formula as given in reference No. 38. This is annotated in section 22.(d).)

Friele evaluated the FCM formula by determining the

correlation between formula colour differences and visual judgements transformed to a "d" scale which was directly proportional to numerical colour difference. Comparison was made with the CIELAB and CIELUV formulae. Friele found that the FCM formula had no distinct advantages over CIELAB or CIELUV in the case of the Morley data. In the case of the data sets in the following table, improvements in correlation between d scale values and formula colour differences were obtained:

	Correlation: total data set		
	CIELUV	CIELAB	FCM
Davidson and Friele	0.57	0.55	0.76
Metropolitan	0.71	0.67	0.81
Robinson	0.76	0.82	0.95
VVVR	0.50	0.43	0.76

For the above data, the d scale was that proposed by Rich, Billmeyer and Howe⁹⁶, defined by Friele as follows:

$$\text{Percentage acceptance}/100 = \exp(-d^2)$$

$$\text{i.e. } d = [-\ln(A/100)]^{\dagger}$$

The FCM formula therefore gives a significantly better correlation with visual observation in terms of the d scale than either the CIELAB or CIELUV formulae. It should be noted that the definition of d makes it necessary to exclude all samples with percentage acceptability values of zero.

Friele detected evidence of tilt in the Y direction for some of the fitted ellipsoids, but he considered that the evidence for tilt was unsystematic and inconclusive.

18. Further amendments to the ANLAB formula

Refs. 78, 82, 105, 106

Gailey and McDonald¹⁰⁵ reported that whilst the ΔE_a equation of McDonald⁸² resulted in significant improvements in agreement with visual perceptibility judgements, when the ΔE_a formula was applied in an industrial situation, the level of agreement with visual acceptability decisions was not always very high. Colour differences from matching experiments with a collection of 88 colour pairs assessed by 8 observers, and 453 colour pairs assessed by a different panel of 8 observers, were split into the components of lightness, hue and metric chroma and these components were plotted against the metric chroma and against the lightness of the standards.

The metric chroma and the hue tolerances were shown to increase as the metric chroma of the standards increased, and the lightness tolerance increased in a non-linear fashion as the lightness of the standards increased. Limit lines were fitted by eye to the plotted data and equations derived to define these lines. The following equations resulted for ANLAB (40) space:

$$L_t = 0.409 (L - 13)/(1 + 0.08 (L - 16))$$

$$C_t = 0.044 C + 1.6$$

$$H_t = 0.08 C/(1 + 0.019 C) + 0.3$$

$$\Delta E = [(\Delta L/L_t)^2 + (\Delta C/C_t)^2 + (\Delta H/H_t)^2]^{\dagger}$$

An alternative to the ellipsoid formula reported was a cuboid formula in which each attribute of colour difference (lightness, metric chroma and hue) were individually compared with the tolerance limits L_t , C_t and H_t above. The disagreements with visual observation on two sets of samples assessed by a panel of eight observers and on the Davidson and Friele data were as follows for the ellipsoid formula:

	Av. visual observer		Formula		ΔE_a	
	No.	%	No.	%	No.	%
88 J. & P. Coats Shades	7	8.0	9	10.2	31	35.2
81 J. & P. Coats Shades	13	16.0	14	17.3	21	25.9
287 Davidson and Friele shades	49	17.1	41	14.3	45	15.7

It was noticed in the dyehouse that the ΔE_a formula tended to be too slack in brown shades and too tight in turquoise shades compared to the visual observer, and some device to alter the ΔE_a formula to compensate for this irregularity was sought. By moving the origin from which the metric chroma of standard was calculated for the ΔE_a equation into the brown quadrant of the ANLAB chromaticity diagram it was found that the anomalous behaviour of the ΔE_a equation could be compensated and the performance improved. The movement of the origin exercise was repeated with the Davidson and Friele and with the Morley data. In each case improvement in performance exemplified by increase in correlation coefficient and reduction in disagreements with visual observation was obtained. With all sets of data, best performance was obtained with the moved origin in the brown quadrant, although for each set of data the optimum position of the moved origin was different. (See table below.)

	Origin		Disagreements		Correlation
	a	b	No.	%	
88 J. & P. Coats Shades	0	0	19	21.6	0.375
	8.0	2.9	17	19.3	0.459
81 J. & P. Coats Shades	0	0	15	18.5	0.544
	0.8	0.8	15	18.5	0.545
Davidson and Friele	0	0	45	15.7	0.684
	5.6	1.3	41	14.3	0.704
Morley 525	0	0			0.745
	0.8	4.8			0.765

		Origin		Correlation	Weightings		
		a	b		L	C	H
D. and F./HATRA 705	ΔE	0	0	0.698	1.0	1.0	1.0
	ΔE_a	0	0	0.718	1.0	1.0	1.0
	ΔE_a	4.8	4.8	0.744	1.0	1.0	1.0
	ΔE_a	4.8	4.8	0.770	*0.5	1.0	1.8
Morley 518	ΔE	0	0	0.714	1.0	1.0	1.0
	ΔE_a	0	0	0.733	1.0	1.0	1.0
	ΔE_a	4.8	4.8	0.768	1.0	1.0	1.0
	ΔE_a	4.8	4.8	0.778	*2.0	1.0	1.7

*Optimum weightings

At the same time as these investigations were taking place, McLaren¹⁰⁵ was independently investigating the optimum relative weightings of lightness, metric chroma and hue in relation to the combined Davidson and Friede, and HATRA samples (705 pairs) and the Morley data (518 pairs). McLaren tested the effect of moving the origin as suggested by Gailey and McDonald, and then altered the weightings to his optimised values to obtain the following results. (See table above.)

The McLaren weightings for L, C and H were, therefore, tried by Gailey and McDonald¹⁰⁵ on the Coats data, re-optimising the movement of the origin for the ΔE_a equation to give. (See table at bottom of page.)

The plots of metric chroma and of hue tolerance versus metric chroma of standard in the paper show that the ratio of hue tolerance to metric chroma tolerance is fairly close to the ratio found by McLaren from the Davidson and Friede/HATRA data.

Movement of the origin was also carried out for the ellipsoid formula and the cuboid formula derived in the paper. Again, in general, improvement was obtained when the origin was moved:

	Origin		Disagreements			
	a	b	Cuboid		Ellipsoid formula	
			No.	%	No.	%
88 J. & P. Coats Shades	0	0	9	10.2	9	10.2
	3.2	4.0	9	10.2		
81 J. & P. Coats Shades	0	0	13	16.0	9	11.1
	3.2	0.8	10	12.3		
D. and F. Shades	0	0	41	14.3	41	14.3
	3.2	0.8	34	11.8	35	12.2

Finally, Gailey and McDonald¹⁰⁵ tested the cuboid and

ellipsoid formula on 1,085 dyehouse production shades visually passed by one observer:

	Formula	Disagreements	
		No.	%
1085 J. & P. Coats Shades	ΔE_a	175	16.1
	Ellipsoid formula	151	13.9
	Ellipsoid formula + visual check of 101 pairs	109	10.0

It was concluded that in ANLAB space, a standard ΔE tolerance value was not adequate to describe the complexities of visual pass/fail judgements. In particular, the relative weightings of lightness, metric chroma and hue as defined by ANLAB space were not equal when acceptability judgements were being made. By incorporation of altered weightings into the ΔE_a equation, improvement in correlation with visual judgement could be obtained, and further improvement could be obtained if the origin was moved to the brown quadrant of the chromaticity plane. The fact that improvement in visual correlation could be obtained when the origin was moved indicated that some hue dependent factor in visual judgements was not completely explained by the ANLAB formula. It was suggested that the ΔE_a formula with McLaren's weightings represents a simplified version of the more complex relationships derived in the paper. The modified ΔE_a formula also did not take full account of the findings of the investigation that Lt was independent of metric chroma and that Lt was dependent on lightness. All the modified formulae gave performances significantly better than the standard ANLAB formula.

McLaren⁷⁸, in a comprehensive review of developments in instrumental shade passing and sorting, traced the evaluation and screening of colour-difference formulae leading to the standardisation on ANLAB space by the

	Origin		Disagreements		Correlation
	a	b	No.	%	
88 J. & P. Coats Shades	0	0	11	12.5	0.637
	2.4	4.8	11	12.5	0.705
81 J. & P. Coats Shades	0	0	12	14.9	0.664
	4.0	2.4	11	13.6	0.686
287 D. and F. Shades	0	0	40	13.9	0.729
	3.2	0.8	34	11.8	0.741

	Best established equation	D and F	Coates Rigg <i>et al.</i>	McDonald McLaren	Keuhni	Jaeckel	Friele	McConnell
D and F	0.63 (NBS)	0.77 ^c	0.64	0.75 ^b	0.78 ^c	0.68		
HATRA	0.71 M ₁		0.72	0.72	0.75 ^a	0.72		
JPC169	0.33 (ANLAB)			0.75 ^c				
DFRKM	0.63 (FMC-2)				0.76 ^{c,d}		0.74 ^c	
KM	0.64 (ANLAB)			0.74 ^c				
MMB	0.72 (CIELAB)			0.80 ^c	0.84 ^{c,d}			0.78 ^b

a = 5.0% level significance, b = 1.0% level significance, c = 0.1% level significance, d = optimised individual ellipsoids – not an equation (ref. 101)

Society of Dyers and Colourists in 1970. Cooper and McLaren's investigation¹⁰⁶ showed that for surface colours the psychological primaries, red, green, yellow and blue did not lie on the ANLAB chromaticity chart, a,b axes, but to one side. McLaren drew attention to the psychological difficulty of interpreting Δa , Δb differences. A better method of splitting ΔE was to utilise the cylindrical co-ordinates of ANLAB space L, C and H because all three were more closely related to one of the most widely recognised sets of perceptual variables: lightness, hue and saturation. Cylindrical co-ordinates were, however, abandoned around 1939 because a given change in hue angle represented a much greater difference in hue for colours of high C value than for those of low C value, and this could only be overcome by the use of an equation involving a cosine term. However, in 1973 Cooper and McLaren¹⁰⁶ and the committee responsible for developing the German Standard on colour-difference measurement, independently derived the method of calculating hue differences which were not chroma dependent and were also in ANLAB units, as follows:

$$(\Delta E)^2 = (\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2$$

$$C = (a^2 + b^2)^{1/2}$$

$$(\Delta E)^2 = (\Delta L)^2 + (\Delta C)^2 + (\Delta H)^2$$

$$\therefore \Delta H = [(\Delta E)^2 - (\Delta L)^2 - (\Delta C)^2]^{1/2}$$

McLaren also outlined investigations into the anomalous relationship between hue, lightness and metric chroma differences and the terminology used and understood by the dyer: hue, brightness and strength¹⁰⁶. In particular, the dyer's perception of strength differences of dyes inferred changes in lightness and in chroma which follow the characteristic strength paths through ANLAB colour space of the dyes in the sample being examined, i.e. for pale shades, such as yellows, increase in strength would mean mainly an increase in chroma, for medium shades mainly a decrease in lightness, and for heavier shades a decrease in lightness and in chroma. The dyer's term "brightness" inferred change in both lightness and chroma. The term "hue difference" inferred a change in hue angle ΔH as previously defined. McLaren¹⁰⁶ described a computer program based on the hue-brightness-strength (HBS) descriptions which had been evaluated by 14 dyehouses in the UK.

McLaren⁷⁸ tabulated the correlation coefficients achieved by optimisation by various workers. (See table above.)

Using ANLAB as the chosen colour-difference formula, McLaren optimised the relative weightings of L/C/H and obtained the following values:

Data	Type	l	c	h	Correlation	
					l,c,h=1	l,c,h opt.
D and F	acce.	1	1.0	2.0	0.570	0.629
HATRA	acce.	1	0.9	1.3	0.699	0.715
JPC169	acce.	1	1.1	5.3	0.326	0.533 ^c
KM	acce.	1	0.6	1.4	0.643	0.730 ^b
MMB	perce.	1	0.5	0.7	0.715	0.743

b = 1.0% level significance, c = 0.1% level significance

McLaren chose an overall weighting factor of 1.0 for both lightness and metric chroma, and from further graphical analysis chose a value of 2.0 for the hue weighting factor. He noted that the MMB perceptibility data weightings were significantly different from those of the acceptability data sets. The optimum value for the denominator constant in the ΔE_a equation was then determined from the above sets of data and the following optimised ΔE_a equation resulted, the HATRA data being ignored because it alone did not respond to the ΔE_a optimisation:

$$\Delta E_a = \frac{[(\Delta L)^2 + (\Delta C)^2 + (2\Delta H)^2]^{1/2}}{1 + 0.02C}$$

When the HATRA data was included, the denominator constant was altered to 0.005C and the performance of the ΔE_a equation was reduced for all the other data sets:

Data	ANLAB	ANLAB 1:1:2/0.005	ANLAB 1:1:2/0.02	Set-optimised ANLAB
D and F	0.570	0.676 ^b	0.726 ^c	0.748 ^c
HATRA	0.699	0.707	0.670	0.720
JPC169	0.326	0.522 ^b	0.614 ^c	0.753 ^c
KM	0.643	0.728 ^b	0.733 ^b	0.744 ^c
MMB	0.715	0.701	0.712	0.797 ^c

b = 1.0 level significant, c = 0.1% level significant

McLaren also listed the instrumental/visual percentage disagreements for each of the data sets. (See table below.)

Data	Visual observer	ANLAB				Set- optimised
		ANLAB	1:1:2/0.005	1:1:2/0.02	ANLAB	ANLAB
D & F	17.2	21.0	14.7	12.9	12.2	
HATRA	24.2	22.2	22.1	19.7	21.6	
JPC169	14.7	29.0	18.9	15.4	9.5	
KM	20.6	15.6	14.2	13.5	14.9	
MMB	17.9	23.6	23.4	19.1	18.3	

McLaren noted that, in contrast to the correlation coefficient, the disagreements criterion indicated that the ANLAB equation 1:1:2/0.02 gave the best performance with the HATRA data. It will be noted that correlation coefficients, as is often the case, do not agree with other estimates of goodness of fit, in this case the disagreements criterion.

19. Effect of sample/standard dividing line on visual assessment and colour-matching formulae

Refs, 107-110

Nunn¹⁰⁷ found that colour matchings established under spatially uniform conditions were disturbed by the introduction of spatial modulation in one half of the adaptation field, even though the mean illumination level and the spectral composition of the spatially non-uniform adaptation was the same as that of the uniform adaptation field. It was deduced that any differences in spatial structure between the matching fields could cause shifts in colour matching obtained under symmetric field conditions. Thus, care should be taken in colorimetry to reduce differences in the two half-fields and to eliminate dust particles whose images might add structure to the visual image. This work may relate to the effect of structure in confusing the visual observer matching textile materials.

Zeller and Hemmendinger¹⁰⁸ carried out a colour-difference scaling experiment using three paint pigments: a moderate chroma red, a moderate chroma yellow, and a high chroma yellow. Tolerance ellipses calculated from the equations CIELAB, FMC-2 and CIELUV were compared. Plots of the unit ellipses for the three colours in the CIE xy chromaticity diagram showed that in the high chroma colour, the CIELAB ellipse was almost at right angles to that of FMC-2 and CIELUV; FMC-2 and CIELUV were almost identical. In the other two regions, FMC-2 gave the smallest ellipse, CIELUV slightly larger, and CIELAB larger still. Paired comparisons were carried out by several observers who were asked to allocate a numerical grading of "0" if the two pairs of colour differences were equally large, "1" if one difference was slightly larger than the other and "2" if one difference was clearly larger than the other. Only differences equivalent to those normally encountered in industrial practice were viewed. If the pair of samples which was visually selected as being the larger was described by the colour-difference formula as being the smaller, then the visually assigned score was changed in sign. This gave a visual scale from -2 to +2, which was then plotted against the ΔE from the different formulae. Correlation coefficients were then determined for each formula. The exercise was repeated for each individual and from the correlation coefficients the best fit formula for each of the colour areas was determined for each observer. The number of times each formula was preferred was as follows:

	FMC-2	CIELAB	CIELUV
Moderate chroma red	0	17	5
Moderate chroma yellow	24	1	18
High chroma yellow	18	0	6

CIELAB was the preferred formula for moderate chroma reds whereas FMC-2 or CIELUV were the preferred formulae for yellows. CIELAB appeared completely unsatisfactory for moderate and high chroma yellows.

The investigation also contained a lightness scaling experiment in which the observers were asked to equate chromaticity differences with a five step lightness pair series. From the data of 39 observers, a plot of L versus chromaticity was obtained, $L = 0 + bC$. The following gradients were obtained:

	Gradient	SD
FMC-2	0.35	0.07
CIELAB	0.26	0.05
CIELUV	0.20	0.04

Thus, in these experiments the lightness difference was perceived 3-5 times more readily than predicted by the formula. Zeller drew attention to Judd's original definition of the NBS unit of colour difference which allowed for a scaling factor on lightness difference that could vary from 3 to 12 depending on the width of the dividing line between the samples¹⁰⁹. In the Zeller study the dividing line was extremely narrow since the observed samples consisted of two paint spots drawn down side by side. In such cases, Judd recommended the higher value of 13. Zeller also drew attention to work of Berger and Brookes¹¹⁰ in which they showed that they could obtain good agreement of calculated colour differences with visual judgements of light fastness scales, only if they increased the weighting of lightness in a MacAdam type formula by a factor of three. Zeller observed that there was need for exactly the same increase in weighting of lightness in the use of FMC-2 and a still larger factor for CIELAB and CIELUV, in his investigation. Zeller considered that the use of a variable scaling factor for lightness differences relative to chromaticity differences was necessary to obtain values of ΔE which conform well to visual observations under different observing conditions, and suggested that each industry should determine and use the scaling factor most appropriate to the observing conditions it normally found in practice.

20. The current position in relation to colour-difference assessment

Refs, 14, 25, 26, 39, 77, 111, 122

Kuehni¹¹¹ has commented that both the CIELAB and CIELUV formulae³⁹ correlate to about the same, less than satisfactory, degree with available small colour differences. He considers that the colour-difference problem is the major unsolved problem of colorimetry. The ideal perceptually-uniform colour-difference formula should be equally applicable to the small colour differences of interest for colour tolerance work, to large colour differences such as those occurring in colour reproduction. The evidence, mostly indirect, for the difference in the perception of large and small colour differences, leads to the conclusion that different constants

and parameters are likely to be required for large and for small colour differences. The evidence is mainly from comparisons of unit colour-difference contours based on threshold data and on large colour-difference data. A formula used for a particular purpose should, in the absence of a detailed understanding of the colour-difference perception mechanism, be based on data established under comparable conditions. Thus a formula for colour-difference thresholds should be based on threshold determinations, whilst one for colour tolerance work should be based on visual colour-difference data between threshold and 5-8 just noticeable difference steps, and one for large colour differences on corresponding visual data. In the first two cases it may not be possible, and indeed not essential, to have a formula that can be associated with a colour space.

Kuehni goes on to survey the available matching data. For larger colour differences there are principally the Munsell data and now also the OSA uniform colour scales data, the latter determined with greater scrutiny and in more depth. He thinks that the OSA uniform colour scales formula or another one fitted to the same data will remain the last word on larger colour differences for a long time. At the other extreme there are the determinations of the colour matching error by MacAdam²⁵ and by Brown and MacAdam²⁶, which are believed to be related to the threshold level of discrimination, the threshold determinations by Wyszecki and Fielder¹²², and the limited object-colour threshold determinations by Rich. In regard to the supra-threshold small colour differences are of greatest interest to most industrial users; however, the amount of data is limited if the so-called acceptability data are disregarded. Acceptability data determined in neutral experiments, such as the study by the AATCC Metropolitan Section, are considered by the CIE to be biased, even though there is no unequivocal evidence of such bias, and at the same time mounting evidence of the absence of bias.

If the Morley-Munn-Billmeyer⁷⁷ data are also disregarded, because the study involves relatively larger differences (averaging approximately four CIELAB units), only data for some 17 micro-spaces remain, namely: Robinson, Friele, VVVR data (ten standards), and the six sample sets evaluated in the ISCC Problems Subcommittee¹⁴. These are not sufficient as a basis for a new colour-difference formula. The next major effort in regard to colour differences should be in the area of suprathreshold small colour differences. It should involve the determination of a representative set of 30 to 40 unit colour-difference contours to cover the chromaticity diagram, where the unit is, for example, about two just noticeable differences from the standard.

Additional research must involve the question of unit contour expansion as a function of lightness, the weight of the lightness difference in the total colour difference, the influence of the background or surround on colour-difference perception, the question of contour tilting, and the effect of sample separation. An attempt must be made to determine the "standard small colour-difference observer".

21. Conclusions

Refs, 41, 82-84, 87, 97, 100, 102-105, 111, 114

The screening tests and other matching investigations carried out over the last 20 years have led to colour-

matching formulae which give reasonable agreement with the visual observer. However, the work of Kuehni^{84,87,97,100,104}, McLaren⁸³, McDonald⁸², and Gailey and McDonald¹⁰⁵ and others reviewed in this section has clearly shown that expansion of chromaticity tolerance occurs with increase in chroma and possibly with change in hue of the colours compared, also that chromaticity tolerance is probably not affected by changes in lightness of the colours compared. The investigations of McLaren¹⁰², Kuehni¹¹¹ and Lozano¹⁰³ indicate that differences in the pass/fail criteria of observers judging perceptibility and those judging acceptability are, as a first approximation, either non-existent or unimportant since the current established equations are placed in the same order of merit regardless of the matching criteria selected. However, at a more critical level, there does seem to be some evidence that the relative weighting of lightness to chromaticity varies according to the judgements criteria adopted.

Deficiencies have been noted in some of the more comprehensive data sets, such as those of HATRA and of Morley, and in other data sets the numbers of colours involved only represent very small fractions of the colour solid. There was, therefore, clearly a need for more comprehensive visual colour-matching data on which to test and develop improved colour-difference equations.

A series of papers by McDonald¹¹²⁻¹¹⁴ describes the preparation of such a set of comprehensive visual colour-difference pairs covering 640 samples grouped around 55 colour centres uniformly distributed throughout colour space. The samples consisted of spun polyester sewing thread dyed to match specific colour co-ordinates in ANLAB colour space by means of computer recipe prediction techniques. The samples, in the form of flat wound cards, were assessed for commercial acceptability by a panel of eight experienced colour matchers on five occasions. The resulting 25,590 pass/fail decisions were analysed to provide acceptability ratings for each of the sample pairs. The data provided information on the "within" and "between" observer errors in commercial acceptability matching and on the reproducibility of the panel. The experiment provided a useful data set for an evaluation of colour-difference formulae.

Methods of fitting tolerance ellipsoids in ANLAB(50) space to the experimental matching data and to the Davidson and Friede⁴⁴ matching data were described. The fitted ellipsoids varied in size according to their position in colour space. In particular, the hue and metric chroma axes of the ellipsoids were found to expand in size as the metric chroma of the colours increased, and the lightness axes were found to expand as the lightness of the colours increased. The hue axes were found also to be dependent on the hue angle of the colours. Various colour-difference equations were derived to describe these variations and these were found to give better correlation with visual observation than other colour-difference formulae. The most successful colour-difference equations were those which incorporated a hue-dependent term in the definition of colour tolerance.

Also described in the same study is an examination of a much larger group of pass/fail judgements carried out by a single observer in a commercial dyehouse, involving 8,454 visual decisions and 599 different colour standards. These data were analysed to provide curvilinear equations which define the dimensions of the colour-tolerance ellipsoid in different regions of colour space. These equations also

Performance of JPC 79 formula for pass/fail matching

Data	Disagreements (%)	No. of dyelots	No. of assessments
1976-77	9.7	617	25580
1977-78	13.6	8454	8454
1.6.78-6.10.78	10.2	1934	1934
1.3.79-16.2.80	10.8	4369	4369
All J. & P. Coats data	12.2	15374	40337
Lowest disagreement between a single observer and majority decision of matching panel	10.2	640	25580
Mean of individual observers disagreements with majority decision of matching panel	13.2	640	25580
Lowest disagreement between panel observers	9.5	640	25580
Mean disagreement between panel observers	17.3	640	25580

show that colour tolerance varies with the metric chroma and with the hue angle of the colour standard. The resultant hue-dependent colour-difference equation, known as the JPC79 equation¹¹⁴, was found to give improved agreement over published colour-difference equations, not only to the J. & P. Coats dyehouse data, but also to the matching panel data described above and to other published sets of matching data, viz. Davidson and Friede, Morley, HATRA 589, Kuehni-Metropolitan and ISCC data.

The single-observer colour-difference equation was subsequently tested for approximately one year in the dyehouse. During this period a further 6,303 pass/fail judgements were made and agreement between the formula and visual observer was approximately 90 per cent. No systematic deficiencies in the formula were found during this period. Half of the disagreements with visual judgement were found to lie in the borderline region within ± 10 per cent of the numerical pass/fail limit.

The JPC79 colour-difference formula¹¹⁴ derived, is considered to provide a viable alternative to visual pass/fail colour matching in the industrial field. Its effectiveness is summarised in the table above.

It should be noted that the improved pass/fail formulae derived by Kuehni^{84,87}, McLaren^{78,83}, Gailey and McDonald¹⁰⁵, and McDonald^{82,113,114} all depend on an accurate determination of the position in colour space of the colours involved. For this reason it becomes essential that the measuring instruments involved have absolute accuracy in addition to their capability of measuring colour difference.

22. Source list of colour-difference formulae

Details of colour-difference formulae and sources have been given in the following publications:

(a) "Colour Science" by G. Wyszecki and W. S. Stiles, *John Wiley & Sons Inc.*, 1967.
Adams (1942) Chromatic Valence Space

Adams Chromatic Value Diagram (ANLAB)
Saunderson and Milner (1946) Zeta Space
Glasser, McKinney, Reilly and Schnelle (1958) Cube Root System
Judd Hunter (1942)
Scotfield (1943)
Hunter (1948, 1958) Lab System
Wyszecki (1963) CIE UVW System (CIE 1964 space)
MacAdam (1942, 1943) Brown MacAdam Ellipsoids

(b) "Colour Metrics" by J. J. Vos, L. F. C. Friele and P. L. Walraven, *Institute for Perception TNO Soesterberg*, Holland, 1972.

A Review by L. F. C. Friele, pages 380-385, gives full details of each of the following formulae. From Friele's review the original sources are given below:

NBS formula (1942)	<i>JOSA</i> , 1942, 32, 509.
Hunter Lab (1958)	<i>JOSA</i> , 1958, 48, 985
CIE 1964	<i>JOSA</i> , 1963, 53, 1318
Nickerson Index of Fading (1936)	<i>Text. Res.</i> , 1936, 6, 509.
Balinkin	<i>Amer. J. Psychol.</i> , 1939, 52, 428.
Godlove (1951)	<i>JOSA</i> , 1951, 41, 760.
Munsell Renotation (1967)	<i>Colour Eng.</i> , 1970, 8, 36.
Adams, Nickerson and Stultz	<i>JOSA</i> , 1944, 34, 550.
Adams, Nickerson Chromatic Value (1944)	<i>JOSA</i> , 1944, 34, 550.
Saunderson, Milner and Zeta Space (1946)	<i>JOSA</i> , 1946, 36, 36.
Reilly Cube Root (1958)	<i>JOSA</i> , 1958, 48, 736.
Friele (1969)	1st AIC Progress "Colour 69", 275.
Simon Goodwin (1958)	<i>Amer. Dyestuff Rep.</i> , 1958, 47, 105.
Friele (1965)	<i>JOSA</i> , 1965, 55, 1314.
FMC-1 (1967)	<i>JOSA</i> , 1967, 57, 537.
FMC-2 (1967)	<i>JOSA</i> , 1971, 61, 118.
MacAdam Geodisc (1969)	<i>Die Farbe</i> , 1969, 18, 77.
DIN (1955)	<i>JOSA</i> , 1955, 45, 223.

(c) "Colour 73", *Adam Hilger*, London, p.21-51.
Wyszecki gives details of the following formula: CIE 1964, ANLAB, Cube Root, FMC-2, Godlove Munsell.

(d) *Colour Res. & Appn.* 2, 1977, 1, 13.
R. D. Lozano lists details of the following formulae: Reilly Cube Root, FMC-1, FMC-2, CIELUV, CIELAB, Judd-Hunter, Hunter-Schofield, MacAdam Geodisic Space, ANLAB, Saunderson-Milner Zeta Space.

(e) The remaining formulae mentioned in this review can be obtained from the following sources:

Friele FMC (1978) *Colour Res. & Appn.* 3, 1978, 2, 53.

NOTE: The equation on page 60 defining "δ" is incorrect. The correct equation is given on page 58.

CIELAB (1976, 1977) *JSDC*, 1976, 92, 337.
JSDC, 1977, 93, 428.

Kuehni MCR (1972) *J. Colour & Appn.*, 1972, 3, 4.

McDonald ΔE_a (1974) *JSDC*, 1974, 90, 189.

McLaren ΔE_a (1976) *JSDC*, 1976, 92, 317.

Gayley and McDonald (1977) *Can. Text. J.*, 1977, March, 57.

JPC 79 (1980) *JSDC*, 1980, 96, 486.

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References

- Judd, D. B. and Wyszecki, G., "Colour in Business, Science & Industry", *J. Wiley & Sons Inc.*, New York, 1967.
- Wright, W. D., "The Measurement of Colour", *Hilger & Watts*, 1969.
- Billmeyer, F. W. and Saltzmann, M., "Principles of Colour Technology", *Interscience*, 1966.
- Wyszecki, G. and Stiles, W. S., "Colour Science", *J. Wiley & Sons Inc.*, New York, 1967.
- "Colour Metrics", Helmholtz Memorial Symposium, Driebergen, 1971 AIC/Holland, c/o Institute for Perception TNO, Soestereberg, 1972.
- McLaren, K. and Coates, E., *JSDC*, 1970, 86, 368.
- McLaren, K., *JSDC*, 1970, 86, 354.
- McLaren, K. and Coates, E., *JSDC*, 1972, 88, 28.
- McLaren, K. and Rigg, B., *JSDC*, 1976, 92, 337.
- Birren, F., *Col. Res. & Appn.*, 1979, 4, 14.
- Nickerson, D., *Col. Res. & Appn.*, 1976, 1, 7.
- Nickerson, D., *Col. Res. & Appn.*, 1976, 1, 69.
- Nickerson, D., *Col. Res. & Appn.*, 1976, 1, 121.
- Nickerson, D., *Col. Eng.*, 1969, 7(5), Sept/Oct.
- Strocka, D., "Colour '73" AIC Meeting, York, *Adam Hilger*, 1973, p.453.
- Billmeyer, F. W., *Col. Eng.*, 1968, 6(1), Jan./Feb., 34.
- Judd, D. B., MacAdam, D. L. and Wyszecki, G., *JOSA*, 1964, 54, 1031.
- McLaren, K., *JSDC*, 1962, 78, 261.
- McLaren, K., *JSDC*, 1965, 83, 438.
- McLaren, K., *JSDC*, 1976, 92, 407.
- Nimeroff, I., *Col. Eng.*, 1967, 5, March/April, 24.
- Leete, C. G. and Lytle, J. R., *Col. Eng.*, 1966, Jan./Feb., 27.
- Stenius, A. S., *Col. Eng.*, 1971, May/June, 19.
- Wright, W. D., *Proc. Phys. Soc.*, London, 1941, 53, 93.
- MacAdam, D. L., *JOSA*, 1942, 32, 247.
- Brown, W. R. J. and MacAdam, D. L., *JOSA*, 1949, 39, 808.
- Brown, W. R. J., *JOSA*, 1957, 47, 137.
- Brown, W. R. J., *JOSA*, 1952, 42, 252.
- Brown, W. R. J., *JOSA*, 1952, 42, 837.
- Brown, W. R. J., *JOSA*, 1951, 41, 684.
- MacAdam, D. L., "Colour 69", Vol. 1, 293, *1st AIC Congress*, Stockholm, 1969, Muster-Schmidt, Göttingen, 1970.
- Newhall, S. M., Nickerson, D. and Judd, D. B., *JOSA*, 1943, 33, 385.
- Ladd, J. H. and Pinney, J. E., *Proc. Inst. Radio Eng.*, 1955, 42, 1137.
- Glasser, L. G., McKinney, A. H. and Reilly, C. D., *JOSA*, 1958, 48, 736.
- Wyszecki, G., *JOSA*, 1963, 53, 1318.
- McLaren, K., *Col. Eng.*, 1969, Nov/Dec., 38.
- Shklover, D. A., "Colour 69", 312.
- Friele, L. F. C., *Col. Res. & Appn.* 3, 1978, 53.
- Foster, R. S., *Col. Eng.*, 1966, Jan./Feb., 17.
- MacAdam, D. L., *JOSA*, 1943, 33, 18.
- Davidson, H. R. and Friede, E. J., *JOSA*, 1953, 43, 581.
- Simon, F. T. and Goodwin, W. J., "Rapid Graphical Computation of Small Colour Differences", *Union Carbide Corporation Plastics Division*.
- Davidson, H. R. and Hanlon, J. J., *JOSA*, 1955, 45, 617.
- Blackwood, N. K. and Billmeyer, F. W., *Col. Eng.*, 1966, March/April.
- MacAdam, D. L., "Colour Measurement and Tolerance", *Official Digest Federation of Societies for Paint Technology*, 1965, 37, 1487.
- Davidson, H. R. and Simon, F. T., *Am. Dyestuff Rep.*, 1958, 47, 105.
- Vos, J. J., *Colour Res. & Appn.*, 1979, 4, 208.
- Wyszecki, G., *JOSA*, 1963, 53, 1318.
- Wyszecki, G. and Wright, H., *JOSA*, 1965, 53, 1166.
- Glasser, L. G., McKinney, A. H., Reilly, C. D. and Schnelle, P. D., *JOSA*, 1958, 48, 760.
- Adams, E. Q., *JOSA*, 1942, 32, 168.
- Godlove, I. H., *JOSA*, 1951, 41, 760.
- Billmeyer, F. W. and Smith, R., *Col. Eng.*, 1967, 5(6), Nov/Dec, 28.
- Chickering, K. D., *JOSA*, 1967, 57, 537.
- Robinson, D., *JOCCA*, 1969, 52, 15.
- Thurner, K. and Walther, V., "Colour 69", vol. 2, 671.
- Jaekel, S. M., *Applied Optics*, 1973, 12, 1299.
- Jaekel, S. M., *JSDC*, 1975, 91, 242.
- Jaekel, S. M., "Color Metrics", *AIC, Holland*, 1971, 266.
- Berger, A. and Brockes, A., "International Farbtagung Lucern, 1965", *Musterschmidt-Verlag*, Göttingen, 1966, 331.
- Kuehni, R., *Col. Eng.*, 1970, 8, No. 1, 47.
- McLaren, K., *JSDC*, 1970, 86, 389.
- Strocka, D., *Appl. Optics*, 1971, 10, 1308.
- Coates, E. and Warburton, F. L., *JSDC*, 1968, 84, 467.
- Coates, E. and Rigg, B., *JSDC*, 1970, 86, 40.
- Coates, E., Day, S. and Rigg, B., "Colour 69", 641.
- Coates, E., Day, S. and Rigg, B., *JSDC*, 1969, 85, 312.
- Coates, E., Provost, J. and Rigg, B., "Color Metrics".
- Mudd, J. S., "Color Metrics", *AIC, Holland*, 1964, 48, 452.
- Mudd, J. S. and Woods, M., *JOCCA*, 1970, 53, 852.
- Schultze, W., "Color Metrics", 254.
- McLaren, K., *JSDC*, 1970, 86, 389.
- McLaren, K., *JSDC*, 1976, 92, 338.
- McLaren, K., *JSDC*, 1953, 69, 404.
- Vos, J. J. and Walraven, P. L., "Color Metrics", 69.
- CIE Colorimetry Committee, *JOSA*, 1974, 64, 896.
- Morley, D. I., Munn, F. and Billmeyer, F. W., *JSDC*, 1975, 91, 229.
- McLaren, K., *JSDC*, 1976, 96, 317.
- Robertson, A. R., *Col. Res. & Appn.*, 1977, 2, 7.
- ISO/TC38/SCI Committee 10th Meeting, Paris, 1974.
- McLaren, K. and Rigg, B., *JSDC*, 1977, 93, 428.
- McDonald, R., *JSDC*, 1974, 90, 189.
- McLaren, K., "Color Metrics", 296.
- Kuehni, R., *J. Col. & Appearance*, 1971, 1(1), 30.
- Strocka, D., *J. App. Optics*, 1971, 10, 1308.
- "Colour 69", 1st AIC Congress, Stockholm, 1969, *Muster-Schmidt*, Göttingen, 1970.
- Kuehni, R., *J. Col. & Appearance*, 1972, 1(3), Nov/Jan, 4.
- Metropolitan Section, *Textile Chem. & Col.*, 1971, 3, 248.
- Billmeyer, F. W., "Color Metrics".
- Schultze, W., "Color 69", Stockholm, vol. 2, 621.
- Steen, P. and Tonnquist, G., "Color 69", Stockholm, vol. 2, 717.
- Schultze, W. and Gall, L., *J. Col. & Appearance*, 1971, 1(1), 17.
- Brown, W. R. J. and MacAdam, D. L., *JOSA*, 1949, 39, 808.
- Glasser, L. G., et al., *JOSA*, 1958, 48, 736.

95. Padgham, C. A. and Rowe, S. C. H., *Col. Eng.*, 1973, 2(1), Spring.
96. Rich, R. M., Billmeyer, F. W. and Howe, W. G., *JOSA*, 1975, 65, 956.
97. Kuehni, R., *JSDC*, 1975, 91, 68.
98. McLaren, K., *JSDC*, 1975, 91, 376.
99. Jaeckel, S. M. and Ward, C. D., *JSDC*, 1976, 92, 353.
100. Kuehni, R., *Col. Res. & Appn.*, 1977, 2, 5.
101. Kuehni, R., *JOSA*, 1976, 66, 497.
102. McLaren, K., *JSDC*, 1976, 92, 364.
103. Lozano, R. D., *Col. Res. & Appn.*, 1977, 2, 13.
104. Kuehni, R. G. and Marcus, R. T., *Col. Res. & Appn.*, 1979, 4, 83.
105. Gailey, I. and McDonald, R., *Can. Textile J.*, 1977, March, 57.
106. Cooper, A. C. and McLaren, K., *JSDC*, 1973, 89, 41.
107. Nunn, R. J., *Col. Res. & Appn.*, 1977, 2, 171.
108. Zeller, R. C. and Hemmendinger, H., *Col. Res. & Appn.*, 1979, 4, 71.
109. Judd, D. B., "Colour in Business Science and Industry", 3rd ed., *Wiley*, New York, 1975, p.317.
110. Berger, A. and Brockes, A., *Die Farbe*, 1962, 11, 263.
111. Kuehni, R., *Col. Res. & Appn.*, 1977, 2, 187.
112. McDonald, R., *JSDC*, 1980, 96, 372.
113. McDonald, R., *JSDC*, 1980, 96, 418.
114. McDonald, R., *JSDC*, 1980, 96, 486.
115. Nickerson, D. and Stultz, K. F., *JOSA*, 1944, 34, 550.
116. Glasser, L. G. and Troy, *JOSA*, 1952, 42, 652.
117. Opler, Meikle and Charlesworth, *JOSA*, 1953, 43, 550.
118. ASTM Designation D1482 (1957).
119. Friele, L. F. C., *Farbe*, 1961, 10, 193.
120. Wyszeccki, G., *JOSA*, 1968, 58, 290.
121. Gailey, I., *JSDC*, 1967, 83, 481.
122. Wyszeccki, G. and Fielder, G. H., *JOSA*, 1971, 61, 1135.

Milligram determination of formaldehyde in a resin using ammonium hexanitratocerate (IV) as an oxidant

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Summary

In this paper a method is described for the milligram determination of formaldehyde in solution and in modified phenolic resin. The sample under examination was reacted with an excess of Ce(IV) solution in an acetic acid medium for two minutes on a water bath. After the reaction, the unreacted Ce(IV) was determined by titrating against Fe(II) using ferroin as an indicator. A blank experiment was also run under identical conditions, and

the determination of the percentage of the formaldehyde present was calculated from the difference in the two readings. The method is easily operable under ordinary laboratory conditions and does not involve the use of sophisticated instruments. The Ce(IV) reagent is stable in all climatic conditions and does not decompose on storage.

Keywords

Raw materials for coatings binders (resins, etc.)

phenolic resin

Raw materials used in manufacture or synthesis of ingredients for coatings

formaldehyde

Processes and methods primarily associated with analysis, measurement or testing

analytical method

La détermination, au moyens de l'hexanitratocérate (IV) d'ammonium en tant qu'oxydant, de formaldéhyde se présentant en quantités milligrammiques dans une résine synthétique

Résumé

Dans cet article on décrit une méthode pour la détermination de formaldéhyde où il se présente en quantités milligrammiques, soit dans une solution, soit dans une résine formophénolique modifiée. On fait réagir l'échantillon, pendant deux minutes sur un bain-marie, avec un excédent chiffré d'une solution en l'acide acétique de Ce(IV) ions. Après que la réaction fût terminée, la quantité de Ce(IV) ions inaltérés était déterminée par titrage avec Fe(II) en se servant de ferroïne comme indicateur. Un essai

en blanc était effectuée sous les conditions identiques, et le titre de l'échantillon est dérivé de la différence entre les deux lectures de la burette. La méthode se fait facilement sous les conditions normales de laboratoire. Elle ne fait aucun appel aux appareils avancés. Le réactif Ce(IV) est stable sous toutes conditions climatiques et n'est pas susceptible à se dégrader lors du stockage.

Die Bestimmung, mittels Ammoniumhexanitratocerate (IV) als Oxidationsmittel, des sich in Milligrammquantitäten und in einem Kunstharz befundenen Formaldehyd

Zusammenfassung

In diesem Aufsatz wird es eine Methode zur Bestimmung entweder in einer Lösung oder in einem modifizierten Phenolformaldehydharz des sich in Milligrammquantitäten befundenen Formaldehydes. Der Muster lässt sich während zweier Minuten mit einem bestimmten Übermass von einer Essigsäurelösung der Ce(IV) Ionen auf einem Wasserbad reagieren. Als die Reaktion geendet hatte, wurde die nichtreagierten Ce(IV) Ionen durch Titration mit Fe(II) und Ferroïne als Indikator bestimmt. Ein

Blindversuch unter den selben Bedingungen wird auch durchgeführt und der Titer des Musters wird aus dem Unterschied zwischen den beiden Versuchen bestimmt. Die Methode wird unter gewöhnlichen Laborbedingungen leicht durchgeführt. Sie befasst sich nicht mit komplizierten Geräten. Der Ce(IV) Reagent zeigt sich stabil bei allen klimatischen Bedingungen und zerstört sich nicht bei der Lagerung.

Introduction

Refs. 1-6

Phenolic resins are well known to the paint and varnish industries. Their main uses are in oleoresinous varnishes.

The effect of the resins, whatever their type, is to decrease drying time since the resins are hard in their normal states and require only solvent evaporation for drying. It should be noted that the addition of resins means that solvent (white spirit, turpentine or aromatic solvents) will be required to reduce the viscosity of the paint, though the

low molecular weights of the oils, resins and oleoresinous products allow medium high solids at application viscosities. The phenolic resins also improve properties of paint films, such as gloss, hardness (though flexibility is reduced), outdoor durability and chemical resistance.

For the standardisation of these resins it is necessary to know the percentage of formaldehyde used in them. The available procedures^{1,2} for the determination of formaldehyde in a solution (formalin) and in a resin are too complicated and not applicable on a small scale. The present work reports on a rapid and convenient method for the determination of formaldehyde in formalin and in a modified phenolic resin using ammonium hexanitratocerate (IV) as an oxidative reagent on the microscale.

Several organic and inorganic compounds can be determined by using different types of ceric reagents. Diethylene tetraammonium sulfatocerate was first used by Singh and Verma³ for the oxidative determination of thioureas. Benrath and his co-workers⁴ used ceric sulfate for the determination of several nitrogenous compounds. Cerimetric estimation of some thioureas in a sulfuric acid medium has also been reported⁵. Recently, Beg, Usmani and Shukla⁶ reported a good oxidative micro-procedure for the sulfur containing amino acids using ammonium hexanitratocerate (IV) as the reagent.

Experimental

Reagents

Ammonium hexanitratocerate (IV) solution (0.15N)

20g of ammonium hexanitratocerate (IV) (AR, BDH) was accurately weighed and dissolved in 8.3ml of 15N nitric acid and made up to 250ml with distilled water.

Ferrous ammonium sulfate (0.025N)

4.9016g of ferrous ammonium sulfate was accurately weighed and dissolved in distilled water followed by the addition of 10ml of concentrated sulphuric acid and the solution was made up to the mark with distilled water in a 500ml volumetric flask.

Glacial acetic acid

(AR, BDH)

Sulfuric acid (1N)

A (1N) solution of sulfuric acid was prepared by dissolving AR, BDH (v/v) in distilled water.

Sample solution

0.5ml of formaldehyde solution (formalin) was made up to 500ml with distilled water.

The sample solution of modified phenolic resin was prepared in the following way. 300mg of the sample was accurately weighed and dissolved in carbon tetrachloride in a 100ml volumetric flask. The solution was made up to the mark (100ml) with carbon tetrachloride.

1,10-phenanthroline

Ferrous sulfate indicator 0.02N solution.

Procedure

An aliquot (1-12ml) of the sample was placed in a 250ml conical flask followed by the addition of 5ml of glacial acetic acid. 5ml of 0.15N ammonium hexanitratocerate (IV) was added. The mixture was allowed to react for two minutes on a water bath. After the reaction, the conical flask was cooled and 10ml of 1N sulfuric acid was added. The unreacted Ce(IV) was titrated against standard ferrous ammonium sulfate using one drop of indicator solution. A reddish orange colour develops at the end point.

A blank experiment was run under identical conditions using all the reagents except for the sample solution. The amount of formaldehyde in the sample was calculated by the difference between the titre values of the ferrous ammonium sulfate Fe(II) from the blank and from the experiment.

$$\text{Percentage formaldehyde (mass)} = \frac{(B-S) N \times 0.3}{M}$$

Where:

B = Volume in ml of standard ferrous ammonium sulfate solution used in blank experiment.

S = Volume in ml of standard ferrous ammonium sulfate solution used in experiment.

N = Normality of ferrous ammonium sulfate solution.

M = Mass in grams of material taken.

Results and discussion

This method was successful in the milligram determination of formaldehyde in a solution (formalin) and in a modified phenolic resin. The results obtained are shown in tables 1 and 2. The percentages of formaldehyde obtained for the sample were fairly constant with the varying sample size, 1-12ml. 5ml of glacial acetic acid was essential for making the medium acidic. Increasing the concentration of acetic acid did not lead to any improvements either in the consistency of results or in the speed of the reaction.

The reaction time was established in the following way.

Table 1
Milligram determination of formaldehyde in formalin with ammonium hexanitratocerate (IV)

Aliquot (ml)	Amount of formaldehyde present (mg)	Value (B-S) (ml)	Recovery of formaldehyde (%)
1	1	5.00	37.50
1	1	5.00	37.50
1	1	5.00	37.50
2	2	9.98	37.42
2	2	9.98	37.42
2	2	9.98	37.42
3	3	14.96	37.40
3	3	14.96	37.40
3	3	14.96	37.40
4	4	19.92	37.35
4	4	19.92	37.35
4	4	19.92	37.35

Table 2
Milligram determination of formaldehyde in
modified phenolic resin with ammonium hexanitratocerate (IV)

Aliquot (ml)	Amount of formaldehyde present (mg)	Value (B-S) (ml)	Recovery of formaldehyde (%)
2	4.720	2.72	4.32
2	4.720	2.72	4.32
2	4.720	2.72	4.32
4	9.440	5.44	4.32
4	9.440	5.44	4.32
4	9.440	5.44	4.32
6	14.160	8.14	4.31
6	14.160	8.14	4.31
6	14.160	8.14	4.31
8	18.880	10.86	4.31
8	18.880	10.86	4.31
8	18.880	10.86	4.31
10	23.600	13.58	4.31
10	23.600	13.58	4.31
10	23.600	13.58	4.31
12	28.320	16.26	4.30
12	28.320	16.26	4.30
12	28.320	16.26	4.30

The reaction mixture was allowed to boil on a water bath for different time intervals, 1, 2, 3, 4, 5 and 10 minutes. It was observed that the consumption of the Ce(IV) reagent

ceased after two minutes reaction time. Increasing the reaction time beyond this did not result in any increase in the amount of formaldehyde determined. For accurate results it was observed that about twice the amount of Ce(IV) reagent normally consumed was required; while a larger excess gave poorer results. The amounts of formaldehyde determined in the solution and in the modified phenolic resin were 37.5 per cent and 4.3 per cent respectively.

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References

1. Indian standard specification, IS 3321, 1973.
2. Indian standard specification, IS 354, Part II, 1971.
3. Singh, B. and Verma, B. C., *Mikrochim. Acta.*, 1974, 1, 123.
4. Benrath, V. A. and Ruland, Z., *Anorg. Chem.*, 1920, 114, 267.
5. Yadav, K. L. and Jain, S. K., *The proceedings of National Academy of Sciences India*, Section A, 1966, 34, 521.
6. Beg, M. M., Usmani, Q. S. and Shukla, I. C., *Mikrochim. Acta.* (Wien), 1977, II, 221.

Next month's issue

The Honorary Editor has accepted the following papers for publication. They are expected to appear in the April issue of the *Journal*:

Room temperature organic phosphating by G. Guidetti and R. I. Jones

Structural changes in polymer films. Part 1: the influence on the transition temperature on the electrolytic resistance and water uptake by J. E. O. Mayne and D. J. Mills

New modified polyester-type resins by F. A. Nassar, M. Moustafa and A. M. Naser

Influence of the use of chlorinated rubber on the anticorrosive properties of paints for ships' hulls by V. Rascio, C. A. Giudice and J. C. Benitez

Coatings for the internal lining of concrete crude oil storage tanks*

By O. C. Vorster

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Summary

This paper deals with the evaluation of three coating systems for the internal coating of very large concrete crude oil storage tanks.

Three different approaches to the problem are discussed, namely:

- (i) a complete epoxy system
- (ii) a system consisting of an emulsion-based slipcoat followed by an epoxy topcoat, and
- (iii) a complete emulsion-based system.

Keywords

Types and classes of coatings and allied products

emulsion paint
epoxy paint
tank coating

Types and classes of structures or surfaces to be coated

concrete

Revêtements pour les surfaces internes de citernes en béton pour le stockage de pétrole brut

Résumé

Cet article traite de l'évaluation de trois systèmes de revêtements pour les surfaces internes de grosses citernes en béton pour le stockage de pétrole brut.

On discute trois diverses tentatives pour résoudre le problème en question, à savoir:

- (i) Un système exclusivement époxyde.
- (ii) Un système comprenant une légère sous-couche à base d'une émulsion suivie par une couche de finition époxyde; et
- (iii) Un système exclusivement à base d'émulsion.

Beschichtungen für die inneren Oberflächen der Roherdölvorratsgefäße aus Beton

Zusammenfassung

Dieser Aufsatz befasst sich mit der Auswertung dreier Beschichtungssysteme für die inneren Oberflächen der grossen Roherdölvorratsgefäße aus Beton.

Es wird drei verschiedenen Versuche diskutiert, das Problem zu lösen, nämlich:

- (i) Ein vollständiges Epoxidsystem.
- (ii) Ein System, das aus einem auf Emulsion gegründeten Vorlack und einem folgendem Epoxidüberzug besteht.
- (iii) Ein vollständiges aus einem auf Emulsion gegründeten System.

1. The problem

Refs. 1-3

Surface coatings are usually applied to concrete to protect the concrete from the environment to which it is exposed, or to provide it with required aesthetic properties.

The painting of the inside of concrete tanks serves another purpose, namely that of containing liquid and thus preventing leakage and contamination of the surroundings.

The consequences of leakage of petroleum products can be disastrous. An incident has been reported where an underground tank, which was used to store about 1,000 litres of petrol, leaked causing the loss of several thousand litres of fuel resulting in the permeation of dangerous fumes into basements within a radius of some 100 metres¹.

The main disadvantage of concrete is its very poor capability of carrying tensile loads. This can, however, be overcome by reinforcement with steel. In prestressed concrete, high tensile steel wires are used to maintain the concrete under compression. This steel can only function successfully if it is free from corrosion. Provided the covering is adequate the steel will not corrode, but as hairline cracks are inherent in a concrete structure as a result of shrinkage, water can reach the steel reinforcement and, with time, the alkalinity of the concrete surrounding the steel will decrease and corrosion will take place. It is therefore necessary to protect the concrete against the ingress of liquids that may cause corrosion of the steel.

It may also be necessary to protect the concrete itself from the liquids stored in the tanks, especially if the liquids are acidic.

*Paper presented at the South African Division's 8th National Symposium.

In an early study of the penetration of concrete by aviation fuel, it was reported that a medium sized unlined tank of dense crackfree high quality concrete might be expected to lose about 1 per cent of its capacity of fuel during the first few months of service.²

In large concrete tanks, differential settling of the tanks is a distinct possibility. Fairly large cracks may therefore be expected in the concrete, and coatings will have to be relied upon to provide the necessary "crack-bridging" to enable the tank to contain the liquid successfully.

In these large concrete tanks two distinct types of cracks are bound to be present:

- (i) Cracks due to shrinkage and thermal movement of the concrete. These cracks will have to be covered by the coating system and may or may not exhibit movement after the coating is cured.
- (ii) Cracks due to settlement of the tank during testing or filling operations. Here the coating system will have to cope with cracks that appear in the concrete after the coating is applied. These cracks can be up to 0.2mm in width.

According to Closner³, concrete tanks provide the following features that render them suitable for oil storage:

- Savings in steel usage
- Savings in land
- Shock resistance
- Fire resistance
- Low maintenance
- Good Holding properties
- Larger capacity tanks

2. Requirements for a suitable coating

The requirements that are expected of a coating system for concrete crude oil storage tanks can be summarised as follows:

(i) Product resistance

The coating system has to be resistant to crude oil, sea water and the sulfate reducing bacteria present in crude oil.

(ii) Permeability

In order to be effective as a lining, low permeability is a very important requirement.

(iii) Adhesion

The coating should adhere well to the substrate even after prolonged periods of immersion, and the intercoat adhesion of the various layers should be good.

(iv) Crack-bridging properties

The coating system should be able to cope with cracks of up to 0.2mm in width that appear in the concrete after application of the coating.

(v) Rheology

In order to provide a uniform film over both the high as well as low points on the substrate, the coating should have the correct rheology. This will also lead to effective crack-bridging properties.

(vi) Application properties

As very large surfaces are to be coated, usually in a very short time period, the coating should be easy to apply preferably with unsophisticated equipment.

(vii) Acceptable to environment

Due to the large volumes of paint involved, pollution of the environment is a distinct possibility and great care should be taken in this regard.

(viii) Cost

Finally, but not least in importance, the cost should be reasonable.

3. Survey of some related work in this field

Refs, 2, 4-6

In 1943 the Bureau of Reclamation, US Department of Interior², demonstrated that alkylate gasolines could be stored in good quality concrete tanks. There was some seepage through these tanks initially, but gums formed, gradually sealing the pores and the very small cracks that inevitably exist in concrete. The same study showed, however, that highly aromatic gasolines would dissolve these gums, eventually resulting in leakage. Hence, discretion should be exercised in the choice of products to be stored in concrete tanks.

Cowling, Eggert and Alexander⁴ evaluated a whole range of products for their suitability as coatings for concrete fuel storage tanks. The range included nylon, vinyl acetate and vinyl chloride copolymers, furans, polyesters, epoxies, phenolics, polysulfide rubber, acrylonitrile rubber, neoprene, and acrylonitrile vinylidene chloride copolymers. With the exception of the nitrile rubbers and neoprenes, many products based on the other materials displayed good to fair inertness towards the test fuels.

The nylons, furans, phenolics, epoxides and polyesters were considered to be impractical due to problems associated with application and extensibility. The epoxides were, in fact, considered excellent materials but for their lack of extensibility. However, it was felt that this property might be improved upon in the future.

The approach in this investigation was to devise a coating with the product resistance of the vinyls combined with the flexibility of the polysulfide rubbers.

The outcome of this work was the US Navy specification NAFAC TS-09801, Lining System, Interior for Concrete Storage Tanks (for Petroleum Fuels).

The coating described in this specification is, however, not suitable for the storage of crude oil as the mercaptans in the crude oil degrade the polysulfide rubber used as a plasticiser in this coating.

Makansi⁵ reported that when reinforced with glass fibre, an epoxy-based coating remained intact when the concrete substrate was cracked. This cracking was in the form of many very small cracks over a large area around an initial crack.

Marijs and Bonafont⁶ evolved a theory which allows membrane stresses and strains to be calculated as a function of the mechanical properties of the constituent materials and of the associated substrate movement.

4. Description of coating systems

The investigation reported here covers the following three coating systems:

Coating system A

This consists of a first layer of an aromatic amine cured epoxy reinforced with a glass fibre cloth (191g m^{-2}).

The topcoat was a pigmented aromatic amine cured epoxy coating applied at a coating mass of 500g m^{-2} . The intercoat time was 24 hours and the material was applied by means of two-component hot airless spray equipment.

Coating system B

The first coat consists of a flexible sliplayer based on an acrylonitrile/butyl acrylate copolymer emulsion. The sliplayer was slightly tinted and applied by means of airless spray equipment at a coating mass of 500g m^{-2} .

The topcoat used was the same as in system A and the intercoat time was 72 hours.

Coating system C

The coating system consisted of three layers of a pigmented acrylonitrile/butyl acrylate copolymer emulsion. The PVC was less than 10 per cent and the individual layers were applied at a film mass of 400g m^{-2} . The various coats were applied at 48 hour intervals by means of airless spray equipment.

Preparation of concrete substrate

The concrete was sandblasted to remove all traces of laitance and cleaned to a dust-free condition before application of the first layers.

5. Comparison of the different coating systems

Resistance to crude oil

The coating systems were immersed in crude oil both on a concrete substrate and as free films for periods of up to 18 months. After this immersion period, the coatings were compared with control samples by means of various physical tests such as hardness, scratch resistance, abrasion resistance, tensile strength, stiffness and change in glass-transition temperature.

The emulsion-based coatings used in system C and as a slipcoat in system B showed less change upon immersion in crude oil than the epoxy-based coating used in coating system A and as a topcoat in B.

Resistance to sea water

After an immersion period of eighteen months no significant difference in sea water resistance between the coating systems could be detected. However, it should be noted that the emulsion coatings should be aged for at least 2 weeks before exposure to sea water to ensure removal of residual solvent.

Resistance to sulfate reducing bacteria

After exposure to the bacterium *Desulphovibrio desulphuricans* and facultative mucoid bacilli for a period of 8 months at 25°C , none of the coating systems showed any breakdown.

Permeability

When the permeability to crude oil was determined by means of an inverted Gardner-Park cup, the following results were obtained:

Coating system	Permeability ($\text{g day}^{-1}\text{m}^{-2}(100\text{ microns})^{-1}$)
A	0.64
B	0.08
C	0.58

Adhesion

The adhesion to the concrete substrate as well as the intercoat adhesion was found to be good. This was true even after very long periods of immersion in both crude oil and sea water.

Crack-bridging properties

Coated concrete beams were loaded progressively at the middle while being supported at both ends, the crack width in the concrete was then noted when failure of the coating occurred.

The following results were obtained:

Coating system	Maximum crack width (mm)
A	0.5
B	0.3
C	0.5

It should be noted however, that, as the epoxy coatings tend to become brittle with immersion in crude oil, the ability to bridge cracks will decrease with time.

Rheology

It was found that due to the rheopectic nature of the emulsion-based coatings, they tended to form even coatings over the very uneven sandblasted substrate.

Application properties

Although no coating should be applied to an improperly

prepared and cleaned substrate, coating system A is less susceptible to dust than the other two systems.

The equipment used for the application of coating system C was far less complicated and costly than those used for the epoxy systems. For system C, less breakdown was experienced, fewer people were needed to operate the equipment and there was no need for maintaining a required temperature and mixing rate as for the epoxies.

The application times for the different systems were in the ratio 2:1:0.75 (A/B/C).

Here the emulsion-based coatings have a distinct advantage over the epoxy coatings. In practice it meant that the sandblasting and spraying operation could be separated. This meant that less contamination of the substrate took place during spraying operations.

No problems were experienced with coating system A when the atmospheric temperature and humidity changed, but when temperatures were low and the relative humidity was very high the emulsion coatings took a long time to dry. Correct planning of the spraying programme did, however, solve this problem.

During application of a coating system the need for repairing damaged areas frequently arises. With the crosslinked epoxy coating, the surface had to be re-sandblasted, also a key area on the adjacent undamaged epoxy had to be sandblasted before repair could be carried out.

With the emulsion systems, no intercoat adhesion problems were experienced and only the substrate had to be cleaned from dust.

Quality control

The emulsion coatings were far easier to control.

Only film thickness and film sequence had to be controlled. With the epoxy coatings the film thickness, mixing ratio and intercoat times had to be controlled.

Environmental hazards

The emulsion-based coatings were far less of a problem than the epoxies. Although the emulsion-based coatings contained mercury, the level of mercury in the air during the spraying operation was well below the accepted TLV.

Cost

The cost of preparation of the substrate, material, labour, overheads and profit to contractor were as follows:

Coating system	Cost (Rand m ⁻²)
A	22.10
B	15.20
C	8.30

6. Conclusions

The advantages of the various coating systems as affected by the requirements for the successful coating of concrete crude oil storage tanks are given in the following table.

The code used is as follows:

- Indicates a disadvantage
- Indicates no advantage or disadvantage
- + Indicates an advantage

Summary of requirements

Property	Coating system		
	A	B	C
Cost per tank	-	○	+
Resistance to crude oil	-	○	+
Resistance to sea water	○	○	○
Permeability to crude oil	○	+	○
Crack bridging	○	+	+
Adhesion	○	○	○
Bacteriological resistance	○	○	○
Surface preparation	+	○	○
Application equipment	-	○	+
Application rate	-	○	+
Effect of environment on application rate	+	○	-
Ease of repair	-	○	+
Quality control	-	-	+
Environmental hazards	-	-	+

From the above table it can be concluded that coating system C is technically and economically the most suitable for the coating of large concrete crude oil storage tanks.

It is of interest that the cheapest of the three systems is also the most suitable. This is a very rare occurrence in the coating world.

Acknowledgement

Ref. 7

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References

1. "The migration of petroleum products in soil and ground water. Principles and counter measures", *American petroleum institute*, Publication No. 4149, 1972, December.
2. Laboratory Report CH-40, *Bureau of Reclamation*, 1943, May.
3. "Design and application of prestressed concrete for oil storage", *American society for mechanical engineers*, Petroleum mechanical engineering conference, Tulsa, Oklahoma, 1975, September.
4. Cowling, J. E., Eggert, I. J. and Alexander, A. L., *Industrial and engineering chemistry*, 1954, September, 46, 1977.
5. Makansi, L., "Epoxy-based membranes for the impermeability of concrete structures", *ICP International Symposium*, Liège, 1977, June.
6. Marijs, P. D. and Bonafont, R. L., *Journal of applied chemistry*, 1970, 20, 11.
7. Vorster, O. C., "Coating systems for the internal lining of concrete crude oil storage tanks", Dip.Tech. Thesis, 1980, December, Technikon, Pretoria.

OCCA meetings

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London

Inks and print technology

A one-day symposium entitled "Inks and print technology – a survey of current advances" was held by the London Section in conjunction with Thames Polytechnic at the Polytechnic, Woolwich, SE18 on Wednesday 18 November 1981.

Ninety-three delegates drawn from the whole of the UK were registered at the symposium which was chaired in the morning by Mr B. F. Gilliam, Chairman, London Section OCCA, and in the afternoon by Mr L. Randall, Chairman, Society of Printing Ink Manufacturers Training Board.

Adhesion of printing inks to plastic films

The first lecture was presented by Mr P. Jones, Lorilleux International, on the "Adhesion of printing inks to plastic films and their subsequent lamination". In this well illustrated paper Mr Jones firstly examined the different types of adhesion:

- physical – such as absorption into paper substrates
- physico-chemical – on e.g. polyethylene or orientated polypropylene, which is a mixture of hydrogen bonding, Van de Waals forces etc. between reactive sites on the ink resin and the substrate
- chemical – reaction between reactive inks and functional sites on the substrate

The adhesion of inks onto two commonly used laminating films was discussed in detail.

PVDCI coated cellulosic films were easily wetted by both water-borne and solvent-borne inks, the inks critical surface tension being about 40 dyne cm^{-1} . Particularly good adhesion could be achieved from polymeric resin-based ink solubilised in alcohol/ester solvents and plasticisers.

Basic polyethylene and polypropylene films were much more difficult to get adhesion to. They were inert, having a wettability tension of 32 dyne cm^{-1} and were not wetted by printing inks. To effect adequate adhesion, the surface of the film had to be modified, e.g. by flame treatment or corona discharge. Exposure of the film to corona discharge resulted in a free radical initiated increase in the amount of oxidised species on the surface of the film. All the oxidised species were polar and the surface tension was increased. STs in the range $38\text{-}40 \text{ dyne cm}^{-1}$ were preferred.

It was as a result of these highly active polar sites that other reactive groups, such as those in polyamide resins, allowed inks to adhere to polyethylene or polypropylene films.

Similar pretreatment was required when cast orientated or co-extruded polypropylene films were to be printed on. Inks for these substrates fell into two areas. Low specification end-users were served by relatively simple polyamide based co-solvent inks, which exhibited excellent adhesion.

High specification inks were more difficult to achieve. Such inks needed to have, for example, high heat resistance properties to allow for printability onto areas that could be heat sealed. Polyamide inks did not have heat resistance and instead either nitrocellulose based inks (modified to give adhesion) or two-pack inks were used. The latter approach was the best for achieving high adhesion elastomeric films on polypropylene, although both real and psychological problems may exist for the printer.

Mr Jones then considered inks which were subsequently adhesive laminated. The composition of the particular ink, in both the selection of the resins and the types and levels of additives, was very critical.

Film to film laminating adhesives were usually two-pack isocyanate/hydroxyl containing polyester or polyether resins. Polyamide inks could not be used as the presence of amide groups in the ink would upset the critical -NCO/OH ratio through a competing reaction with -NCO and reduced bond strengths would result.

Amongst other properties, the inks needed a high level of physico-chemical adhesion and to provide a highly wettable surface to the laminating adhesive both when wet and in the period between drying and laminating. Laboratory testing of inks could only be adequately carried out by laminating printed films and checking bond strengths over a period of at least 30 days.

Bond strength was imprecisely defined. Different tests gave different values. It was considered that the most suitable method was to use a constant-pull delaminating machine, such as an Instron, and to display the force used to delaminate graphically. Typical bond plots such as steady bond strengths and zippy bonds were described.

A number of possible causes of zippy bonds (uneven bond strength) were discussed and included:

- Not enough adhesive
- Poor ink adhesion
- Adhesive overcured
- Poor wettability of the ink

The possible areas of bond breakdown within the laminate were discussed in more detail. The co-operation of the convertor, the end-user, the packaging machine manufacturer, the film supplier and the ink and adhesive manufacturer were all necessary to ensure expensive claims and scrap were to be avoided.

Possible combinations leading to delamination, which were discussed in detail, were:

- Film/coating failure
- Ink/film failure
- Ink/adhesive failure
- Adhesive/second film failure
- Ink/ink failure

Recent advances in screen printing

The second paper was presented by Mr G. Summers of Sericol Ltd who at very short notice stood in for Mr H. Lavell. Mr Summers discussed "Recent advances in screen printing".

The screen printing process was first reviewed in detail. The screen or mesh was made of nylon, stainless steel or polythene. Inks were pushed through areas of the screen which were not blocked by a photographically produced stencil. The same basic principle was used regardless of the application technique and applied equally to slow hand presses as it did to fully automatic machines.

The screen printing process resulted in the application of relatively thick films compared with other printing processes. Litho, letterpress and gravure applied around 5 microns or below. Thin film screen printing applied up to 15 microns and thick film up to 40 microns.

The high film thicknesses applied and the printing method allowed a wide variety of substrates to be printed on a wide range of resin systems to be used.

In discussing the advances in screen printing inks, the pressures of the escalating costs of oil-derived raw materials and the increasing cost of evaporating organic solvents were first discussed. These pressures inevitably influenced the direction of developments.

Water-borne inks, either fully water-borne and dilutable with water, solvent-borne and dilutable with water or solvent/water-borne and water-dilutable, were discussed. Whilst water-borne inks were widely used in textile printing, their use on paper substrates was limited due to cockling of the paper. Extra heat was required to evaporate the water and this could negate the savings made in using non-oil derived solvents. Microwave heaters could be used but their use was restricted to the fully water-borne systems, organic solvents not being polar enough to be evaporated. A further limitation of water-borne systems was the need to waterproof the stencil system.

UV cured inks offered a number of advantages over conventional and water-borne inks in meeting the pressures noted above. They were solvent-free and very fast curing upon exposure to UV light. However, they were more expensive and were, unlike most screen inks, chemically cured coatings.

UV screen ink composition was discussed in detail and the benefits they offered were examined.

Whilst the very high solids resulted in minimal volatile emission, they did present application problems. To achieve economic dry film thicknesses, very fine screens had to be used in the range of 180 linear/cm (usual value 120 linear/cm). Even so, film thicknesses of ink could still be too high and calendering of one side, to flatten the mesh, could be used. This technique will reduce the amount of ink deposited by up to 30 per cent.

The lecturer stressed that whilst both water-borne and UV cured inks were commercially available, the products that were currently on the market were not the ultimate in terms of technical performance and further work was continuing to produce improved inks.

Inks for deinking

In the third morning lecture, Dr M. L. Burstall of the 1982(3)



University of Surrey described some of the work that had been carried out by the University of Surrey Ink Research Unit into "Inks for deinking". Deinkable inks were becoming more important as more and more paper was recycled to produce paper fibre due to lower availability of timber.

The present techniques of deinking paper, washing or flotation, were not particularly applicable to all potential end-uses since the paper was frequently contaminated with ink specks or coloured an overall grey shade.

In the washing method, paper was pulped together with a non-ionic surfactant/emulsifier and filtered through a screen. The paper fibres did not pass through, whilst the ink and emulsifier did.

The flotation method used a mixture of pulp and calcium soaps. The soaps emulsified the inks and these were removed from the surface of the pulp.

Work carried out at Surrey University had shown that off-set and UV cured inks were particularly difficult to remove after ageing, especially when printed onto uncoated paper.

The Ink Research Unit had examined the possibilities of developing inks which could be removed in the currently used deinking processes. One approach was to look at "unzippable" polymers. By choosing a suitable combination of components, it was possible to introduce groups which could be hydrolysed during the deinking process thus leading to the breaking up of the crosslinked polymer.

Partly hydrolysed linseed oil-based inks were found to be particularly encouraging in laboratory scale deinking trials.

Another route was to incorporate a silicone containing compound. Silicone-oxygen bonds were easily broken under alkaline conditions. Dialkoxo-silanes were reacted with a long oil alkyd containing free hydroxyl groups to produce a resin containing about 2 per cent Si in the alkyd and about 0.12 per cent Si in the ink. Inks based on this resin printed well. Deinking trials in the laboratory again indicated encouraging results and on storage showed better deinking properties than conventional inks. A large scale printing and deinking trial was carried out but results were less encouraging. Only a marginal improvement in deinking characteristics was obtained.

Work on this route was subsequently dropped for a number of reasons including patent problems. There is still an interest in this approach to the development of deinkable inks.

Recent work carried out at Surrey University on deinkable UV cured polymers by the incorporation of acylsilicone linkages had resulted in inks with dramatically increased deinking characteristics. However, rub resistance was very poor.

occa meetings

The commercial acceptance of such an approach depends very much on both commercial and technical factors being correct.

Security printing

Dr A. C. Healey presented a lecture entitled "Security printing". Security printing covered a number of different end-uses but a common feature was prevention of some fraudulent activity, e.g. to prevent reproduction of banknotes and travellers cheques, alteration of cheques and premature sight of confidential documents such as examination papers.

A combination of different designs and printing process was used to make the design as complicated as possible. All the common printing processes, and in addition plate printing, were used. The plate printing technique was almost exclusively restricted to use in security printing.

Usually the main design was direct plate printed and the background printed by offset letterpress or litho. Normal printing techniques were used for the background. However, one or two special techniques were used. One such was rainbow printing where different inks were fed into the duct so that the design showed several different colour bands.

Itaglio plate printing processes were used (i.e. ink only in the engraved area), and the need to force the paper into the recessed areas resulted in a thick film printed, embossed document. Photogravure and depress printing were similar to itaglio printing in that recessed areas only were inked.

Plate printing allowed for the very finest of lines to be printed, which was particularly important in preventing forgery.

Some of the problems associated with plate printing were discussed. For instance, the technique of damping the paper to improve the print quality resulted in a weakened substrate and registration problems.

One phenomenon peculiar to plate printing was that of feathering of the print, caused by the ink being forced into the interstices between the fibres of the paper during printing. By varying the depth of engraving, it was possible to alter the shade of the print.

Opaque inks varied very little in shade regardless of film thickness and it was not possible to obtain variations in shade or colour from them. Thus, relatively transparent, tinctorially strong pigments in combination with a small proportion of opaque, large particle size pigments could be used in plate printing inks to obtain the maximum difference in shade. It was also possible to use a lower pigment content in plate printing inks compared with litho or letterpress inks because of the thick films applied. Low tinctorial strength, large particle size inorganic pigments could thus be used which could not be considered in litho

or letterpress inks and was another way of identifying plate printed documents.

Numbering of security documents was always the last process. Direct letterpress was invariably used. The use of sequentially rotating number cylinders presented particular problems of correct ink rheology and drying properties, as the higher digits were used only infrequently but were required to print properly immediately they were rotated into the printing station.

In the printing of bank notes, the maximum complexity of design was used to prevent fraudulent copying. A number of interlocking designs were produced by different printing processes. In addition, other security features such as watermarks, metal strips and coloured fibres in the paper were used. In commercial papers the watermark was usually a thinner area of the paper but in banknote paper it could be thicker, thus looking more opaque when viewed against a light source. By combining thinner and thicker watermarked areas a range of shades from light to dark could be obtained.

Developments in printed metal decoration

Dr A. Gamble, J & C Printing Inks Ltd, presented a paper on "Developments in printed metal decoration". It was within the metal decoration area that the lithopress ink industry had seen its most dramatic developments and changes.

The metal decoration market could be divided into five main market areas. The major two were the open top (beverage and beer) and general line markets, with drums, closures and miscellaneous markets much smaller.

Within the open top area, the greatest rate of change was occurring. Traditionally, flat sheet tinplate was pre-coated with the coatings which were thermally cured, and then fabricated into the can body. Lithographic inks were commonly used. They were formulated so that they dried under the stoving schedules used, were tough to prevent scuffing damage and were able to accept subsequent varnishes whilst still in the uncured or "wet" state.

UV cured inks have made some inroads into this market area for economic reasons. Both interdeck and set stack printing units were used. With interdeck the UV lamps were positioned between the printing presses. Inks cured using set stack were dried to a degree that allowed them to be stacked immediately after printing.

In recent years the two piece or drawn and wall ironed (DWI) can, had made massively significant inroads into the open top market, for aesthetic and technical reasons.

DWI cans were more attractive visually, having all-round decoration, and without a side seam were extremely unlikely to leak. Both aluminium and tin plate cans were produced.

The major difference between the traditional can and the DWI can was that the latter was preformed before decorating. Traditional lithographic printing techniques could not be used. The process of producing finished cans ready for use was an in-line process from start to finish. Cans were fabricated at very high speeds. As a result highly catalysed inks were required which would cure in the short bake schedules permissible. Cans were printed at the rate of 800-1,000 cans per minute. Dry off-set polyester based inks were used. The inks have been formulated carefully to be non-misting as the heat generated

through printing at the line speeds used was significant. They also needed to exhibit high surface slip as the print design was no longer varnished as on the traditional cans.

The general line market covered a very wide range of container shapes and sizes, e.g. food cans, trays and tin boxes. There had been far fewer changes in can "technology" in this market that affected ink formulation. The general line market continued to use traditional lithographic inks. However, UV cured inks had taken a greater share than in the open top markets. As in the open top market, the adoption of UV inks allowed the printers to eliminate oven passes previously required to cure lithographic inks.

In concluding, a number of predictions of future changes were made. It was likely that there would be continued growth in the use of UV inks in the general line and drum markets and possibly in DWI can production. Another possible alternative was the development of lower energy curing inks. The use of water-borne technology was more likely to be restricted to coatings rather than ink development. Finally, the inroads plastics could make into the metal decoration market was not predictable and would remain a continuous challenge.

Press conversions

Mr R. L. Bascombe, print advisor, United Newspapers Ltd, spoke on "Press conversions". Machine conversion was not new. Before the War, presses had been converted from rotary letterpress to offset on one side only. Momentum in press conversion started in the late 60s/early 70s when photocomposition began to make inroads into the composing area. Web offset began to replace stereo letterpress systems. More significant was the conversion of letterpress presses to direct lithography (dilitho). Various methods of damping the litho plate were evaluated e.g. spray, damping rollers.

Each existing press that was converted had to be looked at as a unique entity and had to be converted singly. Roller layout, blanket composition, ink formulation and paper quality all had to be correctly combined to ensure that an acceptable finish was obtained.

The introduction of polymer and diazo wipe on plates of thin aluminium made the lithographic printing process more economically attractive.

Following on from the conversion to dilitho, systems allowing for a much wider conversion of the letterpress machine were introduced. Gutting and replacement of the complete set of printing rollers allowed for faster start-ups and the use of various weight papers.

Another development allowed for the conversion of letterpress machines into web offset presses. Conversion was much less expensive than re-equipping with a new web offset unit (typically £500,000 each).

The advantages and disadvantages of a number of these conversions were discussed in detail. In the future there was going to be continued development in machine conversion along these lines.

A review of progress in paste ink technology

In the final paper Mr G. H. Hutchinson, technical director, Croda Inks Ltd, presented "A review of progress in paste ink technology".



Factors influencing the developments in paste inks had been the trend towards faster press speeds and the use of the inks on a wider range of substrates. In the future both materials and energy availability and environmental pollution considerations would be important in the development of inks.

Inevitably, inks would have to become cheaper for the ink industry to survive. Streamlined production methods and reduced dispersion times were typical areas where costs could be reduced. Pigments which were easier to disperse, which could be dispersed with novel dispersing agents or which were solvent dispersed or flushed were ways in which pigment dispersion costs could be lowered.

Some of the advances made in paste ink technology were illustrated by reference to the various ink drying mechanisms. Using home made models, Mr Hutchinson demonstrated the different drying mechanisms and the structures of the polymer films subsequently formed.

Penetration (e.g. news inks), oxidation (e.g. litho, letterpress, four colour publication work), precipitation (water-miscible inks), evaporation (heat-set press), UV curing and accelerated methods such as microwave, infrared and radio-frequency drying were discussed and demonstrated.

It was suggested that future constraints on product development, such as the EEC Sixth Amendment, would force ink makers to turn away from novel technology and re-examine existing or even redundant technologies and develop these to meet the future requirements.

One problem that had been looked at for a number of years was that of eliminating the need for set-off powders to prevent sticking in the stack when using quick set inks. Initially, additives such as starch compounds were incorporated in the inks. These were of limited usefulness and subsequently compounds such as rosin modified phenolics or maleics were found to be much more valuable, particularly when incorporated into the alkyd resin or oil. Cold blending of oil and phenolic resin led to an ink which would dry very rapidly but which would be of very low gloss, whereas heating the oil and phenolic resins at high temperatures would give a high gloss, relatively slower drying ink. By combination of these two resin types it was possible to produce a compromise ink which had both gloss and fast drying characteristics.

Medium wave infrared drying had been around for a number of years and had made some impact since the late 70s. In 1977 more significant advances had been made when short wave infrared driers, small enough to fit to presses, were introduced.

Water-borne technology would be a major development in flexo and gravure. Particularly attractive was the idea of using a water-borne varnish in the fourth printing station on a four colour press, applying it via the damping rollers.

occa meetings

This would allow for a uniform gloss, rapid drying film applied over the inks, without the need for offset powders or sprays.

UV inks offered many advantages in eliminating solvent emissions, energy consumption etc. The responsible attitude taken towards incorporation of only non-toxic components into UV inks in the UK would ensure that this technology would expand into areas such as aluminium foil, carton board and labels, pharmaceutical and plastic containers.

Reduction in the drying temperatures of heat-set inks was the final area examined. Developments in recent years had enabled set temperatures to be reduced from 150 to 100°C. Additional benefits were less tendency to blister on drying and mark-off when slitting and cutting.

A. J. Newbould

Ontario

Dispersion in aqueous systems

Mr Michael Frantz of Daniel Products Company was the guest speaker at the November technical meeting. His profusely illustrated talk dealt with the design and manufacture of aqueous dispersions; it described the factors which affect degree of dispersion and the advantages which are gained as "ideal" dispersion is approached.

The advantages include improvement in stability, viscosity and end-use suitability of the dispersion, but the main benefit derives from full development of the inherent value of the pigment: its tinting strength, cleanliness of shade, and transparency or opacity (depending on the pigment type). Factors governing degree of dispersion for any specific pigment were given as the vehicle, the dispersion equipment and the skills of the formulator and the operator. When the vehicle and the equipment are specified, the formulator must depend wholly on his selection of pigment and, if necessary, surfactant or dispersing agent.

Mr Frantz demonstrated that the degree of dispersion

can be determined readily and reliably by tests of relative tinting strength (i.e. density of colour imparted to an opaque white base).

The final selection of pigments and dispersing agents was shown to depend to a large extent on trial and error. Good test results (in terms of flow and tinting strength) appear to be more reliable indicators of promising combinations than do predictions based on alleged or theoretical considerations such as surface interaction models.

During the lively discussion period Mr Frantz ably answered a number of pertinent questions. These dealt mainly with types of dispersion equipment, the selection of surfactants, pretreatment of pigments and the applicability of theoretical concepts (such as HLB values) to dispersions and dispersing.

Mr Derek Laming, Section Chairman, introduced Mr Frantz and moved the vote of thanks. Members and guests were reminded that the December meeting date had been reserved for the annual ladies' evening.

J. F. Ambury

Hull

Some recent developments in pressure polymer emulsions

The third lecture of the present programme was delivered by Dr D. Wilson of Vinyl Products Ltd, on Monday 7 December 1981. The venue was the Duke of Cumberland, Market Square, Cottingham, N. Humberside.

The lecturer outlined the various feedstocks for pressure polymer emulsions such as ethylene and vinyl chloride, their production and hence the commercial considerations arising from them. A comprehensive account of the physico-chemical properties of the resulting copolymers included examples of results obtained using commercially available emulsions.

A review of the pressure polymer emulsion process and the necessary restrictions and opportunities offered by this process together with the quality control and analytical procedures required for such a production method followed. Finally, a discussion on the most recent developments, particularly those relating to the paint industry, prompted a question period.

The lecture, having been well presented by the use of slides and equally well received by an appreciative, if small, audience, was concluded by a vote of thanks offered by Dr G. Crawforth and enthusiastically endorsed.

S. Heyes

news

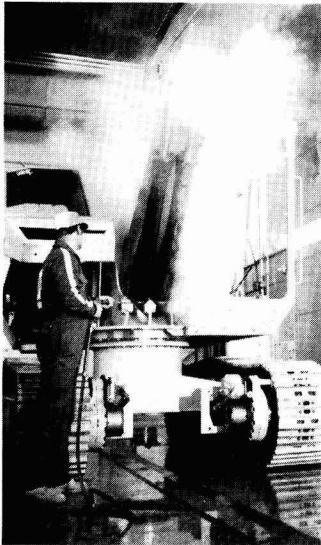
Further information on any items mentioned below may be obtained by circling the appropriate Reader Enquiry Service number on the form at the back of the *Journal*. Enquiries will be forwarded to the organisation concerned.

Management buy-out

Filling machine manufacturer Neumo and its associated packaging systems division has been acquired in a management buy-out by managing director Mr Brian Page.

The owner, Paxall Inc. of Chicago which bought the company in 1966, sold Neumo through its UK operating company Paxall Ltd for around £400,000.

Reader Enquiry Service No. 31



Steam lance being used to clean a B series excavator prior to hot air drying and spray painting

Haden Drysys plant for JCB

Reduction of paint plant pollution to virtually zero, improved working conditions, minimum maintenance and an improved finish are said to be just four of the benefits enjoyed by J. C. Bamford Excavators since installing a complete Haden Drysys finishing plant within its Rocester, Staffs factory.

The plant provides final painting of excavators and other mechanical handling equipment.

The five-stage finishing line at Rocester incorporates Haden Drysys' patented Hydrosprin spraybooth design and one of the company's Hydropac waste paint removal systems. In addition, mobile operator-controlled lift platforms are installed in the spraybooth, enabling painters to gain unhindered access to all surfaces of even the largest JCB products during painting.

Reader Enquiry Service No. 32

Sheen expands by acquisition

Sheen Instruments, established for 40 years and well known in the paint and surface coatings industries, is now the senior partner in a group of three companies including Voss Instruments and Startronic Ltd.

Sheen, which already exports more than 60 per cent of its production, has twenty five overseas agents and has established Sheen Instruments Corporation in New York, the United States being one of the most promising export markets along with South America and, of course, Europe.

Reader Enquiry Service No. 33

Macpherson in further acquisitions

The board of the Donald Macpherson Group Ltd has announced that it has acquired A. G. W. Britton & Sons for £350,000, and Briggs & Townsend Ltd from Johnson & Firth Brown (JFB) for £1.8m.

Brittons, with their administrative offices in South East London and freehold factory site in Herne Bay, Kent, specialise in the manufacture and supply of high quality printing inks to the poster and metal packaging industries and also supply general printing inks. Net assets are valued at £265,000.

Briggs & Townsend is reported as having one of the most broadly based polyurethane manufacturing activities in the UK and operates from Birch Vale, near Stockport, Cheshire. It has been a supplier to Donald Macpherson for several years. Its products comprise speciality plasticisers, polyester polyols and polyurethanes which are widely used in the plastics, rubber, surface coatings, ink, adhesive, lubricant, footwear and engineering industries.

Reader Enquiry Service No. 34

UCB expansion

UCB's Chemical Sector has expanded its radiation-curable monomer/resin manufacturing plant at the Speciality Division located near Brussels, at Drogenbos, Belgium.

The expansion raises UCB's total radiation-curable monomer/resin capacity by 40 per cent and was undertaken to meet market demand increase. UCB say that in Europe alone the market is growing at an annual rate of 15 to 20 per cent and is now estimated to be between 3,500 to 4,000 ton/year.

UCB's monomers and resins are used widely in electron beam and ultraviolet cured coatings, printing inks, printed circuit boards, adhesives and many other end-use applications.

Reader Enquiry Service No. 35

Europe's largest pressure polymerisation reactor

Vinyl Products Ltd, a wholly-owned subsidiary of Unilever Plc, has successfully commissioned what is claimed to be Europe's largest pressure polymerisation reactor for the manufacture of vinyl acetate-ethylene and vinyl acetate-vinyl chloride-ethylene copolymer emulsions at its Warrington factory.

The fully computer-controlled plant, representing an investment of £3m, is the third unit of its kind on the Warrington site, and more than doubles the company's production capacity for pressure polymer emulsions. Vinyl

products ranks among the leading world suppliers of these important industrial materials, and claims to be the only company to manufacture them in the UK. Gaseous ethylene for the process is received via the trans-Pennine pipeline from ICI's Wilton complex; its availability in this way was a vital consideration in the original choice of Warrington as the company's UK base for pressure emulsion polymerisation.

Vinyl Products commissioned its first commercial-scale pressure emulsion plant in 1974 and its second in 1978. The products are marketed under the Vinamul trademark, and are used in a large number of applications such as decorative paints, textured coatings, wallpaper, building products, adhesives, carpets, non-woven fabrics, textile finishing and coating, and specialised agricultural treatments. Since their introduction little more than seven years ago, pressure emulsions have grown to a point where they account for about a quarter of the company's total emulsion business.

The UK market for pressure emulsions has grown considerably over the past few years. In spite of recession, demand has increased by almost 20 per cent in the last twelve months. High growth is expected to continue and this reinforces the decision taken two years ago to proceed with this latest capital investment, in spite of the overall down-turn in demand for industrial chemicals.

The most important element of the plant is the pressure polymerisation reactor, believed to be the largest of its type in Western Europe. Another major element is the Sybron-Taylor computer system, which represents a significant advance in process control for the manufacture of polymer emulsions. It is capable of running every polymerisation batch from start to finish, and is programmed to provide a very high degree of batch-to-batch consistency. It will also significantly reduce process times, so ensuring maximum output and lower operating costs.

Reader Enquiry Service No. 36

Grilon name change

Grilon (UK) Ltd the UK distribution leg of Emser Werke AG of Switzerland has announced the change of its name to: EMS-Grilon (UK) Ltd.

Reader Enquiry Service No. 37

news

CVP visits China

Dr John Peter Burden, assistant managing director of Cray Valley Products Ltd, visited China recently at the invitation of the China International Trust & Investment Corporation (CITIC). Dr Burden visited the Canton Fair and various ministries in the capital Beijing (formerly Peking).

The main purpose of the visit was discussions with representatives of the surface coatings industry of Liaoning Province in the city of Shenyang (formerly Mukden) in north east China. This was the first visit by any representative from CVP to the People's Republic of China. The discussions covered a wide range of subjects within the surface coatings field and, as was expected, the discussions were very searching and detailed.

Dr Burden reports that the contacts at all levels were on a most friendly basis and conducted with charm and expertise. It was evident that a considerable amount of homework had been done by the Chinese, and that they have very clear objectives for trading with Western partners which will require considerable flexibility on the part of those wishing to do business with the People's Republic of China.

Reader Enquiry Service No. 38

Middle East success for Valspar

The contract to supply paint for the re-decoration of the Cairo Museum has been won by Liverpool based Goodlass Wall & Co. Ltd. The specification includes both gloss and emulsion paint from the company's Valspar range, both of which will be produced under licence in the Middle East to quality standards set by chemists at the Speke headquarters.

This is the third prestigious Middle East project for which Goodlass Wall coatings have been specified in the last 12 months.

A few months ago the company was specified as the paint supplier for the Cairo Plaza which is one of the world's tallest buildings, it incorporates a hotel, luxury apartments and offices. The Weathercover finish used to decorate the exterior had been specially formulated to resist the abrasive effects of sandstorms as well as high degrees of ultraviolet. Finishes for the interior include gloss, undercoat, emulsion, eggshell lustre and polyurethane, again from the company's Valspar range.

The recently completed Suez Tunnel is also protected both internally and externally by Valspar. Externally, the concrete tunnel which runs beneath the canal had to be safeguarded for life against the extremely acidic local sub-soil. The internal steel which supports the road deck and ceiling is coated to give ten years maintenance free protection. And the concrete plinth of the pedestrian walkway required a finish which could be easily brush cleaned to remove the oil and oil laden dust which is splashed from the adjacent road. A sample of the tunnel was taken to the Speke laboratories to enable Goodlass Wall chemists to devise formulations to meet not only the protective aspects but to enable the paints to be applied by unskilled local labour using rollers instead of the more usual spray techniques.

Reader Enquiry Service No. 39

Demo phosphating plant

W. Canning Materials Ltd has installed a full scale spray phosphating line for the trial and demonstration of its processes under production conditions.

The 48 foot long line has five stages: cleaner, cold water rinse, phosphate, cold water rinse, hot demineralised water rinse. It can handle components with up to 30 ins drop, 36 ins with conveyor, and 12 ins width. Among the special features are interchangeable stand pipes which give rapid conversion between V or swirl spray jets. To give maximum ease of cleaning and to avoid contamination, all the solution tanks are made of stainless steel and the pipework of polypropylene.

Existing and potential customers can have test panels or trial components phosphated under controlled production conditions without interrupting work on their own plant. The line can give three, four or five stage applications at various temperatures and spray pressures.

Reader Enquiry Service No. 40

new products

Formaldehyde-free preservative

Sterling Industrial has announced the introduction of Parmetol K40, a formaldehyde-free preservative with low toxicity characteristics.

Specially formulated for use in aqueous-based products such as water-based paints, dyes, inks, adhesives and glues, soaps etc., Parmetol K40 does not incorporate phenols or heavy metal substances.

Parmetol K40 is claimed to have a wide bacteriocidal and fungicidal effect. Its main active ingredient is a heterocyclic sulfur-hydrogen compound in special dissolving intermediaries which ensure optimum distribution of the antimicrobial substances in the medium to be preserved.

Reader Enquiry Service No. 41

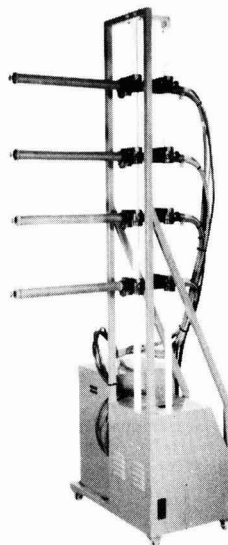
New waggler unit

A new and improved waggler unit which can carry up to eight automatic electrostatic powder coating guns has been introduced by Volstatic Coatings Ltd.

It is designed to impart angular movement to each gun in order to create a better dispersion of charged particles inside the spraybooth, thereby improving both transfer efficiency and the coverage of certain types of workpiece.

Setting the static positions of the guns exactly right is vital for achieving optimum results and Volstatic have made this easier to achieve by designing the MkIII Waggler so that all initial gun adjustments are governed by a single control.

Reader Enquiry Service No. 42



A Mk III Waggler, which can carry up to eight automatic electrostatic powder coating guns

Improved print quality

Warwick Chemical Ltd has introduced a new additive for the preparation of thixotropic gels used in the manufacture of printing inks.

Known as Surkogel 55, the new additive improves printability and sharpness of image whilst increasing cohesion and water resistance in the finished product.

Other claimed advantages are improved stability and effective stabilisation of ink surfaces, thus retarding considerably the formation of undesirable crusting and skinning.

Reader Enquiry Service No. 43



New from Volumair is the T2 and Tank, it is designed for spraying heavy exterior finishes

Heavy materials turbospray kit

The new Turbospray T2 plus tank kit was designed expressly to meet a need among small to medium sized building and decorating firms for an economical means of applying heavy textured exterior coatings.

Volumair, inventor of the turbine air-powered low pressure spraying system, developed the new kit which utilises a two-stage, portable T2 turbine unit in conjunction with a 10 litre hand pressure tank and Model 200 thick materials spray gun complete with easily interchangeable 1.5, 2.5 and 3.5 mm nozzels and needles.

Air power for the Turbospray T2 is provided at very low pressure (2 psi maximum) from a two-stage, 500w turbine unit in which the blades rotate at speeds up to 16,000 rpm. The air is warmed to 20°C above ambient by the blade friction, which speeds surface drying time. The unit provides an air volume of 2,000 litres per minute which, the company claims, has proved in tests to be ample for the application of heavy exterior coatings.

The unit is also fully capable of being used for the application of materials lighter in viscosity by simply changing to smaller gun needle and nozzle sizes. The Turbospray can readily apply primers, undercoats, emulsions, varnishes and glosses.

Reader Enquiry Service No. 44

Heat recovery for textile dyers

Alfa-Laval has developed a skid mounted heat recovery unit for use in textile dyeing which is generally carried out as a batch process.

1982(3)

The batch processing aspect has been a problem in the development of heat recovery equipment and the new system overcomes this problem by using a completely self-contained system which can be used as required.

The system is made to measure for individual applications. A typical unit consists of an insulated buffer or retention tank which stores "make-up" water, two pumps, one to discharge dye from the tank the other to supply fresh water to the plate heat exchanger, controls and filtering equipment, all of which are mounted on a simple skid.

Reader Enquiry Service No. 45

Colour measurement

The new Erichsen Colorimeter 511 is a three-filter (tri-stimulus) colour measuring instrument.

On the basic model, colour values XYZ are displayed; Lab (Hunter) values can also be obtained with a small modification.

Operation is simple, and precise measurements can be made by untrained personnel without any danger of operating errors. A digital readout is included with the basic instrument.

Valuable optional additions are a modern economic desk computer with central memory, large 9 inch screen and magnetic tape cassette station. This allows automatic calculation of such values as CIELAB and Hunter Lab colour difference.

Reader Enquiry Service No. 46

High-pressure cleaning units

A range of compact cleaning units operating at pressures up to 207 bar, (3,000 lb/in²) is newly available from Megator Pumps & Compressors Ltd.

Designed for an array of industrial, marine, agricultural and municipal cleaning jobs, and using cold water only, the Megator washers are said to be able to clean away old paint, dried-on mud, rust, grease, graffiti, etc.

Despite their wide application, the units weigh only 28 kg (62 lb), and are extremely compact, fitting easily into the boot of a Mini.

Reader Enquiry Service No. 47

Powder sampling

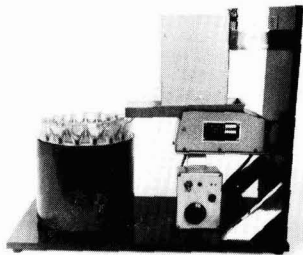
Microscal Ltd has announced the availability of the next generation of its Spinning Rifflers, used for the production of representative samples of powders.

Since their inception ten years ago, Spinning Rifflers have developed in three respects. Firstly, models have diversified, they can provide a complete split of samples into sub-samples, or they can provide one or a number of small fractions of a quantity of powders, the remainder being bulked for ease of handling.

Secondly, the maximum capacity before riffling has been raised from 1 litre to 40 litres.

Thirdly, all models have now been made suitable for sampling cohesive as well as free flowing powders.

Reader Enquiry Service No. 48



An example of Microscal's Spinning Rifflers

news

Gloss meter

Elektro-Physik, the UK agent for Byk-Mallinckrodt, has introduced into the UK a new portable gloss meter.

Known as the Pocket-Gloss, it is battery operated and is available in 20 or 60 degree geometry. The gloss units are shown on a liquid crystal display and the instrument is accurate to \pm one unit.

Reader Enquiry Service No. 49

New test sieve shaker

Endecotts Ltd has introduced a new bench top variable speed shaker for test sieving. The shaker has a unique mechanical action which imparts a circular motion to the sample ensuring it progresses over the surface of the sieve. At the same time a rapid vertical movement assists in the continuous clearing of the apertures.

The electromagnetic drive has no rotating parts to wear out and the whole unit weighs only 28 Kg.

Known as the EVS1, the new shaker has many features including continuous or intermittent operation, 0-60 minute timer, infinitely variable vibration control from 0-3 mm.

A quick release clamping device holds up to seven full height or fifteen half height sieves of 200 mm (or 8 ins) diameter. Adaptor rings for 100 mm diameter sieves are also available.

Reader Enquiry Service No. 50

literature

New resins

Three data sheets have been made available from BIP Chemicals Division describing new Beetle amino coating resins.

A two-page leaflet gives brief details of five methylated melamine resins, a four-page data sheet gives information on a modified urea formaldehyde resin, and a third data sheet, also of four pages, gives provisional information on a high solids methylated urea resin for use in both water-reducible and conventional solvent based systems.

Reader Enquiry Service No. 51

Tioxide R-CR3

The Tioxide Group Plc has published a booklet, "Tioxide R-CR3", on its titanium dioxide pigment R-CR3. Information is included on properties and performances obtainable when using R-CR3.

Reader Enquiry Service No. 52

Calculation techniques in resin formulation

"Calculation techniques in the formulation of alkyd and related resins" is a new publication from Paint RA. The various calculation techniques are demonstrated by specific examples, comments are made on the related general principles, and practice examples are given so that the reader can gain confidence in handling the calculations. Price: £40, Paint RA members £34.

Reader Enquiry Service No. 53

Antifoams for the textile industry

ICI has produced an information booklet on its Silcolapse Antifoams used in the textile industry. The scope and method of application of these antifoams in textile processing are outlined.

Reader Enquiry Service No. 54

Anticorrosive pigments

R. H. Chandler Ltd has published a review entitled "Modern anticorrosive pigments".

Many pigments are included only in comparative experiments, and the review of individual pigments is followed by a series of research reports which summarise the pigment comparisons. The relatively small amount of patent literature is dealt with by means of individual abstracts and there are author, patent number and patentee indexes. Price per copy is £10, \$30 or DM50.

Reader Enquiry Service No. 55

meetings, etc.

Association dinner and dance

The Association will be holding its biennial dinner and dance as usual in the Savoy Hotel, Strand, London. This year it will take place on the middle day of the Exhibition, OCCA-34. Anyone interested in attending should contact the Director & Secretary at the Association's offices or fill in the application form on page iii.

SA Division symposium

The 9th National Symposium of OCCA's South African Division will be held at Sun City, Bophuthatswana on 13 and 14 October 1982.

The theme of the Symposium will be "Economic aspects of protective coat-

ings" and the organising committee is calling for support and participation from all interested parties.

Previous symposia have offered both local and overseas speakers an opportunity of addressing a wide cross-section of people involved in the protective coatings industry, including chemists, manufacturers, specifiers and end-users.

For further information contact: The Symposium Chairman, OCCA, PO Box 2356, Primrose 1416, SA.

Gordon Research Conferences, USA

The Pastore Chemical Laboratory of the University of Rhode Island has announced the programme for the Gordon Research Conferences which will cover the physics and chemistry of coatings and films. The Conferences will be held at various locations in New Hampshire, USA from 14 June to 27 August 1982. For further information contact: Mr A. M. Cruickshank, Gordon Research Conferences, Pastore Chemical Laboratory, University of Rhode Island, Kingston, Rhode Island 02881, USA, Tel: 401-783 4011/3372.

appointments

John S. Fraser has been appointed corporate managing director, Ciba-Geigy Plastics and Additives Company, in succession to Dr K. W. Humphreys. Mr Fraser will also retain his existing responsibilities as head of the Ilford Photographic Group, managing director and chief executive of Ilford Limited, and as a member of the board of Ciba-Geigy (UK) Limited.

Following the retirement of Mr Eric Bowker, with effect from 1 January 1982, Mr Len Holland, an executive director with Hoechst UK Limited, takes over full responsibility for the line management of Industrial Division II (Colour and Surfactants) in addition to his present responsibilities as site director of Hoechst UK's northern offices, technical service laboratories and warehousing facilities at Stainland near Halifax.

Michael Boyce has been appointed managing director of Volstatic Coatings Limited. He is also president and chief executive officer of Volstatic Inc., the company's subsidiary in the USA. Mr Boyce succeeds Mr Bob Lever, the founder of Volstatic, who remains as chairman.

John Gearing has joined Polymer Laboratories Ltd of Church Stretton, Salop as sales manager. After graduating from Oxford in engineering science, John has spent the last eleven years as a technical representative, the last six of which have been with Du Pont (UK) Ltd.



OCCA-34 Exhibition

27-29 April 1982

Cunard International Hotel
Hammersmith, London W6

OCCA news

EXHIBITION LECTURE PROGRAMME

No charge for admission

Shown below is the list of lectures to be presented at OCCA-34 together with dates, times and summaries of lectures which have so far been received.

Admission to the lectures will be by ticket only, although no charge will be made. Those wishing to attend the lectures may obtain tickets either in advance by completing the form on page iii or on the day from the Association's Information Centre at the Exhibition at least half an hour before the stated times of the lectures.

TUESDAY 27 APRIL

10.30 a.m.

Ciba-Geigy, Plastics & Additives Co. will be presenting a lecture on each day of the Exhibition entitled "A novel resin system"*.

Summary

Demands for conservation and reduced solvent emission have led to increased interest in water-based can coatings for both food and beverage applications. The exacting requirements for these coating resins severely restrict the chemistry that can be utilised. The chemistry and technology of a novel resin system developed by Ciba-Geigy to meet these requirements, including FDA acceptability, will be described.

11.30 a.m.

C & W Specialist Equipment will be presenting a lecture on two days of the Exhibition on "Prohesion testing"†.

Summary

Prohesion testing is arguably the most realistic method of accelerated evaluation of paint systems. It incorporates unavoidable application malpractices, identifies levels of adhesion and predicts ageing characteristics of paint coatings.

12.15 p.m.

SBA Commercial systems will discuss "The economic use of computers in the surface coatings industries".

2.30 p.m.

The International Tin Research Institute will give a talk entitled "Tin chemicals for industry". Discussions and questions will be encouraged, and it is possible that a 15-20 mins. film describing the work of the Institute and its liaison with industry will be shown.

Summary

1. The Institute's organisation and function.
2. Facilities for chemical research.
3. Current research into (a) ceramic pigments, (b) primer paints, (c) anti-fouling paints, (d) wood preservatives, and (e) tin-stabilised PVC.
4. Services offered to industry: (a) publications and leaflets, (b) technical advisory service, (c) library and information, and (d) films and visual aids.

3.30 p.m.

Institution of Corrosion Science and Technology: "Painting inspection".

WEDNESDAY 28 APRIL

10.30 a.m.

C & W Specialist Equipment: "Prohesion testing" (see above†).

11.30 a.m.

Silberline Ltd will discuss "Aluminium pastes in surface coatings" with particular reference to printing inks.

Summary

Silberline will be presenting two short discourses at OCCA-34. Dr D. R. King, managing director of Silberline (UK), will present a study of the performance of Eternabrite, a new leafing grade aluminium paste being produced in Europe this year, against similar leafing type pastes. Various examples and data will be discussed.

The role of aluminium pastes in metallic printing inks, their choice, dispersion and adaptability in the demanding world of design will be presented by T. G. Adams, market development executive.

12.15 p.m.

Carri-Med will give a talk on "Measurement of important rheological parameters using the controlled shear stress technique".

Summary

A comparison is made between techniques of rheological measurement using controlled shear stress and controlled shear rate. The advantage of one over the other is discussed with a brief mention of historical development. The presentation is concerned essentially with the practical side of rheological measurement and avoids complex mathematical treatment and theory.

2.30 p.m.

Ciba-Geigy, Plastics & Additives Co.: "A novel resin system" (see above*).

3.30 p.m.

Pacific Scientific (Gardner/Neotech Division) will present a lecture entitled "Colour measurement".

Summary

Gardner is using microprocessor technology, a "Smart" CRT terminal, advanced software and fibre optics to produce a new colour measuring instrument. This Spectrogard spectro/colorimeter is being shown for the first time in England at OCCA-34, 1982. Spectrogard features accuracy, reliability, exceptional ease of operation, speed and flexibility; all at a remarkably low cost. The optical system is a diffusing sphere double beam with 5 second continuous scanning holographic grating from 380 to 720 nm. Low cost is achieved by using fibre optics instead of an expensive optical bench construction. The control/display unit is a "Smart" CRT terminal with 12 inch screen, mini disk memory and screen prompting software.

(Wednesday programme continued overleaf)

OCCA news

4.15 p.m.

Bison will talk on "Intermediate bulk containers and powder handling systems".

THURSDAY 29 APRIL

10.30 a.m.

Polymer Laboratories will give a lecture on "The direct determination of coating material parameters on a substrate by the PL-DMTA".

11.30 a.m.

Ciba-Geigy, Plastics & Additives Co.: "A novel resin system" (see above*).

12.15 p.m.

Microscal will talk on "Sampling of

powders, particle size analysis, light fastness testing, and flow microcalorimetry".

Summary

The development of Microcal's range of instruments continues to concentrate on sampling and certain properties of powders and surfaces.

Sampling of powders: This is an important and now widely accepted prerequisite to good analysis. Our range of Spinning Rifflers is becoming increasingly used on an international basis. These instruments are now joined by our Suspension Samplers for the accurate sampling of particles already dispersed in liquids.

Particle size analysis: The advent of Microscal's computerised photodensitometer makes the analysis of powders in the size range 2-75 µm rapid and effective, both by surface and by weight.

Light fastness testing: Although the fading of textiles is still the most significant application, a wide range of other materials - plastics, rubber, paper, printing inks, printed goods and packaging materials, are evaluated with Microscal's instruments on a routine basis. Less familiar applications are: the testing of

anodised aluminium and architectural materials, degradation studies of pharmaceutical products and foods.

Flow microcalorimetry: The surfaces of powders and the interactions which take place upon them are elucidated by measuring heats of preferential adsorption and desorption.

In addition to the study of pigments, minerals, photochemistry, etc., the surface of coal particles and lubrication are interesting and important areas which provide fresh examples of the power of the flow microcalorimeter.

2.30 p.m.

SBA Commercial Systems will lecture on "Hazard labelling in the surface coatings industries".

3.30 p.m.

Durham Chemicals will discuss "Biocides in paint".

Summary

The talk will concern the microbial breakdown of paints and methods of preventing this.

New exhibitors

Since the first list of exhibitors was published in the February 1982 issue of JOCCA, six further applications to exhibit have been received:

Bison (Bernt Iversen & Son)
Carri-Med
John Godrich
Polymer Laboratories
SBA Commercial Systems
Union Camp Chemicals (formerly BOC)

Social highlight

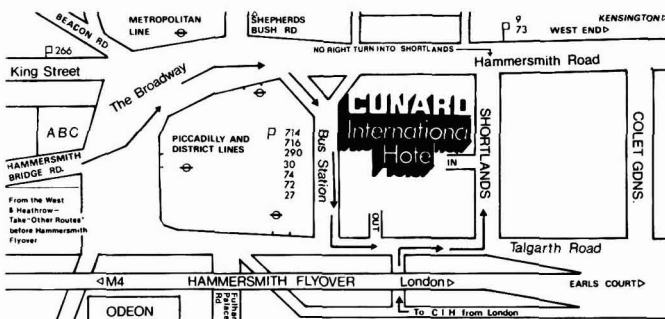
As the social highlight of the Exhibition, the prestigious biennial dinner dance at the Savoy Hotel, London, WC2 has been arranged for the middle day of the Exhibition (Wednesday 28 April), thus affording exhibitors an excellent chance to entertain their customers. Exhibitors who usually hold social functions during OCCA Exhibitions are asked not to hold them on this evening.

Tickets are priced at £25.00 (plus VAT at 15 per cent) each and can be obtained from the Association's offices.

Dates, times and layout of exhibition

The Exhibition will be open from 27-29 April 1982 at 9.30-17.30 on each of the three days. It will be in two sections: on the ground floor - forming the entrance to the Exhibition - and in rooms on the mezzanine - directly above the ground floor where the lecture theatre will also be situated. A fully licensed bar and seating area will be installed in the New Hall.

Admission to the Exhibition will be free and visitors will be asked to complete



Location of the Cunard International Hotel

registration forms at the entrance to the Exhibition.

Aim of the Exhibition

The aim of the Exhibition, which is known as the "international focal point for the surface coatings industries", is the presentation of technical and commercial information relating to raw materials, plant and equipment used in the paint, polymer, printing ink, colour, adhesive and allied industries, in manufacture, processing and application.

Travel facilities and admission

Once again the venue for the "international focal point" is the Cunard International Hotel, which is situated near Hammersmith Station on the Piccadilly Underground line, between Heathrow Airport and the centre of London. Visitors from overseas may board the Piccadilly Line at Heathrow Central

station in the Airport complex, which will take them direct to Hammersmith station or to central London where they may be staying. Car parking space at the hotel will be limited, but there is a large NCP car park close by in Kings Mall. However, those travelling to the Exhibition by car are advised to leave their vehicles outside central London and travel to the Hotel by the Underground system.

The Official Guide

Copies of the *Official Guide* will be charged at £1.50 and will be available, with registration cards, at the entrance to the Exhibition. Copies of the *Official Guide* and registration cards are also available in advance - pre-payment only - from the Association's offices (£1.50 inc. p&p). Each member of OCCA will be sent a copy of the *Official Guide* and a registration card without charge.

OCCA news

News of members

Mr A. Kjellin appointed vice-president of Becker Group

Anders Kjellin has been appointed vice-president of the Becker Group, Stockholm. Mr Kjellin was previously managing director of Soab AB from 1979; he will be succeeded by Mr Raimo Eronen.

West Riding Section

Annual dinner and dance

The West Riding Section held their twenty-third annual dinner and dance on Friday 27 November 1981 at the Crown Hotel, Harrogate. Despite the economic climate the event was very well supported. The principal guest was the President, Don Morris accompanied by Mrs Morris. Other top table guests were the Chairman of Thames Valley, Manchester and Newcastle sections, namely Vincent Moore, Frank Redman and Alan Watson accompanied by their ladies, and the Director & Secretary, Robert Hamblin.

After dinner the President had the pleasure of presenting Norman Cochrane with his Commendation Award. This was a particularly appropriate occasion because, quite apart from his many other offices, Norman had organised this function for many years prior to his recent retirement. The Chairman of West Riding Section, Ron Chappell, also presented the

West Riding Chairman's Golf Trophy to the winner of the 1981 competition, Mr Tony Wood.

After the formalities everybody adjourned to the ballroom and relaxed to some dancing in an air of general frivolity.

R.A.C.C.

Ontario Section

Colour with flair at ladies' evening

Members and guests were treated to a most entertaining presentation at the annual ladies' evening in December. The speaker was Mr Dave Beech, interior designer and colour consultant for C-I-L Paints Inc.

After announcing that he would not be speaking on the subject of paint colourant systems (which had been advertised as his topic), Mr Beech proceeded to give a fascinating slide show which illustrated the broad context in which style and design exist.

He showed that even the most effective stylists and interior designers do not actually set trends, rather they interpret in their work the trend signals which appear in other areas. Colour trends appear first in clothing, cosmetics and automobiles; earlier and more subtle signals can be ascertained by assessment of lifestyle indicators such as sociological patterns and leisure activities. Some of the illustrations showed recently designed interiors whose stylists had read their signals well; for the most part the effects were fresh and original but not jarring or "trendy".

Turning to current developments in colour fashion, Mr Beech explained that most of the "now" colours are subdued shades or tints of the vivid hues that were seen in the seventies. Burgundy, maroon and rose are replacing reds and pinks, oranges are giving way to burnt orange and umber, blues are less saturated and more grey, olive greens are "out", while soft forest greens are "in". All the earth colours, from light ochre through brick red to dark brown, are fashionable. The overall trend is away from synthetic brightness and toward "natural" effects.

To conclude, Mr Beech amused all (and perhaps slightly embarrassed some) by revealing what personality traits are said to be typical of people who prefer certain colours or colour groups.

Mr Derek Laming, Section Chairman, presented a certificate of appreciation to the guest speaker, and moved the vote of thanks which was accorded with enthusiasm.

J.F.A.

London Section

Ladies' night

The London Section's 1980 ladies' night held on Friday 6 November at the Abercorn Rooms, Great Eastern Hotel, Liverpool Street EC2 marked a return to central London after several years in the suburbs.

The principal guest was Dr F. M. Smith, the Immediate Past President. In his speech, Dr Smith put various laws encountered in everyday life in a different perspective.

Mr B. Gilliam, Chairman of the London Section, proposed the toast to the ladies and guests.

Present as top table guests were the Director & Secretary, Mr R. H. Hamblin, and the Chairmen of Bristol, Newcastle, Thames Valley, West Riding and Manchester sections and their wives.

After the meal, dancing commenced and was highlighted by a square dance organised by Mr D. Sharp who had also acted as toast master. The dancing continued until 1.00 a.m. A most successful and enjoyable evening was had by all present.

B.A.C.



Shown in the photograph from left to right are: Mr Redman (Chairman, Manchester Section), Mrs Chappell, Mr Chappell (Chairman, West Riding Section), Mrs Redman, Mr Fowkes (Chairman, Bristol Section), Mrs Fowkes, Mr Gilliam (Chairman, London Section), Mrs Gilliam, Dr Smith (Immediate Past President), Mrs Smith, Dr Banfield, Mrs Banfield, Mr Watson (Chairman, Newcastle Section), Mrs Watson, Mr Moore (Chairman, Thames Valley Section), Mrs Moore and Mr Hamblin (Director & Secretary)

British Standards

The publications listed below are new and revised British Standards. An existing BSI publication bearing a number identical to one announced below is automatically withdrawn.

6138:1981 ADC/9
"Glossary of terms used in the adhesives industry" 24 page A4 size Gr 7
Terms relating to components, finished adhesives, bonding processes, properties and testing of bonded assemblies, pressure sensitive adhesive tapes. No current standard is superseded (*ISBN 0 580 12270 0*)

684: OFC/3
Methods of analysis of fats and fatty oils

684: Section 2.13: 1981 Determination of iodine value (=ISO 3961) 4 page A4 size Gr 2

Reaction with Wijs reagent (iodine monochloride solution) and determination of excess reagent. Supersedes BS 684: Section 2.13: 1976 (*ISBN 0 580 12490 8*)

5729:
Guide to stock control
5729: Part 2: 1981 Demand assessment 8 page A4 size Gr 5
Outlines some basic forecasting procedures suitable for stock control. No current standard is superseded. (*ISBN 0 580 12443 6*)

6199: PCL/2
Methods of measurement of liquid flow in closed conduits using weighing and volumetric methods
6199: Part 1: 1981 Weighing method (=ISO 4185) 20 page A4 Gr 8
Gives a method of liquid flow rate measurement by measuring the mass of liquid delivered into a weighing tank in a known time interval. Covers the measuring apparatus, the procedure, method for calculating the flowrate and the uncertainties with the measurement. No current standard is superseded. (*ISBN 0 580 12474 6*)

Amendments

1101:1977 PVE/1
Specification for pressure containers for paint and other substances

Amendment No. 1 Gr 2 AMD 3828

2011: GEL/15
Basic environmental testing procedures

2011: Part 2.1J: 1977 Test J. Mould growth

The publications listed below and their prices are obtainable from: BSI Sales Counter, 195 Pentonville Road, London N1 9ND (personal callers). BSI Sales Department, 101 Pentonville Road, London N1 9ND (orders by post). Telephone: 01-837 8801. Telex 23218.

Amendment No. 1 Gr 0 AMD 3675

2011: Part 2.2J: 1977 Test J. Mould growth

Amendment No. 1 Gr 2 AMD 3676

1042: PCL/2
Methods for the measurement of fluid flow in pipes

1042: Part 2A: 1973 Pitot tubes. Class A accuracy

Amendment No. 1 Gr 0 AMD 3724

1042: Part 3: 1965 Guide to the effects of departure from the methods in Part 1
Amendment No. 1 Gr 0 AMD 3723

Reprints

3900:
Methods of test for paints

3900: Part F4: 1968 Resistance to continuous salt spray. *Incorporates AMDs 1620 and 2808*

New work started

Determination of "soluble" lead will revise BS 3900: Part B3 to align it with Appendix 2 of the Approved Code of Practice "Control of Lead at Work" (published by the Health and Safety Commission) providing practical guidance in respect of the Control of Lead at Work Regulations, SI 1980, No. 1248 which took effect on 18 August 1981. These regulations revoke the Lead Paint Regulations to which the present edition of BS 3900: Part B3 was aligned. PVC/10

New ISO standards

ISO 787:
General methods of test for pigments and extenders.

ISO 787/2: 1981 Determination of matter volatile at 105°C 2 page B. *To be implemented as a revision of BS 3483 Part B6*

ISO 787/7: 1981 Determination of residue on sieve - water method - manual procedure 3 page C. *To be implemented as a revision of BS 3483 Part B3*

ISO 787/9: 1981 Determination of pH value of an aqueous suspension 2 page B. *To be implemented as a revision of BS 3483: Part C4*

ISO 787/11: 1981 Determination of tamped volume and apparent density after tamping 3 page C. *To be implemented as a revision of BS 3483: Part B10*

ISO 6191: 1981
Light olefins for industrial use - determination of traces of water - Karl Fischer method 8 page E

ISO 6796: 1981
Polyglycols for industrial use - deter-

mination of hydroxyl number - phthalic anhydride esterification method 3 page C

ISO 2909: 1981
Petroleum products - calculation of viscosity index from kinematic viscosity 6 page D

ISO 755:
Butan-1-ol for industrial use-methods of test

755/1: 1981 General 3 page C

755/2: 1981 Determination of acidity - titrimetric method 2 page B

755/3: 1981 Sulphuric acid colour test 3 page C

ISO 759: 1981
Volatile organic liquids for industrial use - determination of dry residue after evaporation on a water bath - general method 3 page C

ISO 787:
General methods of test for pigments and extenders

ISO 787/4: 1981 Determination of acidity or alkalinity of the aqueous extract 2 page B \pm BS 3483: Part C3: 1974

ISO 2715: 1981
Liquid hydrocarbons - volumetric measurement by turbine meter systems 15 page J

ISO 3923:
Metallic powders - determination of apparent density

ISO 3923/2: 1981 Scott volumeter method 4 page C

ISO 4493: 1981
Metallic powders - determination of hydrogen reducible oxygen content 9 page F

ISO 4783:
Industrial wire screens and woven wire cloth - guide to the choice of aperture size and wire diameter combinations

ISO 4783/2: 1981 Preferred combinations for woven wire cloth 7 page E *No equiv. BS*

ISO 756:
Propan-2-ol for industrial use - methods of test

ISO 756/1: 1981 General 3 page C. *To be implemented in revising BS 1595*

ISO 756/3: 1981 Test for miscibility with water 2 page B. *To be implemented in revising BS 1595*

ISO 1388:
Ethanol for industrial use - methods of test

ISO 1388/1: 1981 General 2 page B \pm BS 507: Appendix C&A: 1966

ISO 1388/2: 1981 Detection of alkalinity

or determination of acidity to phenolphthalein 2 page B. *±BS 507: Appendix E: 1966*

ISO 1388/4: 1981 Estimation of contents of carbonyl compounds present in moderate amounts – titrimetric method 3 page C. *±BS 507: Appendix F: 1966*

ISO 1388/5: 1981 Determination of aldehydes content – visual colorimetric method 3 page C. *To be implemented in revising BS 507*

ISO 1388/6: 1981 Test for miscibility with water 2 page B. *±BS 507: Appendix D: 1966*

ISO 1388/7: 1981 Determination of methanol content (methanol contents between 0.01 and 0.2% (v/v) – photometric method 4 page C. *To be implemented in revising BS 507*

ISO 1388/8: 1981 Determination of methanol content (methanol contents between 0.1 and 1.5% (v/v) – visual colorimetric method 3 page C. *To be implemented in revising BS 507*

ISO 1388/10: 1981 Estimation of hydrocarbons content – distillation method 5 page D. *No equiv. BS*

ISO 1388/11: 1981 Test for detection of furfural 2 page B. *No equiv. BS*

ISO 1388/12: 1981 Determination of permanganate time 3 page C. *To be implemented in revising BS 507*

ISO 1543: 1981 Benzole industry – vocabulary 6 page D. *No equiv. BS*

ISO 1995: 1981 Aromatic hydrocarbons – sampling 13 page H. *±BS 3195: Part 1: 1978*

ISO 4630: 1981 Binders for paints and varnishes – estimation of colour of clear liquids by the Gardner colour scale 5 page D. *To be implemented as a BS*

ISO 6377: 1981 Light olefins for industrial use – determination of hydrocarbon impurities by gas chromatography – general considerations 4 page C.

ISO 6378: 1981 Butadiene for industrial use – determination of hydrocarbon impurities – gas chromatographic method 7 page E. *No equiv. BS*

ISO 6379: 1981 Ethylene for industrial use – determination of hydrocarbon impurities – gas chromatographic method 4 page C. *No equiv. BS*

ISO 6380: 1981 Propylene for industrial use – determination of hydrocarbon impurities – gas chromatographic method 5 page D. *No equiv. BS*

**bsi
news**

ISO 6381: 1981 Ethylene and propylene for industrial use – determination of traces of carbon monoxide and carbon dioxide – gas chromatographic method 6 page D. *No equiv. BS*

ISO 6793: 1981 But-2-ene-1,4-diol for industrial use – determination of iodine value 3 page C. *To be implemented as a BS*

ISO 6794: 1981 Butane-1,4-diol industrial use – determination of degree of unsaturation 2 page B. *To be implemented as a BS*

ISO 2834: 1981 Printing inks – preparation of standardised prints for determination of resistance to physical and chemical agents 4 page C.

Professional Grade

At the meeting of the Professional Grade Committee held on 24 February 1982, the Committee authorised the following:

Transfer from Associate to Fellow

Clement, Donovan Harry (*Midlands*)

Garratt, Peter Garth (*General Overseas – Austria*)

Admitted as Associates

Adefarati, Francis Babasola (*General Overseas – Nigeria Branch*)

Borer, Keith (*Newcastle*)

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

Ordinary Members

BANDYOPADHYAY, BASABJIT, BChem, 1 Dhakuria Station Lane, Calcutta – 700031 W B, India (*General Overseas*)

BENNETT, PAUL, GradRSC, 13 Mill Meadow Way, Etwell, Derbyshire (*Midlands*)

EXELBY, JEREMY, BSc, Reckitt & Colman, PO Box 2993, Cape Town, Republic of South Africa (*Cape*)

HAWTHORN, JOHN, 1 Meadowside, Thornbury, Avon BS12 2EN (*Bristol*)

HODASI, VICTOR, BSc, BP 4709, Lome, Togo (*General Overseas*)

**new
members**

NILSSON, PER, PhD, Swedish National Testing Institute, PO Box 857, S-50115 Borås, Sweden (*General Overseas*)

ZUVČENKO, DINAH MARGARET, BSc, 14 De Montfort Road, Reading, Berkshire RG1 8DL (*Thames Valley*)

Registered Students

CAIN, STEPHEN, H. H. Robertsons UK Ltd, Cromwell Road, Ellesmere Port, South Wirral (*Manchester*)

new members

FRYER, CHRISTINE JANIS, 29 Nairn Close, Chester-le-Street, County Durham (West Riding)

KIRBY, STEVEN THOMAS, 5 Carr Hill Nook, Calverley, Pudsey, West Yorkshire LS28 5QF (West Riding)

NODEN, ANDREW, FEB (GB) Ltd, Albany House, Swinton Hall Road, Swinton, Manchester M27 1DT (Manchester)

occa diary

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

March

Monday 1 March

Hull Section: Ladies' evening, a local speaker will discuss "Stained glass". Venue to be decided.

Tuesday 2 March

West Riding Section: "Paint containers present and future" by W. J. Walton, marketing executive of Metal Box Ltd. To be held at the Mansion Hotel, Roundhay Park, Leeds 8, commencing 7.30 p.m.

Thursday 4 March

Newcastle Section: "Decorative paints - market pressures on the formulator" by R. D. Mearns, Goodlass Wall & Co. Ltd. To be held at the Students' Common Room, St Mary's College, Elvet Hill Road, Durham, commencing 6.30 p.m.

Thursday 4 March

Scottish Section - Eastern Branch: Joint Eastern Branch/Institute of Printing meeting in the Albyn Rooms, Queen Street, Edinburgh. "Developments in printing inks" by Jeff Hutchinson, Croda Inks, commencing 7.30 p.m.

Monday 8 March

Manchester Section: Lecture "New two-pack systems without isocyanate" by Dr Mondt, Hoechst. To be held in the New Administration Building, Manchester Polytechnic, All Saints, Manchester, commencing 6.30 p.m.

Thursday 11 March

Midlands Section - Trent Valley Branch: "Radiation cured coatings" by a speaker from Cray Valley Products Ltd. To be held at the Sutton Centre, High Pavement, Sutton-in-Ashfield, Nottinghamshire, commencing 7.15 p.m.

Scottish Section: Lecturer from Barr & Stroud, Glasgow, subject to be confirmed. To be held at the Albany Hotel, Glasgow, commencing 6 p.m.

Friday 12 March

Manchester Section: Informal buffet dance to be held at the RAF Association Club, Oakfield Road, Sale. Details to be announced.

Thursday 18 March

Midlands Section: "Super gourmet meal" followed by the Newton Friend Lecture to be held at Halesowen College, Whittingham Road, Halesowen.

Thames Valley Section: "Safety forum", three speakers and a question and answer session. To be held at the Beaconsfield Crest Motel (White Hart), Aylesbury End, Beaconsfield, Buckinghamshire, commencing 6.30 p.m. for 7 p.m.

Friday 19 March

Bristol Section: "Ultraviolet and electron beam - energy efficient methods of curing" by M. V. Holder, Cray Valley Products Ltd. To be held at the George and Dragon, High Street, Winterbourne, Nr. Bristol, North Avon, commencing 7.15 p.m.

Friday 26 March

Bristol Section: Ladies' night. To be held at the Unicorn Hotel, Bristol. Details to be announced.

Irish Section: "Powder coatings". Details to be announced.

April 1982

Thursday 1 April

Newcastle Section: AGM.

Scottish Section: AGM to be held at the Beacons Hotel, 7 Park Terrace, Glasgow G3 at 6 p.m.

Friday 2 April

Manchester Section: AGM at 6.00 p.m. in the Members' Bar at Lancashire County Cricket Club, Old Trafford followed by a supper.

Monday 5 April

Hull Section: AGM at the Grange Park Hotel, Willerby, Hull, commencing 6.45 p.m.

Tuesday 6 April

West Riding Section: AGM at the Mansion Hotel, Roundhay Park, Leeds 8, commencing 7.30 p.m.

Wednesday 14 April

Scottish Section - Eastern Branch: AGM followed by a talk by R. H. Wardman, lecturer at the Scottish College of Textiles, Galashiels, in the Murrayfield Hotel, Edinburgh.

Thursday 15 April

Thames Valley Section: AGM.

Friday 16 April

Irish Section: AGM at the Clarence Hotel, Wellington Quay, Dublin 2, commencing 8.00 p.m.

Midlands Section - Trent Valley Branch: AGM followed by buffet and dance. Details to be announced.

Thursday 22 April

London Section: AGM. Details to be announced.

Midlands Section: AGM. Details to be announced.

Tuesday 27-Thursday 29 April

OCCA-34 Exhibition at the Cunard International Hotel, Shortlands, Hammersmith, London W6, from 9.30 a.m. to 5.30 p.m.

Friday 30 April

Bristol Section: AGM followed by film on veteran cars by BP Ltd, at the George and Dragon, High Street, Winterbourne, Nr. Bristol, North Avon, commencing 7.15 p.m.

Scottish Section: Ladies' evening, "Hypnotism" by A. Hearne in the Bothwell Suite, Albany Hotel, Glasgow at 7.30 p.m.

OIL & COLOUR CHEMISTS' ASSOCIATION



Annual General Meeting – Luncheon Lecture

Wednesday, 16 June 1982

On the occasion of the 1982 Annual General Meeting, the London Section has arranged a luncheon and lecture which will precede the Annual General Meeting and take place at the same venue, i.e. The Piccadilly Hotel, London W.1.

The lecturer will be Dr Rhodes Boyson, MA, MP, Parliamentary Under Secretary of State for Education, who will deliver a lecture entitled:

“THE ROLE OF GOVERNMENT IN EDUCATION AND SCIENCE”

The programme of events will be as follows:

- 12.30 p.m. Reception in the Margaret Suite (Cash Bar)
- 1.00 p.m. Luncheon – Margaret Suite
- 2.00 p.m. Lecture – Edward Suite
- 3.00 p.m. (or as soon thereafter as the lecture shall have terminated) Annual General Meeting – Edward Suite

Members not wishing to attend the luncheon and lecture will, of course, be able to participate in the Annual General Meeting at the time shown above. **Please notify me so that seating arrangements can be made.**

Tickets for the luncheon/lecture are priced at £11.50 each, inclusive of wine and VAT.

Application for tickets should be made on the form below as soon as possible.

R. H. HAMBLIN,
Director & Secretary.

March 1982

Office Use Only

Date Received
Receipt No.
Ticket No.

**OCCA ANNUAL GENERAL MEETING
LUNCHEON/LECTURE – 16 June 1982**

To: The Director & Secretary,
Oil & Colour Chemists' Association,
Priory House, 967 Harrow Road,
Wembley, Middlesex HA9 2SF

Please send me tickets (£11.50 each, inclusive of VAT) for the OCCA Annual General Meeting Luncheon/lecture on Wednesday, 16 June 1982 for which I enclose my remittance for £

NAME
(BLOCK LETTERS PLEASE)

ADDRESS
.....
.....

Cheques should be crossed and made payable to "Oil & Colour Chemists' Association".



**OCCA-34
LECTURE
PROGRAMME**

**27-29 April 1982
Cunard International Hotel
London W6**

There is no charge for admission to the lectures, and application can be made by post prior to the Exhibition on the form below.

For details of the lectures to be presented see page 80.

**APPLICATION
FOR LECTURE TICKETS**

Name

Address

.....
.....

Please reserve for me a ticket at the following lecture(s). **I understand that I must collect ticket(s) from the Information Centre (Stand 120) not later than 45 minutes before the stated starting time of the lecture(s)**

Title of Lecture(s)	Date	Time
---------------------	------	------

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Note: Unreserved tickets subject to availability may still be obtained on the day concerned at the Information Centre **up to 30 minutes** before the starting time of the lecture.

Please complete and return to:

**Oil and Colour Chemists' Association
Priory House, 967 Harrow Road
Wembley, Middlesex HA0 2SF
England**

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FLAME PROTECTED BATTERY ELECTRIC FORKLIFT TRUCKS!!!

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Applications in writing to include C.V. to:

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Alvechurch Road
West Heath
Birmingham B31 3PC

INDEX TO ADVERTISERS

Further information on any of the products advertised in this *Journal* may be obtained by circling the appropriate number on the *Reader Enquiry Service (RES)* form. The *RES* numbers are shown in brackets below. Enquiries will be forwarded to the organisations concerned.

A	
Atlas Electric Devices Co.	(175) ii
G	
Graco (UK) Limited	(174) ii
N	
NL Chemicals	(173) Cover
O	
OCCA Conference	(199) Cover
OCCA-34 (lectures)	iii
OCCA-Dinner and Dance	iii
S	
Sanyo-Kokusaku Pulp Co. Ltd	(112) ii
Sub-Tropical Testing Service Inc	(117) Cover

EXPERIENCED CHEMIST Wanted for R & D Labs

We are a leading international company in the field of timber preservation and are seeking an experienced chemist to take up a senior position in our Research and Development laboratories.

The successful applicant will be responsible for the development of coloured wood preservative formulations and provide additional expertise in the formulation, manufacture and application of decorative timber finishes.

Suitable applicants will probably hold a degree in a relevant subject and have had several years industrial experience, probably in the paint, printing ink or pigment industries.

The company offers excellent conditions of service which includes a contributory Pension and Life Assurance scheme; and in excess of 4 weeks holiday.

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Applications to:

**The Personnel Manager,
Hickson's Timber Products Ltd,
Ings Lane, Castleford,
West Yorkshire WF10 2JT
Tel: 0977 556565**

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Mr. C. Hubbard Davis, Founder, Sub-Tropical Testing Service, Inc. (1904-1977)
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Phones: (305) 233-5341
Cable: SUBTROPIC, Miami

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JOCCA

READER ENQUIRY SERVICE – MARCH 1982

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Name

Job Title

Company

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Please also send information on the following items
relating to the above:

Country Telephone

Photocopy or cut out this form and send to:

Journal of the Oil and Colour Chemists' Association

Priory House, 967 Harrow Road, Wembley, Middx., HA0 2SF, England
Telephone: 01-908 1086 Telex: 922670 (OCCA G)

OCCA CONFERENCE 1983

YORK

15-18 JUNE

1983

CALL FOR PAPERS



THE EFFICIENT USE OF SURFACE COATINGS

The next OCCA Biennial Conference will be held at the Viking Hotel, York from 15-18 June 1983 with the theme "The efficient use of surface coatings".

There will be four technical sessions under the headings:

- (I) Formulation including manufacturing etc.
- (II) The efficient use of coatings application
- (III) The use of computers in surface coatings
- (IV) Maintenance of quality and prediction of performance

Following the innovation at the 1981 Conference there will be a discourse session included in the fourth technical session.

The Hon. Research & Development Officer now invites offers of papers for presentation at this Conference. Anyone wishing to submit a paper for consideration should notify his intention as soon as possible to: **The Director & Secretary, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, England (Tel: 01-908 1086; Telex: 922670 OCCA G).**

Reader Enquiry Service No. 199