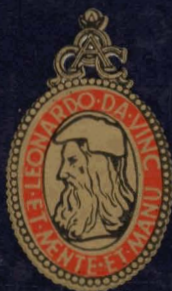


JOURNAL

OF THE

OIL AND COLOUR CHEMISTS' ASSOCIATION



Vol. 54 No. 2

February 1971

The fibre optics colorimeter and its applications in
paint manufacture *I. G. H. Ishak*

Polyurethane finishes for the coil coating process
F. Blomeyer

Papers from the Scottish Symposium

Dispersion in aqueous media *W. Carr*

The influence of non-aqueous media on dispersions
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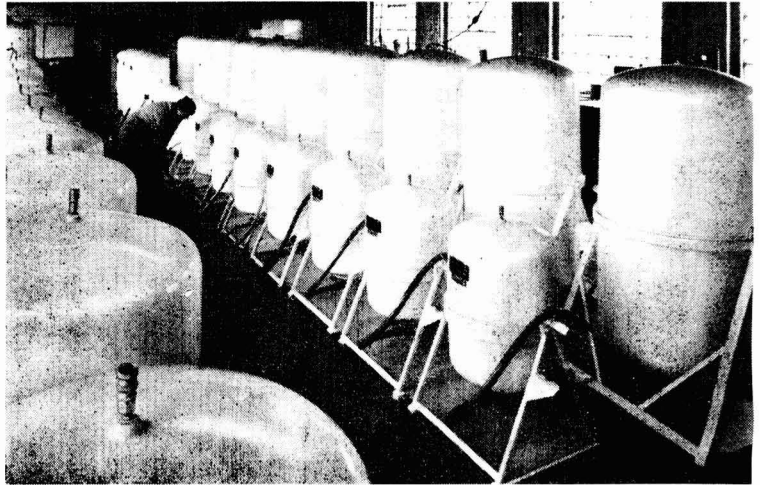
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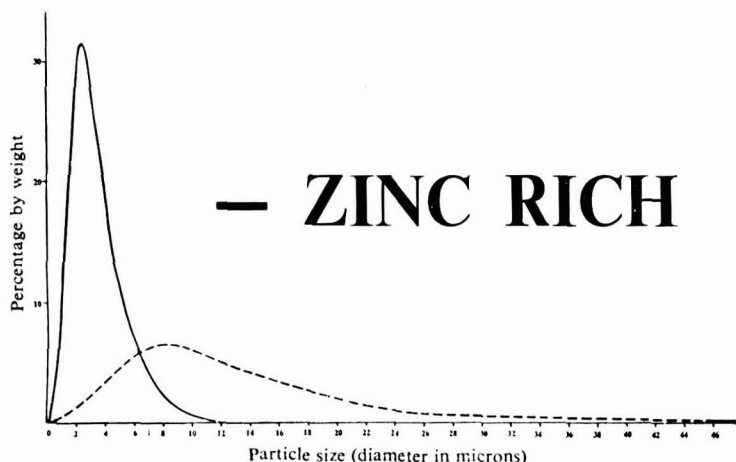
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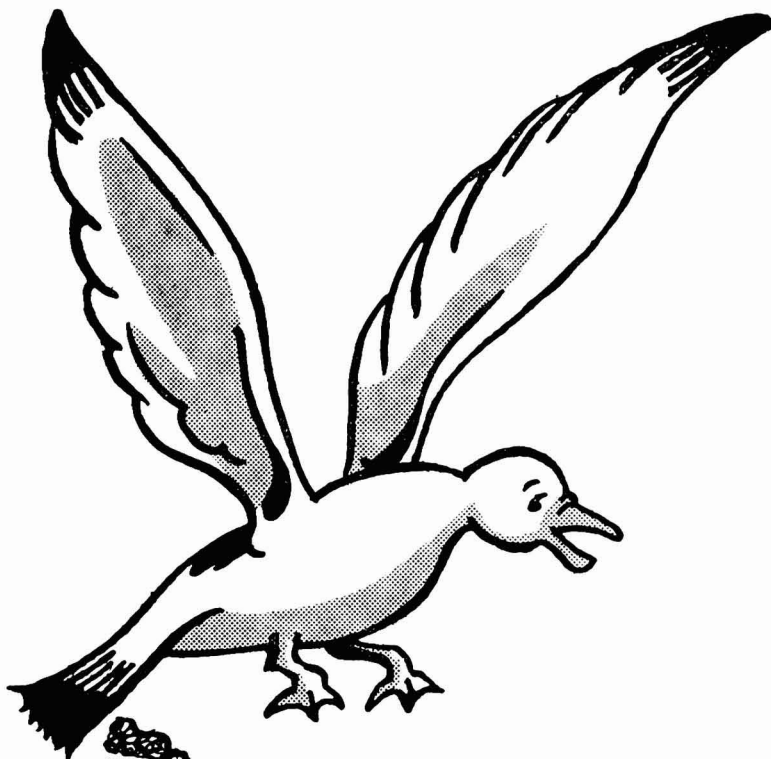
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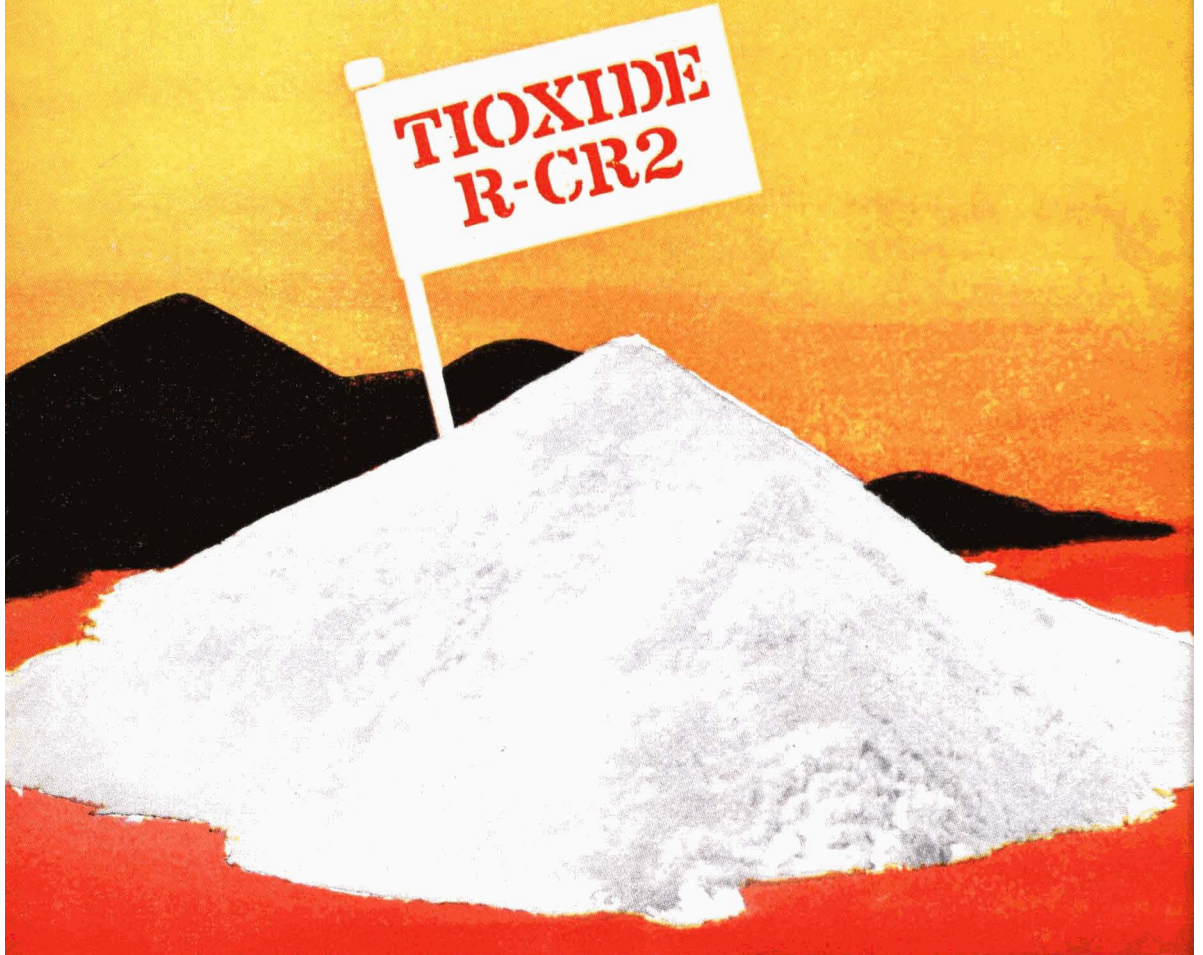
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Transactions and Communications

The fibre optics colorimeter and its applications in paint manufacture

By I. G. H. Ishak

Paint Research Association, Teddington, Middlesex

Summary

The fibre optics colorimeter developed at the Paint Research Association is briefly described. Its applications to colour problems in paint and other colour-based industries are discussed. Measurements have shown that the instrument is highly sensitive to colour differences and the results obtained are reproducible.

Keywords

Equipment primarily associated with analysis, measurement or testing
colorimeter
glass fibre optics

Processes and methods primarily associated with manufacturing or synthesis
colour control
colour matching

Un colorimètre à l'optique de fibres et ses applications à la fabrication de peintures

Résumé

On décrit brièvement le colorimètre à l'optique de fibres mis au point par la Paint Research Station. On discute son emploi pour résoudre des problèmes de couleur dans l'industrie de peintures et dans des autres où la colorimétrie est d'une grande importance. Les mesures ont démontrés que l'appareil est extrêmement sensible aux différences en couleur, et également que les résultats sont reproductibles.

Das Fiberoptiks-Colorimeter und Seine Anwendung in der Anstrichfarbenfabrikation

Zusammenfassung

Das von der Paint Research Association entwickelte "Fibre Optics Colorimeter" wird kurz beschrieben. Seine Anwendungsmöglichkeiten für Farbprobleme in der Lackfabrikation und anderen mit Farbe verbundenen Industrien werden erörtert. Messungen haben erwiesen, dass das Instrument gegenüber Farbünterschieden höchst empfindlich ist, und dass die erhaltenen Resultate reproduzierbar sind.

Фибро-листовой оптический цветомер и его применения в красочной промышленности

Резюме

Кратко описывается фибро-листовой оптический колориметр, разработанный Обществом для Исследования Красок. Обсуждаются его применения в проблемах возникающих в красочных и других смежных промышленности. Измерения показали что прибор обладает высокой чувствительностью к цветовым различиям и что получаемые результаты вполне воспроизводимы.

Introduction

One of the research projects at the PRA is aimed at automatic colour control in paint manufacture. A colorimeter capable of colour measurements and control of wet paint in a batch or on line production is needed for such a project. Since the colorimeters available on the market are useful only for laboratory work and could not easily be modified to meet the requirements for process colour control, the possibility of utilising fibre optic light guides for remote measurement and control of colour was suggested. It was this suggestion that led to the development of a differential colorimeter with high sensitivity and reproducibility, which is suitable for on-line colour measurement and control of paint making, as well as other colour-based industrial processes.

Fibre optics colorimeter

Description

The principle and design of the instrument is published elsewhere¹; Fig. 1 gives a schematic diagram of the colorimeter. A light source, run at a constant current to give a colour temperature of 2854 Å (CIE standard illuminant A)¹, illuminates one end of a fibre optic element (the illuminating element), whose other end is connected to a sensing head. The sample to be measured is placed against the sensing head and is illuminated normally. The light, diffusely reflected from the sample at 45°, is collected by six other fibre optic elements (collecting elements) which are arranged symmetrically around the illuminating element. The collecting elements connect the sensing head to the detector unit.

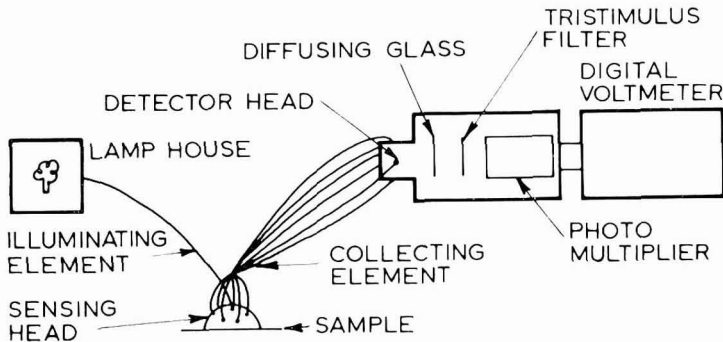


Fig. 1. A schematic diagram showing the different parts of the fibre optics colorimeter

Each fibre optic element is a bundle of thousands of small diameter glass fibres. The glass fibres are cemented and polished at the ends and held by metal ferrules. The fibre element is encased in a flexible sheath of suitable material. Each fibre has a central core of highly refractive optical glass surrounded by a low refractive index glass jacket. When light falls on one end of a glass fibre, it is conducted to the other end by total internal reflection (as illustrated in Fig. 1a). Owing to their small cross-section, the glass fibres are flexible and may be bent as required. The light can be conducted along a curved path without loss of light.

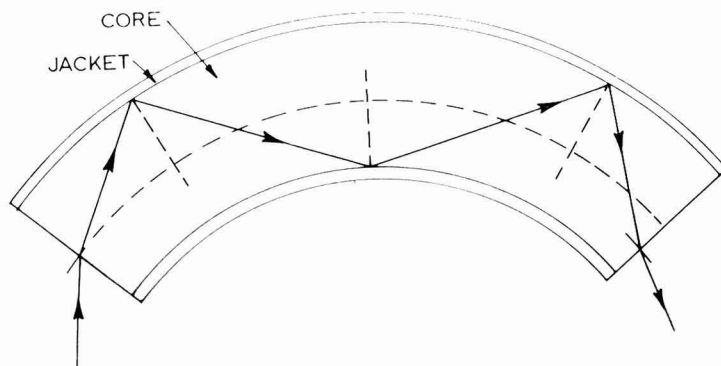


Fig. 1a. Conduction of light through a glass fibre by total internal reflection

The light emerging from the collecting elements falls on a diffusing glass plate and passes through one of three tristimulus glass filters before falling on the cathode of a sensitive photomultiplier. Each of the three tristimulus filters modifies the spectral response of the photomultiplier to approximate one of the CIE colour matching functions \bar{x}_λ , \bar{y}_λ and \bar{z}_λ weighted by the relative energy distribution of the CIE standard illuminant C . The output from the photomultiplier across a suitable load resistance is read on a digital voltmeter whose scale can be adjusted to read directly the tristimulus values X , Y and Z for illuminant C , of the sample under test, when the corresponding filters are inserted in the light path.

The spectral responses of the instrument as a whole were measured and the values of \bar{x}_λ , \bar{y}_λ and \bar{z}_λ curves are shown in Fig. 2, against the corresponding CIE and computed values. The responses obtained were not as close to the CIE specifications as required for absolute colorimetry. This limits the instrument's applicability to differential colour measurements only. However, the deviations from the CIE specifications are of the same order as those obtained for other colorimeters, and for the purpose of controlling the colour of paint, the fibre optics colorimeter as it stands is adequate. However, the design of the instrument offers enough degrees of freedom for a very close duplication of the CIE functions, if this is needed in the future.

Sensitivity and reproducibility

Using the fibre optics colorimeter, several determinations were made on pairs of samples exhibiting small colour differences similar to or smaller than colour tolerances in the paint industry. The pairs of samples used included the following:

paint panels,

vitrolite white and coloured opaque glass tiles,

a complete set of Wright's grey tiles⁵, ranging from near white to near black in nearly equal steps of reflectance; the set comprised 44 tiles, and each successive pair was compared, giving 43 comparisons.

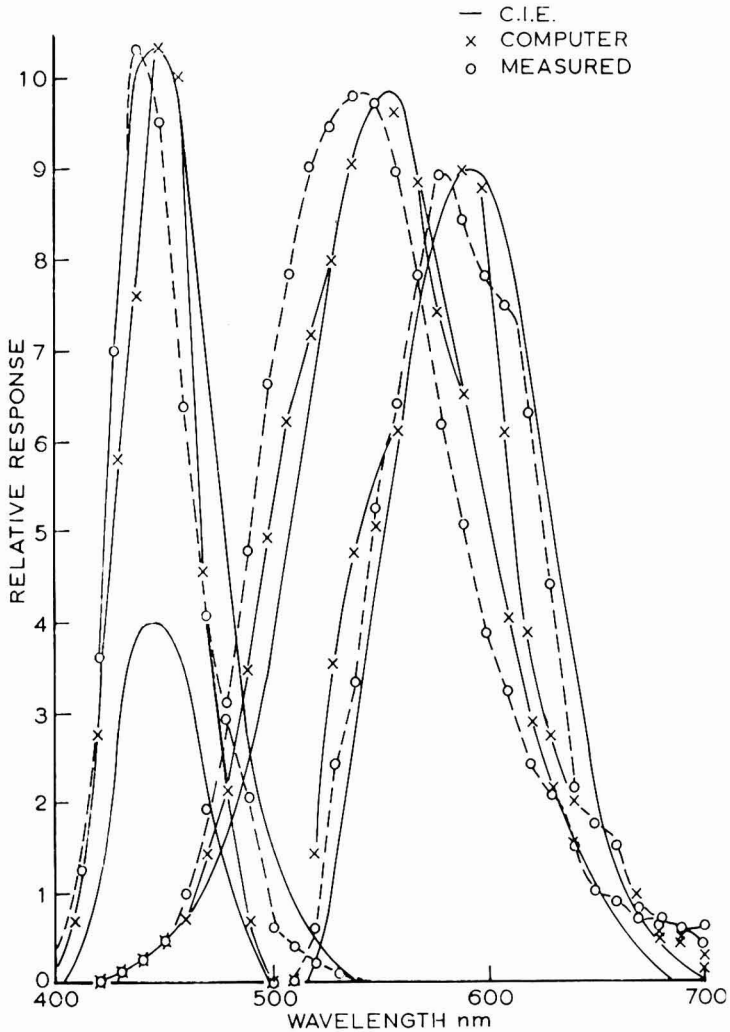


Fig. 2. The CIE colour matching functions weighted by the relative energy distribution of standard source C shown as a continuous line against the corresponding values obtained by calculations (cross) and by measurements (open circles)

The results obtained from the repeated measurements of the colour difference between each of the above mentioned pairs of samples, with the exception of Wright's darkest (black) pair of tiles, showed a spread of not more than 0.2 per cent. Also, the magnitude of the difference in colour for any pair, as measured by the fibre optics colorimeter, was in good agreement with the corresponding values obtained using a Colormaster instrument. The spread of the results of measurements on the black pair of tiles was about 2 per cent on the fibre optics colorimeter, while measurements on the same pair using the Colormaster did not give reproducible results.

It can be safely concluded from the measurements taken with the fibre optics colorimeter that the instrument is extremely sensitive to small colour differences, and that the results obtained are highly reproducible. Any colour difference that can be detected by the human eye under favourable conditions of viewing could be easily and very quickly measured by the instrument. It can also be claimed that the instrument is more sensitive than any available colorimeter.

In the paint industry, it can be used to compare the colours of standard panels with production batches to a very high degree of accuracy.

Advantage of fibre optics colorimeter over conventional colorimeters

Flexibility in measurements: Conventional colorimeters suffer from the restriction that the material to be measured has to be presented in a certain direction to a viewing port on what is often a massive instrument containing sensitive components. By using fibre optic light guides, the colour of any surface, in any direction, or of a bulk of a liquid, can be measured by a suitable probe attached to the recording instrument by flexible leads of up to several yards long. Moreover, the fibre optic elements can be encased in a plastic sheath terminating in a glass or plastic window so that the probe can be immersed in a liquid to monitor the colour at any point inside the liquid container over a temperature range between -195°C and 400°C without affecting the optical properties of the fibre optic elements. This flexibility makes the colorimeter particularly suitable for colour control in many industrial processes.

Versatility in the geometry of illumination and viewing conditions: In instrumental colour control in industry, it is important to choose an instrument which gives measurements of the colours or colour differences that correlate with visual estimates as judged by experienced colour matchers. To achieve good correlation between visual and instrumental results, the geometry of illumination and viewing used by colour inspectors should be reproducible instrumentally. In 1931, the CIE¹ recommended $45^{\circ}/0^{\circ}$ geometry as standard practice. This geometry is particularly useful to exclude the effect of specularly reflected light from glossy surfaces on the measurements. For a number of reasons, other geometries were used in spectrophotometers and colorimeters. The CIE has recognised the need for various types of geometry and in 1967 the Colorimetry Committee of the CIE recommended four alternative arrangements. Depending on the surface characteristics of the test material, one geometry may be more suitable than the others, and consequently, conventional colorimeters, usually utilising one geometry, could be useful only for colour measurements on a limited number of materials. With the fibre optics colorimeter, colour measurements can be obtained for any geometry, by using different sensing heads which are easily and quickly interchangeable. Also, where colour varies over a surface, integration over a desired area can be achieved by using a suitable sensing head.

Duplication of the CIE colour matching functions: Since 1931, when the CIE¹ adopted a set of tables to define the colour-matching functions (\bar{x}_{λ} , \bar{y}_{λ} , \bar{z}_{λ}) of a standard observer, many investigators have attempted, with varying degrees of success, to duplicate these functions by physical means. Details about such

attempts and on the merits and limitations of the available tristimulus colorimeters are given by different authors, Judd and Wyszecki⁶, Wright⁸ and Wyszecki and Stiles⁹, to name a few.

The method used in all photoelectric colorimeters is to modify the spectral response of the photo-detector by the use of coloured filters. The energy distribution of the source and the spectral transmittance of the optical components used are taken into consideration. The filters could be positioned in the path of the light before it is incident on the detector, in (i) series arrangement (subtractive), or (ii) side by side arrangement (sometimes called Dresler principle³, or mosaic or additive), or (iii) a combination of both arrangements (i) and (ii). Theoretically, the CIE functions can be reproduced to a high degree of accuracy by using a large number of filters with subtractive and additive arrangements (see Davies and Wyszecki)². Colorimeters of such design can be calibrated to show directly the tristimulus values X , Y and Z of the sample under test. However, to use a large number of filters presents a difficult practical problem with colorimeters of conventional optical design. For this reason, the number of filters used is restricted to achieve a reasonable approximation to the required functions. This is why none of the photoelectric colorimeters at present available can be recommended for high accuracy colour measurements. They are useful only for differential colorimetry (Johnson et al)⁵.

The design of the fibre optics colorimeter offers enough degrees of freedom to duplicate the CIE functions to a very close approximation without any practical limitations as to the number or arrangement of the filters required and without appreciable loss in sensitivity.

Again, it has been reported in several investigations that measurements on the same sample, using different instruments of the same make, do not agree satisfactorily (Robertson and Wright)⁷. The reason for the discrepancies in the measurements is mainly the variation in the spectral responses of photocells of the same type. To select photocells of the same response or to make corrections on conventional instruments for the variations of the photocells is a costly process. Furthermore, the spectral response of the existing instruments can be determined only by calculations based on a number of measurements (the spectral response of the detector and the spectral transmittance of each filter used and of other optical components), and therefore the values calculated for their response curves are subject to cumulative errors of the individual measurements as well as errors due to internal reflections and stray light in the system. With the fibre optics colorimeter, the spectral response for the instrument as a whole can be measured directly and the accuracy will depend only on one measurement. Also, deviations from the required functions caused by variations in the detector or any other source can be comparatively easily corrected, by changing or adding filters in one or more of the paths of light in the different fibre optic elements.

Measurements on wet paint

Although it is fully appreciated that colour matching will be much quicker if it is based on measurements on wet paint than using dry paint films, yet, in practice, wet colour matching is seldom used in the paint industry. One of the main reasons is the practical difficulty in getting reproducible and reliable

results on wet paint. This is not unexpected, because most wet paint measurements and observations have been made on paint films and not liquid paint in bulk.

Wet paint film v. wet paint in bulk

A wet paint film is a continuously changing system, both the medium and pigment particles undergoing rapid changes that affect the colour appearance of the system. Also, unless very thick wet films of paint are used, the colour of the substrate and the thickness of the film will affect the colour. Without reproducible results on the colour of wet paint, the correlation with the corresponding dry film colour could not be established. Perhaps most of the views regarding the inadequacy of measurements on wet paint for the colour control of paint production are due to taking the colour of wet films of paint as representing the colour of the wet paint.

On the other hand, a wet paint in bulk, with the pigments adequately dispersed in the medium, represents a steady state of equilibrium between the pigments and the medium, at least for a period long enough to take measurements on its colour which could be reproducible. This will enable a correlation between the colour of a wet paint and the corresponding colour of a dry film to be derived.

Measurement on wet paint in bulk was therefore adopted in the present research programme.

Methods for the colour measurement of wet paint in bulk

There are three possible methods in which the fibre optics colorimeter can be used to measure the colour of a wet paint in bulk.

Method 1

The fibre optic elements, encased in a plastic sheath and terminating in a glass window fixed at the port of the sensing head, are immersed in the paint.

Method 2

The paint is viewed through a glass window in the paint container.

Method 3

The sensing head is fixed at a suitable distance above the surface of the paint. The colour measured in this case is that of the paint/air interface.

Only the second and third methods were tried, the first method being rejected because of the risk of paint reaching the optical components of the instrument. Cleaning the glass window of the container in method 2 is essential. In the third method, controlling the distance between the sensing head and the paint surface is of fundamental importance with the present geometry of the illumination and collection of light.

Reproducibility of the results on wet paint in bulk

Second Method: A small container with a glass bottom was used for the colour measurement of wet paint in bulk. The glass was thoroughly cleaned and the container was filled with the paint to be measured to a depth of about 30mm.

With the glass bottom against the port of the sensing head, the values of X , Y and Z were recorded. Three readings of X , Y and Z were taken for each one of the five paints of different colours used in this experiment. Before each measurement, the container and glass were cleaned and the paint was stirred for a period of about three minutes before it was poured in the container. The results obtained from the measurements on the five paints showed the same reproducibility as that obtained by measurements on dry paint, i.e. 0.2 per cent. The colour of the wet paint did not change over a period of 15 minutes.

Also, using the second method, comparison has been made between five pairs of wet paints (with the two paints in each pair slightly different in colour) and the corresponding pairs of dry films on glass plates with thicknesses giving near opacity. It was found that the difference in colour between any wet pair was at least equal to the difference in colour between the corresponding pair of dry paints as measured through glass.

Third method: A simple constant level device was constructed (Fig. 3) and used for the measurement of colour. The paint to be measured flows into an inlet tube to a funnel A which is enclosed in a cylindrical container B. The sensing head C of the colorimeter is fixed to the top of the container, which

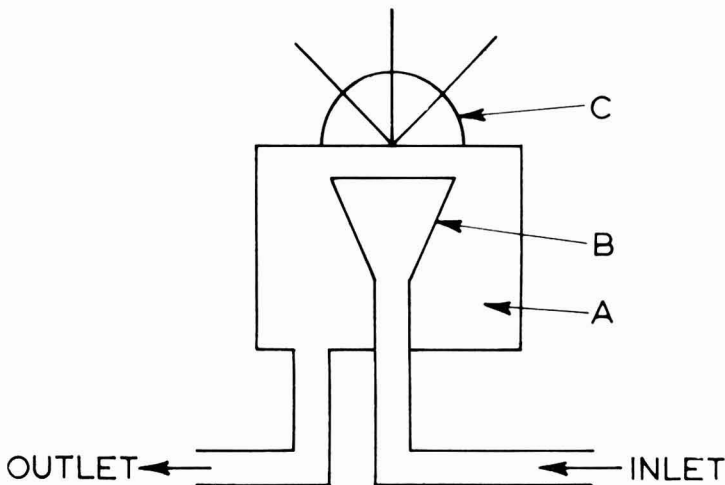


Fig. 3. Constant level device

has an outlet tube at its bottom. The flowing paint fills the funnel to the top and then flows out via the outlet tube. Keeping the edge of the funnel in a horizontal plane gives a constant distance between the surface of the liquid and the sensing head, and makes it possible to measure the colour of the wet paint at a paint/air interface. While the paint was flowing in, readings increased gradually and became constant (for X , Y and Z) when the funnel was filled with the paint. This process was repeated three times using a fresh sample of well stirred paint from the same tin on each occasion, and the results obtained showed the same reproducibility, 0.2 per cent, as with other measurements.

The relation between the colours of wet and dry paint

The usefulness of colour measurements on the wet paint depends on establishing

a relation between the colour of wet paint and the corresponding dry film (for a specified manner of application). The following experiments were undertaken to explore the correlation between the colours of wet paints in bulk and the corresponding colours of dry films.

Experiment 1

Samples from three production batches of each of three paints were provided by a member firm. The relative values of X , Y and Z were measured for the nine samples for both the wet paint in bulk (using the third method) and dry films applied to glass plates. The scale for each measurement was adjusted so that each of the Y tristimulus values read 1,000. Five readings for each of X , Y , Z for each sample were recorded and the average results calculated. Table 1 gives a summary of the ratios between $\frac{X_D}{X_W}$, $\frac{Z_D}{Z_W}$ for the nine samples, where the suffix D refers to dry film and W to wet paint.

Table 1
Relation between wet and dry colours

Paint	1			2			3		
Batch	1	2	3	1	2	3	1	2	3
$\frac{X_D}{X_W}$	0.99	0.99	0.99	1.01	1.00	1.01	0.99	0.99	0.99
$\frac{Z_D}{Z_W}$	1.08	1.10	1.12	1.07	1.08	1.08	1.08	1.08	1.08

For each paint, it can be seen that the variations between the ratios of the tristimulus values of the dry to wet paint for the three samples of the same paint are small. One of the possible reasons for the incomplete correspondence between wet and dry values in this experiment may be batch to batch variation in the refractive indices of the media used. (Measurements of the refractive index for each of six successive batches of the resin used in the paint showed variations which could account for the deviations noticed.) Also, variations in the percentage of the thinner from batch to batch would affect the wet colour.

However, among the six sets of readings, three gave complete correlation, two gave a spread of about 1 per cent and one gave a spread of about 4 per cent.

Experiment 2

Another member firm provided wet samples from each of the different trials during the colour correction for four different coloured paints, but unfortunately not in sufficient quantity to make all the repeat measurements necessary for maximum accuracy. However, the relative tristimulus values of two of the wet paints provided were measured. Five readings for each paint were taken while the paint was flowing in the constant level device (CLD). The relative variations in X , Y and Z for each correcting stage for two paints were measured. Fig. 4 gives the percentage deviation of X , Y and Z from the required colour in the different correcting stages. The samples obtained from the different stages of

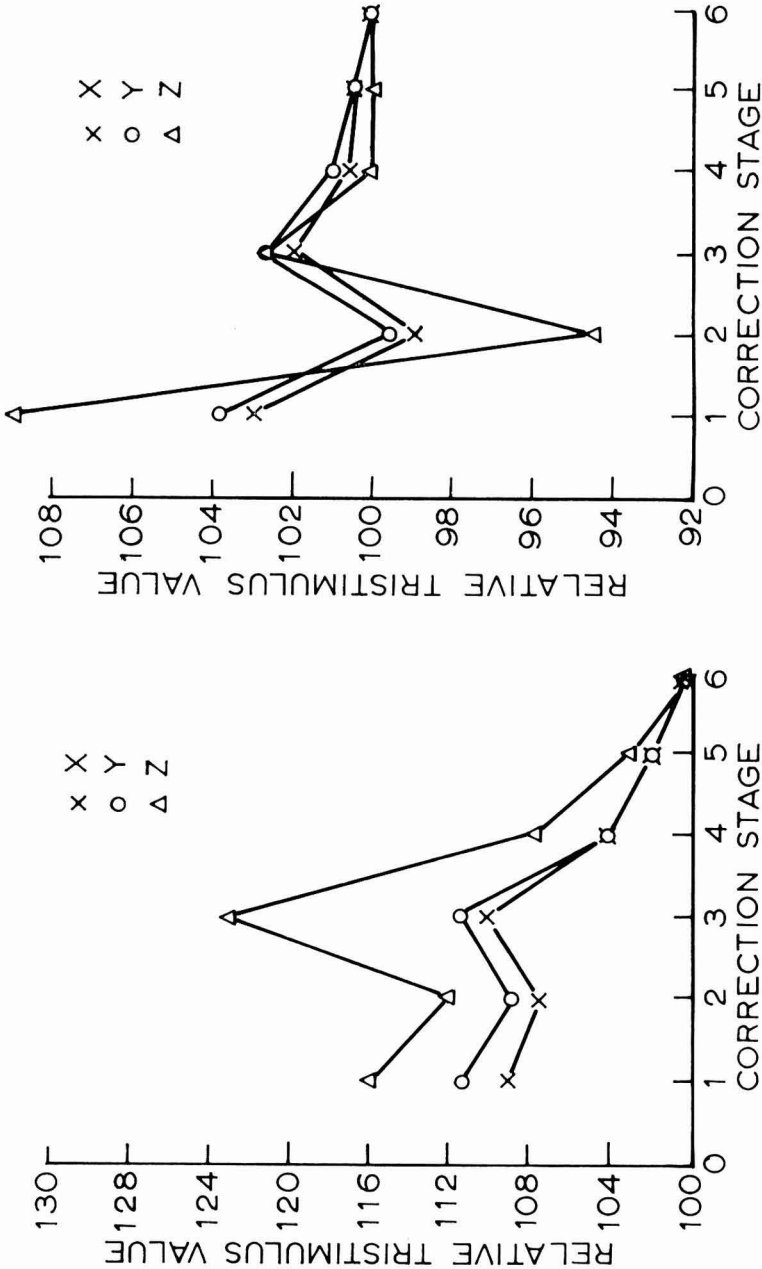


Fig. 4. The relative changes in the tristimulus values during correction stages for two paints

correction of one paint were pumped into the CLD successively. It was noted that X, Y and Z were almost constant for the same sample, and quickly changed when the next sample reached the paint surface that was being measured, then staying constant. This indicates that the paint was delivered to the surfaces without mixing in the CLD during the pumping process. This finding shows

that it should be possible to test the homogeneity of the paint in a batch container by pumping in paint from different parts of the container.

Colour control of paint in batch production

The high reproducibility of the results on wet paint using the third method, together with the satisfactory relation between the colours of wet and dry paints, and the fact that variations in the colour of the paint flowing in the CLD can be detected, make it possible to plan a trial for the colour correction of paint in batch production. It is hoped that such a trial will be arranged soon with the co-operation of member firms.

Colour control of paint on line

It is hoped to explore the possibility of automatic colour control of paint on line at a later date. Fig. 5 is a schematic diagram of the system proposed for this study.

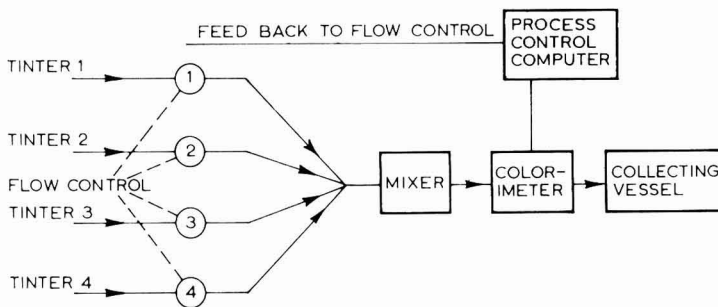


Fig. 5. A block diagram of a system for colour correction of paint on line

Four flow rate regulators connect four reservoirs to a mixer. Each reservoir contains one of the tinters required to give the desired colour of paint when mixed in certain ratios of volume (according to a predetermined formulation programme). The flow rate regulators deliver the paint to the mixer in the required proportions. The tristimulus values of the mixed tinters are measured by the colorimeter while the paint flows from the mixer to a collecting vessel. ΔX , ΔY , and ΔZ , the differences in the tristimulus values between the flowing paint and the required wet colour, are fed to a small process control computer, which is programmed to change the rates of flow of the tinters to correct the colour of the paint. The programme will also ensure that the integrated sums of ΔX , ΔY , and ΔZ , recorded over a certain period of time, will be zero.

Control of dispersion

With the fibre optics colorimeter and the CLD, a study of the possibility of controlling the dispersion process can be made in the following way. While the dispersion of a pigment in the medium is in progress, samples of the paint in full strength or mixed with predispersed white in certain proportions will be pumped into the CLD at suitable intervals. X , Y and Z will be recorded and the dispersion will be assumed to be completed when successive values of X , Y and Z are constant.

Other applications

To demonstrate remote colour control of a bath coloration process a special sensing head was designed, with $0^\circ/45^\circ$ geometry of illumination and collection of light for viewing the samples at a definite distance whilst immersed. The sample was withdrawn when its colour had reached the required predetermined value as shown by a digital voltmeter reading.

Results of colour measurements on samples of fabrics, fibres and on surface coatings have been encouraging. Possible uses of the colorimeter in many other industries, e.g. plastics, paper, ceramics, and other colour based industries are being explored.

Acknowledgements

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Dr G. de W. Anderson, Director of the Paint Research Association, who suggested exploring the possibility of utilising fibre optics for remote colour control of paint, and for his encouragement, which led to the development of the instrument.

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References

1. CIE Proc. 8th Session, 1931 Cambridge. Cambridge Univ. Press.
2. Davies, W. E. R., and Wyszecki, G., *JOSA*, 1962, **52**, 679.
3. Dresler, A., *Licht* 1933, **3**, 41.
4. Ishak, I. G. H., *Opt. Act.* 1970, **17**, 725.
5. Johnson, S., Phillips, D. H., Robertson, A. R., and Wright, W. D., *J. S. D. C.* 1963, **79**, 731.
6. Judd, D. B., and Wyszecki, G., "Colour in Business, Science, and Industry." London: John Wiley & Sons.
7. Robertson, A. R., and Wright, W. D., *JOSA*, 1965, **55**, 694.
8. Wright, W. D., "The Measurement of Colour," Fourth Edition 1969, London: Hilger and Watts Ltd.
9. Wyszecki, G., and Stiles, W. S., "Color Science," 1967, New York: John Wiley & Sons Inc.

Polyurethane finishes for the coil coating process*

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Summary

The coil coating process has developed from continuous metal strip coating, which has been used for about forty years. Towards the end of the fifties it received strong impetus from the aluminium industry, and later the steel industry followed suit. This paper discusses various aspects of the process, and shows how polyurethane coatings can be formulated for it.

Keywords

Processes and methods primarily associated with application of coatings
coil coating

Miscellaneous paint additives
blocking agent

Types and classes of coating
urethane finish

Catalysts, accelerators, inhibitors
aliphatic amine
organo-metallic catalyst

Finitions à polyuréthane pour couchage en continu

Résumé

Le procédé du couchage en continu a été dérivé de la métallisation en continu, qui a été utilisée depuis peu près quarante ans. Vers la fin des années cinquante, il a reçu de l'encouragement vigoureux à partir de l'industrie de l'aluminium, et ensuite de l'industrie de l'acier. Cet article apprécie les divers aspects du procédé et il démontre comment on peut formuler les revêtements polyuréthanes convenables.

Polyurethanlacke für das Bandlackierverfahren

Zusammenfassung

Das Verfahren, Bleche von der Rolle zu lackieren, entwickelte sich aus der laufenden Blechstreifenlackierung, die seit etwa 40 Jahren benutzt worden war. Gegen Ende der fünfziger Jahre erhielt das Verfahren einen starken Impuls von der Aluminiumindustrie, und später folgte die Stahlindustrie nach. In dieser Abhandlung werden die verschiedenen Seiten des Verfahrens bewertet, ausserdem wird gezeigt, wie eine geeignete Rezeptur für Polyurethan enthaltende Lacke zusammengestellt werden kann.

Полиуретановые отделки для процессов покрытия катушек

Резюме

Процесс покрытия катушек был разработан из процесса покрытия сплошных металлических полос, который применялся в течение около сорока лет. В конце пятидесятых годов он получил большой толчок от алюминиевой промышленности а затем и стальная промышленность последовала тому же примеру. Статья оценивает различные характеристики процесса и указывает метод формулировки полиуретановых покрытий для этого процесса.

* Presented to the Southern Branch of the London Section on 10 February 1970

Introduction

The coil coating process was developed mainly in the United States where, by 1967, about 269,000 tons of aluminium and 748,000 tons of steel were processed.

In Europe, plastics-coated strip was developed. The thickness of the plastic coating was approximately 200 to 400 microns. Coatings approximately 10 microns thick were used in packaging and Venetian blinds. Wide strip coating was pioneered in Sweden. Coated metal strips have been used in many applications. At present, about 75 per cent of the output is used for house sidings, roofing, partitions, etc, for the building trade. This field of application should drop to 10 per cent of the total as other outlets appear, of which the following are worth mentioning: metal doors, metal ceilings, dashboards, Venetian blinds, curtain rods, skirting-board heating, shelves, office furniture, lamps, radiator grids, shutters, refrigerators, table tops for camping desks, sandwich construction face sheets with a core of rigid plastic foam for standardised wall elements for exterior use, and pipe insulations. Further uses will probably arise.

The coil coating process was initially an offshoot of the fully-continuous metal strip coating plants developed in the United States. These plants consist of four decoilers and recoilers, two accumulators, steering elements, pre-treatment and chromating baths, coating bath, and ovens (see Fig. 1). Their special advantage lies in the possibility of coating both sides of the strip in one operation. The coated strip must hang free when it is transported through the oven, because thermoplastic material would be damaged at any points of support.

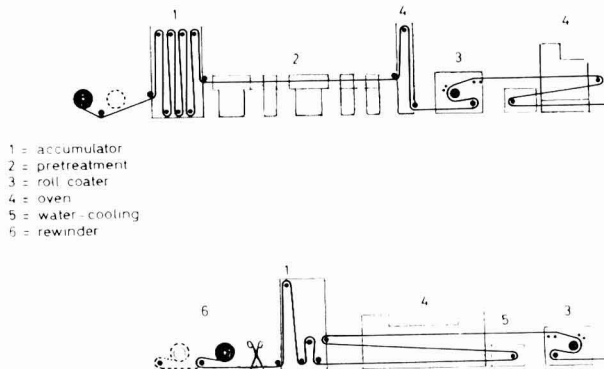


Fig. 1. Typical coil coating installation

Coil coating plants operate at speeds of approximately 100 metres per minute, and the aim is 200 metres per minute. Most plants in existence in Europe operate at lower coil speeds, around 30 to 60 metres per minute.

In practice, coatings are applied only by the roll coating method. Conventional roll coaters operate with applicator rolls and counter-pressure rolls, as shown in Fig. 2 They are not suitable for coatings thicker than 20 microns, and hence, in the United States the "reverse roll coater" has been developed.

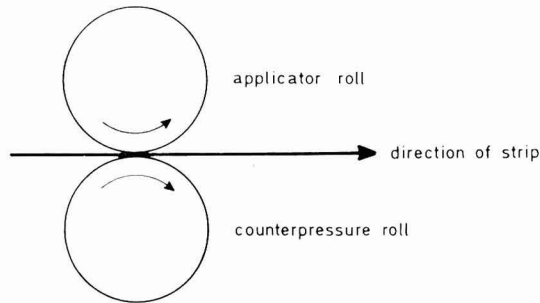


Fig. 2. Conventional roll coater

producing coating thicknesses of up to 1,000 microns (Fig. 3). The coatings so produced are perfectly uniform, which is an important factor in their use and durability. The film thicknesses applied in practice are normally 25 to 35 microns.

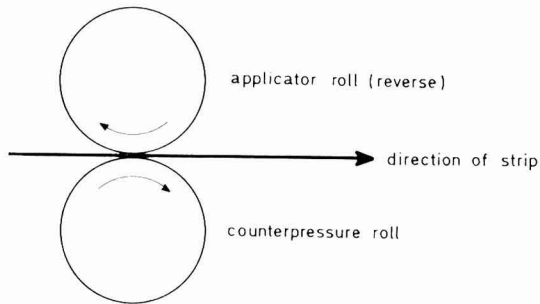


Fig. 3. Reverse roll coater

For higher coil speeds, such as 150 to 200 metres per minute, application by curtain coater would be possible, although, as has been stated, this method is not used commercially at present. The metals used are normally aluminium or galvanised steel, although ungalvanised steel strip has also gained in importance.

Coating properties

Metal strips coated by the coil coating process may be shaped some considerable time after processing. The coating materials should therefore have properties that are suitable for satisfactory subsequent processing. These properties should be internationally standardised. In the United States there is the National Coil Coaters Association (N.C.C.A.) and since 1967 there has been the corresponding European Coil Coating Association (E.C.C.A.), which prepares quality standards. The shaping processes include three-dimensional shaping, bending, embossing, deep-drawing, punching, bevelling, drawing of profiles, etc.

The properties of the coating should be unchanged when it is subjected to one of these processes after normal storage time. The paint film produced by the coil coating process should also show good durability after the shaping

process and should possess the same properties that are demanded of the product. Thus, the coating should not show the following defects when exposed to weathering or to appropriate tests: peeling, splitting off, flaking, blistering or wrinkling, cracking, slight abrasion, changes of colour shade, dirt retention, and formation of rust or mildew.

Forming of coated strip

Shaping is the most important process for coated metal strip. The degree of deformation has been fixed by means of the T-bend test. In this test the thickness of the metal strip is decisive, since it determines the radius of the deformation. Thus bends 0-T, $\frac{1}{2}$ -T, 1-T, $1\frac{1}{2}$ -T, and so on are obtained as shown in Fig. 4.

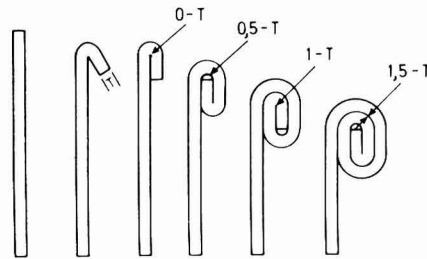


Fig. 4. T-Bend test

The bending capacity is defined by E.C.C.A. in the form of the following formula:

$$\text{bending behaviour } T = \frac{\text{smallest inner bending radius}}{\text{metal thickness}}$$

Since the coated sheets are shaped and a high degree of protection against corrosion is demanded, it seems to be of interest to learn whether the metal surfaces are changed by the deforming process. To study this effect, uncoated metal strips were subjected to the T-bend test and at deformed spots the surface was documented by microphotographs. The results are shown in Fig. 5 for 0.75mm thick aluminium strip, and in Fig. 6 for 0.75mm thick galvanised steel strip.

The greater the bending, the greater the tearing up of the metal surface. This is very noticeable at T-bend 1.

It is obvious that limits to the deformability should be set. House sidings, for example, should be permanently protected against corrosion. Experience, however, shows that such protection is only afforded if an active pigment with anti-corrosive properties is in contact with the metal surface. It is in any case advisable, for this reason, to apply a primer protecting against corrosion. The properties of the primer should be such that the surface cracks of the metal, as they may be formed by the coil deformation, are perfectly bridged and that the primer with its active pigment covers the freshly exposed metal surface.

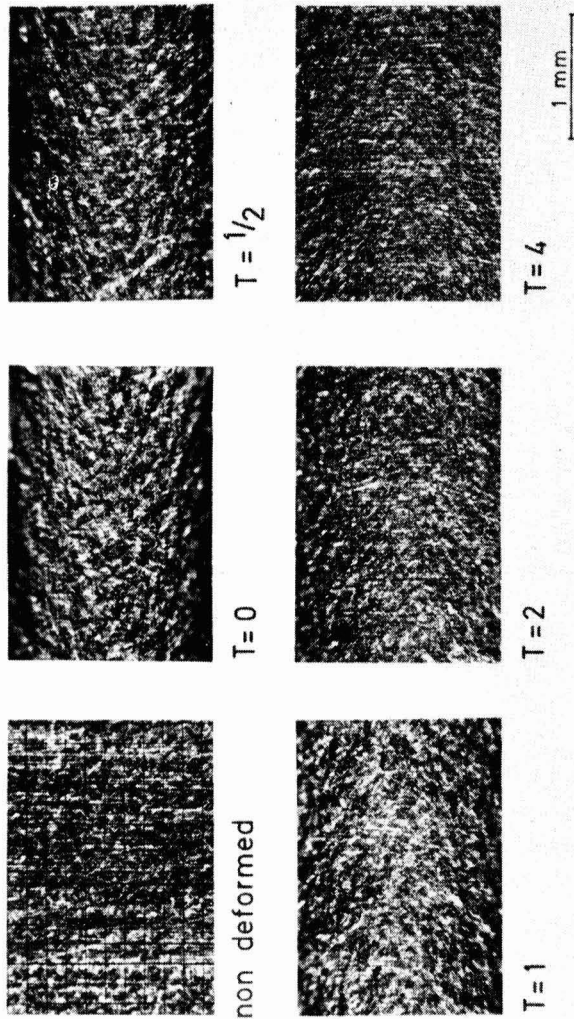


Fig. 5. Deformation of non-coated metal sheets during T-bend test
0.75mm Al; pure

Another important property in connection with deformation should also be mentioned. The primer should adhere to the metal strip and the top coat to the primer. An accelerated test showing up these defects within a short time consists in the drawing of coated metal strips into so-called cups which are then stored at 80 to 100°C for several hours. Fig. 7 demonstrates the result of such a test.

Adhesion is satisfactory if the coating adheres smoothly to the metal surface. The lower cup illustrates bad adhesion.

This simple example leads to the conclusion that all accelerated tests should be carried out on deformed metal strips.

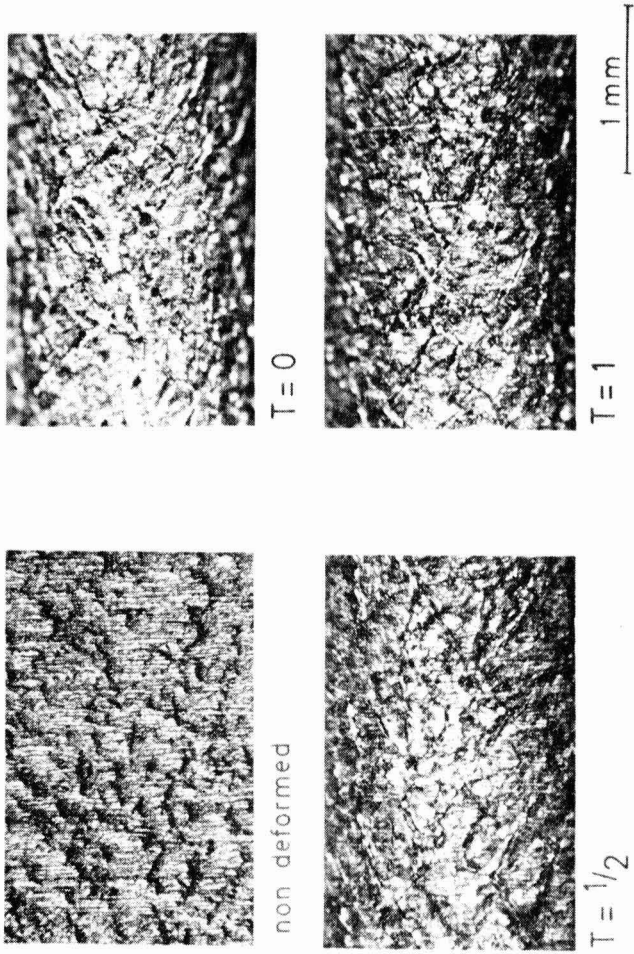


Fig. 6. Deformation of non-coated metal sheets during T-bend test

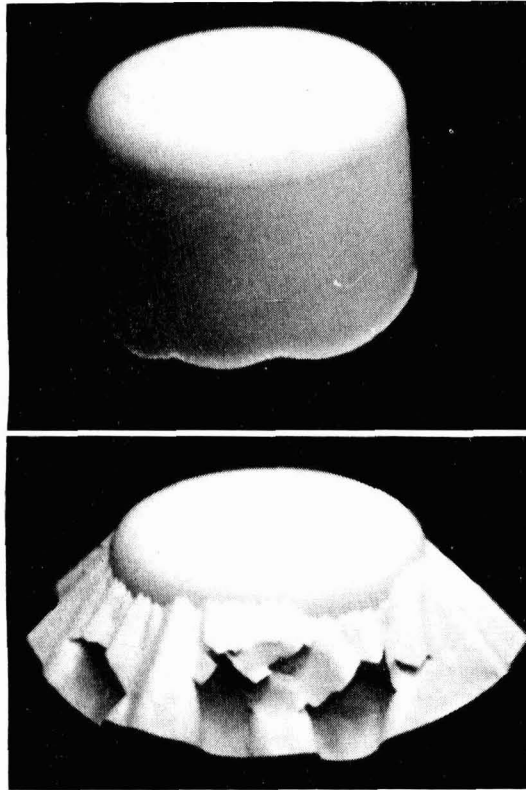


Fig. 7. Results of cupping test for adhesion

Systems for coil coating

Many different binding media are used in the coil coating process, such as alkyd/melamine combinations, vinyl-alkyd compounds, silicone alkyds, acrylates, epoxy solutions, epoxy esters, oil-free polyesters, pvc coatings, organosols, plastisols, polyvinyl fluorides, and polyvinylidene fluorides. Their different properties are listed in Table 1. According to this list, silicone alkyds, acrylates, pvf, and pvdf binding media impart good to excellent weather resistance. Colour retention during permanent exposure to temperature is stated to be good to very good. Gloss varies for silicone alkyds and acrylates from 5 to 95 and for pvc's from 10 to 50. With respect to mar resistance, acrylates are better than silicone alkyds, and pvf products are quite markedly poorer. As far as chemical resistance is concerned, pvf products are superior to all other systems.

Pvf coatings are excellent with respect to deformability and they are not subject to any limits, but silicone alkyds and acrylates can only be deformed within limits governed by the thickness of the coating. Pvf finishes can be successfully used for metal strip coating, with no limits being set on the subsequent use of the strips, whereas with other binding media, there are restrictions.

Table
Prepainted metals and

	Prepainted metals						
	Alkyd-amine	Vinyl-alkyd	Silicone alkyd	Acrylic	Epoxy (solution)	Epoxy (ester)	Polyester
Base metal* and thickness, in.							
Aluminium	0.006-0.080	0.006-0.080	0.006-0.080*	0.006-0.080*	0.006-0.080	0.006-0.080*	0.006-0.080
Cold-rolled steel .. .	0.003-0.075	0.003-0.075	0.003-0.075	0.003-0.075*	0.003-0.075	0.003-0.075	0.003-0.075
Tin mill black-plate steel	0.002-0.015	0.002-0.015	0.002-0.015	0.002-0.015	0.002-0.015	0.002-0.015	0.002-0.015
Electrolytic tin steel ..	n/a	n/a	n/a	n/a	0.006-0.025*	0.006-0.025*	0.003-0.075*
Electrogalvanised steel ..	0.008-0.075	0.008-0.075	0.008-0.075*	0.008-0.075*	0.008-0.075	0.008-0.075	0.008-0.075*
Hot dip galvanised steel..	0.016-0.075	0.016-0.075	0.016-0.075*	0.016-0.075*	0.016-0.075	0.016-0.075	0.016-0.075*
Aluminised steel	0.016-0.075	0.016-0.075	0.016-0.075*	0.016-0.075*	0.016-0.075	0.016-0.075	0.016-0.075*
Preplated steel	n/a	n/a	n/a	0.003-0.075	0.003-0.075*	0.003-0.075*	0.003-0.075*
Film thickness, mils¶ ..	0.1-1.2	0.1-1.2	0.7-1.2	0.9-1.2	0.1-1.0	0.1-1.0	0.1-1.2
Pencil hardness	HB-2H	HB-2H	HB-2H	H-2H	F—> 3H	H-2H	HB—> 3H
Film adhesion†	Good	Good	Good	Excellent	Excellent	Excellent	Good
Mar resistance	Good	Good	Good	Excellent	Excellent	Good	Excellent
Maximum recommended service temperature, F ..	200	150	350	275	300	300	250
Resistance to:¶							
Salt spray	Fair	Good	Good	Excellent	Excellent	Excellent	Good
Humidity	Good	Good	Good	Excellent	Excellent	Excellent	Good
Grease, oil	Good	Good	Good	Excellent	Excellent	Good	Good
Acids, alkalis	Fair	Fair	Good	Good	Excellent	Good	Fair
Food, household agents ..	Fair	Fair	Good	Good	Excellent	Good	Good
Solvents, aliphatic hydrocarbons	Good	Good	Good	Excellent	Excellent	Excellent	Good
Solvents, aromatic hydrocarbons	Good	Fair	Good	Good	Excellent	Excellent	Good
Solvents, oxygenated ..	Fair	Fair	Good	Good	Excellent	Good	Fair
Weathering, pigmented film	Good	Fair	Excellent	Good	Poor	Poor	Good
Weathering, clear film ..	Fair	Fair	Good	Good	Poor	Poor	Fair
Colours available	Full range§	Full range§	Full range§	Full range§	Black, grey	Black, grey, white	Full range§
Colour retention:							
High temperature	Good	Good	Excellent	Excellent	Fair	Fair	Good
Long time	Good	Good	Excellent	Excellent	Fair	Fair	Good
Gloss range (60 deg.), % ..	5.95	5.95	5.95	5.95	5.95	5.95	5.95
Gloss retention at high temperature	Good	Good	Excellent	Good	Fair	Fair	Good
Surface textures available ..	Smooth	Smooth	Smooth	Smooth	Smooth	Smooth	Smooth
Sizes available	←———— Full width coils, 66in wide; minimum or slit width coils, ½in wide;						
Fabrication characteristics..	Fair formability. Suitable for about 3 T-bends without visible hairline fractures. Sustains only slight draws	Fair flexibility. Suitable for roll forming and slight drawing 2 T-bends without hairline fractures are possible	Fair flexibility. Can be roll formed to ⅜ in radii. 2-3 T-bends can be made without hairline fractures	Formability varies with film thickness. Medium and thin film thickness suitable for deep drawing	Excellent film adhesion permits deep drawing and intricate fabrication	Excellent film adhesion permits deep drawing and intricate fabrication	Good to excellent flexibility. Suitable for most forming operations. Can be bent to radii twice thickness
Applications.. .. .	Venetian blinds, drums, pails, tool sheds, toys, louvres, automotive parts, interior uses	Roof decking, baseboard, heating covers, toys, shelving, drapery hardware, licence plates	Exterior building panels, siding, mobile homes, telephone booths, other exterior uses	Wall panels, siding, hot water jackets, refrigerator lining, radio and tv cabinets, business machines	Non-decorative interior uses. Air-conditioners, vending machines, oil filters, electric dryers	Non-decorative interior uses requiring high resistance to chemicals, solvents, humidity and high temperature	Appliance finishes, siding accessories, radio and tv cabinets, business machines, building panels

* indicates most common metal coating combinations. † Based on optimum metal surface condition, primer and film prints. ¶ Film thickness of 0.3in and less are used primarily for prime coats or reverse side protection.

Prepainted metals					Plastic-metal laminates			
Vinyl (solution)	Vinyl (organosol)	Vinyl (plastisol)	Polyvinyl fluoride	Polyvinylidene fluoride	Polyvinyl fluoride	Polyvinyl chloride	Polyester	TFE fluoro-carbon
0.006-0.080* 0.003-0.075* 0.002-0.015* 0.003-0.075* 0.008-0.075* 0.016-0.075* 0.016-0.075* 0.003-0.075*	0.006-0.080* 0.003-0.075* 0.002-0.015* 0.003-0.075* 0.008-0.075* 0.016-0.075* 0.016-0.075* 0.003-0.075*	0.006-0.080* 0.003-0.075* 0.002-0.015* 0.003-0.075* 0.008-0.075* 0.016-0.075* 0.016-0.075* 0.003-0.075*	0.006-0.080* 0.003-0.075 0.002-0.015 0.003-0.075 0.008-0.075 0.016-0.075* 0.016-0.075* 0.003-0.075	0.006-0.080* 0.003-0.075 0.002-0.015 0.003-0.075 0.008-0.075 0.016-0.075* 0.016-0.075* 0.003-0.075	0.006-0.064* 0.003-0.048 0.002-0.015 0.003-0.075 0.008-0.048 0.016-0.052* 0.016-0.075* 0.003-0.075	0.006-0.064* 0.003-0.048* 0.002-0.015* 0.003-0.075* 0.008-0.048* 0.016-0.052* 0.016-0.075* 0.003-0.075*	0.006-0.064* 0.003-0.048* 0.002-0.015* 0.003-0.075* 0.008-0.048* 0.016-0.052* 0.016-0.075* 0.003-0.075*	0.006-0.064 0.003-0.048 0.002-0.015* 0.003-0.075* 0.008-0.048* 0.016-0.052* 0.016-0.075* 0.003-0.075*
0.1-1.2 HB-5H Excellent Good	0.7-4.0 F-H Excellent Fair	4.0—>20.0 n/a Excellent Fair	0.5-2.0 n/a Good Fair	0.5-2.0 n/a Good Fair	1.5-2.0 ‡ Good Good	4.0-25.0 ‡ Excellent Fair	0.5-14.0 ‡ Fair Excellent	1.0-20.0 ‡ Good Good
150	175	200	250	250	225	200	300	400
Excellent Excellent Excellent Good Good	Excellent Excellent Excellent Excellent Good	Excellent Excellent Excellent Excellent Good	Excellent Excellent Excellent Excellent Excellent	Excellent Excellent Excellent Excellent Excellent	Excellent Excellent Excellent Excellent Excellent	Excellent Excellent Excellent Excellent Good	Excellent Excellent Excellent Excellent Excellent	Excellent Excellent Excellent Excellent Excellent
Good	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Poor Poor	Fair Poor	Fair Poor	Excellent Excellent	Excellent Excellent	Excellent Excellent	Fair Poor	Excellent Excellent	Excellent Excellent
Good Poor	Excellent Poor	Excellent Poor	Excellent Excellent	Excellent Excellent	Excellent Excellent	Excellent Poor	Poor Poor	— —
Full range§	Full range§	Full range§	Full range§	Full range§	Full range§	Full range§	Clear or metallised	Clear or metallised
Fair Good 5.95	Fair Good 10.90	Fair Good 10.80	Good Excellent 10.50	Good Excellent 10.50	Good Excellent 10.35	Fair Good 10.80	Fair Good High only	Excellent Excellent High only
Fair Smooth	Fair Smooth	Fair Smooth, striated, embossed	Good Smooth	Good Smooth	Good Smooth	Fair Smooth or textured 54in max. width	Excellent Smooth 60in max. width	Excellent Smooth 36in max. width
maximum steel coil weight, 20,000lb →								
Excellent fabrication. Can be bent 180 deg without visible hairline fracture. Suitable for deep drawing	Excellent formability. Suitable for deep draw- ing, roll forming, stamping	Excellent formability. Films flexible enough to bridge cracks in base metal	Excellent formability. Suitable for all types of fabrication	Excellent formability. Suitable for all types of fabrication	Type and thickness of metal sub- strate limits degree to which laminates can be drawn, bent	Excellent formability. Substrate limits types of fabrica- tion. At high tem- perature film may lift on ex- tremely tight radii	Formability varies with film thick- ness. High film strength may destroy bond in tight bends	Excellent formability. Scoring during fabrication may damage film
Siding, small appliances, metal wall tiles, refrigerator liners, roll formed tubular products, curtain rods, toys, deep drawn parts	Siding, roof shingles, automotive parts, deep drawn parts	Siding, cur- tain walls, auto dashboards, luggage, business machines, furniture appliance kick-plates, embossed parts	Siding, roof shingles, chemical resistant parts	Siding, roof shingles	Siding, chemical research ventilation ducts, laboratory benches, table tops, hospital accessories	Siding, radio and tv cabinets, auto interior trim, air- craft panelling, camera cases, office machines, air ducts, sealing gaskets	Flexible reinforce- ment for brittle metals, light and heat reflectors	Self- lubricating bearings, high release surfaces, heat and light reflectors, high tem- perature parts

thickness. ‡ For details consult appropriate plastics section. § Full range means white, pastels, dark colours, clear and

Price is often an obstacle to the general use of pvf coatings in the coil coating process. Polyurethane coatings are available at a more economic cost, and have remarkable properties, thus closing a gap in the field of coil coating finishes.

The advantage of polyurethane coatings is that they can be formulated not only as air-drying but also as stoving finishes. This results in a considerable advantage in comparison with all other binding media used in the coil coating process.

It has been mentioned that the coated metal strips are subsequently shaped and transported to their point of use. They are then installed. Despite protective films, damage to the coating cannot be prevented. Repair is only possible with air-drying coatings. This constitutes a genuine advantage of polyurethane coatings, which are air-drying as well as stoving systems. A practical test has shown that damage to shaped and installed metal strips coated with polyurethane finishes by the coil coating process was considerably less than finishes based on other media. For repairs, only one-third of the quantity of coating material necessary for conventional coil coating finishes was required for polyurethane systems.

Another advantage is that in, for instance, house sidings, polyurethane coated metal strips can be overcoated to advantage at a later date with air-drying polyurethane finishes that are at the same time weather-resistant and colour-retentive.

Polyurethane systems

For the coil coating process, those systems whose drying time can be reduced by the application of heat to a rate of 30 to 90 seconds are most suitable. Of the polyurethane systems, air-drying two-component catalysed systems fulfill this condition. The polyisocyanates shown below have acquired special importance for coil coating.

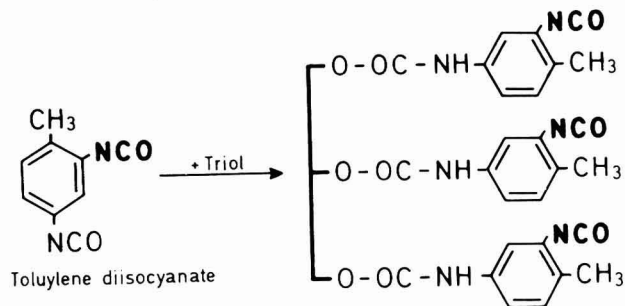


Fig. 8. Polyisocyanate 1

Polyisocyanate 1

A prepolymer of tolylene diisocyanate and trimethylol propane (Fig. 8). Polyurethane films produced on this basis do not show gloss retention during weathering. After a weathering time of only six to twelve months, the gloss decreases to 50 to 60 per cent of the initial value. The decrease in thickness after seven years of weathering is approximately 10 to 20 microns. There is poor colour shade retention. Abrasion resistance, impact resistance, and

chemical resistance are favourable. The main field of application should be for darker colour shades. If gloss retention is required, coatings based on polyisocyanate 3 should be used.

Polyisocyanate 1 can be used in the coil coating process, but it should be noted that the pot-lives of the coatings is not longer than 10 to 100 hours.

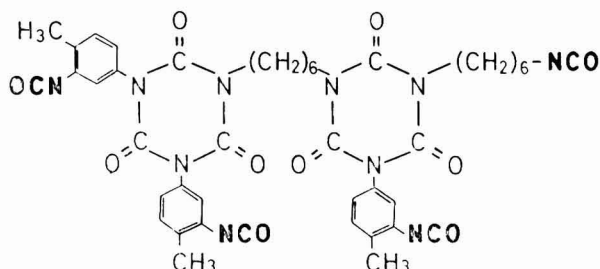


Fig. 9. Polyisocyanate 2

Polyisocyanate 2

A copolymer of tolylene diisocyanate and hexamethylene diisocyanate (Fig. 9). With this product, polyurethane films are obtained which lose about 50 per cent of the initial gloss after weathering for a year. The colour retention of the films is very good. The mechanical and chemical properties are comparable to those of polyurethane 1 films. Coatings based in polyisocyanate 2 should be used mainly where no exposure to weathering is to be expected, particularly in the case of light shades.

Polyisocyanate 2 can also be used in the coil coating process. Pot-lives are of the order of 10 to 72 hours.

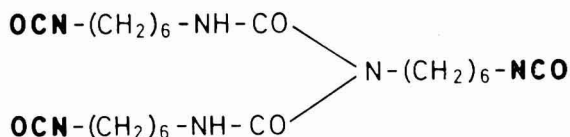
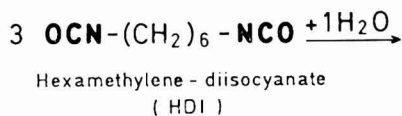


Fig. 10. Polyisocyanate 3

Polyisocyanate 3

A biurette triisocyanate made from hexamethylene diisocyanate and water (Fig. 10). The coatings obtained are resistant to weathering and show good colour and gloss retention. A two-year test in Florida resulted in only a slight decrease in gloss. The coating was undamaged and had maintained its anti-corrosion protective properties. The mechanical properties are remarkable,

particularly for abrasion resistance and resistance to chemicals. Polyisocyanate 3 based coatings can be used for both indoor and outdoor applications. They have pot-lives of about 12 to 120 hours. Application by coil coating plants is now quite common.

Processing of coil applied polyurethane coatings produced from free polyisocyanates, such as the polyisocyanates 1, 2 or 3, in combination with suitable polyhydroxy compounds, is possible and has been practised. A special advantage is that, by application of heat, the drying speed of the air-drying films can be reduced as desired. Temperatures of about 200°C are sufficient to achieve drying within 30 to 60 seconds.

A characteristic feature of all polyisocyanates is the free isocyanate group. This group is so reactive that appropriate polyisocyanates give coatings of only limited pot-life. This property means that these isocyanates can be used only in two-component systems.

Blocked isocyanates

A different behaviour is shown by blocked isocyanates, which do not react appreciably in the temperature range 20 to 100°C. Such blocked isocyanate can therefore be used for the production of one-component polyurethane coatings possessing a shelf life of one year and longer. To achieve reaction with polyhydroxy compounds and thus film formation, it is necessary that the blocked isocyanates are split up so that the reactive isocyanate groups are released. This splitting-up is effected by use of elevated temperature, i.e. during stoving.

The splitting temperature depends on the type of blocking agent and varies over a wide range. Thus, agents such as hydrocyanic acid, acetoacetic ester, and acetyl acetone, which are split at temperatures ranging from 100 to 160°C, are mentioned in the literature. At present, corresponding products have not acquired any importance, partly due to the fact that toxic products are evolved. A substance that has gained importance as a blocking agent is phenol. Products such as polyisocyanate 1a and polyisocyanate 3a are on the market, having a splitting temperature in the region of 160°C, and a stoving time of 60 to 90 minutes.

Monovalent alcohols such as butanol would certainly be interesting as blocking agents. However, splitting temperatures are so high that a prolonged stoving time is necessary. This consequently means that coatings turn dark-yellow to brown. The most favourable performance with respect to splitting temperature and stoving time is shown by oxime-blocked polyisocyanates. For instance, these products split up at 175°C within 20 minutes. Like the air-drying polyisocyanates, they give high-gloss coatings. In contrast, coatings obtained on the basis of phenol-blocked polyisocyanates show a degree of gloss of 60.

The splitting temperatures of blocked isocyanates and stoving times of appropriate coatings can be considerably reduced by catalysts, but this would also shorten the pot-lives. If, for example, tertiary amines are used as catalysts, the pot-life of coatings based on polyisocyanate 1a (phenol-blocked aromatic isocyanate) will be reduced from more than a year to a few weeks, and in the case of primary and secondary amine catalysts, to a few minutes or hours.

The performance of organometallic compounds is considerably more favourable. Their influence on the pot-life is markedly reduced. The splitting temperature and the stoving times approach the value of interest for the coil coating process. Metal catalysts, such as zinc octoate and dibutyl tin dilaurate, should also be mentioned; these are used in concentrations of 1 to 2 per cent and 0.5 to 1 per cent, respectively, calculated on blocked polyisocyanate/polyhydroxy compound.

As has already been mentioned, these catalysts have virtually no influence on the pot-lives. At a stoving temperature of 260°C, a typical figure for the coil coating process, the stoving time is two minutes when using phenol-blocked isocyanates and one minute when using oxime-blocked isocyanates. These are data based on laboratory scale measurements. Tests in practice have shown that, at 260°C, stoving times of 40 seconds are sufficient. The layout of the oven and especially the temperature of the object will play an important part in this connection.

The reaction components used for the free and blocked polyisocyanates are polyhydroxy compounds. They have to be chosen so that stoved films are sufficiently flexible. The coated metal strips are further processed, for example shaped, bevelled, and punched. The polyhydroxy compounds should be selected to give the required properties for these methods of processing.

The desired flexibility can be achieved in two ways. One is to vary the polyisocyanate proportions. If a ratio of NCO:OH lower than 1.0 is chosen, then, as a rule, coatings are obtained that show reduced weather resistance. The flexibility properties are improved only to a negligible extent. A marked improvement of these properties is achieved by using the second method. This involves the use of slightly branched or linear polyhydroxy compounds of higher molecular weight with few hydroxyl groups.

Appropriate polyhydroxy compounds include polyester alcohols made of trimethylol propane, glycerol, butane diol, adipic acid, and dimerised fatty acids, with OH numbers ranging from 45 to 160, or similar branched or linear polyether alcohols, according to the alkoxylation process. The polyhydroxy compounds should, of course, be selected with regard for the nature and properties of the polyisocyanates with which they are combined. One important property in this connection is compatibility. Polyamidoamines may also be used in part as co-reactants for blocked polyisocyanates.

The reagents used with the polyisocyanates should, of course, be selected with a view to the T-bend test requirement. In the case of polyurethane coatings, it is to be expected that the flexibility decreases after ageing. With respect to the coil coating process, this means that the T-bend test value obtained immediately after stoving decreases appreciably after ageing for about eight weeks. It is thus actually possible that after stoving a T-bend value of 0.5 to 1 is obtained, but after storage of the coated metal strip, this value may increase to 2. This change, however, can be eliminated to a very great extent by the selection of the polyhydroxy compound. Thus, for instance, combinations consisting of polyisocyanate 3 with a mixture of a polyester alcohol on the basis of adipic acid, trimethylol propane, butane diol, a polyester alcohol

based on a dimeric fatty acid, glycerol, and butane diol meet the requirements for coil coating.

It is, of course, possible to add to the coatings the conventional auxiliaries. For instance, silicone oils, polyvinyl acetate, or cellulose esters are used as flow-promoting agents. The pigment volume concentration can be varied between 12 and 25 per cent, with the degree of gloss of the films necessarily varying as well.

The individual polyurethane coatings can be used as single-coat finishes if emphasis is placed on adhesion. A two-coat system is always advisable, to obtain adequate protection against corrosion. The coil coating machines are designed for two-coat systems and even for coating the lower side of the strip. Pretreatment primers generally used under polyurethane top coats can also be applied in this case, namely "Alodine 1200" on aluminium and alkyd/melamine or phenol/epoxy resins on galvanised steel or aluminium. Polyurethane primers formulated to give very flexible coatings are extremely suitable too.

The properties of polyurethane coatings are generally improved by stoving. Such properties include film hardness, resistance to abrasion, marring, weathering, and chemicals. Air-drying polyurethane coatings can be used to advantage as repair finishes.

The sum total of all these properties suggests the use of these polyurethane coatings in the coil coating process, and they will find their place among the established coil coating finishes in due course.

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Dispersion in aqueous media*

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Summary

Pigment dispersion is just as important in aqueous systems as in non-aqueous systems, particularly in terms of colour strength. Most aqueous systems are pigmented by the use of pigment pastes, usually supplied by the pigment manufacturer. The constitutions and methods of manufacture of these types of pastes are briefly reviewed. The ICI/Joyce LoebL disc centrifuge can be used to give accurate size distribution curves of the pigment particles in these pastes. From these curves, the degree of dispersion of the pigment can be calculated.

Both anionic and non-ionic surfactants are used in commercial pigment pastes. This is in keeping with current theory, which postulates two separate mechanisms for achieving dispersion stability, namely electrostatic repulsion and steric hindrance. From the results obtained with the centrifuge, there seems to be little to choose between the two as regards effectiveness in aqueous systems.

The relationship between colour strength and particle size has been determined for a number of organic pigments in aqueous systems. The curves vary markedly from pigment to pigment.

It is believed that the dispersion levels achieved in aqueous systems are substantially better than those achieved in non-aqueous systems. It is felt that an investigation of this phenomenon would have considerable theoretical and practical importance.

Keywords

Types and classes of coating
non-aqueous paint
water base paint

Properties, characteristics and conditions primarily associated with:
manufacture and synthesis
dispersion

materials in general
particle size

Le niveau de dispersion pigmentaire en milieux aqueux

Résumé

Le niveau de dispersion pigmentaire est tout à fait aussi important en les systèmes aqueux qu'en non-aqueux, surtout au point de vue du pouvoir colorant. Les systèmes aqueux sont, en général, pigmentés par les pâtes de pigments qui sont usuellement fournies par le fabricant de pigments. On passe en revue brièvement la composition et les méthodes de fabrication de ces types de pâte. On peut utiliser le centrifugeur à disque ICI/Joyce LoebL pour construire des courbes précises de la répartition pigmentaire de ces pâtes. A partir de ces courbes on peut calculer le degré de dispersion pigmentaire.

On emploie les agents tensio-actifs anionique ou non-ionique dans les pâtes de pigments commerciales. C'est en accord avec la théorie d'aujourd'hui qui annonce deux mécanismes différents pour achever les dispersions stables, à savoir, la repulsion électrostatique et l'empêchement stérique. A partir des résultats rendus par le centrifugeur, il apparaît qu'il n'y a pas beaucoup de différence entre ces deux mécanismes en ce qui concerne leur efficacité en systèmes aqueux.

On a déterminé en systèmes aqueux le rapport entre le pouvoir colorant et la grandeur particulaire d'un nombre de pigments organiques. Les courbes varient en grand mesure d'un pigment à l'autre.

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On considère que les niveaux de dispersion que l'on achève en systèmes aqueux sont largement mieux que ceux mis en évidence par les systèmes non-aqueux. On croit qu'une investigation de ce phénomène ait une grande importance à la fois théorique et pratique.

Dispersion in Wässrigen Bindemitteln

Zusammenfassung

Pigmentdispersion ist gerade so wichtig in wässrigen Systemen, wie in nicht-wässrigen, besonders hinsichtlich Farbkraft. Die meisten wässrigen Systeme werden mit Pigmentpasten pigmentiert, die gewöhnlich von der Farbenfabrik geliefert werden. Die Zusammensetzungen und Herstellungsmethoden dieser Pastentyps werden kurz besprochen. Mit der ICI-Joyce Loebel Scheibenzentrifuge können genaue Grössenverteilungskurven der in diesen Pasten enthaltenen Pigmentpartikel bestimmt werden. Von diesen Kurven kann man den Dispersionsgrad des Pigmentes berechnen.

Für Pasten des Handels werden sowohl anionische, als auch nichtionische oberflächenaktive Mittel angewandt. Dies steht im Einklang mit der vorherrschenden Theorie, welche zwei getrennte Mechanismen zur Erzielung von Stabilität einer Dispersion fordert, nämlich elektrostatisches Abstoßen und sterische Hinderung. Von den mit der Zentrifuge erhaltenen Resultaten zu schliessen, scheint kein grosser Unterschied zwischen den beiden hinsichtlich Wirkung in wässrigen Systemen zu bestehen.

Für eine Anzahl organischer Pigmente in wässrigen Systemen wurden die Beziehungen zwischen Farbkraft und Teilchengrösse bestimmt. Die Kurven fallen je nach Pigment ganz verschieden aus.

Es wird angenommen, dass in wässrigen Systemen ein erheblich besserer Dispersionsgrad erhältlich ist, als in nichtwässrigen. Eine Untersuchung dieses Phänomens würde zweifellos erhebliche theoretische und praktische Bedeutung besitzen.

Дисперсия в водных средах

Резюме

Пигментная дисперсия одинаково существенна как в водных так и в безводных системах, в особенности по отношению к стойкости цвета. Большинство водных систем пигментируются применением пигментных паст, обычно поставляемых изготовителем пигмента. Дается краткое описание построения и метода производства этих паст. Дисковая центрифуга I.C.I. Джойс Лобля может быть использована для получения точных кривых распределения величины пигментных частиц в этих пастах. Из этих кривых можно высчитать степень дисперсии пигмента.

Как анионозные так и неионогенные поверхностно-активные вещества применяются в промышленных пигментных пастах. Это согласуется с современной теорией, которая постулирует два отдельных механизма для получения устойчивой дисперсии, а именно электростатического отталкивания и пространственного препятствия. Судя по результатам полученным с центрифугой, не наблюдается существенной разницы между последними, что касается их эффективности в водных системах.

Зависимость между прочностью цвета и величиной частицы определялась для ряда органических пигментов в водных системах. Кривые сильно отличаются среди различных пигментов.

Считается что дисперсные уровни достигаемые в водных системах намного лучше чем в безводных системах и выводится заключение что дальнейшее исследование этого вопроса будет иметь существенное теоретическое и практическое значение.

Introduction

Pigment dispersion is an important study in all types of systems, aqueous and non-aqueous, because certain principles are applicable in all pigmented systems.

First, the pigment must be dispersed in order to develop its colour value. This dispersion can be a slow, difficult and hence expensive process. Secondly, the degree to which it should be carried out is uncertain and the optimum may vary from one application to another. The minimum amount of dispersion is probably that required to ensure that no pigment particles are visible to the naked eye.

The maximum extent to which dispersion is carried is much less certain. As dispersion of the pigment increases, a number of properties of the pigmented system alter, for example:

- flow properties depart more and more from Newtonian
- colour strength of the end product increases
- transparency of the end product increases
- opacity of the end product decreases
- the gloss of the end product increases.

With increasing dispersion, therefore, some application properties will improve and some worsen, and the optimum degree of dispersion will depend on the particular application.

Although these general principles apply to all pigmented systems, aqueous systems warrant a study of dispersion by themselves, by virtue both of their size and economic importance, and also the technical factors which apply to them and not to non-aqueous systems.

There are a considerable number of pigment using industries in which the vehicle is water based. These include:

- plastic emulsion paint manufacture
- viscose rayon manufacture
- paper dyeing applications
- paper coating applications
- oil-bound distemper manufacture
- textile printing applications
- aqueous printing ink manufacture
- aqueous paint manufacture.

These applications represent an important market for pigments and, therefore, any symposium on pigment dispersion must include a study of pigment dispersion in aqueous systems.

The main difference between aqueous and non-aqueous systems is that the former are usually coloured by pigment pastes and the latter by pigment powders.

Pigment pastes

The majority of pigments are made in aqueous systems and begin life as aqueous dispersions. Even where pigments can be made in a non-aqueous phase, as with the phthalocyanines, their after-treatment or conditioning is usually done in an aqueous phase and again they begin their useful life as aqueous dispersions. For use in aqueous applications it is not surprising, therefore, that

these aqueous dispersions should be the starting point. If their pigment content and degree of dispersion could be controlled, they could be incorporated into most systems merely by stirring.

If made by the pigment manufacturer, such properties could be closely controlled and standardised.

The only major drawback to the use of such dispersions would be their low pigment content. After precipitation most pigments are filtered and washed, the end product being a pigment/water press cake in which the solids content would be about 20 to 25 per cent. Speciality pastes made from these would have a pigment content somewhat lower, usually less than 20 per cent. Consequently, for every one part of pigment introduced into a system, at least four parts of water would also be introduced. This dilution effect might not be tolerable, especially in products of strong shade.

This drawback has prevented the successful use of aqueous pigment pastes in aqueous printing inks, but has not prevented their use in the other applications listed.

The pigmentation of all these other systems is now accomplished, almost completely, by the use of specialised aqueous pigment pastes, and any study of dispersion in aqueous media must include a study of such pastes.

The pigment pastes sold for these purposes are speciality pastes in that they are tailor-made for specific applications. This means that they will have an adequate pigment level, adequate dispersion, adequate storage properties, and adequate compatibility with the system for which they are intended.

The pastes are made from the original press cakes by grinding in the presence of surfactants. The types of grinding equipment and surfactants used have been described fully by P. Birrell¹ and will be quickly summarised here.

Preparation of pastes from press cakes

Shearing, milling or grinding must be applied to press cakes because the dispersion of the pigment in these cakes is very coarse. This can be seen by microscopic examination or measured by using the Coulter Counter. They usually exhibit a wide range of particle sizes, the mean being of the order of 2μ . The basic particle size of the pigment calculated from the simple formula $S = 6/\rho d$ where:

$$S = \text{specific surface area in m}^2\text{g}^{-1}$$

$$\rho = \text{density in g.cm}^{-3}$$

$$d = \text{mean diameter in microns}$$

is usually 0.25μ or less and the strong inference is that in the press cake the pigment is in the form of aggregates. The shearing, grinding, milling, etc. is necessary to reduce these aggregates to basic individual particles if possible.

Because the press cake starting material has a relatively low solids content, the viscosity of any dispersions subsequently made from it will only be low or medium and hence the mills used must be suitable for dealing with these low or medium viscosities. Such mills include: ball mills, Kady mills, sand grinders, attritors, vibratory mills.

These mills vary in their efficiency, capacity and rate of throughput. However, no matter which is used, a suitable stabilising agent must be incorporated into the pigment paste or a satisfactory dispersion will not be obtained. The milling process breaks down the aggregates, the stabilising agent is required to prevent the particles re-aggregating.

It is commonly believed that these agents exert their effect by being adsorbed on the surface of the pigment particles and modifying their surface forces. They are consequently called surface active agents or surfactants.

Surfactants

There are three types of surfactants:

- anionic
- non-ionic
- cationic

Anionic surfactants: dissociate in water giving large negative ions which are adsorbed strongly on most powder surfaces, whether they are pigmentary or not. The surface of the pigment particles acquires a negative charge and mutual repulsion of the particles then occurs.

The most widely used anionic surfactant is the sodium salt of dinaphthyl methane disulphonic acid. This is a powerful stabilising agent in aqueous systems: it is cheap, is unaffected by wide changes in pH, and does not give rise to foaming. It is used extensively in aqueous pigment pastes for viscose and plastic emulsion paints, paper dyeing and paper coating.

Non-ionic surfactants: do not ionise in water, and hence their stabilising action must be different. They are usually condensation products from fatty alcohols and ethylene oxide. They are believed to be adsorbed on the surface of the pigment particles with the hydrophilic polyoxyethylene chains reaching out into the water phase. The long molecular chains projecting from any particle interact with the chains from other particles, preventing the particles from coming close enough for aggregation to take place. Non-ionic surfactants are usually unaffected by changes in the pH of the system or by the presence of other surfactants. They usually lower the surface tension of water and hence can give rise to foaming.

A wide variety of them is available commercially and many of them are very efficient stabilising agents for organic pigments in water. Their efficiency appears to vary somewhat from pigment to pigment.

Cationic surfactants: as their name implies, ionise in water to give large cations which can be adsorbed on pigment surfaces, giving the particles a positive charge. This will prevent aggregation by mutual repulsion.

They are more expensive than anionic surfactants and will also give rise to foaming.

Obviously, anionic and cationic surfactants, when both present in the same system, will neutralise one another.

There is no doubt that many cationic surfactants are powerful stabilising agents for pigments, but they are seldom used in commercial pigment pastes. This is due to the fact that the systems to be pigmented are usually anionic

in nature and the presence of the anionic material would destroy the efficiency of the cationic surfactant.

A large number of aqueous pigment pastes have been available commercially for many years, based on either anionic or non-ionic surfactants, and prepared from filter press cakes.

They exhibit a high degree of dispersion, good storage stability and good compatibility with many industrial products.

Their chief drawback, as already mentioned, is their low solids content.

Preparation of pastes from powders

The low solids content is due basically to the fact that the starting material is a press cake. If aqueous pigment pastes are required with higher solids content, the starting material has to be the full strength pigment powder.

Because of their higher solids content, the viscosity of such pastes will be much higher and their preparation will require dispersing machinery that can handle high viscosities. Triple-roll mills and kneading machines of the double Z-blade type are suitable.

The pigment powder used as the starting material has to be wetted out by the water and then dispersed. If the dispersing agent is anionic, a separate wetting agent may be required. If the dispersing agent is non-ionic, a separate wetting agent will not be required as non-ionic surfactants are also good wetting agents.

In the preparation of high solids aqueous pigment pastes, non-ionic surfactants seem to be more efficient than anionic surfactants. With their help, finely dispersed pigment pastes can be obtained with pigment contents of 40 per cent or more. Because they are based on non-ionic surfactants, these pastes have good compatibility with most aqueous systems, because the non-ionic is readily soluble in water and is unaffected by electrolytes present in it.

Measurement of pigment dispersion

Although aqueous pigment pastes have been available commercially for many years and many of them demonstrably have a high degree of pigment dispersion, it has not been possible to measure this degree of dispersion. Usually the pastes are compared with a standard paste for colour value.

The author has approached the problem of measuring the degree of dispersion of aqueous pigment pastes in the following manner.

The surface area of the pigment powder as determined by nitrogen adsorption will give all the available surface area which can come into contact with the water if the aggregates present in the powder are completely dispersed. The actual surface of the pigment in contact with the water can be calculated from the particle size distribution of the pigments in the water, assuming the particles to be spherical. If this surface is equal to the nitrogen surface area, the pigment will be completely dispersed and the degree of dispersion will be 100 per cent. If this surface is less than the nitrogen surface area, the pigment will not be completely dispersed and the degree of dispersion defined as:

$$\frac{\text{actual surface area}}{\text{N}_2 \text{ surface area}} \times 100, \text{ will be less than 100 per cent.}$$

The nitrogen surface area of pigments can be determined by the classical BET method. A modified version of this, using a Sorptometer, has been shown to be suitable for pigments².

Measuring the particle size distribution of pigments in aqueous pastes has been more difficult experimentally. Sedimentation under gravity is too slow; optical microscopy is not sensitive enough; electron microscopy will not handle an actual aqueous paste; the Coulter counter is not sensitive enough. Disc centrifuges are sufficiently sensitive and the ICI/Joyce Loebel disc centrifuge has been shown to be a reliable instrument for measuring the particle size distribution of aqueous pastes³. This instrument employs a line start technique and the physical removal of samples of specific size fractions. These samples have to be analysed separately for their pigment contents. In the author's experience this analytical step presents no major problems for organic pigments, but poses some very difficult problems with inorganics, and with carbon blacks is virtually impossible.

Some of the size distributions obtained with this instrument for various commercial aqueous pastes are given in Figs. 1-6.

Figs. 1 and 2 give the particle size distribution of various commercial aqueous pastes of Green DBN (CI Pigment Green 8). Fig. 1 gives the size distributions of the press cake and the paper paste of this pigment, and Fig. 2 gives the size distributions of Green DBNX, a standard used for viscose. Both the paper paste and the Green DBNX contain anionic dispersing agents and are made from the press cake. This figure also gives the size distribution of Green CPV3 paste. This is a standard intended for plastic emulsion paints. It is made from the Green DBN powder with the aid of non-ionic surfactants.

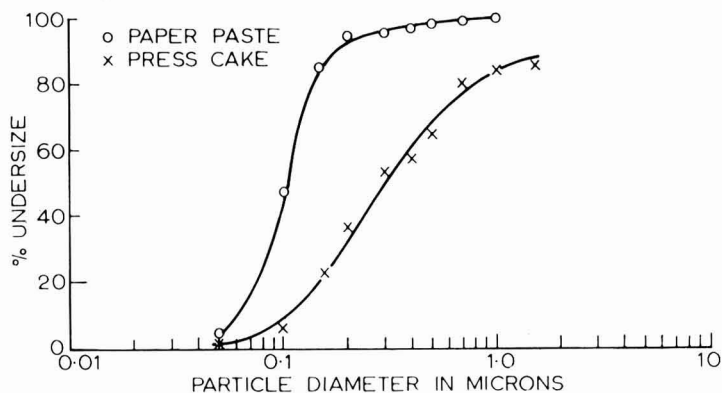


Fig. 1. Particle size distribution of CI Pigment Green 8 (Pigment Green B) in a paper paste and in press cake

Figs. 3 and 4 give the size distributions of the corresponding pastes based on a β -form phthalocyanine blue, Blue GLS, (CI Pigment Blue 15). Fig. 3 gives the size distribution of the press cake and the paper standard (anionic).

Fig. 4 gives the size distribution of the viscose standard, Blue GLX, which is anionic and made from the press cake, and also gives the size distribution of Blue CPV2 paste. This is a standard intended for plastic emulsion paints. It is made from the Blue GLS powder with the aid of non-ionic surfactants.

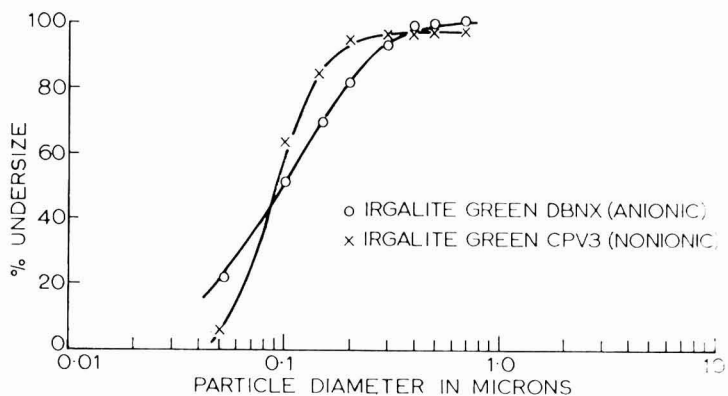


Fig. 2. Particle size distribution of CI Pigment Green 8 (Pigment Green B) in anionic and non-ionic pastes

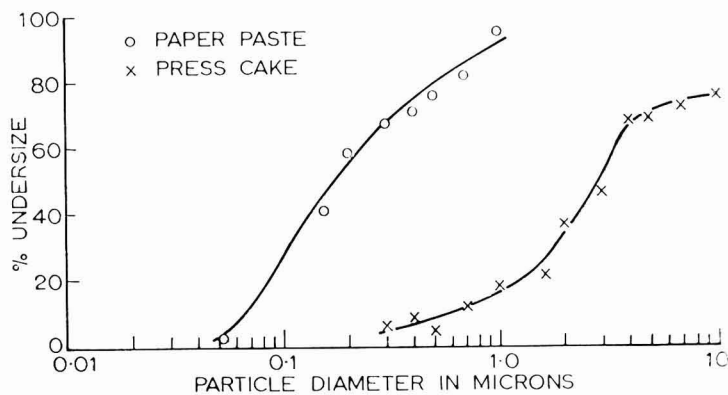


Fig. 3. Particle size distribution of CI Pigment Blue 15 (beta phthalocyanine) in a paper paste and in press cake

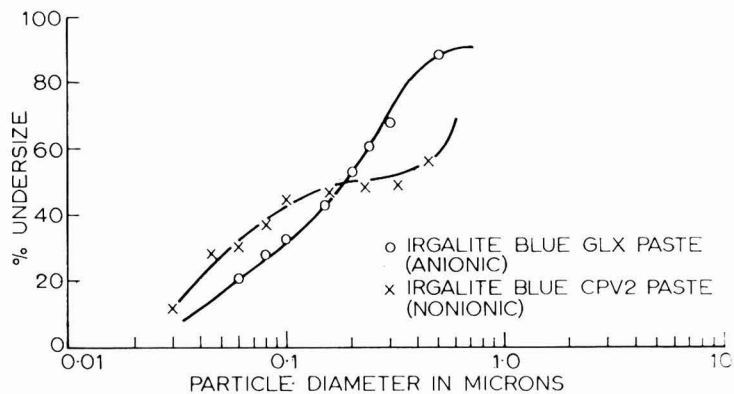


Fig. 4. Particle size distribution of CI Pigment Blue 15 (beta phthalocyanine) in anionic and non-ionic pastes

Figs. 5 and 6 give the size distributions of the corresponding pastes based on a toluidine red, Scarlet RNP (CI Pigment Red 3). Fig. 5 gives the curves for the press cake and paper paste, and Fig. 6 gives the curve for the viscose standard (anionic), Scarlet RNPX, as well as the size distribution of Red CPV2 paste. This is a standard intended for plastic emulsion paints. It is made from the Scarlet RNP powder with the aid of non-ionic surfactants.

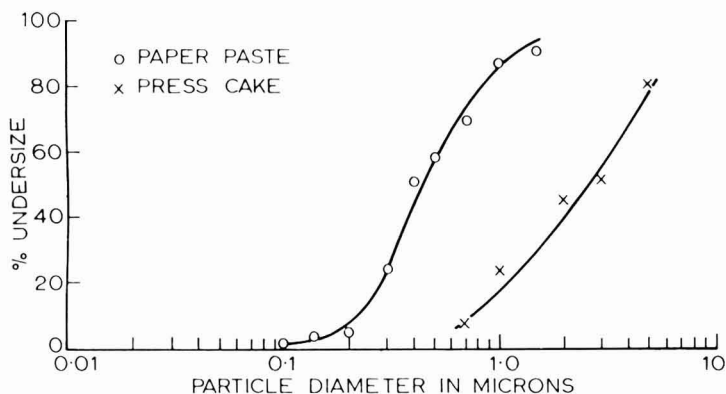


Fig. 5. Particle size distribution of CI Pigment Red 3 (toluidine red) in a paper paste and in press cake

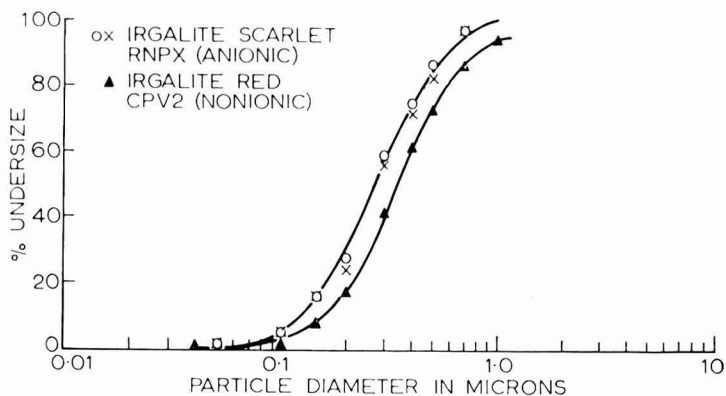


Fig. 6. Particle size distribution of CI Pigment Red 3 (toluidine red) in anionic and non-ionic pastes

The equivalent or effective surface areas of these pastes can be readily calculated from the size distribution curves. This has been done and the figures divided by the nitrogen surface areas of the powders to give a degree of dispersion of the pigments in the various pastes. The results are given in Tables 1, 2 and 3.

Table 1
Aqueous pastes of Green DBN (CI Pigment Green 8)

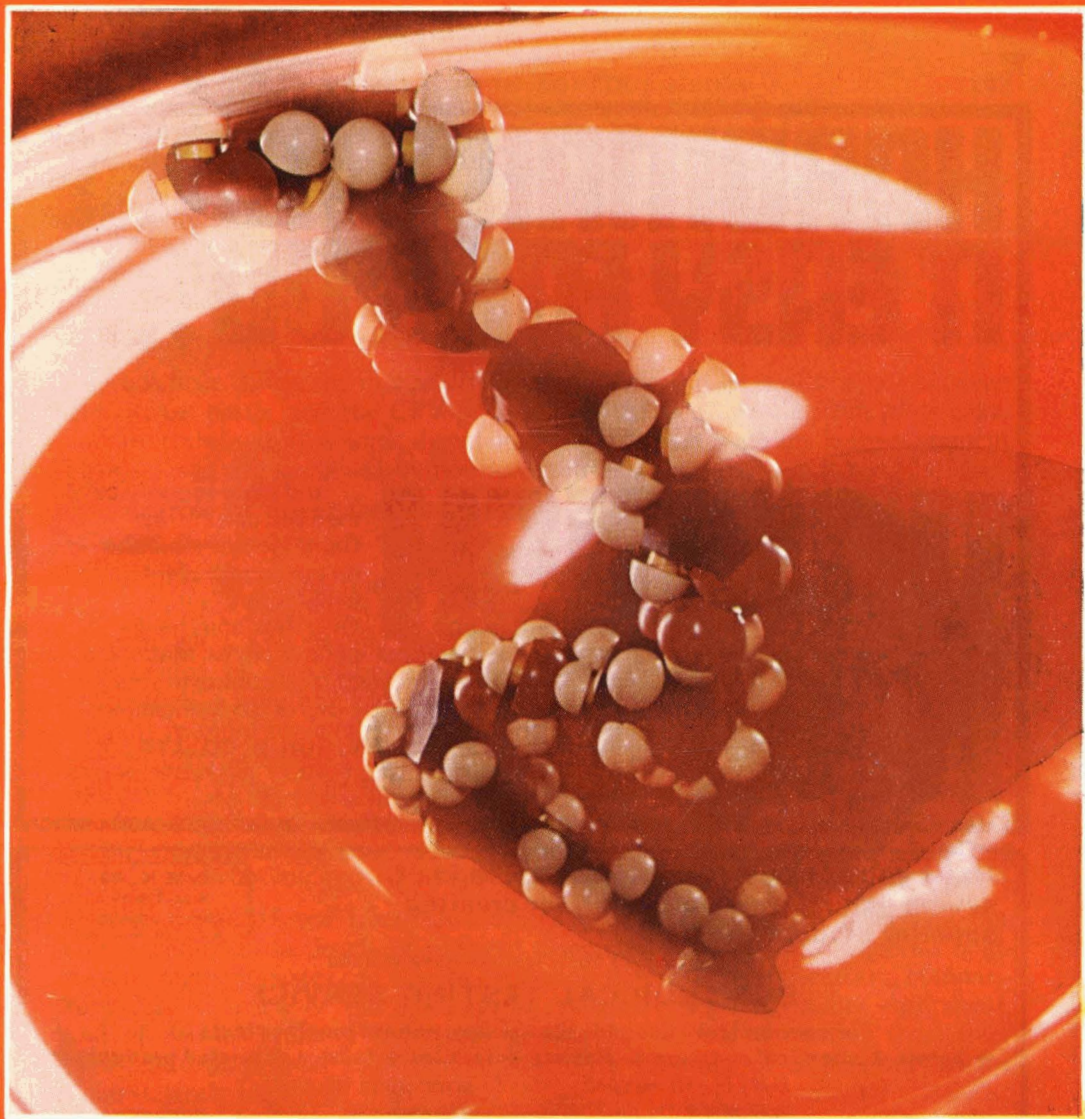
Paste type	Nitrogen surface area of pigment powder (1) m^2g^{-1}	Equivalent surface area from size distribution curve (2) m^2g^{-1}	Degree of dispersion of pigment = $(2)/(1) \times 100$ (%)
Press cake ..	89.3	16.7	18.7
Paper Green DBN	89.3	(i) 41.7 (ii) 36.2	(i) 46.7 (ii) 40.5
Green DBNX ..	89.3	51.5	57.6
Green CPV3 ..	89.3	44.4	49.7

Table 2
Aqueous pastes of Blue GLS (CI Pigment Blue 15)

Paste type	Nitrogen surface area of pigment powder (1) m^2g^{-1}	Equivalent surface area from size distribution curve (2) m^2g^{-1}	Degree of dispersion of pigment = $(2)/(1) \times 100$ (%)
Press cake ..	51.2	2.6	5.1
Paper Blue GLS	51.2	26.8	52.3
Blue GLX ..	51.2	49.9	97.5
Blue CPV2 ..	51.2	50.1	97.9

Table 3
Aqueous pastes of Scarlet RNP (CI Pigment Red 3)

Paste type	Nitrogen surface area of pigment powder (1) m^2g^{-1}	Equivalent surface area from size distribution curve (2) m^2g^{-1}	Degree of dispersion of pigment = $(2)/(1) \times 100$ (%)
Press cake ..	10.4	2.4	23
Paper Scarlet RNP	10.4	(i) 9.7 (ii) 10.2	93.2 98.1
Scarlet RNPX	10.4	(i) 18.4 (ii) 22.3	177 214
CPV2	10.4	13.3	128



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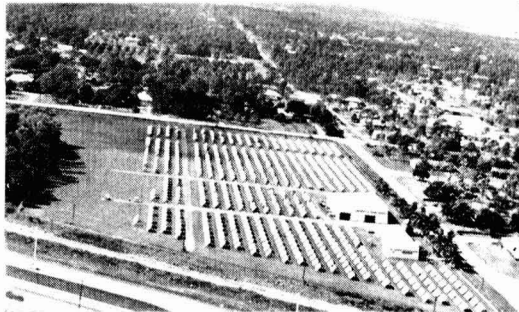
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These results show a number of interesting points.

Experimentally, the sizing technique used gives good size distribution curves, bearing in mind that each point represents a separate experiment.

The progression in fineness from press cake through paper paste to viscose paste is in the correct order, bearing in mind the amount of grinding and the percentage of added surfactant.

The sizing technique is sensitive down to 0.025μ .

There is little difference in size distribution or general level of fineness between the viscose pastes and the CPV pastes. The former are made from press cake, and are stabilised by anionic dispersing agent; the latter are made from pigment powders and are stabilised by non-ionic surfactants.

The degrees of dispersion calculated by dividing equivalent surface area by nitrogen surface area are reasonable and in the correct order.

The only surprising thing about the results is that the degrees of dispersion for some of the toluidine red pastes are much greater than 100 per cent. This pigment has a low specific surface area, indicating a large basic particle. The high degree of dispersion can be explained by assuming that the grinding processes not only break down pigment aggregates to basic particles, but also actually fracture some of the latter, exposing fresh surfaces. Toluidine red is also generally regarded as a pigment having a soft texture. Degrees of dispersion well over 100 per cent have also been found for well dispersed commercial aqueous pastes of other pigments. In each case the pigment powder has a low surface area and is generally regarded as a soft textured pigment. Such pigments include dinitraniline red (CI Pigment Orange 5) and the arylamide yellows.

With the ICI/Joyce LoebI disc centrifuge and the buffered layer and line start technique, the levels of pigment dispersion achieved with aqueous commercial pigment pastes can now be accurately determined. If necessary, comparisons can be made of the efficiency of various types of grinding equipment, and of various types of dispersing agents. The effects of starting from filter press cake or powder can be compared. The stability of dispersions can be quantitatively measured with respect to time, pH and resin content.

As already mentioned, commercial aqueous pastes are stabilised by anionic or non-ionic surfactants. They have adequate storage properties. On standing indoors, i.e. above freezing temperatures, they coarsen slightly over periods of six months but the increase in mean diameter is very slight, of the order of 0.05μ . They are unaffected by changes in pH from 4 to 9. The dispersion is unaffected by dilution with water, provided the dilution is carried out slowly with stirring. They are compatible with the systems for which they are intended, in that they can be incorporated into them without coarsening of the dispersion. This has only been proved in a small number of cases because of experimental difficulties.

Taking the case of a white emulsion paint tinted with Red CPV2 paste, for example, if an attempt is made to determine the size distribution of the toluidine red particles in the paint and compare it with the size distribution in the original paste, certain difficulties arise.

These difficulties are of an analytical rather than a physical nature. Before the paint can be fractionated, it must be diluted to a level where the solids content is low enough to give free sedimentation. Solids here include both the white pigment, titanium oxide, and extenders. If the solids content is reduced to say 0.5 per cent w/w, the amount of organic pigment in the diluted paint will be much smaller. The diluted paint can be centrifuged and the various size fractions removed by the sampling probe, but the very small amount of organic pigment present in each sample makes its quantitative determination inaccurate. This problem can be solved by carrying out the fractionation in quadruplicate, collecting the corresponding size fractions, and estimating the amount of pigment in the combined fractions. This procedure is obviously very slow and tedious, but a small number of such determinations have been made. Fig. 7 gives the size distribution curve for the organic pigment toluidine red in an emulsion paint which had been tinted with Red CPV2 paste in the laboratory. It also shows the size distribution of the pigment in the actual Red CPV2 paste. The same figure shows the size distribution curve for a commercial paint, in which the Red CPV2 paste had been added by the paint manufacturer.

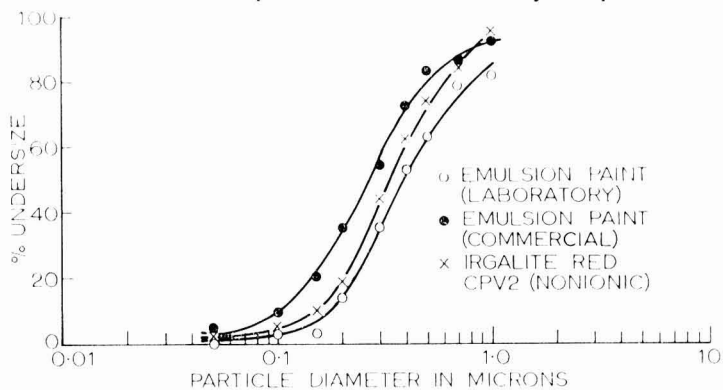


Fig. 7. Particle size distribution of CI Pigment Red 3 (toluidine red) in emulsion paints and in a non-ionic paste

Fig. 8 gives the size distribution curves for Green DBN (CI Pigment Green 8) in an emulsion paint which had been tinted with Green CPV3 paste, as well as the size distribution of the pigment in the actual green CPV3 paste.

Fig. 9 gives the size distribution curves for the organic pigment (CI Pigment Red 112) in an emulsion paint which had been tinted with Red CPV3 paste as well as the size distribution of the pigment in the actual Red CPV3 paste.

It will be seen that there is no significant worsening of the pigment dispersion after incorporation into the emulsion paint.

Earlier, it was pointed out that one application where aqueous pastes are not suitable colouring agents was in the preparation of aqueous flexographic inks. This is because the solids content is not high enough. Pigmented inks of this type can be made by grinding the pigment powder into the aqueous resin solution by suitable means, such as ball milling or sand grinding. Very fine dispersions can be obtained by these methods without the addition of a conventional surfactant. Fig. 10, for example, gives the size distribution of a commercial

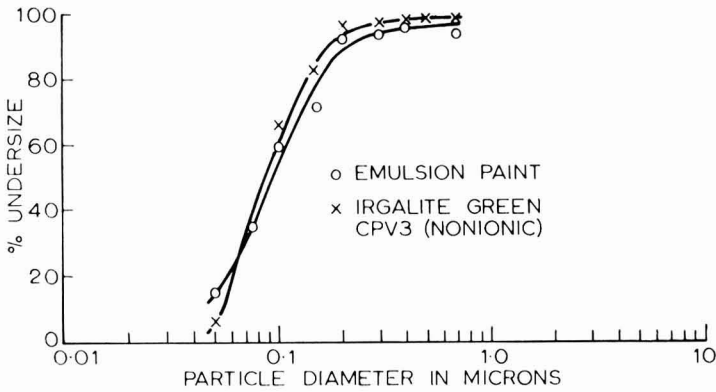


Fig. 8. Particle size distribution of CI Pigment Green 8 (Pigment Green B) in emulsion paint and in a non-ionic paste

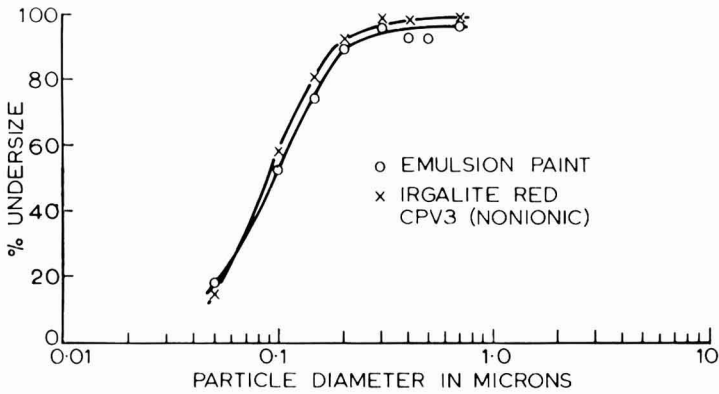


Fig. 9. Particle size distribution of CI Pigment Red 112 in emulsion paint and in a non-ionic paste

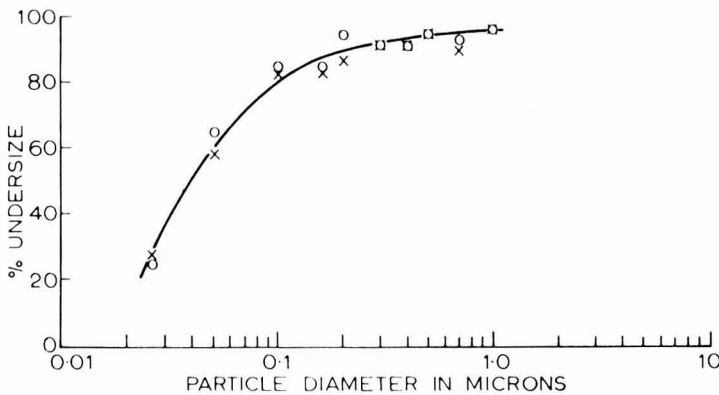


Fig. 10. Particle size distribution of CI Pigment Blue 1 in a commercial aqueous flexographic ink

aqueous flexographic ink made by sand grinding. The pigment in this ink was a PMT basic dye complex (CI Pigment Blue 1) of a specific surface area of $87\text{m}^2 \text{g}^{-1}$.

The graph shows that the dispersion is exceptionally good, 80 per cent by weight of the pigment particles being less than 0.1μ in size. Despite this fineness, the level of dispersion achieved was not 100 per cent. From the graph, the effective surface area of the pigment in the ink was $82\text{m}^2 \text{g}^{-1}$. This means that the degree of dispersion achieved was $(82/87) \times 100$ per cent or 94 per cent.

Dispersion stability

In the above ink, it is believed that the dispersion is stabilised by adsorption of resin molecules on the pigment surface. If the molecules are long enough and enough of them are adsorbed on each particle, they will prevent the particles coming close enough together to aggregate. This interaction of long chain molecules adsorbed on pigment surfaces is called steric hindrance. Current theory argues that steric hindrance is one of the two separate mechanisms by which dispersion stability is achieved. Non-ionic surfactants are also believed to prevent aggregation by this mechanism.

The other mechanism is that of electrostatic repulsion, caused by pigments preferentially adsorbing anions or cations.

Dispersion stability by these two mechanisms has been described by a number of authors in detail^{4,5} and so will not be discussed here. The results given, however, show that, in aqueous systems, there is little difference in efficiency between anionic and non-anionic surfactants, in terms of dispersion levels that can be achieved.

Colour strength

The colour strength of pigments is known to be some function of their degree of dispersion in all types of pigmented systems, aqueous and non-aqueous. This is known from experience. Experience has also shown that the strengths of different pigments increase at different rates with increased grinding times. Now that particle sizes of organic pigments in aqueous pastes can be determined accurately, it is possible to determine experimentally the relationship between colour strength and particle size for such pigments. This determination has been carried out on a number of organic pigments. The experimental procedure is described below.

The starting material was the pigment press cake. This was diluted with water to give a pigment content of 20 per cent, and $12\frac{1}{2}$ per cent (on the weight of dry pigment) of a powerful anionic dispersing agent added. A 2,000g portion of the mix was put into porcelain pots with 1,200g of sand, and the pots were rotated on rollers at 100 rpm for specified times. The aqueous stainers were thus subjected to a ball milling treatment with sand as the grinding agent. This treatment is referred to as sand milling to differentiate it from high speed sand grinding.

The samples were analysed for their size distribution on the disc centrifuge and a size distribution curve was obtained for each sample. In order to represent each curve by a single figure, the 50 per cent diameter was used.

The colour strength of each of the samples was then measured. The sample was stirred into a china clay/casein paper coating mix to give a 1:60 reduction of pigment to china clay. The coloured mix was drawn down on to paper with a bar coater and after drying, it was examined on a spectrophotometer and its k/s value determined. This is directly proportional to its colour strength. Finally, the k/s values were plotted against the 50 per cent diameter.

Four separate pigments were examined, namely Green DBN (CI Pigment Green 8), Red FBS (CI Pigment Red 2), Yellow BAW (CI Pigment Yellow 13) and Blue GLS (CI Pigment Blue 15).

Results

The relationship between colour strength and particle size for each of these pigments, in aqueous systems, is shown in Figs. 11 and 12.

These curves vary markedly from pigment to pigment.

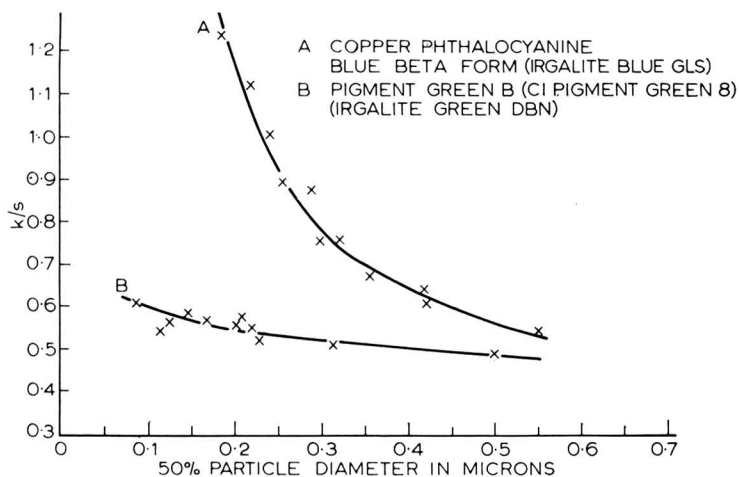


Fig. 11. Particle size of aqueous stainers/colour strength of paper coatings (china clay reductions 1:60)

In the case of the green, the colour strength increases only slowly with reducing particle size, down to very small sizes. This slow increase, coupled with the low price of the colour, means that prolonged grinding of this pigment will never be economical in terms of colour strength. With the phthalocyanine blue, the picture is very different. The colour value increases only slowly at first as the size is reduced, the relationship being linear. The graph then starts to slope upwards very much more sharply and the colour strength becomes very dependent on the actual particle size. This great increase in strength begins at a 50 per cent diameter of about 0.4μ . As the 50 per cent diameter is reduced to 0.2μ , the colour strength increases from 0.64 to 1.16, an increase of 81 per cent. This is a tremendous increase and explains many of the difficulties encountered in standardising pastes of this pigment and comparing competitive samples. Slight changes or differences in degree of dispersion will produce noticeable changes in colour strength.

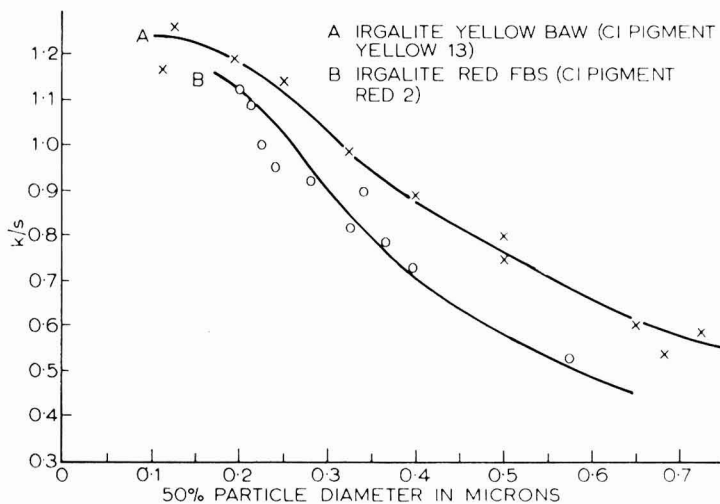


Fig. 12. Particle size of aqueous stainers/colour strength of paper coatings (china clay reductions 1:60)

It will also be appreciated from this graph that, to get the best colour strength from this pigment, it should be ground as finely as possible.

The curves for the red and yellow pigment are intermediate between those for the blue and green pigments.

Aqueous versus non-aqueous dispersion

Experimental evidence is slowly accumulating to show that the dispersion levels achieved in aqueous systems are substantially better than those achieved in non-aqueous systems, even where the same type of mill is used. Some of this evidence is shown in Fig. 13, which shows size distribution curves obtained for two formulations based on Yellow BAW (CI Pigment Yellow 13). In the first formulation, 30 parts by weight of the pigment was premixed for ten minutes

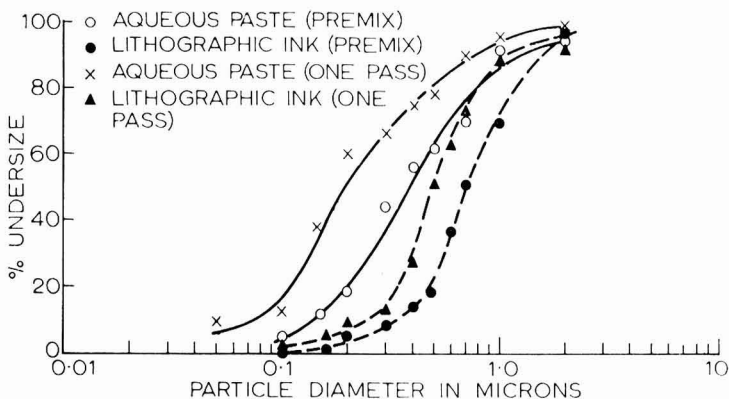


Fig. 13. Particle size distribution of a diarylide yellow (CI Pigment Yellow 13) in a non-ionic aqueous paste and in a mid-lithographic varnish

in 70 parts by weight of a solution of a non-ionic agent (Lissapol NX) in water. The premix was then given three tight passes over a triple-roll mill.

In the second formulation 30 parts by weight of pigment were premixed for ten minutes with a standard mid-litho varnish and the premix was given three tight passes over the triple-roll mill.

The curves show that the dispersion obtained in the aqueous paste was much superior to that in the ink. It is felt that, in view of this and other evidence, the comparison between the dispersion levels achieved in aqueous and non-aqueous systems should be investigated more closely. If this type of result is confirmed on a wider scale, it will be of great interest to both theoretical and practical workers. If the reasons for the difference can be established and the information applied to non-aqueous systems, it may be possible to achieve much better levels of pigment dispersion in non-aqueous paints and inks.

[Received 6 June 1970]

References

1. Birrell, P., *JOCCA*, 1964, **47**, 878
2. Beresford, J., Carr, W., and Lombard, G. A., *JOCCA*, 1965, **48**, 293
3. Beresford, J., *JOCCA*, 1964, **50**, 594
4. Parfitt, G. D., *JOCCA*, 1967, **50**, 822
5. Crowl, V. T., *JOCCA*, 1967, **50**, 1023

Discussion at the Scottish Symposium

MR. W. K. H. LAKIN referred to the figures on the dispersion of toluidine red. He asked if the BET values of the pigment had been determined when it was dispersed in anionic and non-ionic systems to determine whether the surface area was increased. Also, he asked if Dr. Carr could comment on the difference in the degree of dispersion in anionic and non-ionic systems, in particular with respect to the possibility of the dispersing aid affecting the degree of fracture.

DR. W. CARR replied that he assumed that the speaker referred to the possibility of taking an aqueous dispersion of toluidine red that had an observed degree of dispersion of greater than 100 per cent, and extracting the powder from it and determining its nitrogen surface area. This idea had been considered, but had not been followed up owing to the difficulty of extracting pigment from a highly dispersed paste.

With regard to the second part of the question, he felt that it was significant that, while the dispersion of the toluidine red in the non-ionic paste was inferior to that in the anionic, the degree of dispersion of the phthalocyanine blue was virtually the same in both cases. His interpretation of this was that the smaller particle size of the phthalocyanine blue caused greater steric hindrance, thus giving a better stabilising effect. The particle size of the toluidine red was about 0.3 microns, while that of the phthalocyanine blue was 0.12 microns.

MR. D. FAGG remarked that the paper had shown differences in grinding performance between water and lithographic varnishes. Was this not to be expected in view of the different wetting properties of the two substances?

DR. CARR replied that he did not think that it could be proved that wetting affected dispersion. In the case Mr. Fagg had mentioned, the dispersion of the pigments in litho varnish and water, exactly the same procedure had been carried out in pig-menting the two systems to the same level. Both the systems could have a stabilising mechanism caused by steric hindrance. Thus, no difference in dispersion had been expected.

MR. A. S. FOSTER said that, in the work with the Joyce/Loebl disc centrifuge, the undersize fraction had been collected to determine the particle size distribution. It was also possible to collect and examine the oversize fraction. In work he had carried out, the weight median diameters of pigments determined using the undersize fraction had shown significant variations from those for the same pigments when the oversize fraction had been used. No explanation had been arrived at for this phenomenon. Had Dr. Carr any comments?

DR. CARR said that this was a very pertinent point. As Mr. Foster had pointed out, the disc centrifuge extracted the undersize fractions leaving the oversize fractions in the disc. If both the sample removed and the sample remaining were analysed, the result should add up to the original weight of pigment used. Some determinations had been carried out, and reasonable agreement, up to 98 per cent, had been obtained. In some cases, however, particularly with organic pigments, there was some discrepancy. This had been attributed to the fact that small quantities of oversize fractions adhered to the disc, and were not removed with the liquid. Although the amount involved was very small, it was sufficient to cause an error in the small samples of organic pigments used.

MR. N. SCOTT pointed out that, although the paper had suggested that anionic and non-ionic dispersing agents were equally efficient in producing a given state of dispersion of organic pigments, anionics were known to be less effective in dispersing carbon blacks. Had Dr. Carr any comments?

Secondly, was it possible to have too much dispersing agent in a system to give optimum dispersion?

DR. CARR replied that his definition of efficiency was, perhaps, a little different from Mr. Scott's. He had not taken into account any economic factors. The criterion used had merely been that, using optimum quantities, it was not possible to make a paste using a non-ionic in which the dispersion was better than that of a paste made using an anionic. In terms of economic efficiency, the relation would not necessarily hold; for instance, it might be cheaper to use a non-ionic and give a longer grinding time than to use an anionic.

In reply to the second question, he felt that it could be possible to have too much dispersing agent present, but this would depend on the application. A typical case was that of pigment paste for paper. Commercial pastes consisted of press cake, ground to a limited extent with a small amount of anionic dispersing agent. Anionic surfactants could be adsorbed on any solid surface, and so after a layer had built up on the pigment surface, any excess was adsorbed on the fibre of the paper. The electrostatic charges of the surfactant on the paper and the pigment repelled each other, and hence complete coverage was not obtained.

Similar cases where excess of dispersing agent was a disadvantage could be envisaged.

MR. D. M. VARLEY asked if Dr. Carr had any information on the reproducibility of the degree of dispersion of commercially produced batches of any one pigment. In practice, merely the colour characteristics were checked. While it seemed likely that phthalocyanine blue dispersions of the same strength would have a similar degree of dispersion, with pigment green B there could be a wide variation in the dispersion of two batches which had similar strength and shade.

DR. CARR said that he had no information on this point. However, it was obvious from the graphs of colour value against degree of dispersion that the phthalocyanine blue was more sensitive to degree of dispersion than the pigment green B, and so the latter could be more difficult to standardise by judgement of the colour.

MR. K. L. BARGROVE remarked that Dr. Carr was perhaps optimistic in his suggestion that the work on aqueous systems might lead to improved dispersion in non-aqueous media. Was there a possibility that compounds might be developed which ionised in non-aqueous media? If this was not the case, he felt that too much emphasis had been placed on the ionic mechanism described.

DR. CARR said that most of the work had applied to aqueous systems, and here the ionising mechanism was obviously important. However, the fact remained that a technique had been evolved for measuring the degree of dispersion in aqueous and non-aqueous solvents, and this could be used to investigate the differences in dispersion, which might lead to information which could be used to improve dispersion in non-aqueous solvents.

MR. H. F. HUISMAN remarked that Dr. Carr had stated that the time of milling for aqueous and non-aqueous systems was about the same. This seemed strange, as changes in viscosity would affect the milling time.

Also, could Dr. Carr give some idea of the ultimate dispersion level in non-aqueous systems?

DR. CARR said that he had not made any systematic study as yet; experience had shown that dispersion in aqueous media was better than that in non-aqueous. Certainly, if commercial aqueous and non-aqueous pastes of the same pigment were examined, this was almost always the case. The paper was merely intended to show the overall picture.

As far as the point on milling times was concerned, in general the viscosities of aqueous and non-aqueous pastes were very similar.

The influence of non-aqueous media on dispersions*

By K. Pond

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Summary

The selection of media for the dispersion of colourants in printing inks is affected on technical grounds by limitations imposed in three main areas:

- mixing and milling;
- flow of the mixed and milled dispersion;
- characteristics of the printed film.

The performance of the dispersion in each of these three conditions is, it is suggested, critically dependent on the pigment/medium interaction. It is further implied that different portions of the medium have dominant effects at each stage of the preparation and application of the ink.

To illustrate these contentions, a number of test methods have been used to examine the behaviour of two commercially available alkyds when used as the medium for pigment dispersions. To avoid the possible implications that one or other of the materials may be more suitable as an ink vehicle or component, they have been described throughout the text as alkyd A and alkyd B. At the same time the opportunity has been taken to sketch some experimental techniques which can, when used in conjunction, provide a basis for raw material selection and evaluation, with particular reference to printing ink formulation.

Keywords

Types and classes of coating
printing ink

Processes and methods primarily associated
with manufacture or synthesis
dispersion

Equipment primarily associated
with manufacturing or synthesis
three-roll mill

L'influence des milieux non-aqueux sur les niveaux de dispersion

Résumé

Sur le plan technique la sélection des milieux pour la dispersion des colorants d'encre d'imprimerie est influée par les contraintes qui s'imposent dans les secteurs suivants:

- malaxage et broyage
- écoulement de la pâte après malaxage et broyage
- caractéristiques de l'impression

On suggère que le rendement de la pâte sous chaque une des trois conditions se dépend, dans une manière critique, de l'interaction du pigment et du milieu. On suppose, d'ailleurs, à chaque stade de la préparation et de l'application de l'encre, qu'un constituant différent du milieu joue le rôle principal.

Afin d'évaluer ces contentions, on a utilisé un nombre de méthodes d'essai pour examiner le comportement de deux résines alkydes commerciales en tant que milieu de dispersion de pigments.

*Presented at the Scottish Section Symposium, 21-22 May 1970.

Pour éviter les implications éventuelles que l'une ou l'autre des résines soit plus convenable en tant que véhicule ou constituant d'encre, on les a appelé partout dans le texte comme Alkyde A ou Alkyde B. En même temps on a esquissé quelques techniques expérimentales qui peuvent établir une base pour la sélection et l'application des matières premières à l'égard particulier des encres d'imprimerie.

Der Einfluss Nichtwässriger Bindemittel auf Dispersionen

Zusammenfassung

Aus technischen Gründen wird die Wahl von Bindemitteln für die Dispersion von Farbkörpern in Druckfarben von durch in der Hauptsache drei Gesichtspunkten erzwungenen Begrenzungen beeinflusst:

- Mischen und Mahlen
- Verlauf der gemischten und gemahlten Dispersion
- Charakteristika des gedruckten Films.

Es wird die Ansicht vertreten, dass das Verhalten der Dispersion in jedem der drei Zustände kritisch von der Wechselwirkung zwischen Pigment und Bindemittel abhängt. Es wird weiterhin unterstellt, dass verschiedene Anteile des Bindemittels in jedem Stadium der Herstellung und Anwendung der Druckfarbe dominierende Wirkungen ausüben.

Um diese Behauptungen zu illustrieren, wurden mehrere Prüfmethode angewandt, um zwei im Handel befindliche Alkydharze auf ihr Verhalten als Bindemittel bei der Pigmentdispersion zu untersuchen. Um die mögliche Annahme auszuschließen, dass das eine oder andere dieses Harzes sich besser als Druckfarbenbindemittel oder -bestandteil eigne, wurde es überall im Text als Alkydharz A und als Alkydharz B bezeichnet. Zur gleichen Zeit wurde die Gelegenheit benutzt, um einige experimentelle Methoden anzudeuten, welche, wenn miteinander angewandt, eine Basis für die Rohstoffauswahl und -Bewertung, mit besonderer Bezugnahme auf die Rezeptierung von Druckfarben, bilden.

Влияние безводных сред на дисперсию

Резюме

Выбор среды для дисперсии пигмента красителя в печатных чернилах зависит, с технической точки зрения, от ограничений налагаемых в трех главных областях:

- в смешении и размельчении;
- в течении перемешанной и размельченной дисперсии;
- в характеристике печатной пленки.

Считается что рабочие характеристики дисперсии, в каждом из этих трех условий, критически зависят от взаимодействия между пигментом и средой. Предполагается также что различные части среды оказывают преобладающее влияние на каждой отдельной стадии изготовления и применения чернила.

Для проверки этих утверждений, был проведен ряд экспериментальных испытаний для анализа поведения двух коммерчески доступных алкидов, применяемых в качестве среды для дисперсии пигмента. Во избежание возможной интерпретации что тот или другой материал является более пригодным в качестве связующего вещества или компоненты чернила, они описывались в тексте как алкид А и алкид В. В то же время автор воспользовался случаем описать некоторые экспериментальные методы которые, в совместном применении, могут послужить основой для выбора и оценки сырого материала, в особенности в связи с формуляцией печатных чернил.

Introduction and background

As will be well known, oil based printing inks consist of relatively concentrated dispersions of pigment in non-aqueous media. The pigments used include many

of the modern organic colourants and the dispersion medium of a relatively complex mixture of resins, vegetable oils, their derivatives and aliphatic hydrocarbons. The technical requirements which limit the selection of the raw materials include the following.

Production requirements—ease of dispersion, critical pigment volume concentration, resin solubility and inter-compatibility.

Application requirements—flow (viscosity, tack), setting, drying.

Final print requirements—colour, gloss, lightfastness/rub resistance etc.

Naturally, the selection of raw materials against even a generalised specification of this type would be tedious unless simplified test procedures were adopted. Although such test procedures are under continuous review, it could be said that the “standard formula” assessment method is still the most common approach.

Using a highly simplified format, the resin oil and solvent can be separately evaluated by substitution into one or more “typical” vehicles. The ratio between each component to give a given viscosity, tack or drying speed, or any combination of these or other properties, will give useful information about the individual component under test.

The vehicle so prepared could be used as a dispersing medium for a pigment at a given pigment loading and evaluated for its wetting ability. The pigment carrying power, ease of dispersion, gloss, viscosity, and printing and print characteristics can all be assessed using a family of concentrations of pigment mixed into an alkyd under controlled conditions without resorting to the complication of producing a “typical” vehicle. Work of this type has been carried out on the two alkyds which are discussed in the body of this paper.

Without very much more detailed examination, however, the results must be accepted as being characteristic for the material under test and only limited guidance can be given towards the modification or improvement of the product.

By extending the test techniques to include polarity assessments, molecular weight distributions, and film properties, some attempt can be made to define those properties of the materials which are of major significance in the final performance of the dispersion.

Although initially the confusions which arose through the use of a variety of test methods in each of these areas were a source of some difficulty, it is hoped that it will be demonstrated that a more meaningful interpretation of the results was possible purely because so many different techniques had been employed.

Experimental

Alkyd A and alkyd B were used as the basis for dispersions using Reflex Blue, a phthalocyanine blue, a barium lithol and a benzidine orange. Low concentrations of pigment were used in each case. These inks were printed on a FOGRA proof press at 1 g m^{-2} . The paper was Scheufellen brush coated art.

It was observed that in each case alkyd A gave lower gloss and poorer setting and rub resistance than alkyd B. This work, which was part of the routine testing carried out by the company's central research laboratories in France,

took place at a time when the whole question of raw material evaluation was under severe scrutiny. An explanation was offered for this somewhat anomalous behaviour (normally it would be anticipated that dispersions with superior wetting of the pigment, especially where the viscosity of the medium was high, would give better gloss). It was considered possible that, in the case of the dispersions using alkyd A, the pigment was de-wetted on striking the paper and that flocculation of the pigment occurred, this accounting directly for the loss of gloss—the vehicle drainage accounting for the poor rub resistance.

The author's further tests were to print the two alkyds unmodified, pigmented with Reflex Blue and incorporating an oil soluble dye. The dyed and the "neat" alkyd B prints showed greater gloss on the two papers used in the tests. It was interesting to note that the colour development of the dyed print was also very much greater with alkyd B. Furthermore, during printing, alkyd B reticulated on both the forme and the paper. Such an effect could be explained by high surface tensions and according to the Lucas Washburn equation¹ it would be expected that such a material would penetrate more slowly into paper.

At this stage it was felt that a study of the molecular weight distribution of the two alkyds could possibly be of use in explaining the differences observed. The two vehicles were diluted with petroleum ether and passed through an aluminium hydroxide column. The material passing through was collected and the solvent evaporated. This material is the high molecular weight portion.

After eluting the column with acetone and further solvent evaporation, a second fraction was obtained. Despite this solvent washing, material was left adsorbed on the column. This material was expressed as "the loss." The results are shown in Table 1.

Table 1
Results of chromatographic separation

	HMw	LMw	Loss
Alkyd A: Wt %	1.89g 9.45	7.85g 39.25	10.26g 51.3
Alkyd B: Wt %	5.01g 25.0	10.52g 52.6	4.47g 22.4

It is clear from consideration of the results illustrated in this table, that alkyd B has a higher proportion of high molecular weight material.

Taking 25 per cent of the high molecular weight portion of alkyd B together with 75 per cent of the low molecular weight fraction collected and admixing, a viscosity of 50 poise was obtained. The original viscosity of alkyd B was 76 poise. This result suggested that the material retained on the column was indeed low in molecular weight.

By using a shorter and less efficient column, it was possible to obtain extract fractions more complete, which were then printed. The two high molecular weight fractions, when printed on one of the papers used in the earlier tests,

Queen of Arts, gave very similar gloss results. The low molecular weight portion of alkyd A, however, was completely matt. Once again a mottled print appearance was observed.

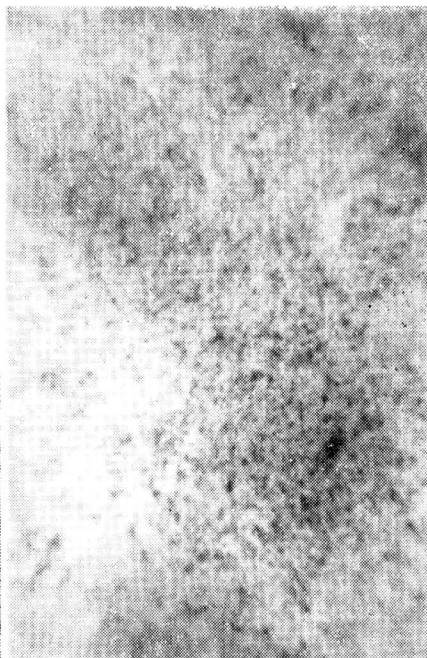
For comparative purposes, the molecular weight distribution was assessed by an alternative technique. This method, which was described by A. Toussaint², gives an indication of molecular weight distribution by quantitative additions of a non-solvent to a known concentration solution of the alkyd in acetone. The non-solvent chosen was water. At each level of added water a given molecular weight range of resin is precipitated. During precipitation the optical density of the medium is measured from which the turbidity (T) is defined as the ratio of the optical density observed over the final optical density.

If V is taken as the ratio of the volume of water to volume of acetone, then T as a function of V gives an integrated weight distribution curve. Plotting dT/dV against V will give the differential molecular weight distribution. This, of course, assumes that the turbidity is a linear function of the concentration of precipitated molecules in the solution if they occupy equivalent volumes. (At each instant for an added volume of water V_1 there is a corresponding precipitation of molecules of the molecular weight M_1 which represents a quantity W_1 .)

A1

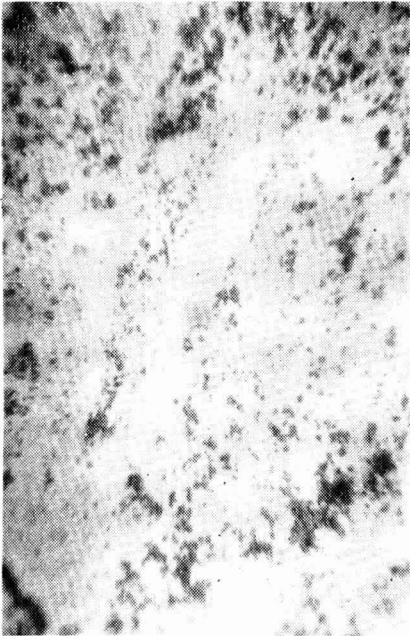
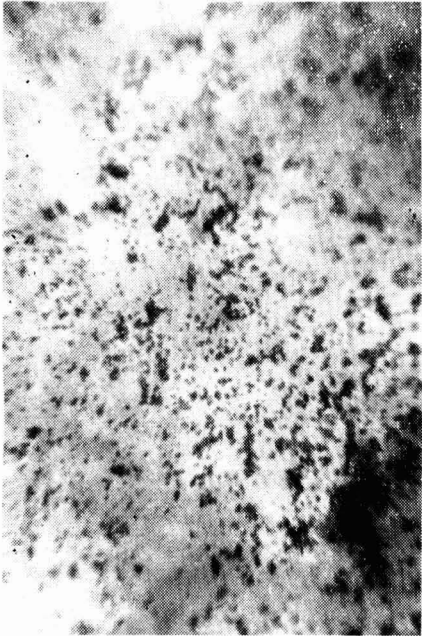
*Alkyd A*

A2

*Alkyd B**Phthalocyanine Blue*

B1

B2



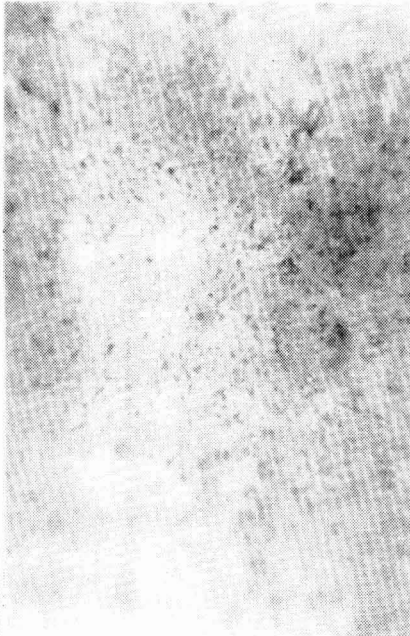
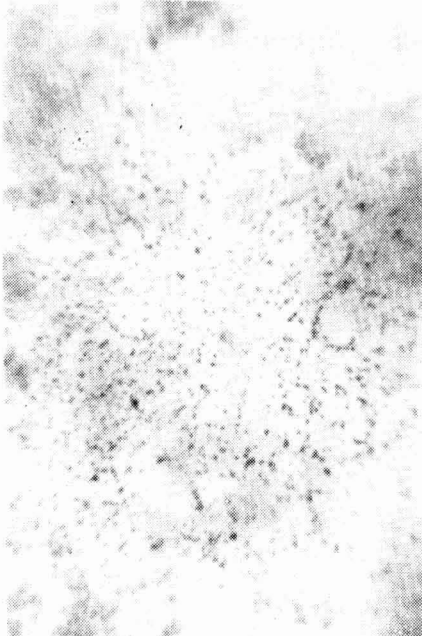
Alkyd A

Benzidine Orange

Alkyd B

C1

C2



Alkyd A

Reflex Blue

Alkyd B

D1

D2

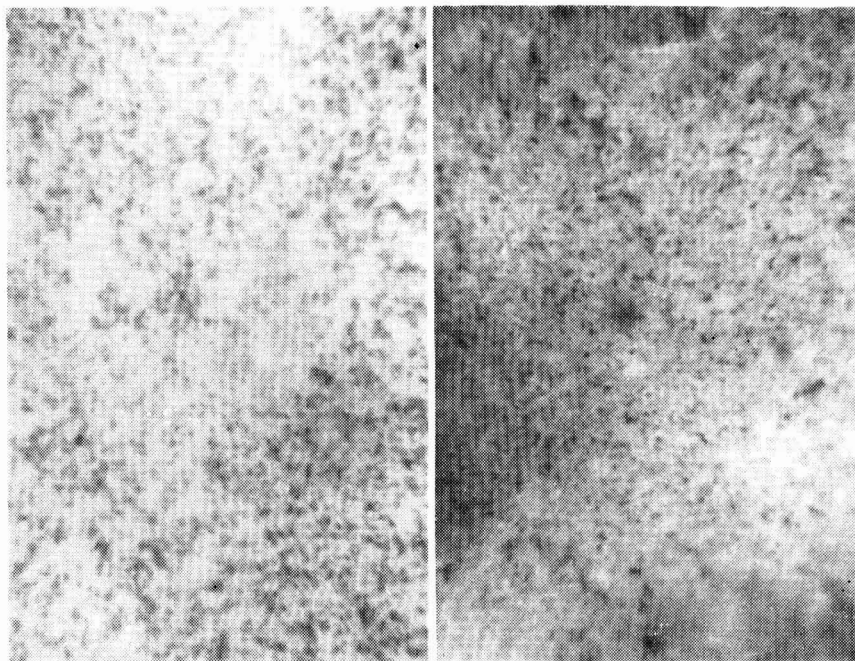
*Alkyd A**Barium Lithol**Alkyd B*

Fig. 1. Photomicrographs illustrating apparent pigment flocculation in the printed film

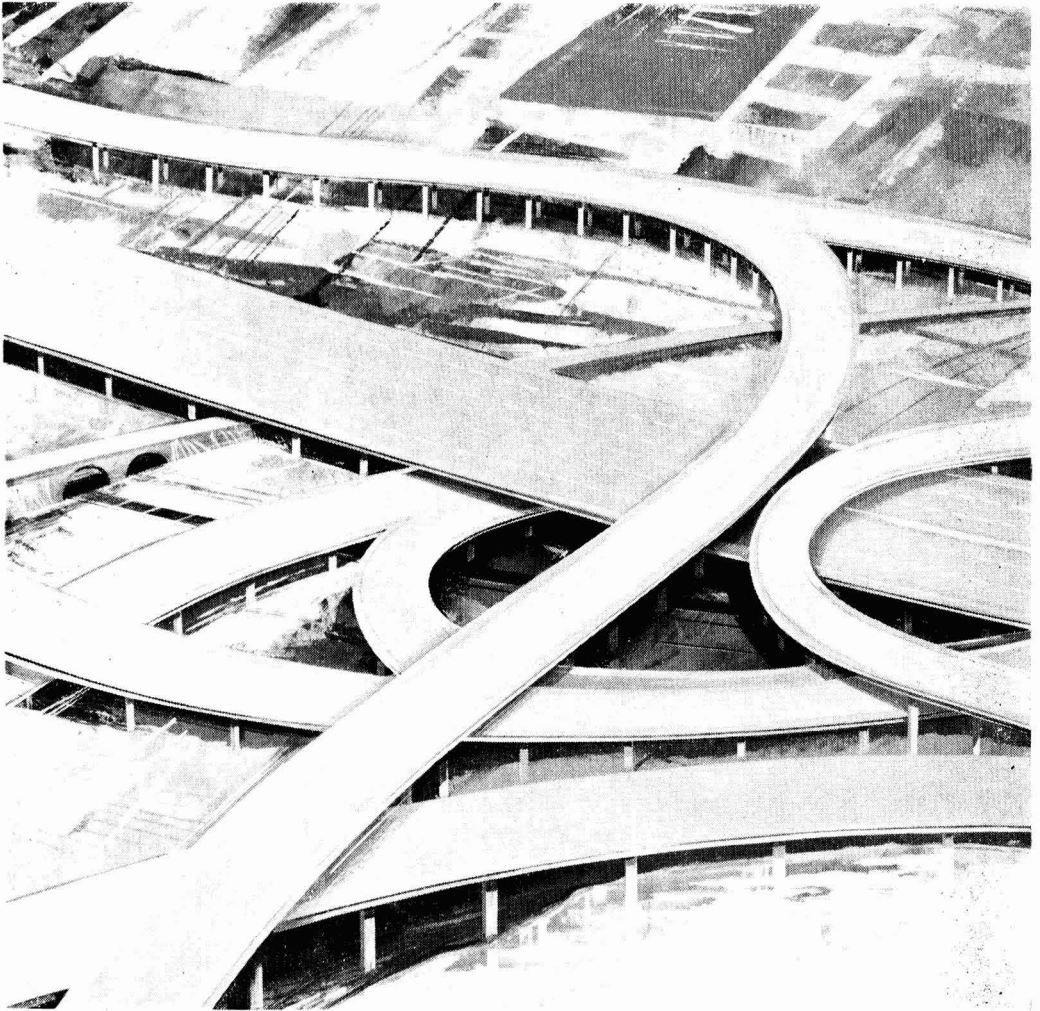
The molecular weight distribution in the case of alkyd A was normal, with a peak at approximately 1,500 molecular weight.

Alkyd B, by contrast, had a distribution with a peak at approximately 3,500 molecular weight, but a small portion of material of molecular weight below 1,000.

These experiments were complemented by molecular weight fractionation using the method of Wilson and Robson³. This method allows more detailed information to be gained about the low molecular weight fraction of the alkyd. Three fractions are obtained:

1. methanol soluble;
2. hot methanol soluble;
3. methanol insoluble.

The results obtained are illustrated in Table 2. The viscosities of the extracts were established and are illustrated in Table 3. Tables 4, 5 and 6 summarise the results of acid value, hydroxyl value and contact angle measurements. Contact angle measurements were made using a defined volume of water of controlled pH and surface tension and a film of the material of a thickness between 15 and 20 microns after a contact interval of five minutes.



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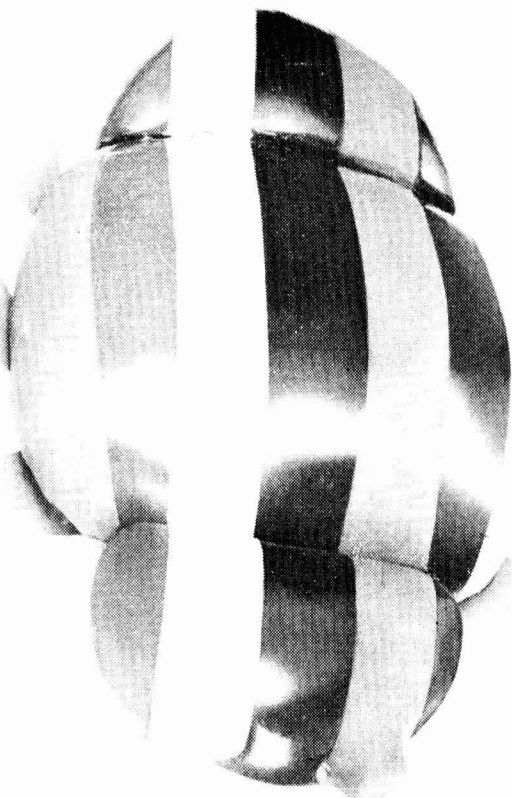
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Table 2
Methanol extraction

Alkyd	Extract	Intermediate fraction	Residue
Alkyd A	20.6	10.4	69.0
Alkyd B	8.1	9.0	82.9

Table 3
Viscosity in poise at 25°C

Alkyd	Extract	Intermediate fraction	Residue
Alkyd A 176 ..	12.3	18.3	94.0
Alkyd B 76 ..	2.6	2.6	42.0

Table 4
Acid value

Alkyd	Extract	Intermediate fraction	Residue
Alkyd A 6.3 ..	28.2	8.9	5.8
Alkyd B 8.4 ..	39.6	9.7	5.3

Table 5
Hydroxyl value

Alkyd	Extract	Residue
Alkyd A 60.0	115.2	60.0
Alkyd B 24.9	88.3	20.3

Table 6
Contact angle (dyne cm⁻²)

Alkyd	Extract	Residue
Alkyd A 27.9	26.0	37.8
Alkyd B 40.0	29.5	35.7

In addition, the alkyd, the extract and the residue were used to produce test varnishes at 10 and 50 per cent weight additions to a standard vehicle of the following form:

rosin modified phenolic	38 per cent
alkali refined linseed oil	37 per cent
petroleum distillate 260/290	25 per cent

The viscosities of the 10 per cent and 50 per cent admixtures were measured. The difference between the measured viscosity and the theoretical viscosity, calculated using a log-linear diagram, was used to assess the peptising power of the extracts, residues and alkyds. A summary of these results is shown in Table 7.

Table 7
Peptising power

	Viscosity	10% addition (wt)			50% addition (wt)		
		Theoretical viscosity	Measured viscosity	Peptising power	Theoretical viscosity	Actual viscosity	Peptising power
A:							
Alkyd	17.6	45.0	14.0	110.7	29.0	94.0	16.3
Extract	12.3	34.0	11.7	68.0	77.0	24.0	81.7
Residue	94.0	53.0	29.0	58.5	69.0	29.0	16.0
B:							
Alkyd	76.0	41.0	16.0	74.7	19.0	62.0	112.8
Extract	2.6	29.0	8.2	72.3	35.0	11.0	74.0
Residue	42.0	49.0	14.0	50.0*	46.0	38.0	105.0*

*Incompatible

Methanol will preferentially solvate materials of high polarity and hydrogen bonding. In alkyds, the highly polar hydrogen bonded material is normally of low molecular weight (since the high molecular weight cross-linked portions are sterically hindered, they have smaller charge separation and are inevitably restricted in movement).

The methanol extraction method will not give a total picture of low molecular weight material, but it does remove material from a lower limit of polarity and hydrogen bonding.

In an effort to establish the polarity of the initial alkyds, solubility parameters were established using a range of solvents. These were toluene for group 1, butyl carbitol for group 2 and 2-ethyl hexanol for group 3A. The alkyds were dissolved in these solvents at 10g plus 50ml of solvent; 2 or 5ml aliquots were taken and titrated with solvents listed below corresponding to the group.

The solubility parameters for these various solvents are listed below.

Solvents—Group 1: toluene	$m = 8.9$
Group 2: butyl carbitol	$m = 8.9$
Group 3A: 2-ethyl hexanol	$m = 9.5$
Titrating solvents—Group 1: (low) silicone fluid MS 200/0.06	
(high) propylene carbonate	$m = 6.75$
Group 2: butyrolactone	$m = 13.5$
Group 3A: methyl alcohol	$m = 15.5$
	$m = 14.5$

The results of these titrations are indicated in Tables 8, 9 and 10. In the case of group 2, dibutyl ether with a solubility parameter of 7 was the lowest available solvent that was compatible with both alkyds.

From the titration results, it was noted that alkyd B showed a large drop in solvency in high hydrogen bonding group 3 situations.

In furthering this aspect of the work, a range of representative pigments was considered and their settling rates studied in a series of solvents—these solvents selected to cover a range of hydrogen bonding from 1 to 18.7 and a solubility parameter from 6.9 up to 14.5.

0.2g of the pigment was shaken in 5ml of solvent and the settling characteristics recorded.

0.5g of alkyd was shaken in 5ml of solvent and examined after 24 hours for clarity, and finally,

0.2g of pigment was shaken in 5ml of a 25 per cent solution of alkyd in xylol and the settling characteristics recorded.

Graphs were plotted for each pigment, showing only the solvents in which the pigment was suspended. These graphs showed considerable variation throughout the pigment range. However, certain very well defined groups were established.

The first group (A) included pigment yellow 1, a xylidide benzidine and a calcium 4B.

Group B included Permanent Red F4R and a Bordeaux F2R.

Group C included Lake Red C and a Barium 2B, together with a second xylidide benzidine.

Group D included a furnace carbon black and a Hansa Yellow 10G.

Group E consisted of a β -form phthalocyanine blue and litho ultra.

The last group (P) consisted of a phthalocyanine green, Permanent Red F2R and Fanal Rose.

Groups A, B and C were all similar, but decreased in solubility from A to C. However, the suspension tests in alkyds did not show a strong relationship between the indicated solubility parameter of the pigment and its wettability by the alkyd.

By dispersing certain of the pigments in a range of alkyds, a direct correlation was established between the alkyd suspension tests and the pigment wetting as indicated by solubility parameter. It would seem from these results

that the concept introduced by Dr. Meyers at the Energy Concepts Symposium held in March 1969 at Battelle Memorial Institute is highly relevant. In principle he associated the dissolution of resin, the wetting of pigment, film adhesion and other effects as being fundamentally dependent upon energy difference.

The second law of thermodynamics, which expresses the change in free energy associated with any spontaneous process, should, therefore, be in our minds in attempting to link observed phenomena with basic properties.

The decrease in free energy on mixing liquid (dissolving resins, wetting pigments, etc.) is larger the more thermodynamically stable the final system. The free energy change is equal to the heat of mixing change minus the absolute temperature times the entropy change.

Clearly, since in any mixture the positional entropy is higher than in the pure components (the system is more disordered), the entropy change will be positive.

Using the same statistical principles as are used for determining the number of free states for an atom in order to determine the contribution to specific heat, a simple expression is obtained for the situation in which the mixture of two pure components is considered.

In the case of polymer solutions, however, account must be taken of the linkage between polymer segments. As a first assumption, each segment could be considered to be of roughly equal size in relation to the solvent molecule and thus take up one lattice site in the mixture. The number of lattice segments will clearly be related to the molecular weight of the polymer and calculations can be made up to the point of phase separation.

The recent advances made in the theoretical description of this type of interaction augurs well for the ability to select materials and understand their performance in the future.

Discussion

Experimental methods have been described which give a picture of the distribution of molecular sizes for two polymers and their polarity as individual components. The fact that alkyd B has a wider range of polar material and that the molecular weight of the high molecular weight fraction is higher than in alkyd A means that there is no requirement for the polar low molecular weight material to solubilise non-polar high molecular weight material.

In alkyd A, this second mechanism is necessary and, on striking the porous substrate, the dispersions of pigment in the two alkyds behave in contrasting fashions.

In the case of alkyd A, the loss of the low molecular weight material insolubilises the high molecular weight fraction, giving rise to a poorly bound matt film with possibly consequent pigment de-wetting.

In the case of alkyd B, the loss of low molecular weight polar material is of less significance, the pigment remains wetted, the high molecular weight fractions remain solubilised and a coherent glossy film is achieved.

By considering the polarity and molecular weight of the two alkyds the ease of dispersion shown in associated work using alkyd A can be readily understood.

This interpretation can also be used to explain the variations in viscosity between the different molecular weight fractions of the two alkyds. It is the author's view that work of this type can usefully be used to interpret the gross and microscopic behaviour of pigment dispersions in non-aqueous media.

As a further example of the ways in which the medium used in dispersing pigments can have a powerful influence on the performance of the dispersion, some work which has been made available⁴ is summarised.

In this work the behaviour of dispersions resulting from different dispersion techniques was studied, and it was established by means of physical and chemical examination that the properties of a pigment in its dry powder form bore no resemblance to the properties of that pigment after it had been made into an ink and printed. The second fact was that when the pigment was dispersed at a fixed concentration in a fixed vehicle, the print resistance to solvents and chemicals varied quite markedly.

A detailed summary of the findings included the points shown below.

The higher the temperature of the three-roll mill during manufacture, the better the ink dispersion, roller pressures on the mill having been adjusted to remain constant during the run.

The characteristics of the dispersion were relatively unaffected by age.

Inks dispersed hot showed improved resistance over the remaining inks with the exclusion of the ink prepared using only a loose grinding pass on a cold three-roll mill.

The test conditions are summarised in the appendix.

It was thought that the physical degree of dispersion which was found to be better in the case of those inks which were dispersed on hot three-roll milling was a contributory factor. Also that chemical changes of both pigment and varnish could have been responsible.

It was argued that although the dispersion factor cannot be discounted, the main cause appeared to lie elsewhere. Electron microscope examination of the pigment did not indicate any reason why this should contribute to improved resistance but, using infra-red spectrophotometry, various changes in the vehicle which could be related to dispersion were the increase in the aldehyde and ketonic groups and increased cross-linking. The drying time of the various inks supported the contention that some polymerisation had occurred during dispersion.

Observations have frequently been made by ink manufacturers that the drying behaviour of inks on printing presses are such that antioxidants must be used. It is interesting to note, however, that the final resistance properties of the print can be so markedly affected by its method of dispersion.

Acknowledgments

The author would like to thank the directors of Lorilleux-Lefranc and Lorilleux & Bolton for permission to use this work and also express gratitude for the helpful discussions and contributions made by colleagues in both France and England.

In addition he is indebted to Geigy (UK) Pigments Division for their help in producing the tabular material in slide form for the lecture at short notice, and to Mr. J. R. Groom of Sandoz Products for permission to include the work referred to in the last section.

It should be stressed that the opinions expressed are those of the author and do not necessarily represent the attitude either of Lorilleux-Lefranc, Lorilleux & Bolton, or indeed his colleagues.

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References

1. Washburn, E. W., *Phys. Rev.*, 1921, **17**, 273.
2. Toussaint, A., Distribution des masses moléculaires dans les alkydes. Rapport de l'IVP, Bruxelles Mai 1965.
3. Wilson, R., Robson, A. H., of Resinous Chemicals Ltd. as reported in *Off. Dig.*, 1955, **27**, 361.
4. Groom, J. R., Private communication.

Appendix

Ink dispersion techniques

<i>Ink</i>	<i>Mixing</i>		<i>Grinding</i>
<i>a</i>	By hand	}	One loose pass—cold three-roll mill
<i>b</i>	By hand		One tight pass—cold three-roll mill
<i>c</i>	By hand		Five tight passes—cold three-roll mill
<i>d</i>	By hand		Ten tight passes—cold three-roll mill
<i>e</i>	By hand		One tight pass—mill temperature 35 °C
<i>f</i>	By hand		Three tight passes—mill temperature 51 °C
<i>j</i>	By hand		One loose pass—cold three-roll mill, 18 °C
<i>k</i>	By hand, then allowed to stand for 24 hours		One loose pass—cold three-roll mill, 18 °C

Temperature of rollers for inks *a*, *b*, *c* and *d* was 18°C. Roller temperatures measured with a surface pyrometer. Inks *j* and *k* were produced to check erroneous variations in print resistances found with ink *a*.

Discussion at the Scottish Symposium

MR J. A. L. HAWKEY asked if Mr Pond could say a little more about hydroxyl and acid values. Normally these were considered of most interest in lithographic inks, because of the water present. Did Mr Pond feel that these values were significant in terms of other properties, such as pigment wetting and adhesion?

MR K. POND said that it was true that acid and hydroxyl values had mainly been of interest for lithographic inks. However, he felt that the total of hydroxyl value and acid value was of some interest in terms of pigment wetting and behaviour. It would be presumptuous to try to give limits for either property, or for their additive value, between which dispersion was adequate, but in studying dispersion he felt it was important to consider the characteristics of the solvent as well. Also, the hydroxyl number could be of interest when considering adhesion, for example when printing on unplasticised pvc. Clearly, however, there were other film forming factors which should be considered at the same time.

MR N. SCOTT agreed that the important criterion in inks and paints was the interaction of pigment and resin. However, most practical systems consisted of a large

number of components, and the results which Mr Pond had obtained on simple systems containing a single alkyd might be modified by the relative attraction of the various components for the pigment surface. Had Mr Pond any comment?

MR POND said that this could be the case. However, it would be very difficult to study this complex effect. The main parameters for vehicle performance were fairly well documented in the literature, and his own work had merely set out to investigate one further factor.

There was little doubt that the relative properties of the various components did affect the properties of the formulation. In many cases, two inks having exactly the same components, but which had been made up by addition of the components in a different order, had very different properties. For instance, to obtain a concentration of 35 per cent of phthalocyanine blue in an ink, it was necessary to disperse the pigment in selected components of the vehicle first. Adequate dispersion of 35 per cent of the pigment in the final vehicle would not be possible; this was probably due to the type of effect that Mr Scott had mentioned. It was true to say that the basic processes of dispersion and application could be much improved if more were known about the detailed interactions.

MR J. C. WATTS asked if Mr Pond could comment further on the use of the hot three-roll mill. Were the results obtained significant, or was the use of cooling water unnecessary?

MR POND commented that he had not carried out this particular work, but had merely been allowed to use the results. The term "hot three-roll mill," in this case, meant a mill which was not cooled. The temperature that the mill attained was around 50°C, as opposed to 18°C, which would be the normal temperature under controlled conditions. It was known that the availability of heat in the dispersion process was advantageous at certain stages, and therefore the ability to control the temperature could be of value.

MR G. N. BELL suggested that it would be better to use a warm premix and a cool mill than the procedure Mr Pond had described.

MR POND said that it would be very interesting to try this.

MR J. GLASS asked if Mr Pond would comment on the correlation of lab assessment and plant assessment.

Secondly, did the premixing time have any effect on the milling time, for instance would a longer premix cut out a proportionate length of time in milling?

Also, he would be interested to hear the criteria for a good pigment for inks. Was there a general standard, or did the necessary properties vary between different ink systems?

MR POND replied that the correlation between laboratory and plant was very difficult, particularly in the case of three-roll milling, as he felt that adequate laboratory three-roll mills were not available. However, in the case of power mixers and high speed stirrers, reasonable correlation was possible.

As far as premixing was concerned, the limited amount of work he had done in this area had shown that carbon black required the same total work input on the mill in spite of the time of premixing. With organic pigments, however, it was sometimes true that additional premixing could save milling time, but it was not possible to generalise.

In answer to the final part of the question, it was not possible to define a general-purpose pigment, as different inks varied widely in their requirements. Pigments which were tailor-made for specific uses were necessary, although this involved higher prices.

MR GLASS asked if there was any effect if the premix was allowed to stand, overnight for instance, before milling.

MR POND said that some laboratory investigation of this had been done, although there was very little information on the effect on a plant scale. Obviously, delays would occur in practice, and the results of letting-down and milling after several hours might be detectable. The laboratory work he had done had involved storing at different temperatures, a fixed amount of work having been done on the dispersion. The most significant effect which had been noticed was a viscosity increase in the dispersion on storage at higher temperatures, but this, in fact, was a polymerisation effect.

MR L. K. D. CAMERON referred to the two photomicrographs of the barium lithols. There was a significant difference in the degree of flocculation between the two. If this was due to experimental variation, it seemed rather large. Had the milling conditions changed?

MR POND replied that two different barium lithols had, in fact, been used.

MR HAWKEY returned to the question of correlating laboratory work and plant conditions. With laboratory work, there was a greater mass of metal in relation to the material being handled than was the case in the plant, and solvent losses were not so great, so that the operating temperature was of greater importance. In fact, the surface temperature of the rolls should be measured, and not the temperature of the emerging water. Many people made this mistake when trying to achieve the same conditions in the lab and the plant.

MR POND thanked Mr Hawkey for his comment. He should have pointed out that it had been roll temperatures which were quoted; these had been measured with a surface pyrometer.

MR J. J. FROGGATT commented that, in his experience with paint, temperature rise during pugging was not advantageous, but it could be helpful after the mixing was complete.

Referring to the discussion of correlation between lab and plant, he said that there were other factors to take into account. Full size roll mills could be supplied with cambered rolls, and often operated at a ratio of roll speeds of 4:1. Lab models could not be supplied with cambered rolls, and nearly always operated at a ratio of 2.5:1. Thus, it was almost impossible to relate one to the other; laboratory work had literally to be carried out in the plant.

Finally, he asked if there was any advantage in the grinding process in the addition of dilatants such as zinc naphthenate?

MR POND replied that he had no information on the effect of dilatant materials.

MR GLASS, continuing the discussion on plant/laboratory correlation, said that one of the difficulties he had encountered was in duplicating conditions on a hydraulic three-roll mill. It seemed almost impossible to achieve reproducible results from day to day using the same machine. Had Mr Pond any experience of this?

MR POND agreed that it was very difficult to establish three-roll mill settings, although this did not apply to many other mixing machines. This, and the remarks made by Mr Froggatt, which he wholeheartedly endorsed, added to the difficulty in applying laboratory results to plant operation.

MR K. L. BARGROVE said that in his view the most important factor in the lack of reproducibility of the three-roll mill was the heat generated. Only a very small proportion of the material being processed was acted upon at any one time—that part which

was in the nip of the rollers. If two different pigments were milled at the same roller settings, the rates of shear would be different causing the temperature in the nip to be different. This would therefore cause a variation in dispersion. If the rolls were cooled, this removed energy from the system, and as it was the imparting of energy into the system which effected the dispersion, again a different value would result.

Surely the reason why reproducible results were not possible on a three-roll mill was that only this very small amount of the mixture was being processed at any time, whereas with other equipment on which reproducible results were obtained, the total volume of material was being treated at all times?

MR POND agreed.

Next month's issue

The Honorary Editor has accepted the following papers for publication, and these are expected to appear in the March issue.

"The determination of chloride on rusted steel panels," *by J. E. Davies*

"Milling—A printing ink variable," *by J. R. Groom*

Papers from the Scottish Symposium

"Determination of gloss haze of paint films containing TiO₂ as a function of the dispersing process," *by R. Amberg*

"The influence of interfacial activity in paint films on their performance," *by W. Funke and R. Brandt*

"Dispersion machinery," *by J. B. Slinger*

"Summing up," *by S. H. Bell*

Correspondence

Colour difference measurement

SIR,—In their very interesting paper on colour difference measurement¹, Mudd and Woods suggest that the term “CIE unit” should not necessarily be tied to the CIE formula but should refer to a particular order of colour difference which can be calculated by using any formula with the appropriate scaling factor. They confirmed my findings² that the appropriate factor for the Adams chromatic value formula, more justly described as Adams-Nickerson³, would be 48, but warn that the use of this factor does not convert individual Adams-Nickerson values into CIE values. This warning cannot be over-emphasised as the actual factors necessary vary from 11.3-93.1⁴ and one cannot know which to use until ΔE has been calculated using both formulae: then it is no longer required!

For this reason, I think it would be most undesirable for the term “CIE unit” ever to be used unless referring to colour differences calculated using the CIE formula. Considerable confusion existed in the USA when the term NBS unit was applied to colour differences calculated by formulae other than those of the NBS.

Scaling factors must be used in most formulae to ensure that the resultant units are of a convenient size. It would, however, be dangerous to select the factor for an established formula (and the Adams-Nickerson formula is one of the oldest, dating from 1950) solely on the basis that the resultant units will be, on average, the same size as CIE units, because many users will erroneously assume that in individual cases there is a high probability that conversions will be meaningful: two-thirds will be more than 10 per cent out, a quarter more than 25 per cent out².

For this reason the Society of Dyers and Colourists, in its recommendation that the Adams-Nickerson formula should be used in preference to any other⁵, selected the factor 42 because it is the one most widely used and, in an attempt to eliminate ambiguity, recommended describing the units as “AN (42) units.” In the Draft British Standard for the assessment of the colour of near-white or near-colourless plastics materials, the term “ANLAB 42 units” is proposed, which is equally unambiguous.

Yours faithfully,
K. McLaren
23 November 1970

*Imperial Chemical Industries Ltd.,
Dyestuffs Division, Hexagon House,
Manchester M9 3DA.*

References

1. Mudd, J. S., and Woods, M., *JOCCA*, 1970, **53**, 852.
2. McLaren, K., *Color Engineering*, 1969, **7**, (6), 38.
3. Idem., *JSDC* 1970, **86**, 354.
4. Idem., *Color Engineering*, 1970, **8**, (4), 21.
5. Colour Measurement Committee, *JSDC* 1970, **86**, 368.

Literature research group

SIR,—The Toronto Society, a constituent society of the Federation of Societies for Paint Technology, is setting up a literature research group to prepare interesting and meaningful collections of important papers on specific paint topics. The hope is that we can supplement the Society's training manuals with some low-cost "Readings in paint technology" in which the paper would be reviewed and tied in to current technology.

I am asking your readers, through this letter, to send me a copy of any paper or patent or article which they have found useful and valuable and feel would merit a place in such a set of readings. The level should not be too advanced as these are intended for student reading. If the paper could be accompanied by a comment explaining its special merit, this would be invaluable.

Yours faithfully,

J. Grey, Chairman
Literature Research
Sub-Committee

16 November 1970

*16 Hills Road,
Ajax, Ontario, Canada.*

Information Received

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

It has recently been announced that **Pekema Osakeyhtio**, the Finnish resin manufacturer, has appointed the **Cornelius Chemical Co. Ltd.** as agents to market its polyolefin products in the UK and Northern Ireland.

ICI Ltd., Mond Division, has published a broadsheet giving details of its activities. The broadsheet, printed in three dual-language versions: English/German, Spanish/French, and Russian/Polish, is said to be the first publication to give a real picture of Mond Division's activities.

The Decorative and Retail Paints Division of **Donald Macpherson Group Ltd.** has recently introduced a new acrylic primer undercoat. The new product, which is available in white only at present, is claimed to dry in 1-2 hours, and to be ready for overcoating in 2-3 hours.

It has recently been announced that two Unilever-owned German oleochemical companies, **Aldag Fettchemie GmbH** and **VSW Germania GmbH**, will amalgamate as from 1 January 1971 to form **Unichema GmbH**. The new company will be based on Hamburg, with factories at Hamburg and Emmerich, and will specialise in marketing oleines, stearines, distilled and fractionated fatty acids, glycerine, catalysts and processed oils.

Price's Chemicals Limited, Unilever's British company in this field, will work in close collaboration with its German associate.

Du Pont has published a 12-page booklet entitled "Du Pont in Europe," giving an outline of the various European Du Pont companies and the products they produce.

Lane Brothers (Tar Distillers) Ltd. has announced that the tar and benzole business that it formerly operated at Scunthorpe in close association with Normanby Park Steelworks has become part of the Chemicals Division of **British Steel Corporation** as from 3 January. The fire at the Scunthorpe tar works on 3 August last year caused a suspension of primary tar distilling, but existing commitments were fulfilled by close and friendly co-operation with BSC; the company is assured by BSC that they will continue to provide the level of service that Lane Brothers has provided in the past.

Two information leaflets, giving full details of the company's range of flexographic inks and liquid inks for film printing, have been issued by **Winstones Limited**.

The *Demi-Finex*, a new, compact, vibratory sieving machine is now available from **Russell Finex Limited**. Originally designed for the separation of extraneous matter from epoxy resin overspray in electrostatic metal coating, the *Demi-Finex* is claimed to be attracting interest from many other industries. The unit comprises a 12in demountable polypropylene sieve, retained and tensioned by quick action spring loaded clips, with a polypropylene cover designed for connection to a feed line, which, when inverted, acts as a funnel for hand feeding. A fractional horse power, totally enclosed, vibrator motor operates the sieve, and the unit is supplied with hollow section steel stand, which is available in two sizes.

The **Research Institute for Printing and Allied Industries TNO** has issued information leaflet W30, giving details of the use of the *IGT Printability Testers A1, A2 and AC2* to measure abrasion and rub resistance.

Swale Chemicals Limited has recently announced the formation of the Swiss company **Swale Chemicals AG**, in conjunction with **Bosshard and Company**, the Swiss surface coatings manufacturer.

The new company will manufacture and market the Swale range of inks and coatings for packaging.

Developed from the compatibility wall chart that was a feature of the **BIP Chemicals Ltd.** stand at OCCA 22, is a new pocket sized wallet of compatibility tables. Each card deals with one of the *Beetle* range of resins, and by sliding the cards into a special key in the lid of the wallet, the resin's compatibility with over forty other film formers, at three different solids ratios, can be seen at a glance.

It has recently been announced that the whole of the share capital of **Laporte Synres Limited** has been acquired by **Coates Brothers and Company Limited**. Under the new ownership, the name of the company has become **CV Polymers Limited**; the production site at Stallingborough will be maintained, but eventually certain functions will be handled centrally by the Coates Brothers Group.

Polyvinyl Chemie Holland NV has issued technical leaflets on *NeoCryl B-722*, a thermoplastic acrylic for modification of nitrocellulose in wood lacquers, and *NeoCryl B-725* as a concrete and asbestos cement sealer.

The **British Titan Products Company Limited** has announced changes in its organisation with effect from 1 January. The name of the company will become **British Titan Limited**, and its UK activities will be transferred to two wholly owned subsidiary companies. British Titan Limited will become a holding company with the same shareholding and board as at present.

The first of the two new subsidiaries, **British Titan Products Company Limited**, will take over manufacturing operations in the UK, while the second, **Tioxide International Limited**, will be responsible for group headquarters and services, as well as sales from both the UK operation and the group's French subsidiary, **Tioxide SA**.

The purpose of reorganisation, say British Titan, is to segregate the headquarters' functions from manufacturing operations, and so provide a suitable framework for further expansion of the group's activities.

Pfizer Ltd. has published a new edition of its list of products, including a range of metal products and pigments.

A new laboratory has been opened by **ICI Ltd., Dyestuffs Division**, at its Manchester headquarters. Aimed at the development of new plastic foams with low flammability, the new laboratory contains facilities for applying BSI and ASTM tests for plastics, as well as most of the individual fire and smoke tests specified by countries throughout the world.

Information on the *Sigmulto* process, a new polychromatic coating system based on synthetic rubber copolymer, is now available from **Pieter Schoen Limited**. The

polymer is emulsified and stabilised in a viscous liquid base, and can be applied in a single spraying operation. Properties claimed for the coating include ease of cleaning with detergent and water, good scratch and chip resistance, ease of touching up, good durability, and an anti-static effect that reduces dirt and dust settlement.

Synthetic Resins Limited has recently announced that it is to be sole UK selling agent for the range of metallic soaps manufactured by **Burts and Harvey Ltd.** The agency was held for many years by James Beadel and Company Ltd., one of the Unilever companies merged to form Synthetic Resins Limited.

Farbwerke Hoechst AG has recently issued technical data sheets on *Permanent Orange GG*, a diazo pigment of the pyrozone class without lake-forming groups, claimed to have high tinctorial strength, very good transparency, excellent gloss and good light fastness, and *Hosaperm Blue AN*, an α -phase copper phthalocyanine pigment to CI Pigment Blue 15.

A new range of plastic-tip retouching pens for retouching damaged or imperfect wood finishes has been introduced by **Sonneborn & Rieck Ltd.** Available in 24 wood finish colours, the pens are supplied filled with mildly solvent, transparent stains that can be used for the direct re-touching of varnish stains. Sealed against drying out, the pens can be cartridge refilled.

Section Proceedings

London

Characterisation of pigment surfaces

A joint meeting of the London Section with the Colloid and Surface Chemistry Group of the Society of Chemical Industry was held at 10 a.m. on 25 November 1970, at Brunel University, Acton, London W3. Attendance was 165. Mr R. C. Tarring, Chairman of the Colloid and Surface Chemistry Group, took the chair for the morning session.

Professor K. S. W. Sing, of Brunel University, gave the first paper *Assessment of area and porosity of pigment surfaces*. In the use of the BET equation with different gases, e.g. nitrogen, butane or propane, varying figures for the specific surface area were frequently obtained. Professor Sing described the derivation of the BET equation, and the significance of the monolayer capacity, V_m , and the constant C , which was related to the heat of adsorption. In spite of theoretical difficulties, the BET was still the preferred method of evaluation of gas adsorption isotherms. The actual range of linearity of the equation was not a criterion of the success of the theory; the real test was to obtain some independent measurement of V_m and C . Unfortunately, most materials examined were very finely divided and porous. Electron microscopy, for example, could only be used for fine non-porous materials. It was necessary to know, in addition to V_m , the molecular area of the adsorbate gas, it being assumed there was a complete monolayer.

The location of the so-called "point B" on Type 2 isotherms was another method of obtaining a value for V_m . Some isotherms were so flat and almost linear in the early stages that visual location of point B was not possible; strictly one should not use the BET equation in such cases.

The energetics of adsorption was related to the change in chemical potential at the relative pressure at which adsorption took place. This could be split into two parts, the differential heat of adsorption and the differential entropy of adsorption. The quantities contributing to the differential heat of adsorption were, according to Kisilov, (1) specific, and (2) non-specific interactions. The latter were the dispersion forces, caused by the fluctuating dipoles or quadrupoles of neighbouring atoms as they moved in phase. As the atoms approached closer, the attractive forces increased until the repulsion barrier was reached. These forces depended upon the polarisability of the species involved, and were related to the density of the solid phase. The specific interactions depended upon some kind of fluctuations in the charge distribution of the adsorbate itself. A polar adsorbate interacted with the field above the solid surface. This effect, for example with nitrogen, could be a very significant contribution to the overall interaction energy. Examples were given of the effect of different types of solid surface on adsorption of various gases. The adsorption of water vapour should clearly be avoided for surface area measurements; it was, however, useful as a means of obtaining information about the nature of the surface.

Professor Sing then considered the effects of porosity. Types 1, 2 and 4 isotherms were very different in character. Type 2 isotherms occurred, for example, with adsorption on a non-porous solid, and it was assumed that multilayer adsorption occurred, extending outwards with no restriction. Type 4 isotherm occurred with capillary condensation in relatively large pores, and was often associated with hysteresis. Monolayer condensation occurred first on the walls of the pores, followed by bulk capillary condensation. Type 1 was the classical Langmuir isotherm, but it was now believed that it was not, in fact, due to formation of a classical monolayer. Rather

it was thought that the primary process was the filling of very narrow pores, owing to the overlap of the dispersion forces of the walls.

Professor G. D. Parfitt, of Brunel University and British Titan Products Company Limited, then spoke on *The chemical characterisation of pigment surfaces*. Professor Parfitt restricted his talk to oxides, and in particular, titanium dioxide pigments. The titanium dioxide surface was very reactive, and needed to be covered up with other oxides for use in surface coatings. Mixtures of oxides were used, developed on a semi-empirical basis over the years. Silica and alumina were the two most important coating oxides. The chemical character of the surface was of greatest importance; infra-red methods had proved to be the most useful techniques to study the nature and if possible the quantity of surface sites or groups.

The pigment surface was covered with hydroxyl groups; it was also necessary to determine the effect of the physically adsorbed water, and the effect of impurities. Professor Parfitt then described the various experimental techniques used, and the methods of interpretation of the spectra. For example, the spectra of hydroxyl groups on the surface could be compared with those of alcohols. The spectrum depended upon the environment, and an example was shown of how the spectrum of butane varied; as a gas, in solution in carbon tetrachloride, and adsorbed on silica glass. The hydroxyl groups could also react chemically, e.g. with an acid to form an ester. The classical work was done before the war on montmorillonite. There were two bands in the hydroxyl stretching region of the spectrum. One of these, at $3,400\text{ cm}^{-1}$ corresponded to hydrogen-bonding, the other, at $3,750\text{ cm}^{-1}$, was an isolated hydroxyl. This could be demonstrated with silica, e.g. Cabosil; as it was heated the bands gradually disappeared, leaving a single band at $3,750\text{ cm}^{-1}$. On dehydration, Si—O—Si bonds were formed on the surface. On re-admission of water to the surface, the multiple bands around $3,400\text{ cm}^{-1}$ reappeared. Water hydrogen-bonded on the surface gave the same spectra as hydrogen-bonded hydroxyl groups. Silica had a relatively simple spectrum and a lot of work had been done on it. It was possible to calculate the number of OH groups on the surface; this amounted to about 4.5 OH groups per 100Å^2 for a fully hydroxylated surface; at higher temperatures this decreased to almost zero. The most recent work on the silica surface had shown that there were two types of site on the surface; one where about 1.4 OH groups per 100Å^2 were directly attached to Si; and one where about 3.2 OH groups per 100Å^2 consisted of a pair of OH groups on adjacent Si atoms bridged by —O—. These latter were all removed on heating to 500°C , leaving behind about 1-1.5 OH groups per 100Å^2 of surface.

Similar investigations had been made with titanium dioxide; however a fully hydroxylated surface was not found, the maximum coverage being only about 50 per cent of the surface. Two types of OH groups were also found, one directly bonded to Ti and the other to the oxygen atom in a Ti—O—Ti bridge. Alumina had a more complicated spectrum, with five distinct bands, depending upon the stereochemical position of the OH group in relation to the oxygen atoms.

In the afternoon session Dr V. T. Crowl of the Paint Research Association took the Chair. The first paper was by Dr G. Eulitz and Dr K. Merkle, of Farbwerke Hoechst, and was entitled *Characterisation of organic pigment surfaces*. Dr Eulitz, in presenting the paper, referred to the great importance in the applications of organic pigments of the particle size distribution. This was normally determined by electron microscopy. The particle size of the pigment was important in the scattering and

absorption of light; this could excite atoms and induce reactions with the medium. In large particles, the light quanta were absorbed only on the surface. The particle surface was of great significance in wetting, rheology, dispersion, etc., and the type of surface was also important.

Measurement of the specific surface presented problems, mainly because of the small size of the crystallites, $< 0.05 \mu\text{m}$. To be sure of reliable results, two or more methods of determination were required. Nitrogen or argon gas adsorption methods were used; a simplified rapid one-point method was used in comparing similar types of pigment, in which the value of V_m was determined by measurement at an argon pressure of 60 Torr. A simple ratio of pigment surface areas was obtained in comparisons by this method, with an accuracy of 2 per cent. Adsorption from solution of phenol or nonylphenol was also used to measure surface areas.

Electron microscopy was used to determine particle size distributions. A Zeiss semi-automatic particle size counter was used with the electron micrographs. This was used to count about 2,000 particles, and the method was rather slow and tedious. However, fully automatic particle counters were unsatisfactory, because they could not distinguish between single particles and agglomerates. The disc centrifuge had also been used successfully to determine particle size distributions, using a buffer line start to overcome streaming. Dr Eulitz described a modification of the Joyce-Loebl disc centrifuge which had been used at Hoechst, in which an optical method was used to determine the particle concentration through the disc; this was very speedy, and was capable of producing reproducible results. A desk-top computer, the Programma 101, was used with electron microscope and photosedimentation data to produce the number, surface, and mass distributions of the pigments.

He then described some work in which the differing behaviour of various batch samples of organic pigments was interpreted by means of surface area and size distribution data. Samples of Pigment Violet 19 showed differences in their properties. The pigment with the higher surface area had higher strength and viscosity in ink media. The lightfastness of the higher surface area pigment was lower than that of the pigment with lower surface area, as would be expected.

Another example was Pigment Yellow 17, samples of which differed in dispersibility in letterpress and offset inks. Electron microscope cross-sections of ink films on paper showed the presence of large numbers of agglomerates in one sample. The Stereoscan was also used to show the irregularity of the surface in films of this latter pigment, which manifested itself as poor gloss. In spite of these differences between the samples, the specific surface areas of the pigments were almost identical. However, X-ray diffraction showed one sample to be more amorphous than the other, resulting in a difference in surface energies.

Another case was that of samples of Pigment Yellow 3 where differences in dispersibility occurred that did not relate to differences in particle size; however, considerable differences in surface area occurred, indicating differences in ultimate crystal size.

Water vapour adsorption isotherms could also be used to determine differences in hydrophobicity. In these and other ways, investigations of the surface chemistry and physics of pigments could be of value in interpretation of their technological properties.

The final paper, given by Dr D. Dollimore of the University of Salford, was entitled *Characterisation of carbon black surfaces*. Dr Dollimore described various forms of carbon; carbon black consisted of graphitic layers of smaller dimensions than normal graphite, and consequently containing more edges of the crystal planes. On

heating carbon black, further graphitisation occurred; hence the different types of carbon black formed by the varying methods of manufacture. The normal data available included particle size from electron microscopy, nitrogen adsorption surface areas, oil absorption, volatile content, and pH of aqueous slurries. A feature of carbon blacks was the formation of chain-like structures, which was related directly to the oil absorption figure. No hysteresis loops were shown in gas adsorption isotherms. With nitrogen adsorption, there were wide variations in the Value of C , from 80 to 500, in the region of V_m . Fortunately, the BET isotherm was insensitive to the actual value of C .

Dr Dollimore presented results on typical carbon blacks, in which the volume of nitrogen adsorbed at V_m was plotted against the absolute temperature to which the samples had been heated. Three types of linear plots were obtained: through the origin, linear but not through the origin, and consisting of two linear portions. It had been suggested that some variations were due to separate regions of homogeneity on the surface. Pierce and Ewing had suggested that nitrogen effectively occupied an area of 20\AA^2 on carbon black surfaces, owing to specific adsorption on the hexagons. Dr Dollimore had used a master isotherm on carbon black for the calculation of t -plots, and had obtained good linear plots. With increasing temperature of oxidation there was a development of surface porosity, possibly pores of only 100\AA diameter, and an increase in surface area, but no decrease in particle size was shown by electron microscopy. The t -plots showed this development of porosity.

Organic molecules adsorbed on normal carbon blacks were not closely packed; methanol, ethanol, carbon tetrachloride and *n*-heptane all occupied larger areas than theoretical. Another group of compounds, e.g. amines, adsorbed on available sites, i.e. there was specific interaction.

Correlations were shown between the nitrogen adsorption surface areas and technological properties. Iodine adsorption depended on surface complexes on the carbons, and there were two sets of relationships, for acidic and for basic surfaces.

Each of the lectures was followed by an extensive discussion. In conclusion, Dr W. Carr, of Manchester Section, proposed a vote of thanks to the four speakers for their excellent and stimulating lectures, and to the authorities at Brunel who had made the administrative arrangements for the meeting.

V.T.C.

Addition copolymers of the vinyl ester of branched chain fatty acids for use in electrodeposition paints

A meeting of the London Section was held at East Ham Technical College on 10 December 1970 with Mr D. E. Eddowes in the chair. Dr W. J. van Westrenen, of Shell Plastics Laboratories, Delft, and Mr W. H. M. Nieuwenhuis, of Shell Laboratories, Amsterdam, presented a paper with the above title.

Dr van Westrenen said that vinyl esters of branched chain fatty acids had been known for some time, being used to make latices; their particular advantages included good alkali resistance and outdoor durability. Alkyds based on these fatty acids had also been examined, and had the same good properties. The present paper was concerned with the design of water-soluble polymers for electrodeposition. There were certain requirements for such polymers which necessitated the use of a multi-component system; these were (a) good water solubility, which necessitated several COOH groups in the chain, giving an acid value of about 50; (b) some cross-linking possibilities for cure, either self-curing or by curing with, for example, an amino resin; (c) monomers to control the hardness of the cured resin, which generally required a combination of hard and soft monomers.

The system chosen for study was a multi-component one consisting of the vinyl ester of the branched chain fatty acids, styrene, and acrylic monomers. Little is published in the literature about such ternary systems, and it was necessary to proceed on an empirical basis. Dr van Westrenen described the experimental work that had been undertaken, and the properties of the range of polymers made, and then considered the evaluation of the resins.

The most important property of the system to be examined was solution stability: the water diluted polymer should be stable for 2-3 weeks' storage at 40°C, with no pH drift. Phase separation on storage was not always due to saponification. The polymers, pigmented with titanium dioxide, were tested in electrodeposition experiments. The polymer was first blended with melamine resin (of the low molecular weight type), then neutralised and let down to mill in the pigment. A circulation test was used to test bath stability.

The electrodeposition results showed good gloss and hardness, and flexibility was satisfactory. Alkali resistance was very good, and salt spray results were fairly good. The gloss was found to be very sensitive to the preparation procedure. Dr van Westrenen concluded by describing some work on a study of the reaction conditions, in which vinyl pivalate was used as a model compound for the branched chain fatty acid vinyl ester.

The lecture was followed by a discussion, after which Mr J. Lloyd, a student at the college, proposed a vote of thanks to the authors.

V.T.C.

Manchester

Chloride titanium dioxide pigments—their value

On Friday 11 December the Section met, under the chairmanship of Mr S. Duckworth, at Liverpool Polytechnic, to hear a paper "Chloride titanium dioxide pigments—their value," presented by Mr F. D. Robinson and Mr J. S. Jordan, of Laporte Industries Limited.

Mr Robinson commenced by dealing with the manufacturing process. TiO_2 production was now 2 million tons p.a., units of 160,000 tons p.a. were now being installed, and there had been no new US plant using the sulphate process for five years. The sulphate process produced both pollutants and effluent as by-products, e.g. 2.5 tons FeSO_4 per ton of TiO_2 , whereas the chloride process by-products were CO and CO_2 which could be vented to atmosphere. The sulphate process calcination to high purity rutile pigments was a critical operation, the oxidation of TiCl_4 being a more controllable process giving a narrower cut size. The impurities affecting brightness—Fe, V, etc., were lower in chloride process products, as were the toxic metals—Pb, Hg, As, etc.

Mr Jordan then followed with a review of technological performance, where hiding power, colour and weathering behaviour in paint systems were compared for products from the two processes. The result was the claim that chloride products could now compete technically in performance, and that the results they produced were in the top rank of those of sulphate process pigments. In emulsion paints, the less aggregated chloride products give better dispersion and colour.

At the close of the discussion the vote of thanks was given by Dr T. I. Kyle.

D.A.P.

The olefine route to new paint latices

The Section met on 13 November at the Bolton Institute of Technology to hear Mr J. A. Wall, of BP Chemicals Limited, present a paper on "The olefine route to new paint latices." Dr F. M. Smith was in the chair and 67 members and guests were present.

Mr Wall recollected that emulsion paints were about 20 years old and in the UK were born during post-war austerity; demand built up quickly and resin capacity was stretched. The available monomers were then vinyl acetate, styrene and butadiene. Va required plasticisation, styrene high proportions of coalescing solvent, and styrene/butadiene discoloured on ageing. Va was the main monomer used, initially with external plasticisation. In the late 50s, internal plasticisation of va by acrylic esters was introduced, and in the mid-60s, acrylic esters of higher alcohols were employed as internal plasticisers, as were vinyl esters of branched chain fatty acids; the latter significantly increased water resistance but were not highly effective plasticisers.

In the US in 1965, va/ethylene copolymers were introduced; these required less stabilisation or thickening, and the incorporation of ethylene effectively removed half of the ester linkages that produced weaknesses in va polymers.

The behaviour of exterior paints based on va/ethylene was illustrated by Mr Wall; experience of this was now being used in the development of second generation paints. Discussion at the Manchester Section Symposium had suggested blending the soft va/ethylene with the harder va/VeoVa. A convenient way of doing this would be by making terpolymers from three of the four monomers. Four terpolymers were theoretically possible, two of which could be eliminated from knowledge of the behaviour of their constituent bipolymers and the lack of effect of the third component.

The two left were va/ethylene/vc, and va/ethylene/VeoVa. Mr Wall referred to a Fatipec paper which concluded that vinyl chloride improved the properties of va/ethylene.

Va had been the mainstay of emulsion paints for 20 years, and during this time cost and performance had been improved. Mr Wall considered that such improvements would continue.

The vote of thanks was proposed by Mr C. Barker and carried with acclamation.

D.A.P.

Midlands

Gloss and semi-gloss latex paints

A meeting of the Midlands Section was held at the Chamber of Commerce House, Birmingham, on 20 November 1970. Mr D. J. Morris, in the chair, introduced Mr J. Clark of British Titan Products Company Limited, who presented a paper entitled "Gloss and semi-gloss latex paints."

Mr Clark explained that flat oil and distemper paints had been almost completely superseded by emulsion paints for flat and satin finishes. This progress had led to the search for a gloss emulsion paint having the advantages associated with emulsion paints of easy clean-up, absence of fire hazards or smell, and rapid drying characteristics.

He illustrated, by a large number of slides, the extensive investigations carried out by his company in evaluating the influence of pigment, thickener, glycol, latex, and formulation on film properties, particularly gloss characteristics.

In the course of an account of exterior weathering properties, Mr Clark admitted that glossy latex coatings left much to be desired. Although the amount of dirt

deposited on the latex coatings was not greatly different from that deposited on an alkyd gloss coating, it was much more difficult to remove the dirt from the latex coating by scrubbing. This was attributed to the dirt particles sinking into the thermoplastic latex film and becoming mechanically bound. Complete removal of dirt could only be achieved by abrasion.

At the conclusion of the paper, Mr Clark dealt ably with a variety of queries raised by members of the audience including Mr D. J. Morris, Mr H. J. Clarke, Mr R. F. Hill, and Mr D. Penrice. The questions included comments on the possible use of silicone resins or UV reactive components to control dirt retention, the influence of different grades of TiO_2 on gloss, the influence of film thickness on gloss and the influence of various substrates on performance.

A vote of thanks was proposed by the President of the Birmingham Paint, Varnish and Lacquer Club, Mr D. Penrice, which was heartily endorsed by those present.

R.F.H.

Trent Valley Branch

Electropainting

A joint meeting with the Institute of Metal Finishing was held at Loughborough University on Thursday 12 November at 7.30 p.m., when Mr J. R. Bourne, of Mebon Limited, spoke to an audience of 50 members and guests on the above subject.

Mr Bourne then gave a brief outline of the history of the electropainting process. As early as the 1930s the potential of such a method was realised by Crosse & Blackwell Limited, when they used it for the coating of food containers. However, for some reason the idea was then dropped and not thought of again until the 1960s. This resurrection was prompted by the increasing demand for corrosion resistance on motor vehicles and in 1962 the first commercial plant was opened. By 1964 the Ford Motor Company were operating the first full scale plant and at present there were something like 400 plants in the world using this process, of which approximately two-thirds were situated in Europe.

In electropainting several processes took place simultaneously; the three major processes were thought to be electrolysis, electrophoresis, and electro-endosmosis.

Mr Bourne outlined typical electropaint formulations, and listed some of the most suitable components. He then described the general make-up of the plant used for electrocoating as comprising cleaning, pre-treatment, drying, electrodeposition, washing, drying and curing at 150-160 C. The importance of circulation in the paint bath was stressed.

As far as the electrical side of the process was concerned, constant current was preferred. However, constant voltage had been found most practical in commercial production. Electrical requirements generally worked out at 2-3 amps per square foot of the article to be coated.

Mr Bourne went on to summarise some of the advantages offered by the electropainting process. One interesting point was that the estimated cost of the paint coverage (at 1 thou thickness) was approximately $\frac{1}{2}$ d per sq ft and the electricity cost was about $\frac{3}{4}$ d for treating 100 sq ft. Spray painting, on the other hand, generally costed out at 2d or more per sq ft.

He also referred to one or two drawbacks. It was essential that a good, smooth, perfect surface was obtained on the metal to be coated; one coat had a very high insulation value, therefore, it could only be a one-coat process; the process was only economic if long runs were possible with similar types of articles; articles made of different metals produced different coating characteristics and therefore varying results could occur.

Mr Bourne estimated that 75 per cent of the electropaint used found its way on to motor vehicles or car accessories. In many areas of metal finishing it was obviously going to find a much broader use. For instance, multi-coat systems were currently being investigated and tested, and development work was going on with one-coat white finishes with good corrosion resistance, mainly for domestic appliances such as washing machines, refrigerators, etc. Other fields in which this type of painting had been tried included the treatment of 60 ft long steel girders and steel coil coating, where it was possible to handle up to 500 ft per min, on a full scale commercial plant.

Mr Bourne's lecture was very fully illustrated by a series of pictorial and technical slides backed up by a small scale practical demonstration of the electropainting process.

Such an interesting and informative talk naturally produced a very full general discussion period when Mr Bourne answered many relevant questions on both commercial and technical aspects.

In conclusion a vote of thanks was proposed by a member of the Institute of Metal Finishing which was heartily endorsed by the rest of the audience.

D.F.G.

Newcastle

Solution polymers for cross-linking with polyisocyanates based on the vinyl ester of Versatic acid

The second meeting of the current session was held at the Royal Turks Head Hotel, Newcastle on Thursday 12 November 1970, when a paper was presented by Mr P. de Carpentier of Shell Research NV, Delft.

Mr Carpentier discussed the preparation and evaluation of isocyanate cured paint films based on hydroxyl containing copolymers of vinyl acetate and the vinyl ester of branched chain fatty acids.

Initially, polymers were prepared by reacting vinyl acetate with VeoVa in solution at a ratio of about 2:1 wt/wt, using benzoyl peroxide initiator. The resultant polymers were then saponified, using an aqueous solution of *p*-toluene sulphonic acid. The reaction time of the hydrolysis step was varied according to the desired degree of hydrolysis of the vinyl acetate required. Hydrolysis of the vinyl acetate by this method yielded a vinyl polymer containing hydroxyl functionality.

Reaction variables which were considered in depth were hydroxyl value, molecular weight, and the presence of carboxyl groups in the vinyl polymer backbone. The polymers prepared in this manner were reacted with various polyisocyanates and examined for film properties.

Some interesting results were obtained, and these were outlined by Mr Carpentier, and, in particular, stress was laid on the rapid drying of these systems, particularly with those polymers prepared with small additions of acrylic acid copolymerised in the vinyl polymer backbone.

The speaker concluded by commenting on the nature of the process for the preparation of the vinyl polymers. He emphasised that, initially, the primary intention was to assess the merits of these VeoVa based materials. Now that it had been demonstrated that these were potentially attractive polymers, attention was being concentrated on improving the process aspects.

Mr Carpentier then dealt with questions from Messrs Davison, Laws, Baxter, Tate, James and Bravey, after which Mr James thanked Mr Carpentier for his interesting paper.

A.L.

Thames Valley

Corrosion and protection

In front of a large audience, Dr T. P. Hoar, of the University of Cambridge, gave a lecture on "Corrosion and protection" at the Thames Valley Section meeting on 20 October 1970 at the Beech Tree Hotel, Beaconsfield.

Dr Hoar began by saying that "corrosion" was a depressing, negative term implying decay and loss. Now that its mechanisms were largely understood, and the means of its control and prevention available in many cases, it was right to lay at least equal emphasis on the aspect of protection.

The speaker briefly sketched the progress in corrosion protection over the past 50 years, from linseed oil based paints through phenolic resin based types to modern polyurethane and epoxy formulations, where air drying, or even solvent evaporation, was often not required. Progress had also been made with inorganic coatings, which were often silica based, setting to an inorganic glass.

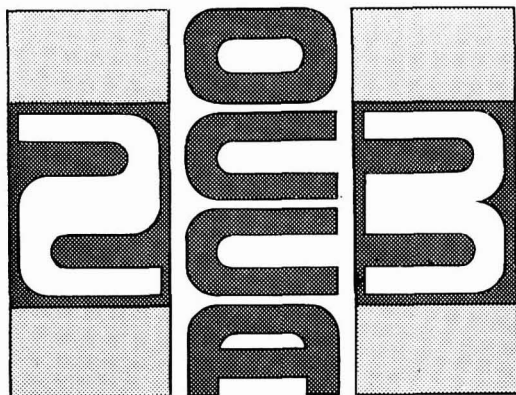
During the same period, pigments had progressed from being merely colour additives until many now imparted both inhibiting and protective properties to the film. In many cases, the greatest advances had been made where properties of vehicles and pigments had been blended, as in the incorporation of micaceous iron oxide in epoxy vehicles to improve salt-spray resistance, and in the formulation of etch primers.

Coatings systems based on a metal-sprayed coat followed by primers and finishing coats were making great strides, after initial resistance from both metal-sprayers and painters, and this had underlined the importance of really good surface preparation, particularly by the use of grit blasting.

However, as more nominally favourable factors were incorporated into a protective system, the necessity for careful control and inspection at every stage increased. Failure to reach the proper standard at any one stage in the process would prejudice its overall success. Thus those responsible for drawing up specifications, and those who carried them out, should be fully conversant with all the pitfalls, as well as with the best processes.

Question time gave rise to some lively discussion, with an interesting contribution from Mr Newnham. Mr Bray, a member of the Section Committee, proposed a vote of thanks, which was heartily endorsed by all those present.

R.E.G.



Technical Exhibition

21-25 June 1971

Additional Exhibitors

The Twenty-Third Annual Technical Exhibition, to be held at the Empire Hall, Olympia, London from 21-25 June 1971, will be the largest ever organised by the Association, a net stand area of well over 35,000 square feet having been applied for.

The Committee is pleased to report that it has accepted late applications from: Elsevier Sequoia SA, and Radiant Color of California NV.

Thus, there will now be 116 stands with direct exhibitors from 11 overseas countries—Belgium, Canada, Denmark, Finland, France, Germany, Holland, Italy, Norway, Switzerland and United States of America. Of the total number of companies exhibiting, 14 have not previously shown at OCCA Technical Exhibitions, whilst 28 others did not show at the 1970 Exhibition.

Arrangements have been made with three hotel groups in London for hotel accommodation for visitors to the Exhibition and details will be published in the *Official Guide*. Copies of the *Guide* will be despatched individually to chemists and technologists on the Continent of Europe and in other countries as well as being sent to all Members of the Association, wherever resident.

A visitors' identification card is

being enclosed in each copy of the *Official Guide* despatched prior to the Exhibition and will also be enclosed in the folders for technical literature which will again be available at the entrance to the Exhibition.

The Committee is pleased to announce that the Rt. Hon. Margaret Thatcher, PC, MP, Secretary of State for Education and Science, has kindly consented to be



Mrs Margaret Thatcher, PC, MP

Guest of Honour at the Exhibition Luncheon which is to be held at the Savoy Hotel on Monday 21 June 1971. A form of application for tickets (price £3.25 each) will be enclosed in each copy of the *Official Guide*.

For the information of visitors to the Exhibition, Olympia is easily accessible from the Gloucester Road Air Terminal and from all main-line stations. Those travelling by underground should board the Piccadilly or District line trains to Earls Court, from which

station a special train service is provided to Olympia.

Facilities available at the Empire Hall during the Exhibition include a licensed restaurant, and two licensed buffets—one on each of the two floors on which the Exhibition will be located. Escalators to and from the first floor will be in operation throughout the hours of opening, and attractive seating areas, which have long been a feature of OCCA Exhibitions, will be provided on both floors.

Biennial Conference 1971

Surface properties and appearance

At the end of November copies of the Conference Brochure were despatched to all members of the Association and to non-members who had written requesting this information. **The closing date for applications on this occasion will be 1 March 1971** and the attention of readers is directed to this date, which is a month earlier than normal since the Conference itself will be held from 4-8 May at the Palace Hotel, Torquay.

Following the practice of previous Conferences, it is intended to despatch pre-prints of the papers, together with full details of accommodation allocated, badges, tickets etc. in the special Conference folder, at the beginning of April 1971.

Four technical sessions have been arranged under the title given above, together with a special session devoted to a management topic—"The management of innovation"—and three Workshop Sessions entitled:

How will pollution control affect the paint industry?

Is the gloss emulsion paint a myth?

Powder coatings—a threat to stoving enamels?

As well as the technical sessions there will be the usual social programme for ladies attending the Conference, together with a Civic Reception for all delegates on 5 May and the Association's Dinner and Dance at the conclusion of the Conference on the Friday evening, 7 May. The usual tournaments will take place, including the golf tournament for the OCCA Conference Golf Trophy, presented by Mr S. Sharp, a former Chairman of the Hull Section.

Council has fixed the registration fees at £15 for Members, £7 10s 0d for Wives and £25 for Non-members, with a concessionary rate for Student and Retired Members of £7 10s 0d. The Chemical & Allied Products Industry Training Board will consider the payment of grant, to firms within scope, for attendance at the Conference. Payment is subject to the content of the Conference being relevant to the needs of the sponsoring company and also to the development of the individual attending.

Readers wishing to receive the Conference Brochure and Registration Form and/or synopses of the papers (as published in the October and November 1970 issues of *JOCCA*) are requested to apply to the Director & Secretary at the Association's office.

Courses and Symposia

Particle size and surface area measurement

A one-week residential course with the above title is to be held from 29 March to 2 April at the University of Bradford. The emphasis will be on practice and interpretation of results. Application forms may be obtained from The Secretary, School of Powder Technology, University of Bradford, Bradford, BD7 1DP.

Corrosion prevention

A one-day symposium on corrosion prevention is to be held at Derby and District College of Technology on Thursday 15 April. The stated aim of the symposium is to present some provocative but constructive aspects of corrosion prevention, particularly from economic and practical considerations, with ample opportunity for audience participation. Full details are available from B. Marshall, Derby and District College of Technology, Kedleston Road, Derby, DE3 1GB.

SDC Biennial Symposium

The Society of Dyers and Colourists has chosen the theme "Colour and processing challenges in the seventies" for its 15th Biennial Symposium, to be held at Aviemore from 15-17 September 1971. A full technical and social programme has been arranged, and applications should be sent to the SDC, Dean House, 19 Piccadilly, Bradford, Yorks.

Advances in the chemistry and technology of pigments

A course on "Advances in the chemistry and technology of pigments," intended as a stimulating course at graduate level for all those interested in organic or inorganic pigments, either as makers or users, is to be held at Leeds University from 13-16 July 1971. Full details of the lecture programme, which will be relatively light to allow plenty of time for discussion, were sent out at the end of January. Any interested person should contact the Director of Special Courses, Special Courses Division, Department of

Adult Education and Extramural Studies, The University, Leeds, LS2 9JT.

Fourth International Lead Conference

The European Lead Development Committee is to organise the fourth International Lead Conference, to be held at the Atlantic Hotel, Hamburg, from 21-24 September 1971. The Lead Development Association is responsible for the technical programme, for which modern visual aids, including closed-circuit television, will be available. Several works visits and social functions have also been arranged. The provisional programme is expected to be ready early this year, and intending delegates should write to the LDA, 34, Berkeley Square, London W1X 6AJ.

Adhesives, sealants and surface coatings industries

A symposium on "World future technical and commercial developments of the adhesives, sealants and surface coatings industries" is to be held in Brussels on 24 and 25 March. The organisers are the International Business Contact Club, Avenue Nouvelle 65, B 1820, Strombeek, Belgium.

Colloid and Surface Chemistry Group

A meeting of the Colloid and Surface Chemistry Group of the SCI will be held at 14 Belgrave Square, London WC1, on Monday 8 March at 6.00 pm, when Dr G. D. Parfitt will speak on "Dispersions of powders in liquids."

News of Members

At the recent A.G.M. of the British Resin Manufacturers' Association, Mr. C. H. Morris, an Ordinary Member attached to the Newcastle Section, and a Vice-President of OCCA, was elected Chairman. Mr. R. F. Bond, an Ordinary Member attached to the Manchester Section, Mr. H. S. Parker, an Associate Member attached to the London Section, and Mr. R. S. Robinson, an Ordinary Member attached to the Manchester Section, were all elected to the B.R.M.A. Executive Committee at the same meeting.

Mr A. G. North, an Ordinary Member attached to the London Section, has been appointed a director of the new Coates Brothers company, C. V. Polymers Limited. Mr North will continue in his position as a director of Cray Valley Products Limited.

Dr A. Bowman, an Ordinary Member attached to the Newcastle Section, is technical director of Tioxide International Limited, the new company formed during British Titan Products Company Limited's recent reorganisation.

Mr C. N. Taylor, an Ordinary Member attached to the London Section, is commercial director of Tioxide International Limited.

Mr B. H. White, an Ordinary Member attached to the West Riding Section, has been appointed divisional marketing manager of Laporte Industries Limited.

New FSPT President

Mr. S. L. Davidson was elected President of the Federation of Societies for Paint Technology at the Federation's Annual Meeting at Boston in October 1970. Mr. Davidson has been President of both Golden Gate and New York Societies, and was Federation Treasurer before his election to President-Elect in 1970.

The FSPT has also announced that a special Golden Anniversary Committee has been appointed to plan the FSPT Annual Meeting and Paint Show that will be held in 1972, the Fiftieth Anniversary year of the Federation, in Atlantic City.

New SLF President

As from 1 January this year, the President of the Federation of Scandinavian Paint and Varnish Technologists is Mr. A. D. Brantsaeter. As reported in the December issue of the *Journal*, Mr. Brantsaeter was appointed President-Elect at the SLF Congress in September, and he commenced his three-year term at the beginning of the year.

Register of Members

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

Ordinary Members

ANDERSON, EDWARD JAMES, 27 Affric Drive, Paisley, Renfrewshire, Scotland.

(Scottish)

DUFFY, BERNARD, 56 Glen Doll, St. Leonard's, East Kilbride, Scotland *(Scottish)*

GIBSON, FRANK, LRIC, 33 Eaton Road, Alsager, Stoke-on-Trent, ST7 2BG.

(Manchester)

HAFFORD, BRADFORD C., The New Jersey Zinc Co., Palmerton, Pa 18071, USA.

(Overseas)

HALL, WALTER, 3 Holystone Avenue, Newsham Farm Estate, Blyth, Northumberland.

(Newcastle)

HAYES, RONALD, 4 Rowan Court, Forest Hall, Newcastle upon Tyne 12. *(Newcastle)*

KAFFENBERGER, THILO HEINZ, c/o Bohler Lackfabrik, 6731 Bohl/Pfalz, Kreis Ludwigshafen am Rhein, West Germany.

(Overseas)

KEELING, ROBERT ALAN, BSc, Glenwood, 12 Westville Drive, Congleton, Cheshire.

(Manchester)

McLAREN, GEORGE, 78 Carrick Road, Rutherglen, Lanarkshire, Scotland. *(Scottish)*

PATEK, JOHN CHARLES, MA, A. B. Fleming & Co., 170 Glasgow Road, Edinburgh.

(Scottish)

REID, ROBERT GRAY, FRIC, Low & Bonar (T & D) Dens Works, PO Box 13-Dundee, DD1 9BG.

(Scottish)

RING, EUGENE FINBARR, Zinkaflex Ltd., Dumer's Lane, Bury, Lancashire.

(Manchester)

Associate Members

HOULTON, WILLIAM, Grays Cottage, Coles Hill, Amersham, Bucks. (*Thames Valley*)
 RICHARDS, PETER HARLEN, 186 Peel Hall Road, Wythenshawe, Manchester 22.
 (*Scottish*)

Student Members

CAPLEN, TIMOTHY BRIAN, Tolkein, The Gables, Rays Hill, Chesham, Bucks.
 (*Thames Valley*)
 DAWSON, SURTEES, 17 Woodlands Terrace, Felling, Gateshead, Co. Durham.
 (*Newcastle*)
 McROBBIE, DAVID MARTYN, 23 Hillstone Close, Greenmount, Nr. Bury, Lancashire,
 BL8 4EZ. (*Manchester*)
 McMAHON, PHILIP, 20 Parkfield Avenue, Hillingdon, Middlesex. (*Thames Valley*)
 MOORE, MICHAEL JOSEPH, 30 Gosling Road, Langley, Bucks. (*Thames Valley*)
 TAYLOR, PAUL, "Sam Remo", Uxbridge Road, Stoke Poges, Bucks. (*Thames Valley*)

Forthcoming Events

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

Monday 1 February

Hull Section: "The use of instrumentation in the evaluation of paint performance" by Mr D. M. Bishop of British Railways, to be held at the Bullock Lecture Theatre, Hull College of Technology, at 7.00 p.m.

Thursday 4 February

Newcastle Section: "Flooring compositions" by a speaker from Synthetic Resins Limited, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Friday 5 February

Thames Valley Section: Buffet Dance at "Great Fosters," Egham.

Tuesday 9 February

London Section—Southern Branch: "New developments in the field of shop and wash primers" by Herr Lampe; given by Dr Lehmann of Farbwerke Hoechst AG. To be held at the Pendragon Hotel, Clarence Parade, Southsea, at 7.00 p.m.

West Riding Section: "Compositional changes of solvent mixtures during the film formation process" by Mr L. A. Tysall and Dr D. H. Shärer of Shell Research Limited, to be held at the Griffin Hotel, Boar Lane, Leeds, at 7.30 p.m.

Thursday 11 February

Scottish Section: "Colour consciousness" by Dr F. M. Smith and Mr D. Malin of Geigy (UK) Limited. Joint Meeting with the Plastics Institute and the British Paper and Board Makers Association. To be held at the St Enoch Hotel, Glasgow, at 6.45 p.m.

Friday 12 February

Manchester Section: "Present and future trends in motor car finishing" by Mr H. L. Quick of Rootes Motors Limited, to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester 1, at 6.30 p.m.

Saturday 13 February

Scottish Section—Student Group: "Organic pigments available to the

paint chemist today" by Mr M. A. Kerr. Geigy (UK) Limited, to be held at the St Enoch Hotel, Glasgow, at 10 p.m.

Wednesday 17 February

London Section: "Techniques of electrographic reproduction" by Mr J. Sloman of Ozalid Limited, to be held at the Polytechnic of the South Bank (Borough Polytechnic), Borough Road, London SE1, at 7.00 p.m.

Newcastle Section—Student Group: "Modern methods of paint application" by Mr K. Baxter of British Paints Limited, to be held at the Newcastle Polytechnic, Ellison Place, Newcastle upon Tyne, at 3.00 p.m.

Scottish Section—Eastern Branch: "Layout of machinery and plant" by Mr D. P. Sullivan of D.H. Industries Limited, to be held at the Carlton Hotel, North Bridge, Edinburgh, at 7.30 p.m.

Thursday 18 February

Thames Valley Section: "Where paint and ink meet" by Mr R. C. Kinsman of Winstones Ltd., to be held at The Beech Tree Hotel, Beaconsfield, Bucks, at 7.00 p.m.

Friday 19 February

Irish Section: "Paper production" by Dr P. Sherry of Clondalkin Paper Mills Limited, to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

Midland Section: "Developments in automobile finishing" by Mr H. L. Quick of Rootes Motors Limited, to be held at the Chamber of Commerce House, 75 Harbourne Road, Birmingham 15, at 6.30 p.m.

Newcastle Section: "Ladies Night" at the Five Bridges Hotel, Gateshead, Co. Durham.

Friday 26 February

Bristol Section: "The glass transition temperature of paint films" by Mr

J. L. Prosser of the Paint Research Association, to be held at the Angel Hotel, Cardiff, at 7.15 p.m.

Monday 1 March

Hull Section: Ladies Evening. A talk on winemaking by a member of the Hull and District Winemakers Guild, to be held at the Queen's Hotel, George Street, Hull, at 7.00 p.m.

Thursday 4 March

Midland Section—Trent Valley Branch: "Solvent-free coatings" by Dr F. Blomeyer of Bayer Chemicals Limited, to be held at the British Rail School of Transport, London Road, Derby, at 7.00 p.m.

Newcastle Section: "Mechanical behaviour of polymers under low temperature high frequency cycling" by Mr J. L. Prosser of the Paint Research Station, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Tuesday 9 March

West Riding Section: "Carbon black in coating application—dispersion and formulation techniques" by a speaker from Columbian International Limited, to be held at the Griffin Hotel, Boar Lane, Leeds, at 7.30 p.m.

Wednesday 10 March

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

Newcastle Section—Student Group: Film show, to be held at the Newcastle Polytechnic, Ellison Place, Newcastle upon Tyne, at 3.00 p.m.

Thursday 11 March

Scottish Section: "Some thoughts on the early development of industry in the Clyde Valley" by Mr A. S. Fraser of Charles Tennant & Co. Limited, to be held in the St Enoch Hotel, Glasgow, at 6.00 p.m.

Friday 12 March

Manchester Section: "The utilisation of isocyanates in seamless flooring systems" by Dr A. Lowe of ICI Limited, Dyestuffs Division, to be held at the Liverpool Building and Design Centre, Hope Street, Liverpool 1, at 6.30 p.m.

Saturday 13 March

Scottish Section—Student Group: AGM followed by a lecture on the student project by Mr I. R. McCallum and Mr R. F. Hill, to be held at the St Enoch Hotel, Glasgow, at 10.00 p.m.

Tuesday 16 March

London Section—Southern Branch: "Metal-rich coatings" by a speaker arranged by the Lead and Zinc Development Association, to be held at the Pendragon Hotel, Clarence Parade, Southsea, at 7.00 p.m.

Wednesday 17 March

London Section: "Applications of the scanning electron microscope to the examination of paint systems" by Mr H. Wells, to be held at the Polytechnic of the South Bank (Borough Polytechnic), Borough Road, London SE1, at 7.00 p.m.

Thursday 18 March

Thames Valley Section: "Additives for paint and printing inks" by a speaker from Hardman & Holden Limited, to be held at the Beech Tree Hotel, Beaconsfield, Bucks, at 7.00 p.m.

Friday 19 March

Irish Section: Annual General Meeting followed by an "Open forum", to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

Midlands Section: J. Newton Friend Ladies' Lecture: "Forensic science" by Mr P. J. Cobb of the West Midland Forensic Science Laboratory, to be held at the Chamber of Commerce House, 75 Harbourne Road, Birmingham 15, at 6.30 p.m.

Wednesday 24 March

Scottish Section—Eastern Branch: "Combustion hazards in industry" by Mr Murray of the Fire Prevention Department, to be held at the Carlton Hotel, North Bridge, Edinburgh, at 7.30 p.m.

Friday 26 March

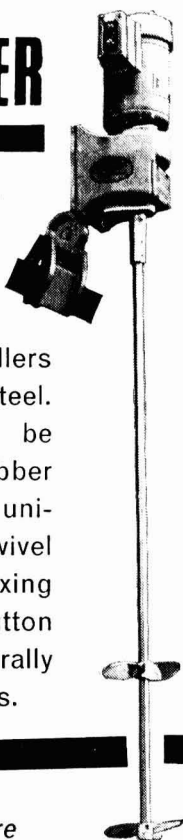
Bristol Section: "Aerosols" by Mr D. T. Trist of Swallowfield Serta Limited, to be held at the Royal Hotel, Bristol, at 7.15 p.m.

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Technical Exhibition

OCCA 23

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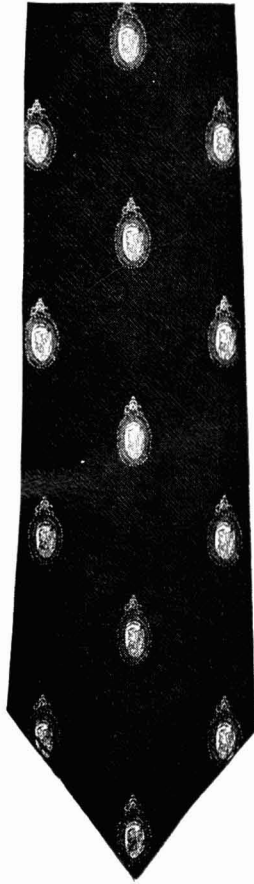
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Lancaster Place, Strand,
London, W.C.2.

To : Thresher & Glenny Ltd., Lancaster Place, Strand, London, W.C.2.
As a member of the Association, please accept my order for the following:

- ... OCCA tie @ 26/6
- ... OCCA blazer badge @ 75/-
- ... OCCA wall plaque @ 44/-
- ... OCCA car badge @ 44/-
(state bar or grille)

(All prices include postage and packing)

If tie is required airmail add 6s. 6d.

Total Remitted

Name

Section/No.

Address

The ties will be supplied from stock; all other items are made to order. Only the tie can be supplied by airmail at an extra cost of 6s. 6d.

LAKE & PIGMENT

COLOURS

for

PAINTS

PRINTING INKS

CELLULOSE FINISHES

LINOLEUM, LEATHERCLOTH

ETC.

We invite your enquiries

HORACE CORY

& CO. LTD.

NATHAN WAY

WOOLWICH INDUSTRIAL ESTATE

LONDON, SE28 OAY