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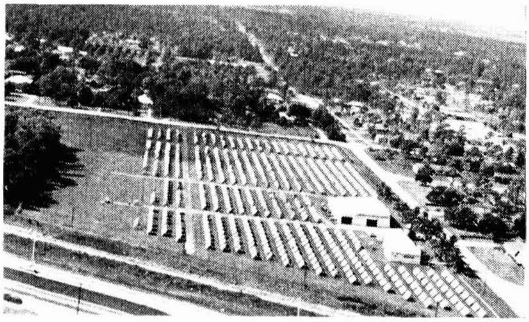

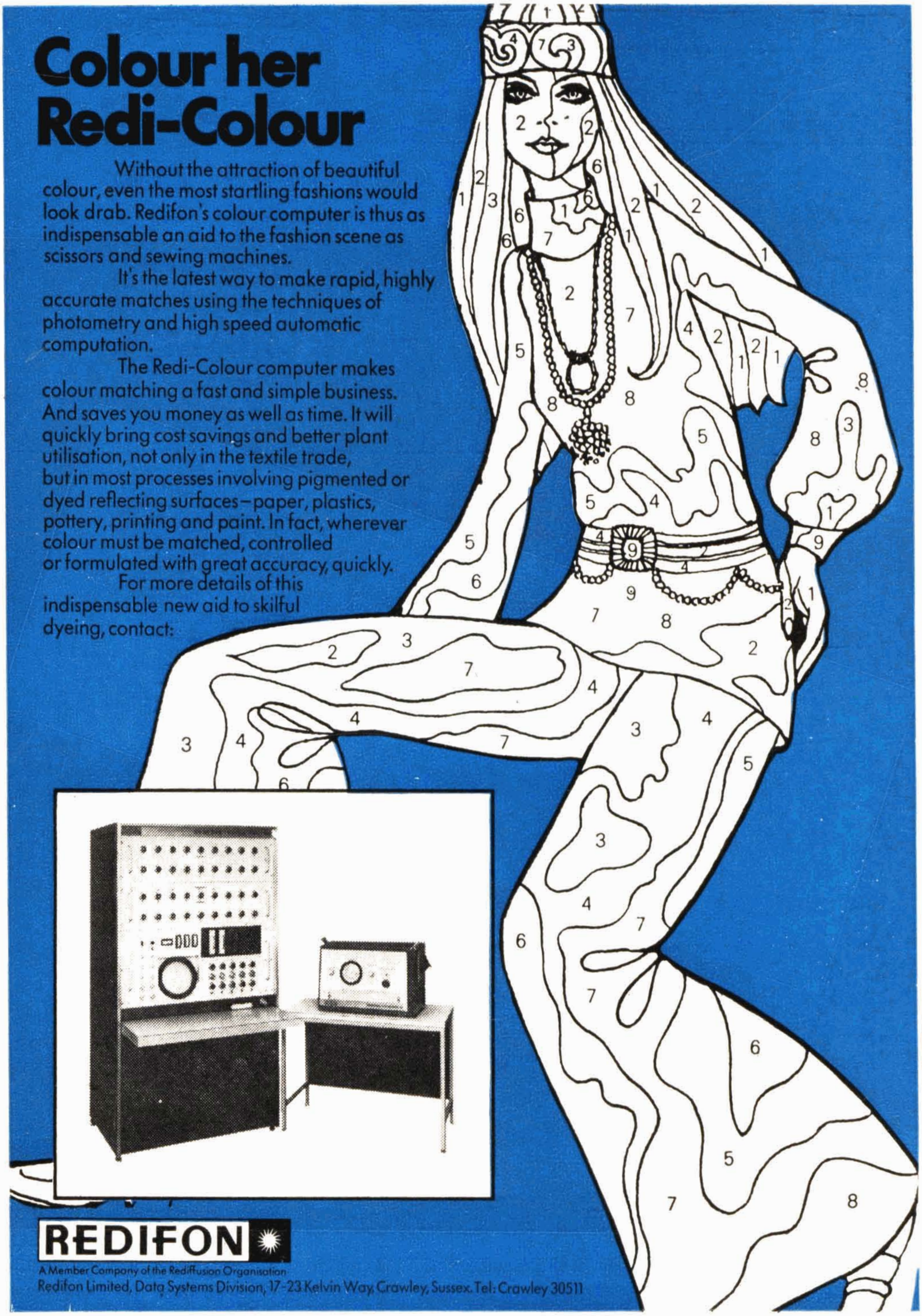

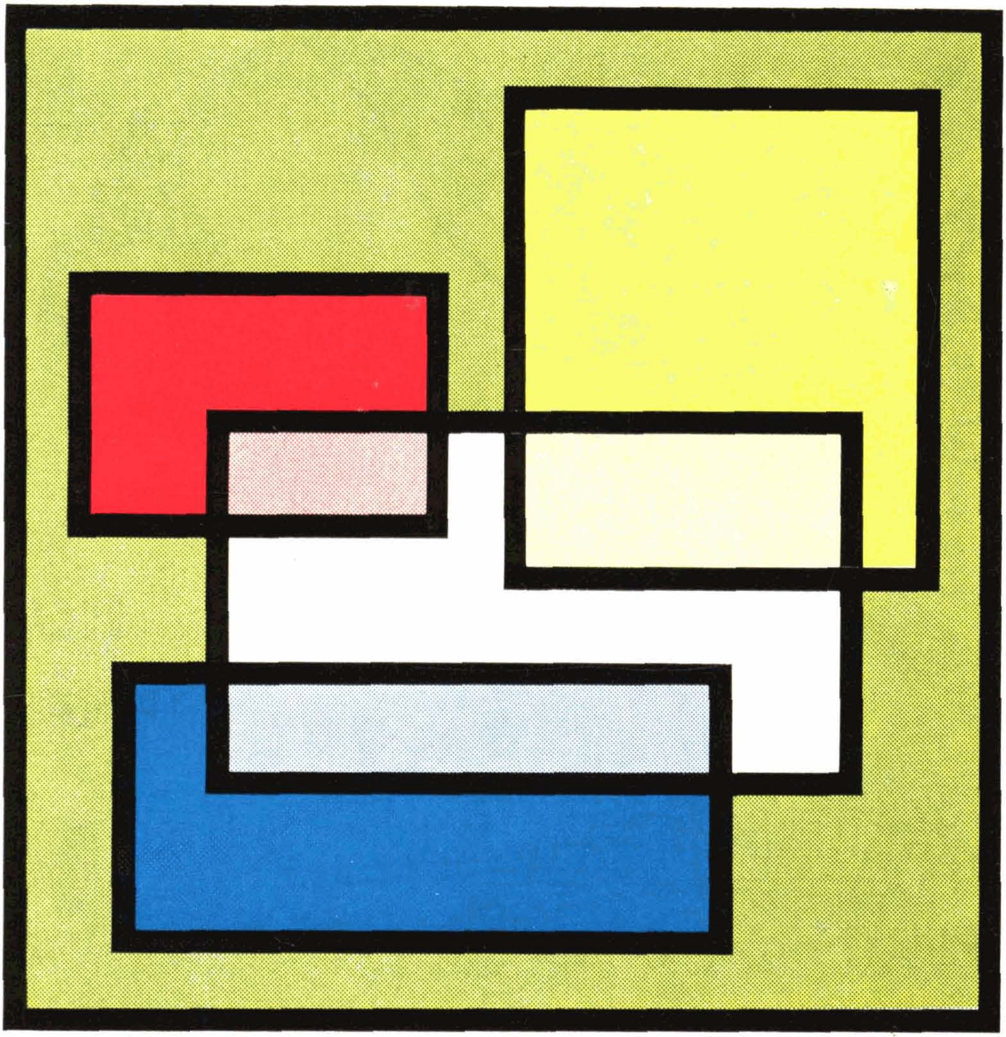

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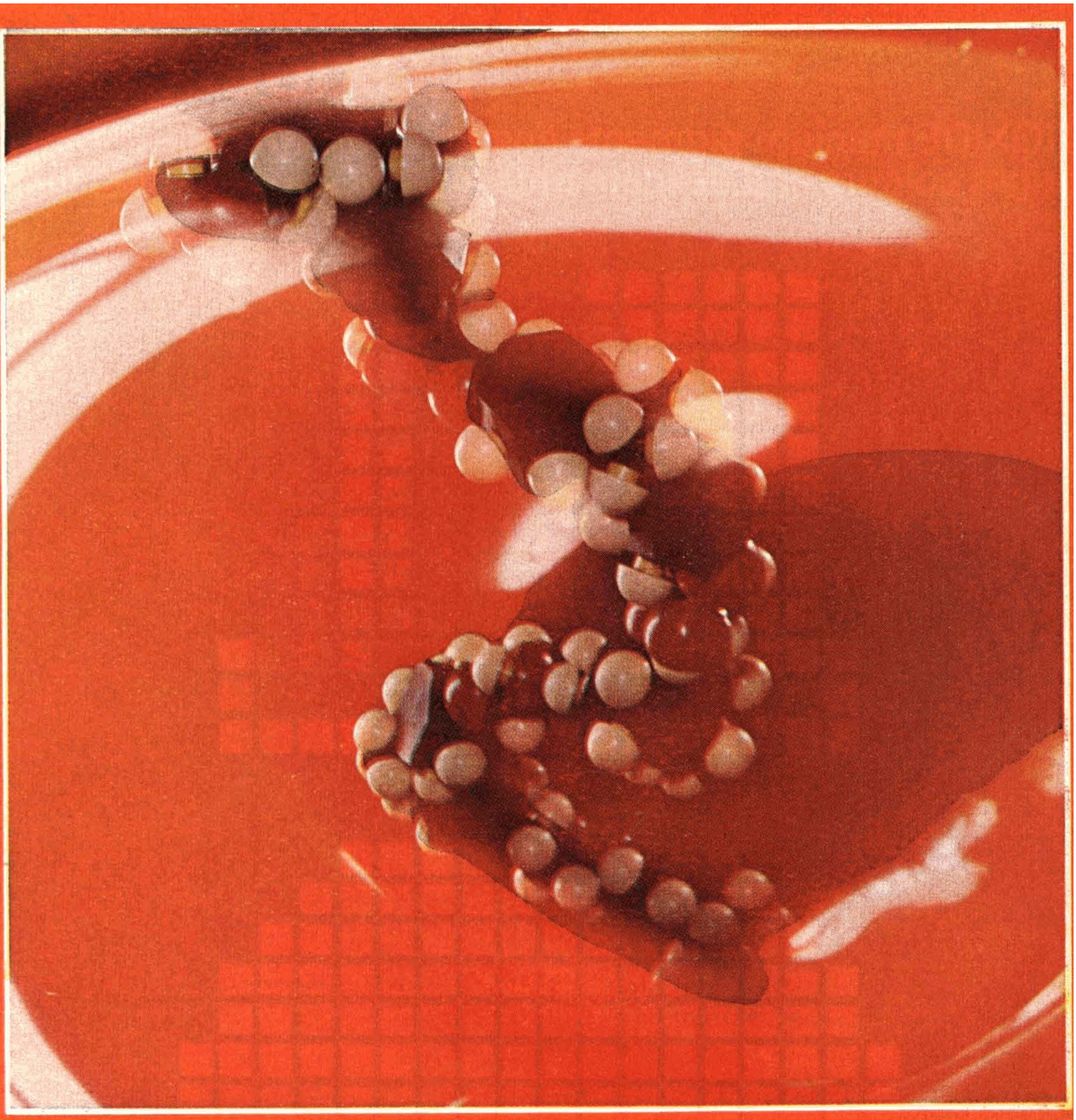

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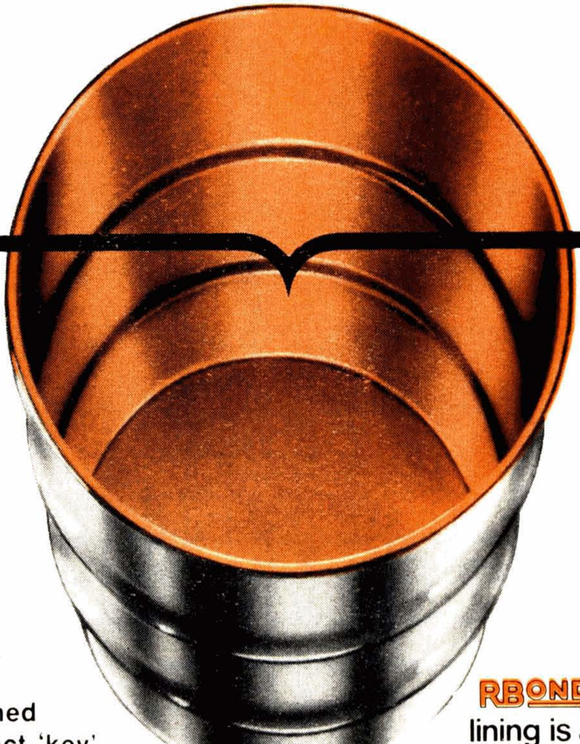

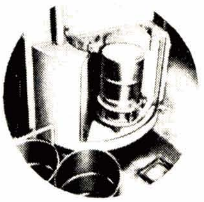

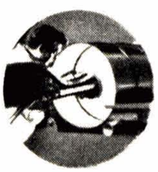

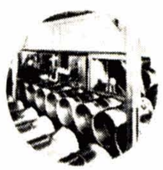

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Transactions and Communications

Formulation of fungus-resistant paints. VIII: Addition of N-trichloromethylthiophthalimide

By E. Hoffmann and A. Saracz

Division of Building Research, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

Summary

The effect of N-trichloromethylthiophthalimide (NTP) as a fungicide has been assessed on panels coated with gloss and flat alkyd enamel paints and exposed at Lae, New Guinea. The mould growth in each case was compared with that on the same paint free of fungicide, and the loss of NTP from the paint films at Lae and other locations was also determined.

Paints containing NTP remained free of mould for up to 2 years at Lae, and were more resistant to the growth of fungus in indoor applications in Melbourne for about 5 years.

Keywords

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

Biologically active agents
N-trichloromethylthiophthalimide

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

8ème. Partie. L'addition de N-trichlorométhylthiophtalimide

Résumé

On a apprécié l'effet de N-trichlorométhylthiophtalimide (NPT) en tant que fongicide en peintures alkydes, brillante et mate, sur éprouvettes exposées à Lae, Nouvelle Guinée. On a en fait comparer la croissance de moisissure auprès de celle de la même peinture exempte de fongicide, et la perte de la NPT à partir des feuils à Lae et à d'autres emplacements a été dosée également.

Les peintures contenant de NPT restaient exemptes de moisissure à Lae pendant une période de jusqu'à deux ans, et aux emplacements à l'intérieure à Melbourne, elles sont plus résistantes à la croissance de végétation mycélienne jusqu'à cinq ans environs.

Rezeptur für Pilzbeständige Anstrichfarben:

8. Zusatz von N-Trichlormethylthio-Phthalimid

Zusammenfassung

An mit glänzenden und matten Alkydharzemaillelacken gestrichenen Tafeln wurde die fungizide Wirkung des N-Trichlormethylthiophthalimids (NPT) bewertet. Die Probetafeln wurden in Lae, Neu Guinea dem Wetter ausgesetzt. In jedem Einzelfall wurde der Schimmelbefall mit einer fungizidfreien Blindprobe derselben Farbe verglichen, und der Verlust des NPT aus deren Film in Lae, sowie auch anderen Orten, bestimmt.

NTP enthaltende Emaillelacke blieben in Lae bis zu 2 Jahren schimmelfrei und waren in Melbourne etwa 5 Jahre lang noch beständiger, gegen Pilzbewuchs, sofern sie innen angewandt worden waren.

Формуляция красок устойчивых против плесени: 8. Добавление N- трихлорметилтиофталимида

Резюме

Оценивалось влияние N- трихлорметилтиофталимида (NTP) как фунгисида на панелях покрытых глянцевыми и матовыми алкидными эмалиевыми красками, и подверженных действию атмосферы в Лае, в Новой Гинее. Прирост плесени в каждом случае сравнивался с плесенью в той же краске без фунгисида и определялась также утеря NTP в красочных пленках в Лае и в других местах.

Краски содержащие NTP оставались свободными от плесени в течение двух лет в Лае и являлись более устойчивыми против прироста плесени при применении внутри помещений в Мельбурне в течение около 5-ти лет.

Introduction

N-trichloromethylthiophthalimide (NTP) has been proposed as a fungicidal additive to paint, and this paper records the results obtained on paints containing NTP and exposed outdoors at Lae, New Guinea, and indoors in Melbourne. In accordance with the method used in this Division for assessing the effectiveness of fungicides, the stability of NTP in a paint film was also determined[1].

Experimental

Analytical work

Flat and gloss alkyd enamel paints containing NTP, and the corresponding blanks, were brushed out on sheets (12in × 6in) of polyethylene terephthalate polyester film, which were then attached to hardboard panels and exposed under the following conditions:

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

The panels at Highett were mounted on racks at an angle of 45° facing north; those at Lae had the painted films attached to both sides and were mounted at 45° facing 31° east of true north.

At intervals of approximately six months, a portion of each film was removed and analysed to determine the loss of NTP. The analysis was carried out by a spectrophotometric method and determination of the chlorine content as described previously[2].

The results are summarised in Figs. 1 and 2.

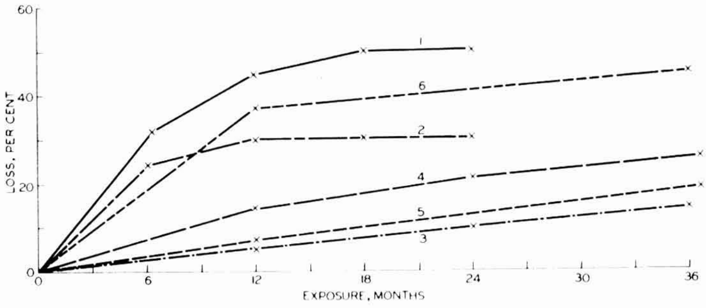

Fig. 1. Loss of NTP from gloss enamel paints

1. Outdoors, Lae, New Guinea (upper side)
2. Outdoors, Lae, New Guinea (under side)
3. Outdoors, Highett, Victoria
4. Fog room
5. Constant temperature room
6. Hot room

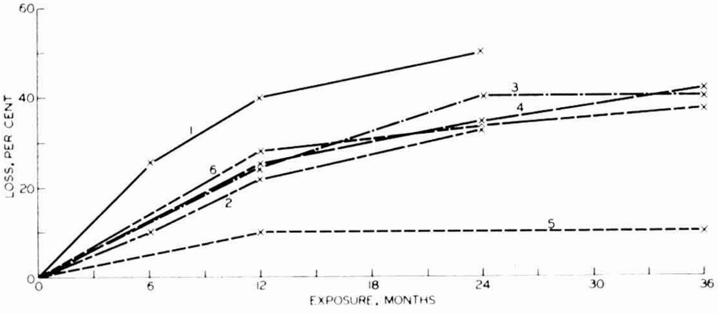

Fig. 2. Loss of NTP from flat enamel paint

1. Outdoors, Lae, New Guinea (upper side)
2. Outdoors, Lae, New Guinea (under side)
3. Outdoors, Highett, Victoria
4. Fog room
5. Constant temperature room
6. Hot room

Evaluation indoors

Evaluation of the paint indoors was carried out in 39 dwellings in Melbourne in which a comparatively high degree of mould growth had made repainting desirable. Of these, 15 dwellings were decorated with a flat enamel paint without fungicide, and 24 with a flat enamel paint containing 1 per cent of NTP. All walls were washed with hypochlorite solution before painting. The houses were inspected after each winter season, when mould growth is strongest, and the growth was then washed off with a hypochlorite solution. The results are summarised in Table 1.

Table 1

Incidence of mould growth in houses painted with a flat alkyd enamel paint containing 1 per cent NTP

	Control		1% NTP		
Inspection (at yearly intervals)	Number* inspected	% affected	Number* inspected	% affected	Significant at probability of
1	11	55	21	10	0.01
2	15	47	23	17	0.06
3	13	77	24	33	0.01
4	12	50	22	23	0.11
5	11	27	23	13	0.31

*Access to some of the houses could not be gained at the time of inspection.

Exposure at Lae, New Guinea

A separate set of hardboard panels painted with flat and gloss alkyd enamel paints, and the corresponding blanks, were exposed at Lae, in the same manner as described earlier. The intensity and the extent of mould growth were assessed at intervals of about three months, and the results are summarised in Tables 2-5.

Discussion

Gloss enamel paint

The loss of NTP from a gloss enamel paint on the upper side of panels at Lae amounted to 50 per cent in two years (Fig. 1, curve 1). Paints containing NTP (Table 1) stayed free of mould on the upper side for a length of time depending on the concentration of the additive. Films from paints containing 1, 2, and 3 per cent NTP showed no growth of mould for 12, 15, and 18 months respectively, whereas the blank was already mouldy after three months.

From the rate of decomposition of the fungicide, it would be expected that coatings from paints originally containing 3 or even 2 per cent would stay free of mould much longer than was actually observed. It could be postulated that the mould becomes adapted to the presence of the fungicide, but this is not the only possible explanation. NTP will first disappear from the surface layer of the

Table 2

Assessment of mould growth on gloss enamel paint films exposed outdoors at Lae: upper side of panels

		Exposure															
Paint	Duplicate	3 months		6 months		9 months		12 months		15 months		18 months		21 months		23 months	
		I	C	I	C	I	C	I	C	I	C	I	C	I	C	I	C
G0F	1	3–4	50	3	60	3	80	3	80	3–4	80	3–4	100	withdrawn			
	2	3–4	50	3–4	70	3	80	3	80	3–4	80	3–4	100				
	3	3–4	50	3–4	70	3	80	3	80	3–4	80	3–4	100				
G1F	1	0	100	0	100	0	100	trace		4–5	25	3–4	100	3–4	100	2–3	100
	2	0	100	0	100	0	100	trace		3–4	20	2–3	100	2–3	100	2–3	100
	3	0	100	0	100	0	100	trace		3–4	15	2–3	100	2–3	100	2–3	100
G2F	1	0	100	0	100	0	100	trace		trace		2–5	100	withdrawn		withdrawn	
	2	0	100	0	100	0	100	0	100	trace		2–5	100	1–4	100	3–4	100
	3	0	100	0	100	0	100	0	100	trace		2–5	100	1–4	100	3–4	100
G3F	1	0	100	0	100	0	100	0	100	0	100	0	100	4–5	100	2–3	100
	2	0	100	0	100	0	100	0	100	0	100	0	100	4–5	100	2–3	100
	3	0	100	0	100	0	100	0	100	trace		trace		withdrawn		withdrawn	

G0F—Gloss enamel paint without fungicide.

G1F, G2F, G3F—Gloss enamel paints containing 1, 2, and 3 per cent NTP respectively.

C = Percentage area covered by colour intensity I.

I = Intensity of colour according to scale 9 (black) → 0 (white) Intensity I = 0 and C = 100 means that the panel is free of mould.

Tr = Trace. C under 5 per cent.

Table 3

Assessment of mould growth on gloss enamel paint films exposed outdoors at Lae: under side of panels

Paint	Duplicate	Exposure															
		3 months		6 months		9 months		12 months		15 months		18 months		21 months		23 months	
		I	C	I	C	I	C	I	C	I	C	I	C	I	C	I	C
G0F	1	0	100	3	20	2–9	60	2–9	70	3–9	100	4–9	100	withdrawn			
	2	0	100	3	20	2–9	60	2–9	70	3–9	100	4–9	100				
	3	0	100	3	20	2–9	60	2–9	70	3–9	100	4–9	100				
G1F	1	0	100	0	100	0	100	3–4	25	4–5	40	2–5	60	1–9	100	1–9	100
	2	0	100	0	100	0	100	3–4	25	3–5	40	2–5	60	1–5	100	4–5	100
	3	0	100	0	100	0	100	3–4	25	3–4	40	2–4	40	1–5	100	1–5	100
G2F	1	0	100	0	100	0	100	3–4	20	3–9	30	3–9	40	withdrawn			
	2	0	100	0	100	0	100	0	100	0	100	0	100	5–6	10	4–6	25
	3	0	100	0	100	0	100	0	100	0	100	0	100	3–4	20	3–4	20
G3F	1	0	100	0	100	0	100	0	100	0	100	0	100	4–5	10	0	100
	2	0	100	0	100	0	100	0	100	0	100	0	100	4–5	10	0	100
	3	0	100	0	100	0	100	trace		trace		trace		withdrawn			

G0F—Gloss enamel paint without fungicide.

G1F, G2F, G3F—Gloss enamel paints containing 1, 2, and 3 per cent NTP respectively.

I—Intensity of colour according to scale 9 (black) → 0 (white) Intensity I = 0 and C = 100 means that the panel is free of mould.

Tr = Trace, C under 5 per cent.

Table 4

Assessment of mould growth on flat enamel paint films exposed outdoors at Lae: upper side of panels

Paint	Duplicate	Exposure															
		3 months		6 months		9 months		12 months		15 months		18 months		21 months		23 months	
		I	C	I	C	I	C	I	C	I	C	I	C	I	C	I	C
F0F	1	3–4	50	3–4	50	3–4	60	3–4	70	3–4	100	3–9	100	3–9	100	3–4	100
	2	3–4	50	3–4	50	3–4	60	3–4	70	3–4	100	3–9	100	3–9	100		
	3	3–4	50	3–4	50	3–4	60	3–4	70	3–4	100	3–9	100	3–9	100		
F1F	1	0	100	0	100	0	100	trace		5–6	20	3–4	100	3–4	100	2–3	100
	2	0	100	0	100	0	100	trace		5–6	20	3–4	100	3–4	100	2–9	100
	3	0	100	0	100	0	100	trace		5–6	20	3–4	100	3–4	100	2–9	100
F2F	1	0	100	0	100	0	100	trace		7–8	20	4–5	100	withdrawn			
	2	0	100	0	100	0	100	0	100	trace		2–3	100	2–5	100	1–2	100
	3	0	100	0	100	0	100	trace		5–6	20	4–5	100	2–5	100	1–5	100
F3F	1	0	100	0	100	0	100	0	100	5–6	20	4–5	100	2–5	100	2–9	100
	2	0	100	0	100	0	100	0	100	5–6	15	2–3	100	withdrawn			
	3	0	100	0	100	0	100	trace		4–5	20	4–5	100	withdrawn			

F0F—Flat enamel paint without fungicide.

F1F, F2F, F3F—Flat enamel paints containing 1, 2, and 3 per cent NTP respectively.

C = Percentage area covered by colour intensity I.

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

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

Tr = Trace, C under 5 per cent.

Table 5

Assessment of mould growth on flat enamel paint films exposed outdoors at Lae: under side of panels

Paint	Duplicate	Exposure															
		3 months		6 months		9 months		12 months		15 months		18 months		21 months		23 months	
		I	C	I	C	I	C	I	C	I	C	I	C	I	C	I	C
F0F	1	9	20	4–9	60	4–9	80	3–9	100	3–9	100	3–9	100	3–9	100	3–9	100
	2	9	20	4–9	60	4–9	80	3–9	100	3–9	100	3–9	100	3–9	100		
	3	9	20	4–9	60	4–9	80	3–9	100	3–9	100	3–9	100	3–9	100	3–9	100
F1F	1	0	100	0	100	0	100	0	100	0	100	0	100	trace		trace	
	2	0	100	0	100	0	100	3–4	10	3–5	10	3–5	10	4–9	50	1–9	100
	3	0	100	0	100	0	100	3–4	10	3–4	10	7–5	10	4–9	50	1–9	100
F2F	1	0	100	0	100	0	100	3–4	10	3–5	20	3–5	20	withdrawn			
	2	0	100	0	100	0	100	0	100	0	100	0	100	0	100	0	100
	3	0	100	0	100	0	100	0	100	0	100	trace		trace		trace	
F3F	1	0	100	0	100	0	100	4–5	10	3–4	50	3–9	75	3–9	100	3–9	100
	2	0	100	0	100	0	100	4-5	20	3–4	60	3–5	50	withdrawn			
	3	0	100	0	100	0	100	3–4	10	3–4	60	3–5	50	withdrawn			

F0F—Flat enamel paint without fungicide.

F1F, F2F, F3F = Flat enamel paints containing 1, 2, and 3 per cent NTP respectively.

C—Percentage area covered by colour intensity I.

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

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

Tr = Trace, C under 5 per cent.

paint, and if its rate of diffusion is too slow, it will not be replenished from the body of the paint film quickly enough to provide an effective fungicidal layer at the surface. That the rate of diffusion is decreased can be seen from Table 6, which shows the concentration of NTP in a drop of water in contact with a fresh paint film and with one which had been exposed for one year. On the fresh paint film, saturation concentration (12μg/ml) is reached after one day, whereas on the exposed film the concentration after five days is only 6μg/ml.

Table 6

Diffusion of NTP from a gloss enamel paint film in contact with a drop of water

Time	Concentration μg/ml of water	
	Fresh paint film	Paint film exposed for 1 year at Lae
4 hr	6	0
1 day	12	2
2 ,,	—	3.6
5 ,,	—	6

Solubility of NTP in water at 20°C, 12 μg/ml.

The loss of NTP from the under side of a panel covered with a gloss enamel paint is slower, only 30 per cent in 4 months (Fig. 1, curve 2). There is also an improvement in the mould resistance of the paint (Table 2), and this is especially evident with the paint containing 3 per cent NTP, which remained free of mould for 18 months.

Flat enamel paint

The losses of NTP (Fig. 2) from a flat enamel paint film were similar to those from a gloss enamel coating. The upper side (Table 4) stayed free of mould for 12 months, whereas a copious growth on paint without NTP occurred after three months. It is perhaps worthwhile to point out that no difference in mould growth was observed with paints containing different amounts of NTP, and 1 per cent NTP seems to impart as much mould resistance as 3 per cent. The reasons for this behaviour are not clear.

On the under side (Table 5), addition of NTP also increased the mould resistance of the paint film, and 2 per cent seemed to have a greater effect than 3 per cent. No explanation can be offered for this peculiar behaviour.

The mould growth in houses painted with a flat enamel paint containing 1 per cent NTP was followed over a 5-year period and compared with the growth on a flat alkyd enamel paint without fungicide. From Table 1, it would appear that, in the fourth and fifth years, the effectiveness declines (as measured by the difference in the percentage of houses affected when a paint free of fungicide is used compared with the percentage affected when a fungicide is included), but there are not enough data available to judge whether this is significant.

NTP is also effective in a gloss enamel paint on inside exposure, as can be seen from Fig. 3. A wall in a dye works was divided into five strips and these were coated with paints H (1 per cent NTP) and G (no NTP).

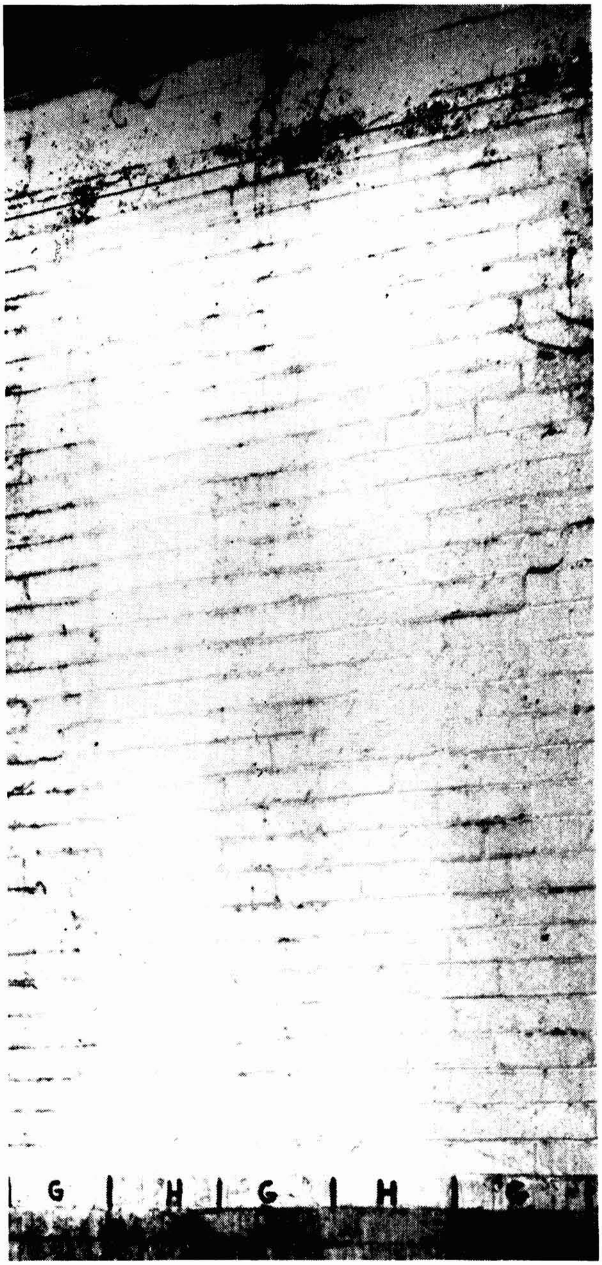

Fig. 3. Mould growth on wall of dye works after $2\frac{1}{2}$ years

G.—Gloss enamel paint without fungicide

H.—Gloss enamel paint containing 1 per cent NTP

Some conclusions as to the way in which NTP disappears can be drawn from the decomposition curves. In the constant temperature room, 18 per cent of the NTP is lost from the gloss enamel paint (Fig. 1, curve 5) in three years, and this is probably lost by evaporation only. The loss from specimens exposed for the same time in the fog room (Fig. 1, curve 4) is 25 per cent, and the additional 7 per cent is probably lost through leaching or decomposition.

The persistence of NTP in a gloss enamel paint film under wet conditions appears to be much greater than was found with the other fungicides which have so far been investigated, except for copper 8—hydroxyquinolate[3-7], and it should therefore prove valuable in very wet conditions.

The loss of NTP from the flat enamel paint in the constant temperature room (Fig. 2, curve 5) is about the same as for the gloss enamel, but in the fog room it is much higher at about 40 per cent (curve 4).

Acknowledgments

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J. Oil Col. Chem. Assoc. 1970, 53, 852-875

Colour difference measurement

By J. S. Mudd and M. Woods*

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Summary

Various methods of calculation have been used to determine colour differences in thirty series of patterns and the results compared with average observer assessments, using a rank correlation coefficient as a measure of agreement. The use of radial tolerances in the 1931 C.I.E. diagram, in place of chromaticity ellipses, has practical significance in colour difference measurement for industrial application. It is shown that relative weighting of chromaticity and luminance differences can be linked with dominant wavelength. Methods of colour difference calculation in common use all give good results in some cases and have an overall accuracy that is comparable with the best that can be expected from any one observer, but on other occasions they fail badly. A method is suggested that has given acceptable results with every one of the thirty series of patterns examined, and with an overall correlation that is significantly better than the observer mean.

Keywords

Properties, characteristics and conditions primarily associated with materials in general

colour

Miscellaneous terms

CIE system

Equipment primarily associated with analysis, measurement and testing

colour difference measurement

La mesure des différences en couleur

Résumé

On a utilisé de diverses méthodes pour calculer les différences en couleur de trente séries de spécimens, et les résultats ont été comparés auprès de l'appréciation d'un "oeil moyen" en utilisant un coefficient de corrélation du rang en tant qu'une mesure d'accord. L'emploi des tolérances radiales à la diagramme de 1931 de la C.I.E., au lieu des ellipses de chromaticité, relève de signification pratique dans le domaine de la mesure des différences en couleur sur le plan industriel. On démontre que la pondération relative des différences en chromaticité et en luminance peut être liée à la longueur d'onde dominante. Toutes les méthodes de l'usage habituel pour calculer les différences en couleur rendent en certains cas de bons résultats et elles ont une précision globale comparable à la meilleure que l'on peut s'attendre à un observateur particulier, d'autre part en certains cas elles échouent gravement. On suggère une méthode qui a donné des résultats convenables dans le cas de chaqu'une des trente séries de spécimens examinées, et en utilisant une corrélation globale, cette méthode est significativement mieux que le moyen des observateurs.

Messen von Farbunterschieden

Zusammenfassung

Zur Bestimmung der Farbunterschiede bei dreissig Serien von Mustern wurden verschiedene Berechnungsmethoden benutzt, und die Resultate mit denen von Schätzungen von Schätzungen von Durchschnittsbeobachtern verglichen. Dabei wurde ein Reihenkorrelationskoeffizient als Mass für Übereinstimmung gebraucht. Die Anwendung radialer Toleranzen im 1931 C.I.E. Diagramm anstelle von Farbartelipsen hat für die Messung von Farbtonunterschieden praktische Bedeutung für industrielle Anwendung. Es wird dargelegt, dass die relative Bewertung von Unterschieden in Farbart und Leuchtdichte mit der vorherrschenden Wellenlänge in Verbindung gebracht werden kann. Alle üblicher Weise benutzten Methoden

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für die Berechnung von Farbunterschieden ergeben in manchen Fällen sämtlich gute Resultate und sind im grossen und ganzen von einer Genauigkeit, welche mit der besten von irgendwelchen Beobachtern erzielten erwartet werden kann; in anderen Fällen ergeben sie jedoch ganz falsche Resultate. Eine Methode wird vorgeschlagen, die bei jeder einzelnen der geprüften dreissig Musterserien brauchbare Resultate ergab und dabei mit einer Gesamtkorrelation, welche wesentlich besser ist, als die von den Beobachtern erzielte.

Измерение контрастности цветов

Резюме

Применяются различные методы вычисления для определения цветовых контрастов в тридцати сериях образцов и результаты сравниваются с средней оценкой визуальных наблюдений, применяя классифицированный, корреляционный коэффициент в качестве меры согласования. Применение радиальных допусков в диаграмме C.I.E. 1931-го года, вместо хроматических эллипсов, имеет практическое значение в измерении разности цветов в промышленной практике. Показано, что относительная оценка цветных и световых контрастов может быть связана с преобладающей длиной волны. Методы вычисления цветовых контрастов в общем пользовании дают хорошие результаты в некоторых случаях и обладают предельной точностью сравнимой с наилучшими показаниями основанными на отдельных визуальных наблюдениях, но в других случаях они намного отстают. Предлагается метод который дал приемлемые результаты с каждым из тридцати серий испытанных образцов, с значительно лучшей общей корреляцией чем средняя корреляция основанная на визуальном наблюдении.

Introduction

There is a general feeling that colour difference measurement, with its obvious application in shade passing, would be much more widely used in industry if one could be really confident that the results would be more reliable than those obtained by visual assessment. It is not necessary to stipulate that the instrumental assessment must be right every time, because visual assessment falls far short of this requirement. The present investigation shows that any observer is likely to make a wrong decision once in five times, and other investigations now proceeding may well show the probability to be once in four times. To be of real value to industry, colour difference measurement must be shown to be more consistently reliable than visual assessment, not necessarily throughout colour space but at least in that part of colour space which can be achieved with coloured materials such as paint, leather, and textiles.

Theoretical considerations

A recent paper by Coates and Warburton[1] on colour difference measurements in relation to visual assessments in the textile field, showed poor correlation between instrumental and visual assessments on the green wool and green viscose fabrics examined. Since reasonable agreement was shown between observers and between instruments, the calculations which form the link between the instrument readings and the colour difference figure, ΔE, must be responsible to a considerable degree for the poor correlation. Several of the colour difference formulae used by Coates and Warburton have, in fact, given results which are much better than the observer mean with patterns of other materials such as paint and leather, and it was felt that an endeavour should be made to find out why they failed so badly in this particular series.

Colour difference formulae have the appearance of being very cleverly calculated from infallible data on observed differences in chromaticity and luminance, whereas they are really rather haphazard affairs.

Wyszecki makes this comment[2]: "We select some chromaticity diagram with approximately uniform chromaticness spacing and some function of luminous reflectance giving approximately uniform lightness spacing. Then we make some kind of guess regarding how the two should be combined to define a unit of colour difference." The quotation is interesting because one can sometimes develop a formula better by "tailoring" it to fit the facts as one finds them than by working from purely theoretical considerations. In the past, there have been interminable arguments about the relative merits of various systems of chromaticity ellipses, but in a paper in 1962[3] the author made the point that the relative weighting of chromaticity and luminance differences in the combined tolerance calculation was more important than the precise shape or orientation of the chromaticity tolerance ellipses.

Some comment first on the less important, but by no means unimportant, problem of tolerance ellipses. In general, the major axis of the ellipse lies along the line of dominant wavelength, which implies that differences in saturation are less readily seen than differences along the line of the minor axis. Whilst this is undoubtedly true in observations on coloured lights and to a lesser extent with transparent or translucent colours, is it always right with regard to the mass of materials with which one is more familiar? Does one assume too readily that the results are applicable to different conditions?

There is evidence that differences in saturation with surface colours are seen as readily as other shade differences. This has to be inferred from the fact that colour difference calculations derived from the results of classical observations on the behaviour of coloured lights do not give sufficiently good agreement with visually observed differences in surface colours.

Surface colour differences are far more important commercially than coloured light differences, and whilst this paper is concerned with a practical approach to the problem of estimating differences in surface colours, the suggestion cannot be avoided that there are fundamental differences in the observation of coloured lights and coloured surfaces which one can only hope will be investigated in due course.

The work of Coates and Warburton shows that, for the green fabric patterns, the discrimination ellipse is very nearly a circle. Circular tolerance areas in the 1931 C.I.E. diagram were considered by a committee of the Society of Leather Trades Chemists in 1964[4], and the statement shown below was made.

"Further consideration of the figure produced by Brown[5] for the discrimination ellipses for twelve observers led to the suggestion that an approximation involving the use of circular tolerance areas instead of the elliptical ones might be justified if the dimensions were adjusted to fit the 1931 diagram. The method was tested, using the series of mixed colour differences referred to in the previous report, and gave surprisingly good results against observer assessment when one considers the approximation involved in using a circle of $r = 0.0040$ in place of an ellipse with semi-minor axis of 0.0015, which occurs in the red region. The correlation coefficient for this method ($\rho = 0.96$) compares with the best previously reported figure of 0.92 for a modified S.L.T.C. method, 0.79 for the N.B.S. method, and 0.83 for the mean of thirty observers. The use of radial tolerances obviously allows a more simple calculation to be used, and this is important if the ordinary works chemist is to be persuaded of the advantages of colour measurement, but the theoretical objections to the approximations involved would almost certainly prevent the use of this method in a wider sphere even if it was accepted by the leather industry".

Some time later, a method was evolved that employed radial tolerances in the 1960 C.I.E. diagram[6], but this gave very poor correlation with the green fabric samples. From the experimental work reported in this paper, it is now obvious that the chromaticity—luminance weighting in this method is such that it will give good results with reds and relatively poor results with greens.

Experimental work

The above data notwithstanding, in view of the very nearly circular tolerance area in the 1931 diagram found by Coates and Warburton, and remembering the experience with radial tolerances in 1964, the temptation to experiment with radial tolerances in the 1931 diagram was irresistible, even though it contradicted what one had been taught—and had taught others—about tolerance ellipses. Using the set of radial tolerances developed for the 1964 work, it was found that by far the greater part of the differences in radius could be equated with the y coefficient, thus giving an easy method of calculation. The authors now had several sets of data which could be reprocessed, and by trial and error were able to arrive at what appeared to be the best proportion between the semi-major and semi-minor axes of the ellipses to use as radial tolerances. The radial tolerance was represented by

$$T_r = 0.0114\ (y + 0.0375)$$

and the chromaticity difference by

$$\Delta c = \frac{(\Delta x^2 + \Delta y^2)^{\frac{1}{2}}}{T_r}$$

The variation of luminance tolerance with luminance factor was derived from the Vy function defined by Nickerson[7] to represent the spacing along the neutral axis in the Munsell system, and reference is made to this in a report of the S.L.T.C. Colour Committee[8]. A modification was made to this giving larger tolerances in the $Y = 0$-20 region, but although a table of values could be used for manual calculation, it was difficult to apply to computer working. A simplified calculation was made possible by using a linear variation between $Y = 8.0$ and $Y = 100$.

$$T_y = 0.0082\ (Y + 22)$$

and a steeper slope for Y values less than 8.0

$$T_y = 0.022\ Y + 0.074$$

the luminance difference $\Delta_l = \dfrac{\Delta y}{T_y}$

and the combined colour difference:

$$\Delta E = (\Delta_c^2 + \Delta_l^2)^{\frac{1}{2}} \quad \text{.................................Method 1}$$

If an electronic computer is available, it is just as easy to use the Nickerson curve according to the formula:

$$\begin{aligned} T_y = {} & 0.855708 + 0.601942\ Y - 0.013104\ Y^2 \\ & + 0.000213576\ Y^3 - 0.00000171774\ Y^4 \\ & + 0.00000000\,540863\ Y^5 \quad \text{.......... Method 1a} \end{aligned}$$

It will be shown later that in practice the linear modification gives rather better results than the Nickerson curve, which suggests that for computer working another curve could be devised which would give better results than either.

It is worth consideration that, although complicated formulae present no real difficulty if a computer is available and may be necessary to ensure accuracy, a very simple formula requiring the use only of a slide rule and squared paper may be more attractive, and even quicker overall, at the point where calculation is most required; at the end of a production line, or in a routine testing laboratory. Such a formula is also required by those who are not fortunate enough to have access to a computer.

Having calculated ΔE for each of the patterns in a given series at a predetermined luminance weighting, the results can be arranged in order and compared with average observer assessment, using a rank coefficient as a measure of agreement. If a sufficient number of such calculations are made, they show that the optimum weighting varies with the nature of the coloured surfaces which are examined. This would apparently explain why most of the well known colour difference formulae give good correlation with visual assessment in some cases and not others. However, a colour difference formula is required that will give good results with a variety of colours and surfaces, in every case with a degree of correlation that is better than can be expected from any one observer. In order to assess the effect of varying the importance given to chromaticity differences and luminance differences in a colour difference calculation, it was necessary to introduce a relative weighting factor, K, by which the luminance differences could be multiplied. As a starting point, the ratio of Δ_c to Δ_l in the S.L.T.C. method was assumed to be 1 to 1; a K value of 2.5 indicates that the permitted luminance tolerance is two and a half times larger than that in the original calculation.

The importance of the relative weighting of chromaticity and luminance differences in a colour difference calculation is generally accepted, but it was disconcerting to find that, when several series of patterns were examined for colour differences by measurement/calculation, some series required an appreciably different weighting factor from others. In particular, some glossy red-brown patterns required about one fifth the luminance tolerance needed for some green wool patterns if reasonable correlation with average observer assessment was to be achieved. This was independent of the normal variation of luminance tolerance, which increases with increase in luminance factor in a manner that is well understood. The first three colour difference series that were examined appeared to indicate a simple relationship between gloss and luminance weighting, and hopes were raised that this relationship would enable more consistent results to be obtained from colour difference measurements. The next three series, however, showed no significant relationship. Green patterns from matt to relatively high gloss required a similar weighting factor, and it was seen clearly that gloss variation was not the answer. This was later confirmed by Coates, Day and Rigg[9]. As other series of patterns, typical of other areas in the chromaticity diagram, were assessed, it was noticed that green patterns required large luminance tolerance and red and blue patterns small luminance tolerance. An attempt was made to link this with the y coefficient, which had proved useful in determining the chromaticity tolerance areas, but there was no significant relationship in this case.

A more promising relationship was found when the optimum weighting factor for several series of patterns was plotted against the dominant wavelength of the patterns taken as the standard in each series, and the curve that was tentatively drawn looked so much like the photopic luminosity curve, (the $V\lambda$ curve), that further investigation was imperative.

Having been misled by having insufficient evidence into thinking that there might be a simple relationship between gloss and weighting, it was decided to follow up the interesting possibility of a relationship between weighting and dominant wavelength with determinations at as many points in colour space as possible. The procedure was the same for each series. Measurements were made with a Colormaster V colorimeter, and in the case of the green wool and green viscose patterns the average values for several instruments were used. Table 1 gives the values for Y, x and y, for the 25 series of patterns used for correlation tests. The 5 series of mixed colours were made up from the 25 series of single colours. At least 10 observers were used to obtain the visual ranking order under standard lighting conditions. The patterns were viewed in a cabinet painted with a matt paint of a colorimetrically neutral grey of luminance factor 25, illuminated by four 5ft fluorescent tubes (Artificial Daylight to B.S.950) so that illumination

Table 1

Series	Y	x	y	Series	Y	x	y
Blue Acrylate				*Green Urethane*			
Standard	3.04	0.2053	0.1772	Standard	7.45	0.2582	0.3900
1	3.45	0.2023	0.1760	1	7.45	0.2594	0.3916
2	3.11	0.1995	0.1673	2	6.96	0.2617	0.3842
3	2.61	0.1992	0.1649	3	8.47	0.2587	0.3869
4	3.05	0.2016	0.1708	4	7.25	0.2553	0.3859
5	3.55	0.2071	0.1823	5	7.55	0.2607	0.3958
6	2.86	0.2038	0.1710	6	7.39	0.2554	0.3913
7	3.13	0.2086	0.1838	7	7.02	0.2583	0.3849
8	2.99	0.2087	0.1848	8	7.53	0.2573	0.3895
9	3.54	0.2107	0.1875	9	7.44	0.2564	0.4035
				10	6.80	0.2459	0.3780
Blue Urethane							
Standard	13.47	0.1710	0.1853	*Green Wool*			
1	10.57	0.1890	0.2076	Standard	12.36	0.2956	0.3614
2	12.98	0.1690	0.1836	1	13.56	0.2964	0.3602
3	14.80	0.1738	0.1898	2	12.80	0.2979	0.3652
4	12.97	0.1724	0.1828	3	11.07	0.2967	0.3609
5	13.83	0.1798	0.2119	4	12.09	0.3018	0.3566
6	12.21	0.1677	0.1794	5	11.60	0.2890	0.3517
7	12.01	0.1804	0.2036	6	13.50	0.2947	0.3654

Table 1—continued

Series	Y	x	y
Green Viscose			
Standard	10.07	0.2818	0.3570
1	9.68	0.2827	0.3572
2	10.48	0.2792	0.3573
3	10.15	0.2847	0.3621
4	9.73	0.2805	0.3486
5	11.37	0.2863	0.3578
6	9.80	0.2747	0.3519
Red Acrylate			
Standard	9.41	0.6054	0.3086
1	9.40	0.6062	0.3094
2	8.79	0.6016	0.3134
3	10.85	0.5760	0.3112
4	8.74	0.6010	0.3098
5	8.63	0.5978	0.3114
6	10.52	0.5700	0.3045
7	10.74	0.5734	0.3068
Green Acrylate II			
Standard	12.17	0.3233	0.4723
1	12.75	0.3226	0.4680
2	12.22	0.3259	0.4730
3	12.26	0.3267	0.4725
4	12.01	0.3232	0.4711
5	12.60	0.3217	0.4666
6	11.45	0.3123	0.4602
7	10.78	0.3102	0.4627
8	12.50	0.3102	0.4489
Crimson Acrylate			
Standard	18.39	0.4828	0.2925
1	18.22	0.4898	0.2944
2	18.90	0.4779	0.2903
3	20.57	0.4645	0.2908
4	16.02	0.5046	0.2944
5	19.64	0.4665	0.2865
6	21.76	0.4586	0.2909
7	19.24	0.4545	0.2893
8	19.26	0.4702	0.2875
Pink Acrylate			
Standard	19.26	0.4702	0.2875
1	19.24	0.4545	0.2893
2	21.76	0.4586	0.2909
3	19.64	0.4665	0.2865
4	16.02	0.5046	0.2944
5	20.57	0.4645	0.2908
6	18.90	0.4779	0.2903
7	18.22	0.4898	0.2994
8	18.39	0.4828	0.2925

Series	Y	x	y
Green G. Paint			
Standard	12.50	0.2915	0.3651
1	12.39	0.2910	0.3683
2	12.04	0.2873	0.3633
3	11.71	0.2908	0.3622
4	12.47	0.2905	0.3644
5	13.45	0.2929	0.3658
6	12.51	0.2928	0.3685
7	12.65	0.2931	0.3631
8	13.06	0.2925	0.3642
Fawn Acrylate			
Standard	23.25	0.3598	0.3439
1	23.95	0.3709	0.3527
2	21.75	0.3566	0.3389
3	24.00	0.3577	0.3408
4	24.02	0.3665	0.3488
5	23.97	0.3543	0.3420
6	27.88	0.3643	0.3494
7	22.45	0.3592	0.3415
8	25.44	0.3579	0.3642
9	23.87	0.3607	0.3436
Magenta Acrylate			
Standard	8.02	0.4588	0.2380
1	7.41	0.4598	0.2345
2	8.67	0.4654	0.2452
3	8.42	0.4744	0.2488
4	7.43	0.4816	0.2543
5	8.60	0.4530	0.2368
6	7.29	0.4669	0.2436
7	8.60	0.4500	0.2354
8	7.95	0.4644	0.2411
Grey Acrylate			
Standard	17.27	0.2994	0.3034
1	18.25	0.2980	0.3008
2	17.07	0.2978	0.3014
3	22.04	0.2991	0.3020
4	16.31	0.2988	0.3026
5	15.48	0.2967	0.3002
6	15.56	0.2983	0.3020
7	17.99	0.2993	0.3028
8	17.41	0.3043	0.3094
Blue-Grey Acrylate			
Standard	25.48	0.2764	0.2853
1	28.23	0.2734	0.2804
2	22.34	0.2765	0.2861
3	27.37	0.2987	0.2617
4	25.35	0.2760	0.2824
5	26.28	0.2799	0.2889
6	28.59	0.2749	0.2820
7	25.05	0.2745	0.2838
8	24.50	0.2748	0.2820
9	31.24	0.2675	0.2790

Table 1—continued

Series	Y	x	y	Series	Y	x	y
Dark Red A				*Violet Acrylate*			
Standard	2.64	0.5261	0.3284	Standard	3.37	0.2904	0.2332
1	2.66	0.5235	0.3290	1	2.81	0.2976	0.2334
2	2.69	0.5266	0.3260	2	3.21	0.2991	0.2350
3	3.12	0.5449	0.3257	3	3.10	0.3044	0.2388
4	3.17	0.5268	0.3287	4	3.34	0.2950	0.2371
5	2.57	0.5387	0.3285	5	3.49	0.2808	0.2277
6	2.95	0.5204	0.3257	6	2.78	0.3222	0.2551
7	2.86	0.5266	0.3255	7	3.68	0.2874	0.2304
8	3.32	0.5169	0.3248	8	2.65	0.3191	0.2451
Orange Acrylate							
Standard	17.99	0.5801	0.3626	*Yellow Acrylate*			
1	19.64	0.5706	0.3702	Standard	73.26	0.4584	0.5013
2	16.59	0.5899	0.3548	1	73.53	0.4599	0.5045
3	16.21	0.5684	0.3667	2	64.33	0.4551	0.5045
4	16.27	0.5792	0.3597	3	71.83	0.4593	0.5044
5	19.04	0.5728	0.3674	4	68.88	0.4585	0.5040
6	17.55	0.5823	0.3605	5	74.58	0.4534	0.4934
7	18.92	0.5725	0.3688	6	58.43	0.4854	0.4703
8	20.06	0.5688	0.3724	7	67.08	0.4688	0.4902
				8	74.01	0.4440	0.4797
Green M. Paint				9	74.30	0.4497	0.4873
Standard	18.54	0.2957	0.3630	10	73.84	0.4484	0.4996
1	17.92	0.2915	0.3583				
2	19.60	0.2964	0.3629				
3	19.21	0.2973	0.3659	*Red-Brown Acrylate*			
4	18.13	0.2976	0.3599				
5	18.31	0.2959	0.3610	Standard	8.34	0.4685	0.3351
				1	7.29	0.4911	0.3362
Green Acrylate I				2	8.71	0.4787	0.3397
Standard	20.04	0.3069	0.4001	3	7.24	0.4631	0.3348
1	18.11	0.3057	0.3908	4	7.41	0.4405	0.3336
2	21.67	0.3014	0.3951	5	8.78	0.4715	0.3371
3	20.32	0.2913	0.3963	6	7.74	0.4688	0.3339
4	18.72	0.3059	0.4027	7	8.20	0.4891	0.3470
5	20.01	0.3095	0.4007	8	8.61	0.4700	0.3328
6	20.03	0.3122	0.4004	9	6.72	0.4652	0.3355
7	18.86	0.3102	0.3923	10	6.67	0.4310	0.3338
8	21.94	0.3066	0.3954	11	8.48	0.4681	0.3317
9	16.53	0.3094	0.4107	12	9.28	0.4659	0.3377
10	21.06	0.2978	0.3940				
Light Brown Acrylate				*Blue-Green Acrylate*			
Standard	11.56	0.4365	0.3487	Standard	9.35	0.2194	0.2808
1	11.23	0.4376	0.3475	1	11.10	0.2202	0.2807
2	12.27	0.4334	0.3508	2	8.81	0.2184	0.2814
3	11.15	0.4460	0.3482	3	8.80	0.2125	0.2724
4	11.75	0.4376	0.3504	4	11.10	0.2309	0.2951
5	12.08	0.4326	0.3490	5	9.29	0.2130	0.2726
6	11.61	0.4364	0.3496	6	11.87	0.2256	0.2861
7	10.90	0.4411	0.3509	7	9.32	0.2205	0.2842
8	10.82	0.4495	0.3466	8	8.63	0.2141	0.2751

Table 1—continued

Series	Y	x	y	Series	Y	x	y
Mixed Poromeric				*Fawn Acrylate II*			
Standard	3.26	0.3574	0.3431	Standard	24.45	0.3657	0.3452
Pattern 1	3.04	0.3576	0.3456	1	22.47	0.3638	0.3415
Standard	2.97	0.3571	0.3473	2	23.72	0.3663	0.3434
Pattern 2	3.27	0.3540	0.3434	3	22.75	0.3629	0.3408
Standard	4.97	0.4068	0.3650	4	22.50	0.3668	0.3439
Pattern 3	4.69	0.3997	0.3645	5	22.58	0.3723	0.3493
Standard	5.24	0.3942	0.3629	6	24.25	0.3713	0.3489
Pattern 4	5.00	0.4062	0.3641	7	24.12	0.3662	0.3455
Standard	5.58	0.4843	0.3623	8	27.77	0.3555	0.3408
Pattern 5	4.50	0.4674	0.3636				
Standard	41.52	0.4398	0.3543	*Dark Brown Acrylate*			
Pattern 6	43.16	0.4366	0.3555				
Standard	51.34	0.3211	0.3254	Standard	2.81	0.4217	0.3440
Pattern 7	46.43	0.3294	0.3325	1	2.80	0.4244	0.3419
Standard	1.54	0.2694	0.2680	2	2.71	0.4355	0.3450
Pattern 8	1.70	0.2722	0.2708	3	2.32	0.4208	0.3422
Standard	33.88	0.3725	0.3851	4	3.21	0.4365	0.3451
Pattern 9	30.34	0.3765	0.3878	5	3.48	0.4141	0.3388
Standard	17.59	0.2391	0.2644	6	2.34	0.4167	0.3418
Pattern 10	16.68	0.2380	0.2623	7	2.91	0.4369	0.3500
				8	2.64	0.4085	0.3484

was at 90° and viewing at 45°. The ranking order obtained from each method of calculation was compared with the visual order by means of the Spearman rank coefficient.

$$\rho = 1.0 - \frac{S\ (6d^2)}{n\,(n^2 - 1)}$$

Where d is the difference in ranking between the observed and measured rating and n the number of pairs involved.

It was decided at this point to present also the values obtained with several well known colour difference formulae, to aid in the assessment of the radial formula and modifications of this which might be developed later. Colour difference values (ΔE) were calculated according to the following formulae :

Method 1 $\Delta E = (\Delta_c^2 + \Delta_l^2)^{\frac{1}{2}}$
at K values 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 4.5

Method 1a As method 1 but using Δ_l derived from the Nickerson curve.
$K = 0.5$ to 4.5

Method 2 S.L.T.C. formula

$$\Delta E = \left\{500[(\Delta u)^2 + (\Delta v)^2]^{\frac{1}{2}} + [R(\Delta Y)^2]^{\frac{1}{2}}\right\}^{\frac{1}{2}}$$

R is the reciprocal of the permitted luminance difference which can be modified by the factor K, as in Method 1 and 1a.

Method 3 Adams chromatic value formula

$$\Delta E = 40\left\{(0.23\Delta V_y)^2 + [\Delta(V_x - V_y)]^2 + [0.4\Delta(V_z - V_y)]^2\right\}^{\frac{1}{2}}$$

Method 4 C.I.E. formula

$$\Delta E = [(\Delta W)^2 + (\Delta U)^2 + (\Delta V)^2]^{\frac{1}{2}}$$

Method 5 Judd-Hunter formula

$$\Delta E = f_g\{([221\, Y^{\frac{1}{4}}\, (\Delta\alpha)]^2 + (\Delta\beta)^2)^{\frac{1}{2}} + [K(\Delta Y)^{\frac{1}{2}}]^2\}^{\frac{1}{2}}$$

Method 6 Hunter-Schofield formula

$$\Delta E = 1.2\, \{[\Delta\, (10\, Y^{\frac{1}{2}})]^2 + [\Delta(70\, Y^{\frac{1}{2}}\alpha)]^2 + [\Delta(70\, Y^{\frac{1}{2}}\beta)^2\}^{\frac{1}{2}}$$

Method 7 Glasser cube—root formula

$$\Delta E = 1.4\, [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{\frac{1}{2}}$$

Method 8 Saunderson-Milner formula

$$\Delta E = 6[(\Delta\xi_1)^2 + (\Delta\xi^2)_2 + (\Delta\xi_3)^2]^{\frac{1}{2}}$$

Method 9 MacAdam—Friele—Chickering formula

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

where $\Delta C = K_1 \Delta C_1$ and $\Delta L = K_2 \Delta L_2$,

$\Delta C_1 = [(\Delta C_{rg}/a)^2 + (\Delta C_{yb}/b)^2]^{\frac{1}{2}}$ and $\Delta L_1 = (P\Delta P + Q\Delta Q)/(P^2 + Q^2)^{\frac{1}{2}}$,

$\Delta C_{rg} = (Q\Delta P - P\Delta Q)/(P^2 + Q^2)^{\frac{1}{2}}$ and $\Delta C_{yb} = S\Delta L_1/(P^2 + Q^2)^{\frac{1}{2}} - \Delta S$,

$\Delta L_2 = 0.279\Delta L_1/a$,

$K_1 = 0.55669 + 0.049434\ Y - 0.82575.10^{-3}\ Y^2 + 0.79172.10^{-5}\ Y^3 - 0.30087.10^{-7}\ Y^4$,

$K_2 = 0.17548 + 0.027556\ Y - 0.57262.10^{-3}\ Y^2 + 0.63893.10^{-5}\ Y^3 - 0.26731.10^{-7}\ Y^4$,

$a^2 = 17.3.10^{-6}(P^2 + Q^2)/[1 + 2.73P^2Q^2/(P^4 + Q^4)]$

$b^2 = 3.098.10^{-4}(S^2 + 0.2015\ Y^2)$

$P = 0.724\ X + 0.382\ Y - 0.098\ Z$

$Q = 0.48\ X + 1.37\ Y + 0.1276\ Z$

$S = 0.686\ Z$

Discussion

The essential difference between the radial and S.L.T.C. methods is that the former employs the considerable approximation of radial tolerances in the 1931 C.I.E. diagram, and the latter the radial tolerances in the 1960 C.I.E. diagram, which are the ellipses computed by Perry [10]in the 1931 diagram. If the values of K are plotted against the correlation coefficient, ρ, the latter, in most cases, will be seen to rise to an optimum value and then fall off again, but if the luminance differences in a series are relatively unimportant compared with the chromaticity differences, there will be little or no change after the optimum is reached. The optimum weighting is taken as the minimum value of K at which the best agreement with average observer assessment is obtained.

Fig. 1 shows the $V\lambda$ curve, modified by illuminant C ($Ec\bar{y}\lambda$) with the optimum values for K found for each series by Method 1. It will be seen that the points fit the curve too closely for it to be mere coincidence. The corresponding points for the S.L.T.C. method follow the same general trend but are much more scattered, which suggests that, where surface colours are concerned, the chromaticity discrimination areas are much nearer to circles than to ellipses, with the possible exception of the red acrylate series, in which this method showed to advantage.

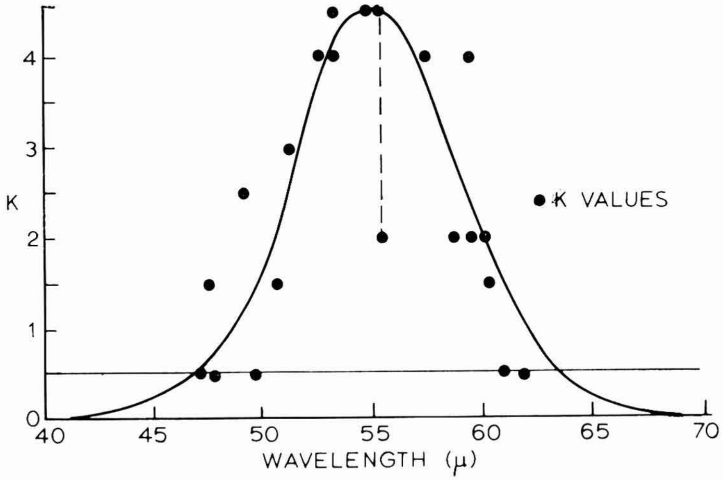

Fig. 1. $V\lambda$ **curve, with optimum** K **values from method 1**

Some series presented difficulties in plotting. For example, the green acrylate II series reached an optimum at $K = 2.0$ (Method 1), but had the same value at $K = 4.5$, where it would apparently belong. At a later stage, the light brown acrylate series, using Method 1b, showed the same correlation at all weightings, a notable exception, and so the mid point was used in this case. The fact that some series gave results that did not conform to the general trend illustrates the importance of making as many trials as possible, as isolated results can be quite misleading.

Obviously, the manner in which a series of patterns is constructed has a bearing on the information that can be obtained from them. It is not easy to prepare a series of patterns that will give the desired results but, by examining a large number of patterns at different points in colour space, it was hoped that the overall correlation would be significant and would correspond to the conditions obtaining in normal commercial practice.

The authors consider that the work involved in calculating the results from 25 series of single colours, as well as the 5 series of mixed colours, was absolutely necessary to give reasonable confidence in the results obtained. Table 2 shows the visual ranking of the blue acrylate patterns by 10 observers, the mean placement, the correlation coefficient for each observer and for the observer mean. It was not considered necessary to publish full tables for all the observer assessments, but only the mean placement and the coefficient for the observer mean, Table 3. A number of observers were called to take part in the tests, according to availability and convenience. They were all engaged in the colour industry but were not all "trained colourists." The "trained colourists" who took part were perhaps a little more consistent in their assessment than the others, but the idea that a good colourist is right every time cannot be entertained. Some observers took part in all the tests, and it is interesting to note that an observer who made a high correlation coefficient in one series might be almost at the bottom of the list in the next series, and vice versa. To one who has watched the observer assessment of the considerable number of patterns involved in this investigation, it seems incredible that the colour passing of batches of material worth perhaps hundreds of pounds should be left to the discretion of any one observer. The correlation coefficient for the observer mean overall was 0.83. To be of real value commercially, a colour difference formula must be relied on to give in every case a result that is better than one can expect from any one observer, and therefore, if with any particular series a method gave a correlation coefficient of less than 0.80, this was regarded as unacceptable and noted accordingly.

Table 2

Blue Acrylate Series *Visual ranking 10 observers*

Pattern	1	2	3	4	5	6	7	8	9	10	Mean Placement
1	5	7	5	9	7	9	7	9	5	7	7
2	9	6	7	7	5	5	5	6	2	9	5
3	7	5	6	3	8	6	9	5	9	8	6
4	3	2	2	5	3	3	2	3	1	2	2
5	6	9	8	7	9	8	4	8	7	5	8
6	2	1	1	4	1	2	6	4	3	3	3
7	1	3	3	1	2	1	1	1	4	1	1
8	4	4	4	2	4	4	3	2	8	4	4
9	8	8	9	8	6	7	8	7	6	6	9
$\rho =$	0.750	0.900	0.833	0.750	0.833	0.917	0.700	0.867	0.516	0.864	

Observer mean 0.780

Table

Mean placement

Pattern	Blue Acrylate	Blue Urethane	Green Urethane	Green Viscose	Green Wool	Green Paint	Green Matt Pt.
1	7	7	2	1	1	5	5
2	5	1	8	2	3	8	2
3	6	2	6	4	2	7	4
4	2	3	4	5	5	1	3
5	8	5	5	3	6	6	1
6	3	4	3	6	4	4	
7	1	6	7			3	
8	4		1			2	
9	9		9				
10			10				
11							
12							
$\rho =$	0.750	0.890	0.853	0.870	0.870	0.615	0.719

Pattern	Pink Acrylate	Magenta Acrylate	Dk. Brn. Acrylate	Dk. Red Acrylate	Grey Acrylate	Bl. Grey Acrylate	Orange Acrylate
1	6	6	1	1	5	7	5
2	5	3	4	2	1	5	7
3	1	6	3	8	8	8	6
4	8	8	7	6	4	2	4
5	3	2	2	3	7	3	2
6	2	7	5	5	6	6	1
7	7	4	8	4	2	1	3
8	4	1	6	7	3	4	8
9						9	
10							
11							
12							
$\rho =$	0.857	0.743	0.814	0.940	0.856	0.850	0.812

While the publication of tables showing the ΔE values for all patterns with each method of calculation would have been interesting and would have indicated the immense amount of work involved in the investigation—the greater part fortunately being done by computer—it is not essential, as sufficient information is given to enable such figures to be recalculated if desired. The really important figures are the correlation coefficients for each method and

3

by observers

Green Acryl. I	Green Acryl. II	Yellow Acrylate	Fawn Acryl. I	Lt. Brn. Acrylate	Red Br. Acrylate	Red Acrylate	Crimson Acrylate
8	3	2	8	2	6	1	2
5	2	6	6	7	7	3	1
9	4	1	3	6	8	7	5
2	1	3	5	3	11	2	7
1	5	4	4	4	4	4	4
4	6	10	9	1	3	6	6
6	8	9	1	5	10	5	8
3	7	8	7	8	2		3
10		7	1		9		
7		5			12		
					1		
					5		
0.820	0.855	0.927	0.838	0.851	0.866	0.575	0.849

Bl. Green Acrylate	Violet Acrylate	Fawn Acryl. II	Mixed Pormeric	Mixed Acryl. I	Mixed Acryl. II	Mixed Acryl. III	Mixed
6	3	6	3	2	6	4	7
2	4	2	2	7	7	1	8
5	5	7	8	1	2	3	6
7	2	4	7	4	1	5	1
4	6	5	10	3	4	8	4
8	8	3	4	6	5	2	5
1	1	1	9	8	3	6	2
3	7	8	1	5		7	3
			6				
			5				
0.940	0.831	0.771	0.897	0.855	0.832	0.912	0.897

each series against average observer assessment. These are summarised in Table 4, which also shows the average correlation coefficient for the 30 series for each method of calculation. It is necessary to recall the examination of the results that was made when only 16 series of patterns had been examined, as this induced the authors to attempt further modification of the radial method, and to make the whole investigation much larger than that originally planned.

Table 4

Method I K Value	Blue Acrylate	Blue Urethane	Green Urethane	Green Viscose	Green Wool	Green Paint	Green Matt Pt.	Green Acrylate I
0.5	0.867	0.964	0.830	*0.120*	*0.659*	*0.547*	*0.400*	*0.418*
1.0	*0.616*	0.929	0.927	*0.315*	*0.542*	*0.620*	*0.400*	*0.418*
1.5	*0.500*	0.929	0.933	*0.600*	*0.258*	*0.740*	*0.400*	*0.684*
2.0	*0.333*	0.929	0.903	*0.600*	*0.258*	*0.740*	*0.700*	0.806
2.5	*0.220*	0.929	0.891	*0.657*	*0.438*	*0.740*	*0.700*	0.915
3.0	*0.220*	0.929	0.915	1.000	*0.714*	*0.798*	*0.700*	0.952
3.5	*0.117*	0.929	0.915	1.000	0.827	0.952	0.900	0.952
4.0	*0.117*	0.929	0.915	1.000	0.827	0.976	1.000	0.964
4.5	*0.032*	0.929	0.927	1.000	0.943	0.976	0.900	0.988

Method I K Value	Pink Acrylate	Magenta Acrylate	Dk. Brn. Acrylate	Dk. Red Acrylate	Grey Acrylate	Blue Grey Acrylate	Orange Acrylate	Blue Green Acrylate
0.5	*0.690*	0.905	*0.008*	0.976	0.952	0.817	0.809	0.881
1.0	0.881	0.881	*0.168*	0.929	0.952	0.917	0.809	0.976
1.5	0.976	0.881	*0.714*	0.857	1.000	0.900	0.905	0.976
2.0	0.976	0.809	0.881	0.833	0.929	0.833	0.976	0.952
2.5	0.976	0.809	0.881	0.809	0.929	0.900	0.952	0.881
3.0	0.976	0.809	0.881	*0.714*	0.857	0.917	0.905	0.810
3.5	0.976	0.809	0.881	*0.714*	0.833	0.950	0.905	0.810
4.0	0.976	0.809	0.881	*0.714*	*0.738*	0.950	0.905	0.810
4.5	0.952	0.809	0.881	*0.714*	*0.738*	0.967	0.929	*0.738*

Method 1A	Blue Acrylate	Blue Urethane	Green Urethane	Green Viscose	Green Wool	Green Paint	Green Matt Pt.	Green Acrylate I
0.5	0.867	0.964	0.830	*0.085*	*0.659*	*0.547*	*0.400*	*0.418*
1.0	*0.466*	0.929	0.927	*0.485*	*0.143*	*0.740*	*0.400*	*0.466*
1.5	*0.236*	0.929	0.903	*0.600*	*0.258*	*0.740*	*0.400*	0.806
2.0	*0.117*	0.929	0.903	*0.657*	*0.438*	*0.740*	*0.700*	0.915
2.5	*0.117*	0.929	0.915	1.000	*0.714*	*0.798*	*0.700*	0.952
3.0	*0.032*	0.929	0.915	1.000	0.827	0.952	0.900	0.952
3.5	*0.032*	0.929	0.915	1.000	0.827	0.976	1.000	0.964
4.0	*0.032*	0.929	0.927	1.000	0.943	0.929	0.900	0.964
4.5	*0.032*	0.929	0.903	1.000	1.000	0.929	0.900	0.964

Method 1A	Pink Acrylate	Magenta Acrylate	Dk. Brn. Acrylate	Dk. Red Acrylate	Grey Acrylate	Blue Grey Acrylate	Orange Acrylate	Blue Green Acrylate
0.5	*0.690*	0.881	*0.119*	0.905	0.952	0.833	0.809	0.881
1.0	0.881	0.881	*0.793*	0.857	1.000	0.917	0.809	0.976
1.5	0.976	0.809	0.881	0.809	0.929	0.900	0.905	0.976
2.0	0.976	0.809	0.881	0.714	0.929	0.833	0.976	0.881
2.5	0.976	0.809	0.881	*0.714*	0.857	0.917	0.905	0.810
3.0	0.976	0.809	0.881	*0.666*	0.833	0.950	0.905	0.810
3.5	0.976	0.809	*0.786*	*0.666*	*0.738*	0.950	0.905	*0.738*
4.0	0.952	0.809	*0.786*	*0.452*	*0.738*	0.967	0.905	*0.642*
4.5	0.952	*0.714*	*0.786*	*0.452*	*0.666*	0.967	0.905	*0.642*

Method 1B	Blue Acrylate	Blue Urethane	Green Urethane	Green Viscose	Green Wool	Green Paint	Green Matt Pt.	Green Acrylate I
0.5	*0.784*	0.822	0.818	*0.120*	*0.659*	*0.531*	*0.300*	*0.418*
1.0	0.867	0.964	0.927	*0.600*	*0.542*	*0.595*	*0.400*	*0.418*
1.5	0.850	0.929	0.927	*0.600*	*0.143*	*0.738*	*0.400*	*0.684*
2.0	*0.716*	0.929	0.964	*0.600*	*0.258*	*0.738*	*0.700*	0.806
2.5	*0.450*	0.929	0.964	*0.657*	*0.258*	*0.738*	*0.700*	0.915
3.0	*0.450*	0.929	0.964	1.000	*0.714*	*0.786*	*0.700*	0.952
3.5	*0.450*	0.929	0.964	1.000	*0.714*	0.952	*0.700*	0.952
4.0	*0.355*	0.929	0.952	1.000	0.827	0.952	1.000	0.964
4.5	*0.355*	0.929	0.952	1.000	0.943	0.976	1.000	0.988

Summary

Green Acrylate II	Yellow Acrylate	Fawn Acrylate I	Lt. Brown Acrylate	Red Brn. Acrylate	Red Acrylate	Crimson Acrylate	Unacceptable	Overall Average
0.810	*0.673*	0.833	0.905	0.832	0.929	0.809	—	—
0.905	*0.709*	0.933	0.905	0.937	0.893	0.881	—	—
0.905	*0.709*	0.950	0.905	0.951	0.893	0.929	—	—
0.952	0.818	1.000	0.905	0.945	0.893	0.929	—	—
0.952	0.895	1.000	0.905	0.937	0.893	0.976	—	—
0.952	0.891	0.905	0.905	0.923	0.893	0.976	—	—
0.952	0.891	0.933	0.905	0.923	0.893	0.976	—	—
0.952	0.964	0.933	0.928	0.923	0.893	0.976	—	—
0.952	0.964	0.917	0.928	0.923	0.893	0.976	—	—

Violet Acrylate	Fawn Acrylate II	Mixed Poromeric	Mixed Acrylate I	Mixed Acrylate II	Mixed Acrylate III	Mixed Acrylate IV	Unacceptable	Overall Average
0.595	0.809	*0.588*	*0.251*	0.857	0.976	0.929	11	0.669
0.857	0.833	*0.611*	*0.070*	0.857	0.952	1.000	10	0.718
0.952	0.833	*0.758*	*0.047*	0.822	0.905	0.976	10	0.793
0.952	0.833	0.891	*0.000*	0.893	0.833	0.976	6	0.809
0.976	0.905	0.867	*0.000*	0.929	*0.738*	0.929	7	0.814
0.976	0.905	*0.794*	*0.000*	0.964	*0.738*	0.833	8	0.827
0.976	0.905	*0.782*	*0.191*	0.893	*0.738*	0.833	5	0.842
0.976	0.905	*0.782*	*0.191*	0.893	*0.738*	0.833	6	0.847
0.976	0.905	*0.782*	*0.191*	0.893	*0.738*	*0.718*	8	0.839

Green Acrylate II	Yellow Acrylate	Fawn Acrylate I	Lt. Brown Acrylate	Red Brn. Acrylate	Red Acrylate	Crimson Acrylate	Unacceptable	Overall Average
0.833	*0.673*	0.900	0.968	0.827	0.929	0.809	—	—
0.929	*0.757*	0.933	0.905	0.930	0.893	0.915	—	—
0.905	0.818	0.984	0.905	0.916	0.893	0.929	—	—
0.952	0.869	1.000	0.905	0.909	0.893	0.976	—	—
0.952	0.869	0.984	0.905	0.881	0.893	0.976	—	—
0.952	0.891	0.933	0.905	0.839	0.893	0.976	—	—
0.952	0.927	0.933	0.928	0.839	0.893	0.976	—	—
0.952	0.964	0.917	0.928	0.839	0.893	0.976	—	—
0.952	0.984	0.867	0.928	0.832	8.893	0.976	—	—

Violet Acrylate	Fawn Acrylate II	Mixed Poromeric	Mixed Acrylate I	Mixed Acrylate II	Mixed Acrylate III	Mixed Acrylate IV	Unacceptable	Overall Average
0.808	0.809	*0.648*	*0.251*	0.857	0.976	0.976	10	0.693
0.952	0.833	*0.721*	*0.047*	0.857	0.952	0.976	10	0.766
0.976	0.833	*0.758*	*0.047*	0.822	*0.738*	0.976	8	0.785
0.976	0.833	0.891	*0.000*	0.929	*0.738*	0.976	8	0.808
0.976	0.905	0.855	*0.000*	0.964	*0.738*	0.833	7	0.824
0.976	0.905	0.806	*0.024*	0.893	*0.738*	0.810	4	0.829
0.976	0.905	*0.782*	*0.191*	0.893	*0.738*	0.810	8	0.832
0.976	0.905	*0.782*	*0.191*	0.893	*0.738*	*0.714*	9	0.818
0.976	*0.738*	*0.782*	*0.191*	0.893	*0.690*	*0.714*	11	0.805

Green Acrylate II	Yellow Acrylate	Fawn Acrylate I	Lt. Brown Acrylate	Red Brn. Acrylate	Red Acrylate	Crimson Acrylate	Unacceptable	Overall Average
0.833	*0.709*	0.833	0.902	*0.797*	0.929	*0.666*	—	—
0.905	*0.758*	0.900	0.902	0.930	*0.796*	0.809	—	—
0.905	0.818	0.911	0.902	0.924	0.893	0.915	—	—
0.952	0.818	1.000	0.902	0.916	0.893	0.929	—	—
0.952	0.891	1.000	0.902	0.909	0.893	0.929	—	—
0.952	0.915	1.000	0.902	0.895	0.893	0.929	—	—
0.952	0.964	0.950	0.902	0.873	0.893	0.976	—	—
0.952	0.984	0.933	0.902	0.852	0.893	0.976	—	—
0.952	0.984	0.933	0.902	0.838	0.893	0.976	—	—

Table 4

Method 1B	Pink Acrylate	Magenta Acrylate	Dk. Brn. Acrylate	Dk. Red Acrylate	Grey Acrylate	Blue Grey Acrylate	Orange Acrylate	Blue Green Acrylate
0.5	*0.690*	*0.787*	*0.007*	0.976	0.952	0.817	0.808	0.881
1.0	*0.786*	0.881	*0.120*	0.929	0.952	0.687	0.808	0.881
1.5	0.881	0.881	*0.420*	0.857	1.000	0.917	0.905	0.976
2.0	0.976	0.881	*0.738*	0.857	0.976	0.917	0.929	0.976
2.5	0.976	0.881	0.881	0.808	0.929	0.833	0.929	0.976
3.0	0.976	0.881	0.881	*0.714*	0.929	0.833	0.905	0.952
3.5	1.000	0.881	0.881	*0.714*	0.929	0.900	0.905	0.881
4.0	0.976	0.881	0.881	*0.714*	0.875	0.917	0.905	0.810
4.5	0.976	0.809	0.881	*0.714*	*0.738*	0.917	0.905	0.810

Method 2	Blue Acrylate	Blue Urethane	Green Urethane	Green Viscose	Green Wool	Green Paint	Green Matt Pt.	Green Acrylate I
0.5	0.833	0.893	0.818	*0.370*	*0.540*	*0.548*	*0.300*	*0.418*
1.0	0.817	0.929	0.842	*0.370*	*0.540*	*0.548*	*0.400*	*0.612*
1.5	*0.716*	0.929	0.891	*0.370*	*0.140*	*0.690*	*0.300*	0.806
2.0	*0.516*	0.929	0.927	*0.771*	*0.657*	*0.690*	*0.300*	0.879
2.5	*0.450*	0.929	0.952	*0.771*	*0.714*	*0.714*	*0.600*	0.915
3.0	*0.400*	0.929	0.952	*0.771*	*0.772*	*0.786*	*0.500*	0.927
3.5	*0.400*	0.929	0.952	*0.771*	*0.772*	0.857	*0.500*	0.927
4.0	*0.400*	0.929	0.952	0.829	*0.772*	0.857	*0.500*	0.927
4.5	*0.400*	0.929	0.952	0.829	*0.772*	*0.690*	*0.500*	0.939

Method 2	Pink Acrylate	Magenta Acrylate	Dk. Brn. Acrylate	Dk. Red Acrylate	Grey Acrylate	Blue Grey Acrylate	Orange Acrylate	Blue Green Acrylate
0.5	0.833	*0.643*	*0.002*	0.976	0.952	0.917	0.929	0.881
1.0	0.881	*0.738*	*0.524*	0.808	0.952	0.917	0.857	0.976
1.5	0.881	*0.523*	*0.690*	*0.714*	0.928	0.917	0.905	0.976
2.0	0.905	*0.523*	*0.690*	*0.714*	0.808	0.900	0.905	1.000
2.5	0.929	*0.523*	*0.690*	*0.618*	0.808	0.917	0.905	0.952
3.0	0.929	*0.523*	*0.642*	*0.618*	*0.738*	0.917	0.905	0.905
3.5	0.976	*0.523*	*0.642*	*0.404*	*0.642*	0.950	0.905	0.809
4.0	0.976	*0.523*	*0.642*	*0.404*	*0.642*	0.967	0.833	0.809
4.5	0.976	*0.523*	*0.642*	*0.404*	*0.642*	0.967	0.833	0.809

Method	Blue Acrylate	Blue Urethane	Green Urethane	Green Viscose	Green Wool	Green Paint	Green Matt Pt.	Green Acrylate I
3	*0.565*	0.929	0.984	*0.485*	*0.772*	0.833	*0.600*	0.964
4	0.833	0.949	0.927	*0.485*	*0.657*	*0.690*	*0.500*	0.964
5	*0.250*	0.929	0.952	0.829	*0.772*	0.857	*0.600*	0.927
6	*0.783*	0.949	0.964	*0.485*	*0.657*	*0.690*	*0.500*	0.964
7	*0.150*	0.929	0.927	*0.485*	*0.428*	*0.726*	*0.500*	0.915
8	*0.234*	0.949	0.939	*0.485*	*0.657*	0.833	*0.500*	0.915
9	*0.666*	0.857	0.818	*0.771*	*0.657*	*0.594*	*0.600*	0.915
1D	0.867	0.964	0.903	*0.657*	0.827	0.976	1.000	0.988
1F	0.867	0.929	0.915	1.000	0.943	0.976	0.900	0.988
1E	0.867	0.964	0.903	1.000	0.943	0.929	0.900	0.964
1G	0.867	0.929	0.915	1.000	1.000	0.929	0.900	0.964
1H	0.867	0.929	0.964	1.000	0.827	0.976	1.000	0.988
2A	0.833	0.893	0.927	0.829	*0.772*	0.857	*0.500*	0.939

Summary—continued

Violet Acrylate	Fawn Acrylate II	Mixed Poromeric	Mixed Acrylate I	Mixed Acrylate II	Mixed Acrylate III	Mixed Acrylate IV	Unacceptable	Overall Average
0.547	*0.762*	*0.588*	0.857	0.857	0.905	0.929	15	0.664
0.738	0.833	*0.648*	0.857	0.857	0.976	0.968	11	0.744
0.857	0.833	*0.752*	0.822	0.822	1.000	0.929	7	0.804
0.857	0.833	0.842	0.822	0.822	0.952	0.929	6	0.848
0.952	0.833	0.867	0.857	0.857	0.952	0.929	5	0.852
0.952	0.905	0.867	0.857	0.857	0.952	0.881	5	0.877
0.952	0.905	0.842	0.893	0.893	0.952	*0.714*	5	0.880
0.976	0.905	0.855	0.893	0.893	0.952	*0.714*	3	0.887
0.976	0.905	0.800	0.893	0.893	0.952	*0.666*	4	0.882

Green Acrylate II	Yellow Acrylate	Fawn Acrylate I	Lt. Brn. Acrylate	Red Brn. Acrylate	Red Acrylate	Crimson Acrylate	Unacceptable	Overall Average
0.714	*0.430*	0.900	0.968	0.866	0.964	0.809	—	—
0.905	*0.745*	0.933	0.905	0.909	1.000	0.929	—	—
0.905	*0.745*	0.984	0.905	0.895	1.000	0.929	—	—
0.905	0.843	0.984	0.857	0.895	1.000	0.976	—	—
0.905	0.867	1.000	0.875	0.902	1.000	0.976	—	—
0.801	0.867	0.978	0.857	0.888	1.000	0.976	—	—
0.801	0.915	0.933	0.875	0.867	1.000	0.976	—	—
0.801	0.915	0.933	0.875	0.867	1.000	0.976	—	—
0.801	0.915	0.900	0.875	0.874	1.000	0.976	—	—

Violet Acrylate	Fawn Acrylate II	Mixed Poromeric	Mixed Acrylate I	Mixed Acrylate II	Mixed Acrylate III	Mixed Acrylate IV	Unacceptable	Overall Average
0.547	0.809	*0.460*	*0.237*	0.857	0.928	0.881	12	0.647
0.875	0.833	*0.679*	*0.286*	0.893	0.976	0.976	10	0.749
0.875	0.833	0.867	*0.190*	0.893	0.928	0.833	10	0.762
0.976	0.833	0.867	*0.401*	0.893	0.909	0.833	9	0.810
0.976	0.833	0.843	*0.500*	0.893	0.909	0.833	9	0.823
0.976	0.833	0.843	*0.500*	0.928	0.909	*0.717*	11	0.810
0.976	0.833	0.830	*0.547*	0.928	0.909	*0.717*	10	0.802
0.976	*0.714*	0.830	*0.547*	0.928	*0.714*	*0.717*	11	0.792
0.976	*0.690*	0.830	*0.642*	0.928	*0.714*	*0.717*	12	0.788

Green Acrylate II	Yellow Acrylate	Fawn Acrylate I	Lt. Brn. Acrylate	Red Brn. Acrylate	Red Acrylate	Crimson Acrylate	Unacceptable	Overall Average
0.952	0.952	0.967	0.970	0.958	0.893	0.976	—	—
0.929	0.915	0.917	0.929	0.937	0.905	0.976	—	—
0.968	0.939	0.900	0.929	0.895	0.964	0.976	—	—
0.929	0.915	0.917	0.970	0.972	*0.000*	0.976	—	—
0.928	0.952	0.933	0.970	0.902	0.893	0.976	—	—
0.905	0.976	0.933	0.970	0.923	0.893	0.976	—	—
0.905	0.939	0.900	0.929	0.842	0.893	0.875	—	—
0.952	0.891	0.950	0.905	0.945	*0.796*	0.809	—	—
0.952	0.891	1.000	0.905	0.951	0.929	0.929	—	—
0.952	0.927	0.933	0.905	0.909	0.893	0.809	—	—
0.952	0.891	0.984	0.905	0.916	0.929	0.929	—	—
0.952	0.984	1.000	0.902	0.944	0.893	0.929	—	—
0.801	0.915	0.978	0.968	0.895	1.000	0.809	—	—

Table 4

Method	Pink Acrylate	Magenta Acrylate	Dk. Brn. Acrylate	Dk. Red Acrylate	Grey Acrylate	Blue Grey Acrylate	Orange Acrylate	Blue Green Acrylate
3	0.976	0.905	*0.333*	0.905	0.929	0.983	*0.785*	1.000
4	0.928	*0.762*	*0.500*	0.976	0.929	0.967	0.833	0.976
5	0.976	*0.774*	*0.690*	*0.738*	0.857	0.967	0.905	0.833
6	0.976	*0.762*	*0.500*	0.976	0.929	0.950	*0.690*	0.976
7	0.929	*0.714*	*0.427*	0.976	0.857	0.967	0.928	0.952
8	0.976	0.809	*0.427*	0.928	0.857	0.967	0.881	0.952
9	0.881	*0.666*	*0.524*	0.857	0.929	0.900	0.857	1.000
1D	0.881	0.881	0.881	0.857	0.952	0.817	0.976	0.976
1F	0.976	0.809	0.881	0.929	0.952	0.917	0.905	0.976
1E	0.881	0.809	0.881	0.809	0.952	0.833	0.976	0.976
1G	0.976	0.809	0.881	0.857	1.000	0.917	0.905	0.976
1H	0.976	0.881	0.881	0.857	0.952	0.917	0.929	0.976
2A	0.881	*0.643*	*0.690*	*0.714*	0.952	0.917	0.905	0.976

It was noted that the best results with a method employing constant luminance weighting were with method 1 ($\rho = 0.882$, K = 4.0), radial tolerances in the 1931 diagram, and a simple linear function for luminance tolerance. This was followed by method 1A ($\rho = 0.869$, K = 4.0), radial tolerances with the more complicated Nickerson curve luminance tolerance, and then method 3 (Adams Chromatic Value formula, $\rho = 0.850$). It was also noted that the best luminance weighting with methods 1, 1A, and 2, was considerably larger than that originally selected by the Colour Committee of the S.L.T.C. Included in the results for the 16 series, methods 1 and 1A each had one unacceptable result, and methods 2 and 3 four unacceptable results. Even at a constant luminance weighting, radial tolerances gave better results than elliptical tolerances for chromaticity differences.

The next step was to use the $V\lambda$ curve to arrive at a variable weighting for luminance tolerance. A line was drawn (quite arbitrarily) at $K = 0.5$ in Fig. 1 because it was felt that K values below this would give excessively large values for ΔE.

Values to the nearest 0.5 K were used from the results already obtained and are shown in the summary under method 1D. There was a rise in the overall correlation coefficient to 0.905. Method 1E was a little better at $\rho = 0.917$. Applied to method 2, the $V\lambda$ modification raised the overall correlation coefficient to 0.838 (method 2A), and halved the number of unacceptable results.

It seems obvious, therefore, that where surface colour is concerned, luminance discrimination varies with dominant wavelength as well as with luminance factor.

It was thought that a better fit to the observed values could be obtained if the $V\lambda$ curve was moved slightly to the left so that the peak value was at 545μ instead of 555μ, and when this was done the correlation coefficient for method 1D rose to 0.930 (1F) and that for Method 1E rose to 0.926. The apparent shift in the $V\lambda$ curve may be due to the original curve being based on observations with a 2° field, whereas a much wider field is used in visual assessment of the patterns. Whatever the cause, the improvement in results appears to justify its use.

Summary—continued

Violet Acrylate	Fawn Acrylate II	Mixed Poromeric	Mixed Acrylate I	Mixed Acrylate II	Mixed Acrylate III	Mixed Acrylate IV	Unacceptable	Overall Average
0.738	0.976	0.818	*0.476*	*0.678*	0.952	0.833	9	0.836
0.857	0.905	0.927	*0.427*	0.857	0.905	*0.785*	8	0.835
0.967	*0.714*	0.867	*0.452*	0.857	*0.690*	*0.690*	10	0.822
0.857	0.976	0.927	*0.310*	0.857	0.952	*0.714*	11	0.810
0.857	0.928	0.903	*0.285*	*0.678*	*0.714*	0.809	10	0.786
0.950	0.928	0.818	*0.262*	*0.678*	*0.714*	0.833	8	0.802
0.905	0.833	0.806	*0.547*	0.928	0.882	*0.767*	9	0.815
0.976	0.905	*0.095*	*0.095*	*0.785*	*0.702*	*0.453*	7	0.822
0.976	0.833	*0.075*	*0.143*	1.000	*0.714*	*0.453*	4	0.854
0.976	0.905	*0.500*	*0.095*	*0.785*	*0.762*	*0.453*	5	0.846
0.976	0.833	*0.524*	*0.143*	1.000	*0.666*	*0.453*	4	0.864
0.976	0.905	0.867	0.810	0.964	0.976	0.976	0	0.933
0.976	0.833	*0.745*	*0.285*	0.857	*0.714*	0.929	8	0.831

At the same time, the problem of what to do with the non-spectral colours was considered, and it was found that the use of the complimentary wavelengths was effective in determining the required K values. This is a purely practical solution and has no theoretical justification. Similarly, if one should find a master pattern that plots on or very near to the white point, an arbitrary value of $K = 4.0$ is suggested.

It is one thing to devise a formula that will give better than average observer ranking with any particular series of patterns, but to be really effective a given value of ΔE should mean the same thing at any point in colour space. Only if this requirement is met can one fix a definite value of ΔE for the passing or rejection of coloured materials, unless such materials are to be produced in one colour only. The problem is much more serious when variable luminance weighting is used as against a formula with constant luminance weighting, and it was seen that ΔE values for blue patterns calculated by method 1D were larger than they should be in relation to the values for green patterns.

It seemed that one way to reduce this disparity would be to increase the size of the radial chromaticity tolerances for the blue patterns, so that to maintain the same relative luminance weighting a higher K value would be required and the numerical value of ΔE would be reduced. The reverse of this would, of course, give a higher numerical value for the green patterns. This would mean that chromaticity tolerances for blue and green patterns would be approximately equal. This does not imply that chromaticity differences are in fact equally spaced in the 1931 diagram. It is merely a convenient way of adjusting the size of the units and simplifying the calculation.

It was decided to test this by using for chromaticity tolerance a constant value of 0.005 in x or y so that:

$$\Delta_c = 200\,(\Delta x^2 + \Delta y^2)^{\frac{1}{2}}$$

the luminance tolerance and ΔE values being calculated as in method 1 . . . method 1B.

This resulted in a compression of the scale of K values required, and compression also in the numerical values of ΔE. In the calculations for method 1H, the K values were read directly from the $V\lambda$ curve plotted between 0.5 and 4.5K

and peaking at 545μ (Fig. 2). Complementary wavelengths were used for the non-spectral colours. The overall coefficient for this method for the first 16 sets was 0.940, and for the 30 sets 0.933.

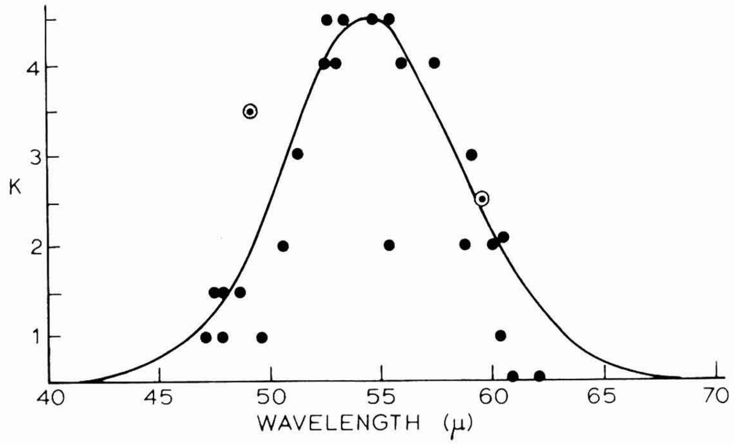

Fig. 2. **$V\lambda$ curve used for method 1H**

The value of this modification, using uniform radial tolerances, was shown when a series of mixed colour differences was examined. In this case the observer was asked to state whether a difference between two green patterns was greater or less than the difference between two red or blue patterns or patterns of some other colour. Going back to one's earlier experiences with colour measurement, it seemed that blue differences had always received a higher rating than they should have done with respect to differences in other colours, irrespective of whether elliptical or radial tolerances were used, and this was substantiated in the first mixed difference series. The radial tolerance method with the $V\lambda$ modification which had in general given excellent results (method 1D) failed in this test to give good correlation with average observer assessment in common with other well known methods, mainly because a pair of blue patterns ranked by observers as the second smallest difference in a series of eight was calculated to be the largest difference in the series. When uniform radial tolerances were used (Method 1H), an acceptable correlation was achieved.

McLaren[11] has drawn attention to the necessity for scaling factors in colour difference formulae in order that values for ΔE obtained by various methods of calculation might have the magnitude implied in the term "C.I.E. units". In the course of this work, the ΔE values of a large number of patterns were calculated by the Adams chromatic value formula (A.C.V.), using scaling factors of 40 and 50 respectively. The authors were a little dubious about the validity of adding the ΔE values by one method and comparing them with the added values by another method for the same 204 patterns, but if the added values for A.C.V. 40, and the added values for A.C.V. 50 are compared with the added values for the C.I.E. method, it is found that one fifth of the difference subtracted from the values for A.C.V. 50 gives the sum of the C.I.E. values. A scaling factor of 48 applied to the A.C.V. values would therefore give overall C.I.E. values. This agrees with the scaling factor given by McLaren. If this method of determining scaling values is valid for the A.C.V. methods, it is likely that it will be valid for the other methods to which it has been applied.

It must be understood that the use of a scaling factor does not convert individual ΔE values to C.I.E. ΔE values, which can only be obtained by using the C.I.E. formula, but it does ensure that the values have the same meaning in terms of colour difference.

If the term "C.I.E. unit" should be defined as referring to a particular order of colour difference, it is not necessarily tied to the C.I.E. formula. Any formula could be used with the appropriate scaling factor but, of course, in any commercial specification, the method to be used for calculating ΔE would be indicated. Values for ΔE were calculated by 49 methods but many of these were variations of the same method using different K values. Table 5 is an abbreviated list of the results obtained with the different methods of calculation. Apart from the overall rank correlation coefficients, the most interesting figures are those for the number of unacceptable results, or those cases where any good observer might be expected to do better than measurement/calculation, and those for the lowest coefficient recorded for any one of the 30 series, indicating the worst agreement one is likely to get under certain conditions. Method 1H heads the list, giving acceptable results with every one of the 30 series, and with an overall correlation that is considerably better than the observer mean.

Table 5

Abbreviated list of results

	Method	Rank coefficient	Not acceptable	Lowest value
1H	Radial Equal circles. Mod. Vλ curve	0.933	0	0.810
1B	(K = 4) Radial Equal circles. Fixed weighting	0.887	3	0.355
1G	Radial Unequal circles. Mod. Vλ curve	0.864	4	0.143
1F	Radial Unequal circles. Vλ curve	0.854	4	0.143
1	(K = 4) Radial Unequal circles. Fixed weighting	0.847	6	0.117
1E	Radial Unequal circles. Mod. Vλ curve	0.846	5	0.095
	Nickerson Luminance curve	—	—	—
3	Adams Chromatic Value	0.836	9	0.333
4	CIE	0.835	8	0.427
1A	(K = 3.5) Radial Unequal circles. Fixed weighting with Nickerson curve	0.832	8	0.032
2A	Ellipses. Vλ curve	0.831	8	0.285
1D	Radial Unequal circles. Vλ curve	0.822	7	0.095
5	Judd—Hunter	0.822	10	0.250
9	MacAdam—Friede—Chickering	0.815	9	0.524
2	(K = 2.0) Ellipses. Fixed weighting	0.810	9	0.500
6	Hunter—Schofield	0.810	11	0.000
8	Saunderson—Milner	0.802	8	0.234
7	Glasser Cube root	0.786	10	0.150
2	(K = 1.0) SLTC. Fixed weighting	0.749	10	−0.540

It has been suggested that this method would be difficult to operate by computer because instead of feeding *R.G.B.* or *X.Y.Z.* values directly into the computer, the coefficients x and y must be calculated first, in order to find the dominant wavelength by plotting in a chromaticity chart, and from this the correct K value. With the K value inserted, the computer programme follows normal procedure. In fairness, it should be pointed out that the K value has only to be determined once for the standard colour. It is a simple operation and the improved results fully justify its use. A skilled colorimetrist could even make a reasonably accurate forecast of the required K value without even seeing the chromaticity co-ordinates. The manual time required to calculate ΔE once the K value has been found is about 2 minutes, using a slide rule and squared paper, against a minimum of 15 minutes for the A.C.V. method, using tables and a calculator.

The best formula using fixed luminance weighting, method 1B at $K = 4.0$, may be expected to give trouble with some blue and red patterns, but still shows a considerable improvement over other methods in common use. Of these there is little to choose between the A.C.V. and C.I.E. methods, the balance perhaps being slightly in favour of the latter, although 8 or 9 failures in 30 tests is not a good recommendation for their general use. Other methods gave even poorer results.

Conclusions

In general, the results indicate that uniform radial tolerances for chromaticity differences give better results than variable radial tolerances, which are in turn better than elliptical tolerances (in the 1931 C.I.E. diagram); that the $V\lambda$ modification is better than any fixed weighting of chromaticity—luminance values; and that for the calculation of luminance differences, two simple linear functions can replace a polynomial calculation.

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Appendix

Radial method for calculating ΔE

If Y is > 8.0

$$\Delta E = 1.3\left\{[200\,(\Delta x^2 + \Delta y^2)^{\frac{1}{2}}]^{\frac{1}{2}} + \left[\frac{\Delta Y}{K[0.0082(Y + 22)]}\right]^2\right\}^{\frac{1}{2}}$$

If Y is < 8.0

$$\Delta E = 1.3\left\{[200\,(\Delta x^2 + \Delta y^2)^{\frac{1}{2}}]^2 + \left[\frac{\Delta Y}{K[(0.022\,Y) + 0.074]}\right]^2\right\}^{\frac{1}{2}}$$

1. The patterns are measured.

2. The dominant wavelength of the standard colour is found by plotting in the 1931 C.I.E. diagram.

3. A factor (K) is obtained by reference to the modified $Y\lambda$ curve.*

4. The permitted luminance tolerance for the standard colour (Ty) is calculated

$$T_y = K\,[0.0082(Y + 22)] \ldots\ldots \text{if } Y > 8.0$$

$$T_y = K\,[(0.022\ Y) + 0.074] \ldots\ldots \text{if } Y < 8.0$$

5. $\Delta_c = 200\,(\Delta x^2 + \Delta y^2)^{\frac{1}{2}}$

6. $\Delta_l = \dfrac{\Delta Y}{T_y}$

7. $\Delta E = 1.3\,(\Delta_c{}^2 + \Delta_l{}^2)^{\frac{1}{2}}$

N.B. The scaling factor (1.3) is used to make the ΔE values comparable with C.I.E. 1964 units.

*This is the $Ec\bar{y}\lambda$ curve with the peak moved from 555μ to 545μ using K values from 0.5 to 4.5 as the ordinate and wavelengths from 400 mμ to 700 mμ as the abscissa.

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The measurement of resin viscosity during manufacture: A high temperature cone and plate viscometer

By P. S. Pond and C. J. H. Monk

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Summary

This paper describes the development of a cone and plate viscometer, thermostatically controlled at set temperatures in the range 25°C-150°C, for the measurement of the melt viscosity of resins during manufacture. Viscosity measurements within the range 0-10 poises, to an accuracy of ± 2 per cent of full scale, can be made on samples straight from the resin plant in less than one minute, and a closer check on viscosity changes during manufacture can be made than by periodical thinning tests.

Keywords

Properties, characteristics and conditions primarily associated with materials in general	*Equipment primarily associated with analysis, measurement and testing*
viscosity	high temperature viscometer

La mesure de la viscosité des résines pendant leur fabrication: Un viscosimètre à cône et disque pour l'usage aux températures hautes

Résumé

Cet exposé décrit le développement d'un viscosimètre à cône et disque pour mesurer la viscosité des résines fondues, lors du procédé de fabrication. Les mesures de viscosité dans la gamme de 0-10 poises à une précision de ± 2% de l'échelle entière, peuvent être effectuées, en moins d'une minute, sur des échantillons prélevés directement de l'installation. L'appareil permet un contrôle plus étroit des changements de viscosité survenant lors de la fabrication que l'on peut achever par les essais de dilution effectués à une cadence périodique.

Das Messen der Harzviskosität während des Fabrikationsprozesses: Ein Kegel-und Plattenviskometer für Hohe Temperaturen

Zusammenfassung

In diesem Vortrag wird die Entwicklung eines Kegel- und Plattenviskometers beschrieben, das für zwischen 25°C und 150°C thermostatisch kontrollierte und eingestellte Temperaturen zur Messung der Schmelzviskositäten von Harzen während ihrer Herstellung bestimmt ist. Es können innerhalb des Bereiches von 0-10 Poisen an direkt vom Harzkessel gezogenen Proben in weniger als einer Minute Viskositätsmessungen mit einer Genauigkeit von ± 2% gemacht werden; ausserdem können Viskositätseinstellungen während der Fabrikation genauer vorgenommen werden, als wenn die diesbezüglichen Prüfungen durch periodisches Verdünnen erfolgen würden.

Измерение вязкости смол во время производства: высокотемпературный конусно-пластинчатый вискозиметр

Резюме

Статья описывает разработку конусно-пластинчатого вискозиметра, с термостатическим контролем при заданных температурах в диапазоне от 25°C до 150°C, для измерения вязкости смол во время производства. Измерения вязкости в диапазоне 0-10 пуазов, с точностью в ±2% шкалы, могут быть проведены на образцах взятых непосредственно из смольно-производственной установки в течение меньше минуты, и более точная проверка изменений в вязкости во время производства может быть произведена чем путем периодических испытаний на разжижение.

Introduction

In resin production, particularly of alkyd and oleoresinous products, measurement of viscosity is one of the criteria by which the completeness of the reaction is judged. The thinning test and bubble tube method commonly used possesses the disadvantages of delay and inaccuracy involved in obtaining a result. The delay is particularly serious for resins that show rapid increase in viscosity towards the end of the reaction, e.g. short oil alkyds. In view of this, the development of a continuously recording viscometer has been considered by several workers, and some have been described.[1,2,3,4] In general, these instruments have been expensive to install and difficult to maintain. As in much resin manufacture it is necessary to sample periodically for other control tests, such as acid value, consideration has been given to the development of a quick, simple and reliable method of determining viscosity on this sample. A modified version of the ICI cone and plate viscometer[5] has been developed which can operate at various set temperatures in the range 25°C-150°C and measures viscosity in the range 0-10 poises. By choosing a satisfactory temperature, the melt viscosity of the unthinned resin can be made to give sensible readings on the viscometer.

Discussion

The commonly used method of measuring the increase in viscosity of a resin during manufacture is to take samples periodically, thin them with a certain percentage of solvent, and measure the viscosity of the solution at 25°C by means of a bubble tube or other simple viscometer. This test takes 15-20 minutes and is limited in accuracy by the thinning technique adopted and the method of viscosity measurement. Such a test is reasonably satisfactory for long oil resins, but it is not so satisfactory for short oil resins which body quickly.

The need for an instrument for continuously recording viscosity during resin manufacture has been recognised for many years; some instruments have been developed but they have not been widely adopted. One of the difficulties of measuring viscosity directly in the cooking vessel is that viscosity changes at the cooking temperature are small and usually in the 0-100 centipoise region. Viscosity measurement in this range involves the use of delicate instruments which are not very suitable for plant use. However, the installation of a suitably designed recording viscometer would not, in general, remove the necessity to sample for other properties. Since this necessity for sampling existed, it seemed desirable to consider a simple viscometer which could give a quick and accurate determination of viscosity on a sample taken directly from the kettle.

Experience gained in developing continuous viscometers had shown it to be advantageous to cool the resin from the kettle to 100°C in order to bring the viscosity in the region of 5-10 poises, in which range it is easy to carry out measurements with a robust instrument. In view of this, thought was given to the development of a thermostatted viscometer that would measure the viscosity of small samples quickly at temperatures below the cooking temperature. This would eliminate the thinning procedure, and give a quick and direct reading of the melt viscosity of the resin at a specific temperature.

The ICI cone and plate viscometer[5] was developed to measure the viscosity of paint samples at 25°C at a rate of shear of 10,000 sec^{-1}. This instrument measures the viscosity of very small samples in the range 0-10 poises and is quick and easy to use and to clean. Consideration was given to the modification of this instrument for hot resin work. The cone and plate principle was considered to be good for this application, as the small sample needed could quickly be brought to temperature, and the simple construction was robust and easy to clean. The high shear rate of 10,000 sec^{-1} appeared to be no disadvantage, as most resin melts are near Newtonian, and the viscosity is independent of the rate of shear.

Experiments with a prototype instrument showed that it was necessary to equip the cone and plate with thermostatic controls that could be set at a variety of temperatures, in order that a wide variety of different resins could be brought to a suitable viscosity for measurement on the standard 0-10 poise viscometer. The temperatures chosen were 25°C, 50°C, 75°C, 100°C, 125°C and 150°C. The 25°C position is intended for calibration purposes and can only be used when the ambient temperature is less than 25°C, as the viscometer is not fitted with the Frigistor used in the standard 25°C instrument.

Most of the modifications are in the base of the instrument, which has a different cone and plate construction to minimise thermal gradients in the resin sample. A multi-range transistorised thermostat has been developed to control the temperature of the cone and plate to the required limits.

Use of the instrument on the plant has shown that the results are satisfactory and that closer and quicker control of the product can be obtained than with the thinning test method.

Mechanical construction

A diagram of the instrument is shown in Fig. 1. It consists of a base, A, which supports a vertical column, B, and a head assembly, C, which can be raised or lowered by a lever, D. The head assembly is mounted on a casting, E, which is a sliding fit on the column. This casting supports a synchronous motor, F, which has its axis vertical and parallel to the column, B. The body of the motor is modified so that it is held in the casting by means of two ballraces, G, and is free to rotate independently of the rotation of the rotor of the motor. This freedom to rotate is restrained by a phosphor bronze strip torque spring, H, which is attached to the motor body at one end and to a zero adjuster, J, at

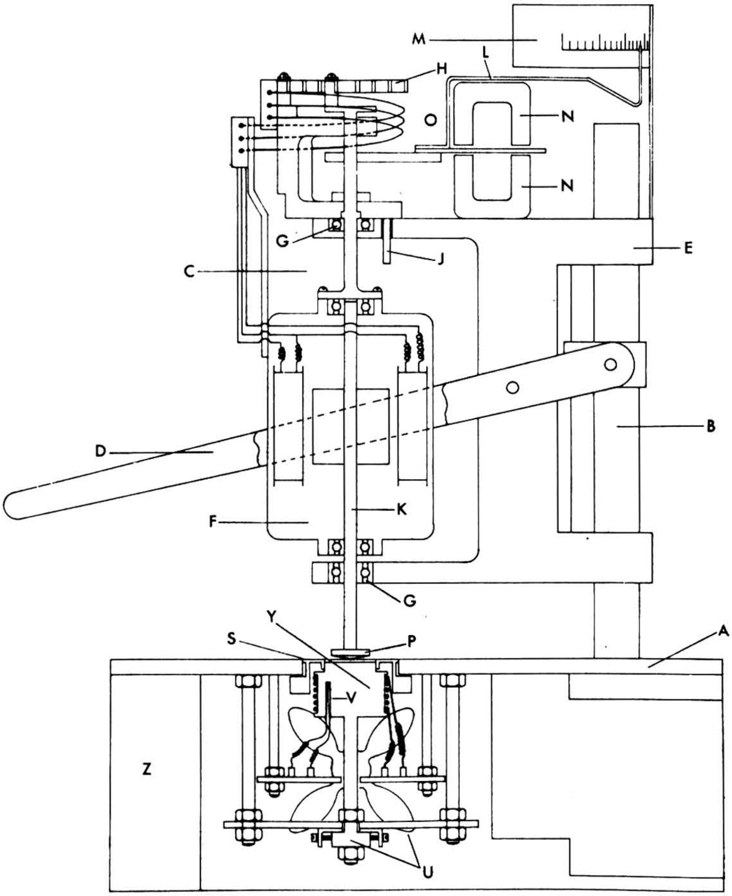


Fig. 1. Sectional diagram of viscometer

the other. In operation, the torque transmitted by the motor shaft, K, gives an equal and opposite torque to the motor body, and this is opposed by the spring. A pointer, L, is attached to the motor body and angular deflections of the motor due to torque are indicated on the scale, M. Damping is arranged by means of an aluminium sector working in the gap of the permanent magnets, N. Three light springs, O, made of phosphor bronze wire insulated with polythene sleeving, serve as electrical conductors to the motor but exert negligible torque compared to the main torque spring. The lower end of the motor shaft carries the detachable cone, P, which is 0.765in in diameter, has an apical angle of 179° and is made of tungsten carbide.

The base of the instrument is formed from the aluminium plate, A, into which is inserted the 1in diameter viscometer plate, Y. The plate assembly is constructed from copper in the form of a waisted cylinder, with a heater winding around its sides; a plate of $\frac{1}{16}$in thick tungsten carbide is brazed to its top and then ground flat. The whole is thermally insulated from the plate by means of the Tufnol collar, S. Fitted into the bottom centre of the plate assembly is a stainless steel threaded tube which passes down through a collar and plate, U, for holding and centring. The temperature sensing thermistors, V, are inserted in drilled holes in the copper base of the plate assembly. A fan is fitted to assist cooling. The base also contains the electronics, W, Z.

Electronics

Several methods of temperature control were considered, and it was decided to use on/off control, providing the sensitivity of the whole system was made sufficiently high to give a short cycling time. The circuit is shown in Fig. 2.

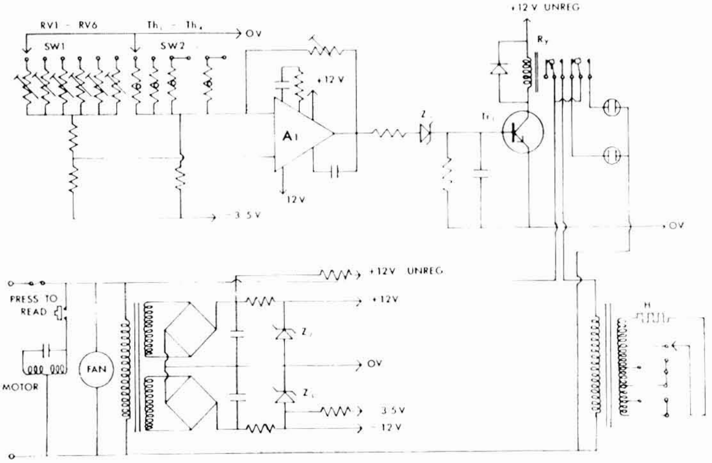
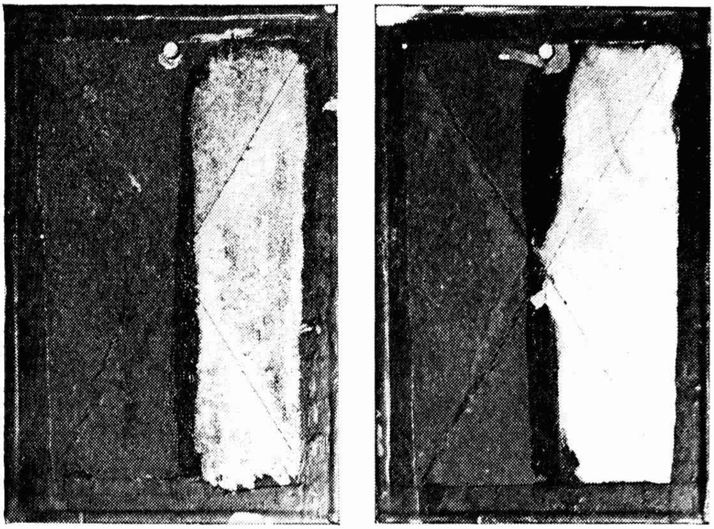


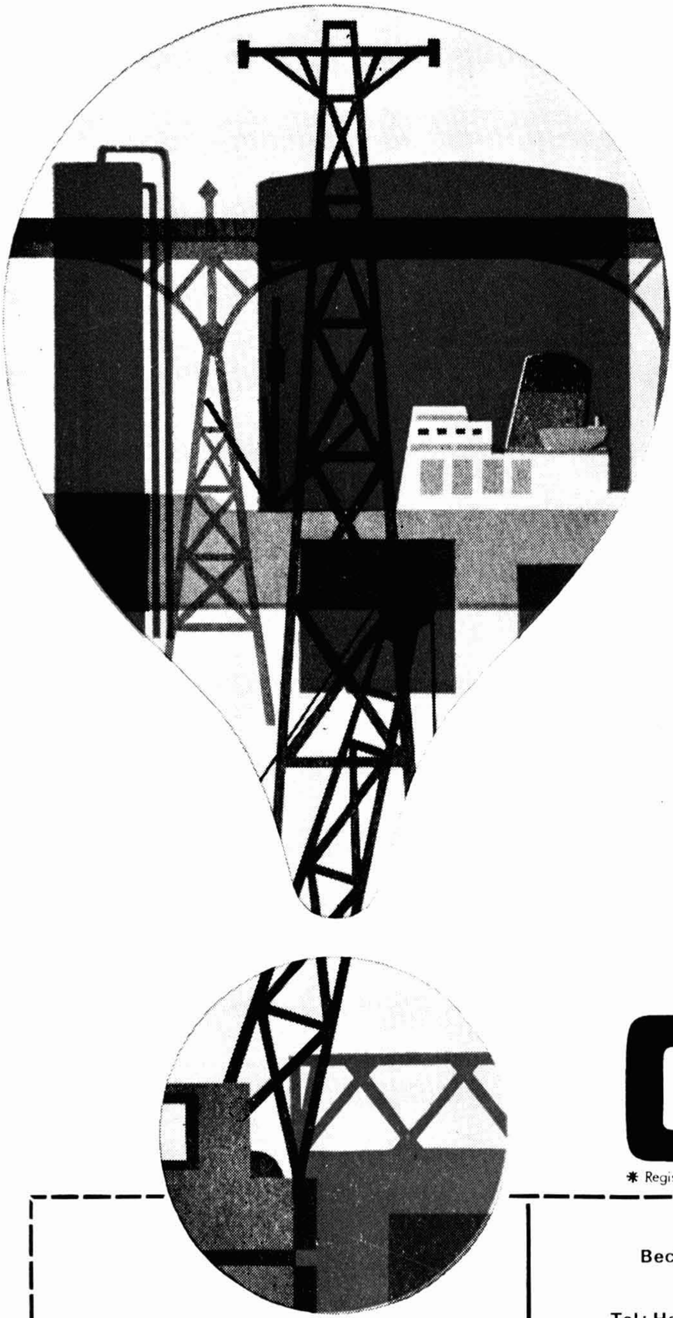
Fig. 2. Instrument wiring diagram

Thermistors were chosen in preference to resistance thermometers or thermocouples, because of their quick response and high resistance/temperature coefficient. Four thermistors, Th_1-Th_4, cover the six temperatures required: the appropriate thermistor together with its balancing preset resistor, RV_1-RV_6, are selected by the range switch, SW_1-SW_2, and enable a DC Wheatstone bridge, balanced at about 1000 ohms, to be used. The out-of-balance signal is fed to a high gain, low drift integrated circuit operational amplifier, A_1. The amplified signal feeds a trigger circuit, Z_1 Tr_1, to operate an electromagnetic relay, Ry, which switches the heater, H, on or off as required. A second set of contacts on relay Ry switch two indicator lamps to show the circuit conditions. The range switch, SW_3, also selects the optimum voltage supply to the heater H. A comprehensive power unit, Zener diode Z_2 Z_3, is incorporated which supplies the appropriate DC voltages, stabilised where necessary, to the amplifier and trigger circuit. The temperature controller was tested by inserting a fine wire thermocouple connected to a Comark temperature indicator in the gap. The control temperature differential at all six set points was better than ±0.2°C over a wide range of ambient temperatures.

Method of use

The instrument should be located in a reasonably draught free position, and connected to a suitable power outlet. The cone and plate should always be in





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contact when not separated for cleaning or loading purposes. The temperature is selected by the range switch and a minimum of 15 minutes allowed for the instrument to reach a steady temperature, which will be indicated by regular flashing of the front panel lights. The zero of the instrument is checked by depressing the push button and adjusting the zero set control as necessary.

The cone is raised and approximately 0.2ml of the sample placed on the plate. The cone is then lowered and approximately 20 seconds allowed for temperature equilibrium, which will again be apparent from the indicator lights. (It is important that sufficient material be used to surround the cone completely when it is in contact with the plate, as the use of insufficient liquid has a serious effect on the viscosity reading whereas an excess has very little effect.) After pressing the push button, the reading may be observed on the scale. The cone should be raised and both cone and plate cleaned with suitable solvent before returning the cone to its rest position in contact with the plate. The loss of volatile components is not significant when this method is used. As indicated above, 15 minutes is a reasonable warm up time for the instrument, but it would normally be switched on permanently in plant use.

Calibration

Initially, the 25°C range was adjusted to the correct temperature by means of the range 1 preset control and a fine wire thermocouple placed in oil between the cone and plate. Standard oils were measured and the torque spring adjusted for correct readings. The remaining 5 ranges were then adjusted to the correct temperature by the same method, using the appropriate preset adjuster.

Viscosity readings for a variety of materials were recorded at three room temperatures i.e. 10°C, 22°C, and 45°C, see Table 1. A range of temperatures

Table 1

Viscosity measurements to determine instrument accuracy at varying ambient temperatures

Range	Material	Viscosity (Poise) at air temperatures		
		10°C	22°C	45°C
150°C	Short oil alkyd Long oil alkyd Shellmex and BP Mexphalte 40/50	6.0 0.6 4.3	6.2 0.6 4.1	6.0 0.65 4.1
125°C	Long oil alkyd Std. oil-196 p @ 25°C	1.1 1.0	1.2 0.9	1.2 0.9
100°C	Long oil alkyd Std. oil-196 p @ 25°C Std. oil-151 p @ 25°C	2.2 2.05 1.8	2.3 2.1 1.8	2.35 2.2 1.8
75°C	Std. oil-196 p @ 25°C Std. oil-151 p @ 25°C Std. oil-98 p @ 25°C	6.2 5.1 3.5	6.2 5.1 3.4	6.25 5.0 3.5
50°C	Std. oil-25 p @ 25°C Std. oil-42 p @ 25°C	4.6 7.1	4.5 7.0	4.45 7.0

was chosen in order to determine the accuracy of the instrument under the high ambient temperature conditions often encountered in resin production plants. It will be seen from Table 1 that, over this range of room temperatures, the viscosity reading variation is less than 1 division and therefore remains within an overall accuracy of ±2 per cent of full scale. A fresh sample of resin or oil was used for each measurement. Self-heating or work heating of the sample is not apparent on the ranges 2-6. Warm up time from 25°C to 150°C at an air temperature of 10°C was less than 10 minutes.

Results

The prototype instrument has been used under plant conditions, where test samples of resin were checked on the high temperature cone and plate viscometer in comparison with the bubble tube test. As shown in Fig. 3, correlation of the two methods was good, the results obtained on the high temperature cone and plate viscometer showing less scatter within the specified limits.

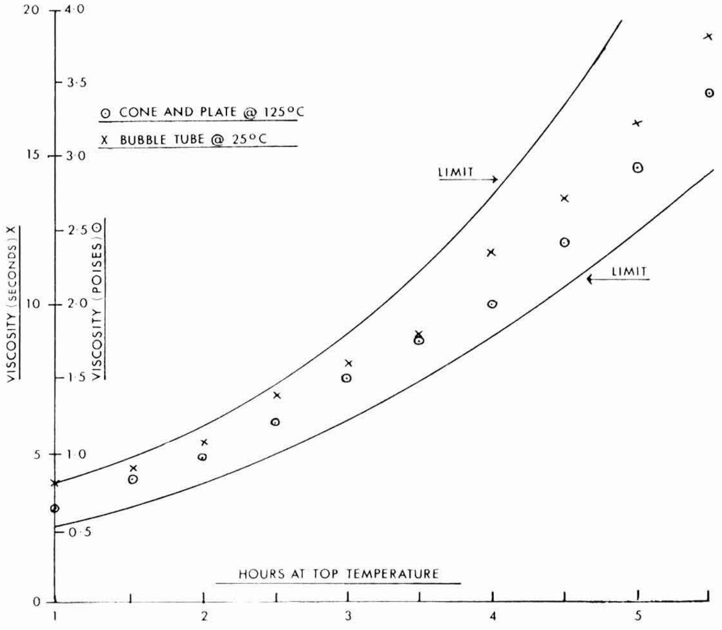

Fig. 3. Study of plant batch of short oil alkyd: Comparison of viscosity by thinning test and cone and plate viscometer

Acknowledgments

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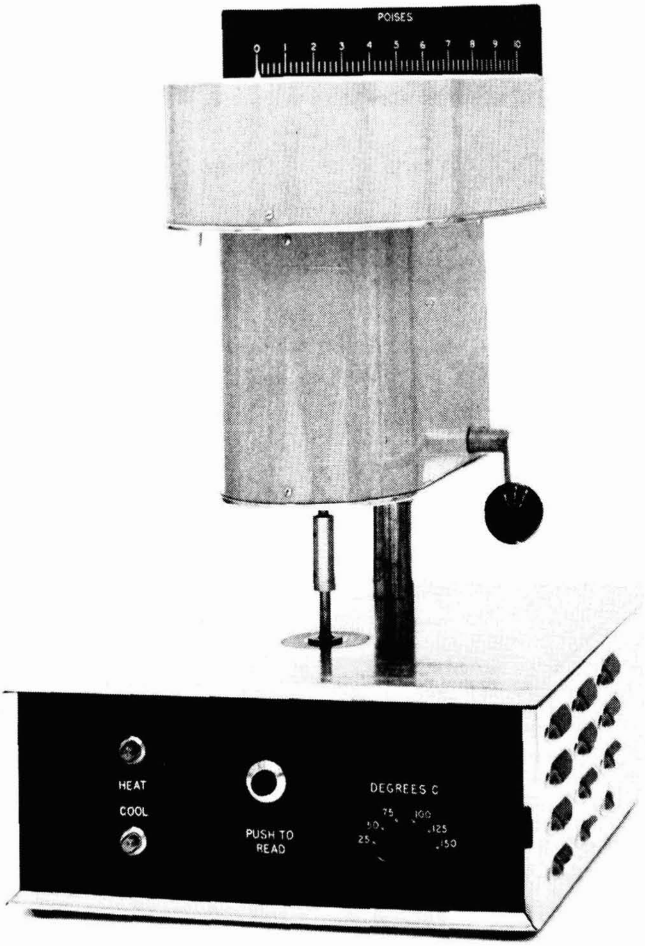

Fig. 4. ICI high temperature cone and plate viscometer

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Sand grinding versus ball milling in relation to pigment particle size*

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Summary

The use of the Joyce-Loebl-ICI disc centrifuge to measure particle size distribution accurately in decorative paint stainers is described.

An attempt is made to use the technique to compare the relative efficiencies of ball milling and sand grinding for three organic pigments in stainer formulations. It is shown that, although sand grinding is, in general, more efficient than ball milling, the relative effect varies with different pigments, and that the current practical use of both mills achieves only a limited degree of dispersion.

The way in which this technique can be used to gain more information on the grinding process, and hence on the physics of paints and inks, is outlined.

Keywords

Equipment primarily associated with:		*Properties, characteristics and conditions primarily associated with bulk coatings*	*Prime pigments and dyes*
analysis, measurement and testing	*manufacturing or synthesis*		
disc centrifuge	ball mill sand mill	particle size	dioxazine violet phthalocyanine blue pigment green B

Broyage à sable contre broyage à billes au point de vue de la grandeur particulaire de pigments

Résumé

On décrit l'emploi du centrifugeur à disque Joyce Loebl-ICI pour mesurer exactement la granulométrie des colorants destinés à la mise à la teinte des peintures décoratives. On fait une tentative d'utiliser cette technique pour faire comparer les rendements relatifs de broyage à billes et à sable lors de la préparation des colorants pour la mise à la teinte à partir de trois pigments organiques. On démontre que, bien que le broyage à sable soit, en général plus efficace que le broyage à billes, l'effet relatif se varie avec de différents pigments, et égalemont que l'emploi couramment suivi en pratique à l'égard de tous les deux types de broyeur n'achève qu'un degré de dispersion assez limité.

On trace les grandes lignes de la manière en laquelle cette technique peut être utilisée pour gagner plus d'information sur le procédé de broyage et aussi sur la physique de peintures et d'encres d'imprimerie.

Sand- und Kugelmühlenresultate Bezogen auf Pigmentpartikelgrösse

Zusammenfassung

Die Anwendung der Joice Loebl-ICI Scheibenzentrifuge zur Messung der genauen Teilchengrössenverteilung in Abtönpasten für Malerlacke wird beschrieben.

Es wird versucht diese Technik zu benutzen, um die relative Wirksamkeit zu vergleichen, wenn drei organische Pigmente in Rezepturen für Abtönpasten auf Kugel- oder Sandmühle gemahlen werden. Dabei erweist sich, dass, obwohl Mahlen mit Sandmühlen im allgemeinen

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*Presented to the Manchester Section on 14 November 1969, and the London Section on 10 December 1969.

wirkungsvoller als mit Kugelmühlen ist, die relative Wirkung bei jedem Pigment verschieden ist, und dass bei der allgemein üblichen praktischen Anwendung beider Mühlen nur ein beschränkter Dispersionsgrad erzielbar ist.

Die Arbeitsweise, mit Hilfe deren diese Technik angewandt werden kann, um mehrüber Mahlprozesse zu lernen und somit auch die physikalische Beschaffenheit von Lacken und Druckfarben, wird skizziert.

Песочная шлифовка в сравнении с шаровой фрезеровкой по отношению к величине пигментных частиц

Резюме

Описывается применение дисковой центрифуги I.C.I. – Джойс Лоебля для точного измерения распределения величины частиц в декоративных красителях.

Делается попытка применения этой техники для сравнения относительной эффективности шаровой фрезеровки и песочной шлифовки, в случае трех органических пигментов в формуляции красителей. Показано что хотя песочное растирание и является в большинстве случаев более продуктивным чем шаровое фрезерование, все же относительный эффект различен для различных пигментов, и что современное практическое применение обеих фрез дает только ограниченную степень дисперсии.

Рассматривается метод применения этой техники для получения более подробных сведений относительно процессов размельчения и тем самым более подробных данных о физике красок и чернил.

Introduction

It is now known from actual measurements that the surface areas of organic pigments are much higher than those of inorganic pigments. These high surface areas mean that the basic particle size of organic pigments is very small, of the order of 0.1 micron. In the manufacture of paints, printing inks, coloured plastics, paper coating mixes, and similar products, the pigment has to be dispersed uniformly throughout the vehicle. It has to be dispersed finely enough to ensure that no visible specks of pigment are left and that a reasonable colour value is obtained from the pigment.

The high surface areas and small basic particle sizes make the dispersion of organic pigments in commercial systems a difficult process. The dispersion process may be a lengthy one or may require considerable energy and sophisticated equipment. Its efficiency will depend on the actual mill used and the type of vehicle used, the pigment concentration and the viscosity of the system. Despite this dependence, and despite the importance of the dispersion process, it has not been possible to measure accurately the extent of the dispersion obtained. It has not, therefore, been possible to compare accurately different methods of dispersing organic pigments.

The aim of the author's work has been to develop a method for measuring pigment dispersion, and the method is described. It is used to compare the efficiency of sand grinding and ball milling processes in the manufacture of paint stainers based on three well known pigments.

Measuring technique

Dispersion has been difficult to measure accurately because measurement of pigment particle size has been a very difficult experimental problem, particularly in non-aqueous systems.

A new approach to the problem was made by Atherton[1] in 1964. He used a disc centrifuge and a sampling probe applying a line start method. The line start made the mathematics of the calculation much simpler. With the sampling probe, samples were taken from a fixed depth whilst the disc was revolving, and the pigment contents of the samples were determined separately. This eliminated uncertainties about the actual pigment concentrations in the various size fractions. In the case of organic pigments, the analysis is relatively simple. The pigment is taken up in a suitable solvent and examined on a spectrophotometer.

A commercial instrument embodying this design was put on the market as the ICI—Joyce Loebl disc centrifuge. All the author's particle size determinations have been carried out on these instruments.

The first problem was to overcome the "streaming" that occurred with the line start method, and to examine critically the instrument and the technique for the determination of the particle size distribution of organic pigments in aqueous pigment pastes. Using a "buffer" layer line start, Beresford[2] reported a high degree of accuracy and reproducibility for such pastes.

With non-aqueous systems, such as paint stainers, the stainer has to be diluted with a suitable solvent or thinner, and a sample of it has to be allowed to sediment in the disc centrifuge, through a suitable spin fluid. This also has to be a solvent or thinner which is miscible with the original stainer.

If the solvents or thinners used attack the disc centrifuge, which is made of Perspex, swelling and distortion of the disc will take place and affect the results. If the organic pigments present in the stainers bleed in the spin fluid, then during the centrifugal sedimentation the particles will slowly dissolve and the results will again be inaccurate.

For the present series of experiments, therefore, the paint stainers used were based on a simple resin system which could be diluted with white spirit or carbon tetrachloride, and the three pigments used were a copper phthalocyanine blue (CI Pigment Blue 15), a pigment green B (CI Pigment Green 8), and a dioxazine violet (CI Pigment Violet 34). All are non-bleeding in white spirit and carbon tetrachloride. Under these restrictions, absence of powerful solvents and using non-bleeding pigments, it was found that the size distribution of organic pigment particles in non-aqueous paint stainers could be determined accurately and reproducibly.

Having tested the technique thoroughly, it was decided to prepare paint stainers of the pigments by two well known grinding techniques, namely ball milling and sand grinding. A large number of stainers were prepared, and each was sand ground or ball milled for a different time, the time ranging from very short periods to very long ones.

The size distribution of the pigment in each stainer was measured on the disc centrifuge.

In this way, the effect of progressive grinding by both milling techniques was followed.

Experimental details

Ball milled stainers

	parts by weight
Pigment	16.0
A long oil soya penta alkyd resin (70 per cent solids) . . . Beckosol P.470	40.0
White Spirit	42.0

This formulation was milled for the required time and then 50 parts of the long oil soya penta alkyd resin was added and the diluted base milled for a further 15 minutes. Finally, a further 47.2 parts of the long oil soya penta alkyd resin was added, together with 4.8 parts of a drier solution containing approximately 10 per cent by weight of methyl ethyl ketoxime, approximately 15 per cent by weight of 6 per cent naphthenate solution and white spirit solvent. The pigment to binder ratio of the stainer composition so prepared was 1 to 6, the medium solids content was 52.17 per cent and the pigmentation level was 8 per cent. The ball milling was carried out in glass jars, capacity 325ml, containing 320 parts of steatite balls of ⅜in diameter (0.975cm), the jars being allowed to revolve on rollers at a speed of 104 revs/minute.

Sand grinding

A mill base was prepared by sand grinding the following formulation for a specified time:

	parts by weight
Pigment	28
A long oil soya penta alkyd resin (70 per cent solids) . . . Beckosol P.470	198.5
White Spirit	73.5
171.4 parts of this mill base containing	
Pigment	16.0
Resin	113.4
White Spirit	42.0

were treated, with stirring, with 4.8 parts of the drier solution (as in the ball milling series) and 23.8 parts of the same resin.

The pigment to binder ratio of the stainers composition so prepared was 1 to 6, the medium solids content was 52.17 per cent and the pigmentation level was 8 per cent.

The sand grinding was carried out on a laboratory sand grinder at 2,580 revolutions per minute, using Ottowa sand. A diagram of the grinder is shown in Fig. 1.

The three pigments used were:

Irgalite Blue GLS, a 100 per cent β-form phthalocyanine blue, (C.I. Pigment Blue 15) having a specific surface area of $50m^2g^{-1}$ and

Irgalite Green DBN Conc. (C.I. Pigment Green 8) having a specific surface area of $99m^2g^{-1}$.

Irgazin Violet 6RLT, a dioxazine violet (C.I. Pigment Violet 34) having a specific surface area of 47.3m^{2}g^{-1}.

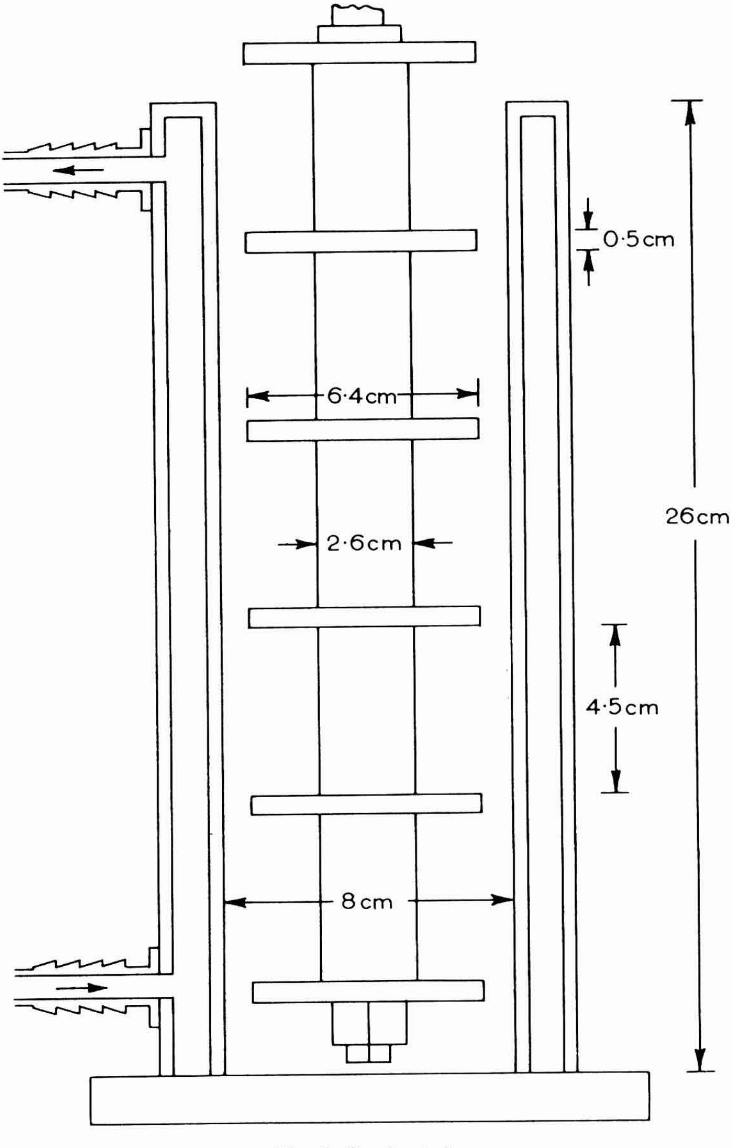

Fig. 1. Sand grinder

The particle size distribution of the pigments in the stainers was determined in the following manner, using the I.C.I.—Joyce Loebl disc centrifuge: samples of the stainers were reduced with stirring to a pigment content of 0.4 per cent with white spirit. A buffered layer technique was used. The spin fluid used was a white spirit/carbon tetrachloride mixture containing 70 parts by volume of white spirit; the buffer layer was 1ml of white spirit, and 1ml of the diluted stainer was injected on to the surface of the buffer layer when the disc was rotating at the selected speed. The disc was allowed to rotate for pre-determined times and then the contents removed to a fixed depth by the sampling probe. The pigment content of the samples was determined by analysis by the methods shown.

Phthalocyanine blue and dioxazine violet

Each sample, representing a specific undersize fraction, was evaporated to dryness on a steam bath. The residue was dissolved in concentrated sulphuric acid and the volume was made up to 50 parts by volume. A 5.0 parts by volume aliquot was then added with stirring to 45 parts by volume of a 0.1 per cent weight/volume aqueous solution of Triton X-100. This is a non-ionic surfactant believed to be a condensation product of tertiary octyl phenol and ethylene oxide.

The optical density at 610 μ for the blue and 630μ for the violet was measured within 5 minutes of the addition. The concentration of the pigment was then read from a previously determined calibration graph.

Pigment Green B

Each sample, representing a specific undersize fraction, was evaporated to dryness on a steam bath. The residue was then dissolved in dimethyl formamide, the volume made up to 50 parts by volume, and the optical density measured at 700μ. The concentration of pigment was then read from a previously determined calibration graph.

In this way the size distribution curve of each stainer was accurately determined.

Results

As the times of ball milling for the green and blue stainers ranged from 1 hour to 72 hours, and the times of the sand grinding ranged from 15 minutes to 8 hours, the number of actual stainers, and hence of particle size distribution curves, is considerable (approximately 50) and it would be impracticable to illustrate all the curves. A selection of them is given in Figs. 2-7.

Fig. 2 illustrates the curves for ball milled stainers of Blue GLS for 2hr, 12hr and 72hr.

Fig. 3 illustrates the curves for sand ground stainers of Blue GLS for ¼hr, 2hr and 8hr.

Fig. 4 illustrates the curves for ball milled stainers of Green DBN Conc. for 4hr, 24hr and 72hr.

Fig. 5 illustrates the curves for sand ground stainers of Green DBN Conc. for ½hr, 2hr and 8hr.

Fig. 6 illustrates the curves for ball milled stainers of Violet 6RLT for 2hr, 12hr and 72hr.

Fig. 7 illustrates the curves for sand ground stainers of Violet 6RLT for ¼hr, 2hr and 8hr.

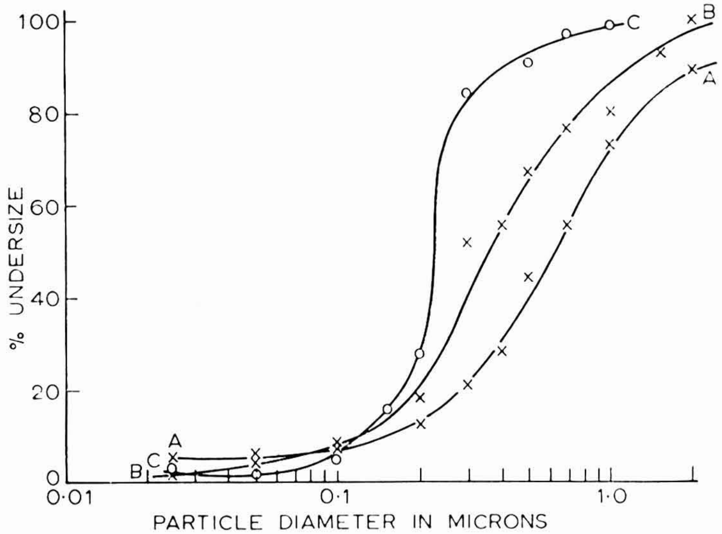

Fig. 2. Particle size distribution of Irgalite Blue GLS after, A 2hr, B 12hr, C 72hr ball milling

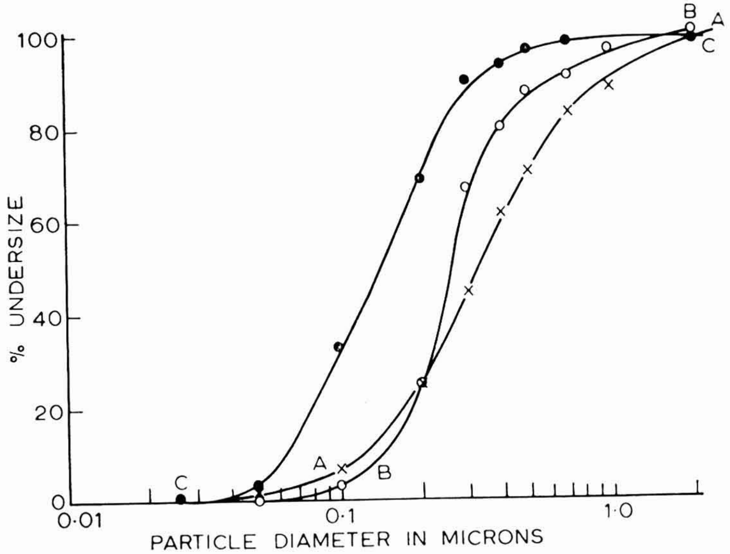

Fig. 3. Particle size distribution of Irgalite Blue GLS after, A 15min, B 2hr, C 8hr sand grinding

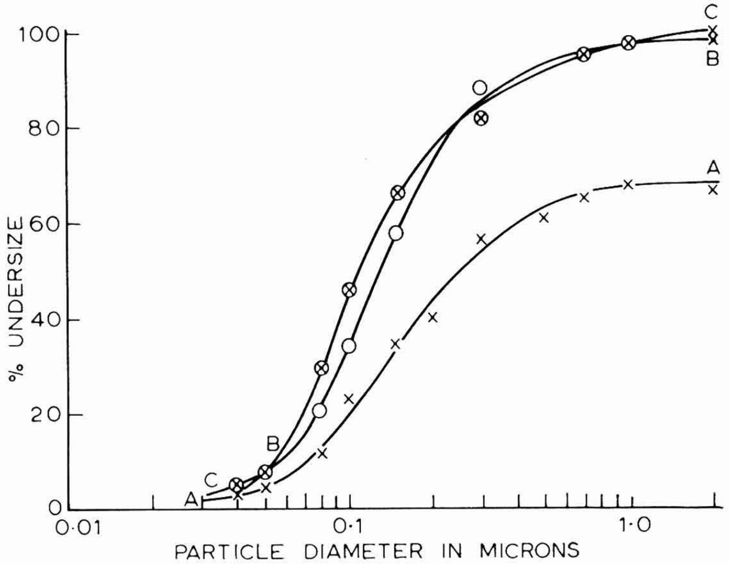

Fig. 4. Particle size distribution of Irgalite Green DBN after, A 4hr, B 24hr, C 72hr ball milling

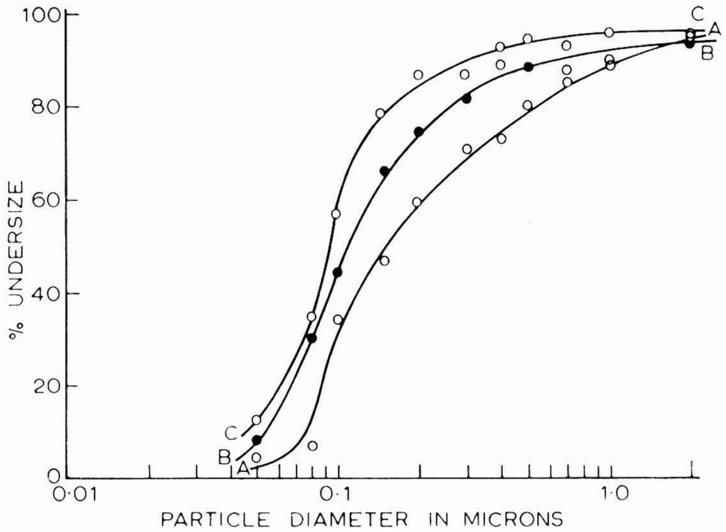

Fig. 5. Particle size distribution of Irgalite Green DBN after, A 30min, B 2hr, C 8hr sand grinding

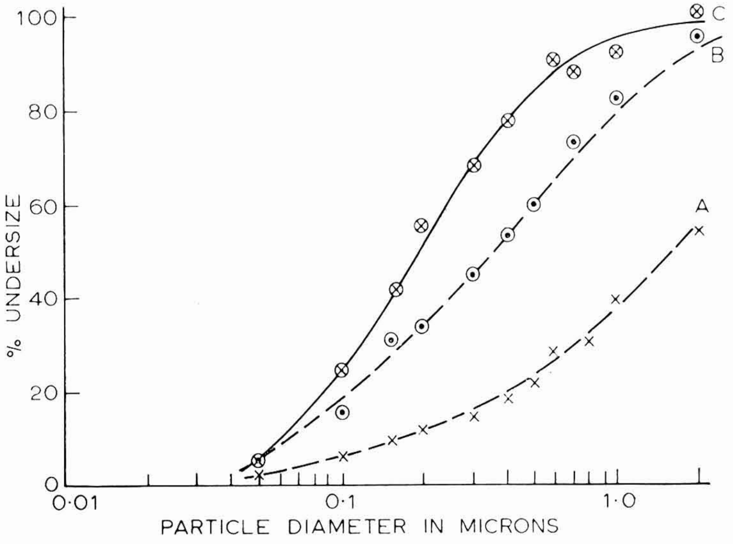

Fig. 6. Particle size distribution of Irgazin Violet 6RLT after, A 2hr, B 12hr, C 72hr ball milling

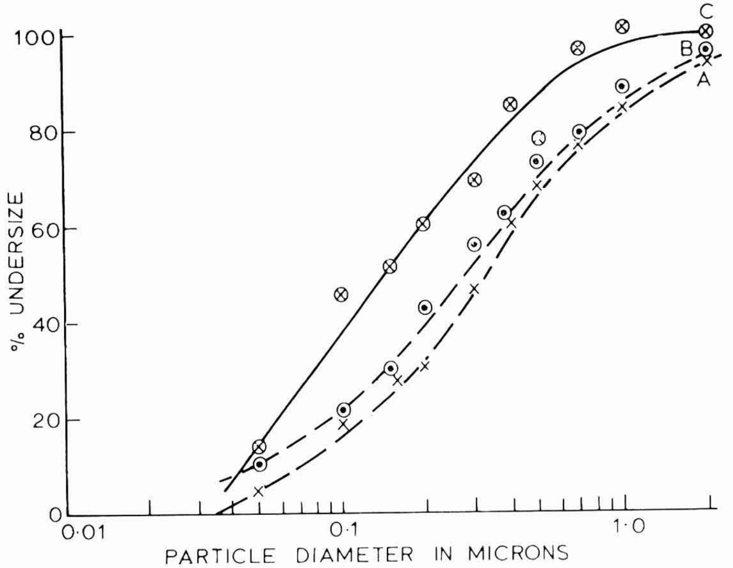

Fig. 7. Particle size distribution of Irgazin Violet 6RLT after, A 15min, B 2hr, C 8hr sand grinding

In order to follow the reduction of particle size of the pigment with time, the various size distribution curves can be represented by a single figure, namely the 50 per cent diameter. This is defined as the size below and above which there is an equal weight of pigment. As the pigment particles in the stainers are not monodispersed, the 50 per cent diameters are not representative of the stainers on an absolute scale, but their use does enaole a fairly concise picture to be obtained of the progress of grinding with time.

Table 1 gives the 50 per cent diameters of the Blue GLS ball milled stainers and the corresponding milling times.

Table 2 gives the 50 per cent diameters of the Blue GLS and ground stainers and the corresponding grinding times.

Table 3 gives the 50 per cent diameters of the Green DBN Conc. ball milled stainers and the corresponding milling times.

Table 4 gives the 50 per cent diameters of the sand ground Green DBN Conc. stainers and the corresponding grinding times.

Table 5 gives the 50 per cent diameters of the Violet 6RLT ball milled stainers and the corresponding milling times.

Table 6 gives the 50 per cent diameters of the Violet 6RLT sand ground stainers and the corresponding grinding times.

Table 1

Ball-milled Blue GLS stainers

Time of ball milling in hours	50% diameter in microns
½	0.675
1	0.565
2	0.565
4½	0.415
6	0.345
7	0.395
8	0.405
10	0.305
12	0.335
16	0.300
20	0.290
24	0.285
30	0.300
36	0.270
48	0.225
72	0.215

Table 2

Sand ground Blue GLS stainers

Time of sand grinding in hours	50% diameter in microns
¼	0.300
1	0.260
2	0.235
4½	0.160
5	0.160
6	0.140
8	0.130

The results given in Tables 1-4 are shown graphically in Fig. 8 and with a larger time scale in Fig. 9.

Table 3

Ball milled Green DBN Conc. stainers

Time of ball milling in hours	50% diameter in microns
½	2
1½	0.834
2	0.465
3	0.465
4	0.265
8	0.160
24	0.120
72	0.100

Table 4

Sand ground Green DBN Conc. stainers

Time of sand grinding in hours	50% diameter in microns
¼	0.135
½	0.155
1	0.125
2	0.110
4	0.110
6	0.096
8	0.095

Table 5

Ball milled 6RLT stainers

Time of ball milling in hours	50% diameter in microns
2	1.60
5	0.695
6	0.54
12	0.345
18	0.401
24	0.255
48	0.215
72	0.19

Table 6

Sand ground Violet 6RLT stainers

Time of sand grinding in hours	50% diameter in microns
¼	0.32
½	0.355
1	0.285
2	0.270
4	0.185
6	0.15
7	0.145
8	0.14

The results given in Tables 5 and 6 are shown graphically in Fig. 10 and with a larger time scale in Fig. 11.

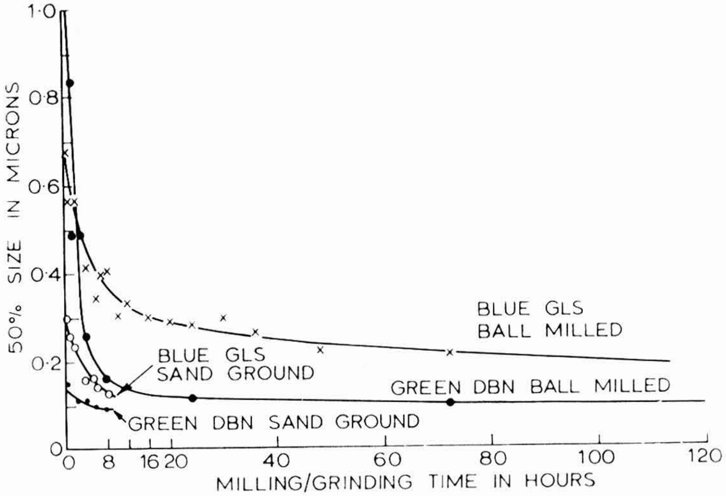

Fig. 8. Milling and grinding times to give 50% diameter for Irgalite Blue GLS and Irgalite Green DBN

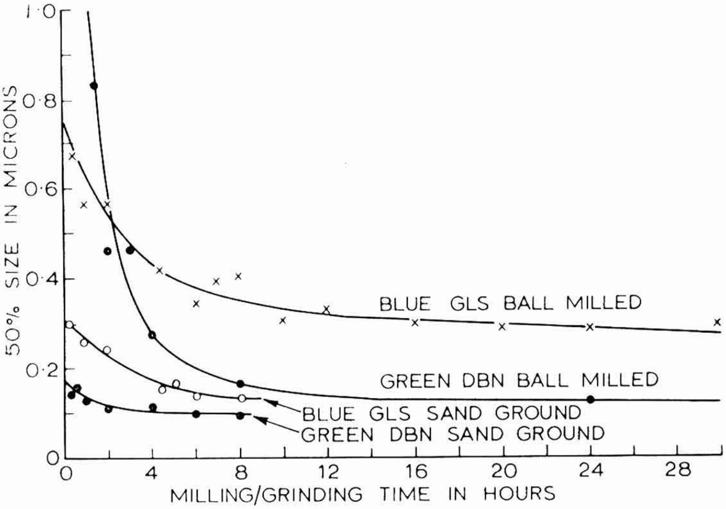

Fig. 9. Milling and grinding times to give 50% diameter for Irgalite Blue GLS and Irgalite Green DBN

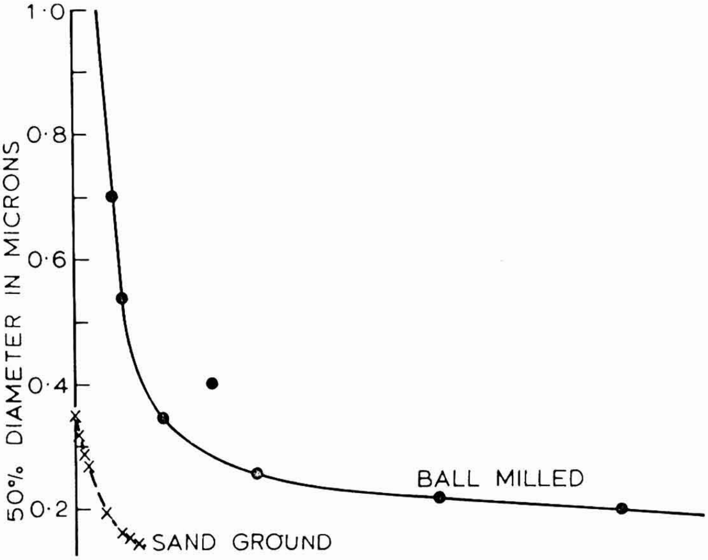

Fig. 10. Relation between milling and grinding time and 50% diameter for Irgazin Violet 6RLT

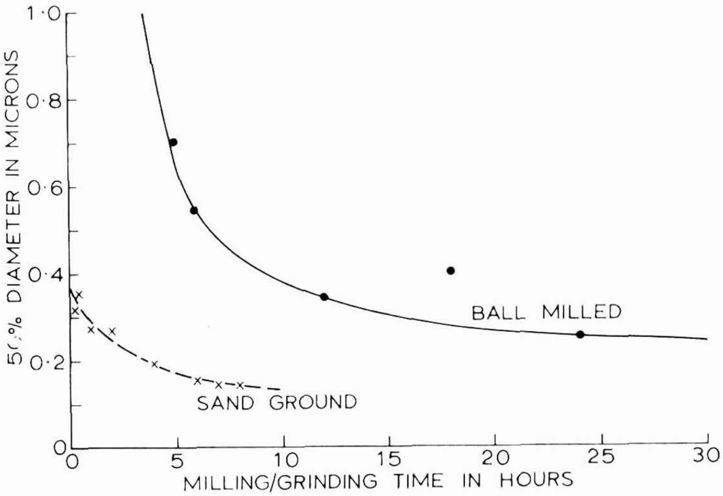

Fig. 11. Relation between milling and grinding time and 50% diameter for Irgazin Violet 6RLT

Discussion

The results can be discussed or assessed in a number of ways. Here they are surveyed from two aspects.

First, a straightforward comparison is made of ball milling and sand grinding in terms of time and the actual degree of dispersion achieved. Secondly, the results are analysed in detail, in order to study the manner in which the various sizes of particles are reduced on progressive grinding.

Comparison of sand grinding and ball milling

A study of the graphs yields a number of interesting points. Sand grinding is very much more efficient than ball milling, both in terms of time and ultimate fineness. This fact is, of course, well known from practical experience, but the graphs show the relationship in more detail. For example, we see that, for the blue, 15 minutes' sand grinding is equivalent approximately to 18 hours' ball milling, whilst approximately $2\frac{1}{2}$ hours' sand grinding is equal to 72 hours' ball milling.

Despite the greater efficiency of the sand grinding process, complete dispersion of the pigment is not achieved even after 8 hours' sand grinding. With the blue, the 50 per cent diameter of the stainer is reduced to 0.130μ, but from the surface area of the powder ($50 m^2 g^{-1}$) and its density (1.5), the basic particle size is known to be 0.08μ. From the actual size distribution curve for the stainer, sand ground for 8 hours, the effective surface area of the pigment in the stainer can be calculated, and is equal to $31 m^2 g^{-1}$. The degree of dispersion of the blue in this stainer is, therefore, given as:

$$\frac{\text{effective surface area}}{\text{nitrogen surface area}} \times 100 = \frac{31}{50} \times 100 = 62 \text{ per cent}$$

For the 72 hour ball mill grind, the degree of dispersion, calculated in a similar manner, is only 38 per cent.

The figures for the degree of dispersions of the stainers ball milled for 72 hours and sand ground for 8 hours of all three pigments are given in Table 7.

Table 7
Degree of dispersions of stainers

Grind	Degree of dispersion (%)		
	Blue GLS	Green DBN	Violet 6RLT
72 hours' ball milling	38	37	59
8 hours' sand grinding	62	46	83

These figures show that ball milling is an inefficient form of grinding for organic pigments in *an absolute sense* i.e. in its ability to break down the pigment aggregates into their basic pigment particles.

Although more efficient, sand grinding of organic pigments for 8 hours is still far from being 100 per cent efficient.

The results given in Tables 2, 4 and 6, and illustrated graphically in Figs. 8-11, demonstrate clearly that the sand grinding times normally used in industry, from 5-20 minutes, are much too short to achieve complete dispersion of the pigments.

The same tables and graphs also show that the rate at which the particle size is reduced by either grinding process varies from pigment to pigment.

A comparison of the effectiveness of sand grinding and ball milling for each pigment can also be made from Figs. 8-11.

Such a comparison is made in Table 8.

Table 8
Comparison of sand grinding and ball milling times

Time of sand grinding	Equivalent time of ball milling		
	Green BBN	Blue GLS	Violet 6RLT
¼ hour	8 hours	20 hours	11-12 hours
½ hour	10 hours	24 hours	13 hours
1 hour	12 hours	36 hours	17 hours
2 hours	80 hours	60 hours	24-26 hours
4 hours			72 hours

Again it will be seen that the comparison between the two grinding processes varies from pigment to pigment. The inference from these results is that each pigment must be treated as an individual in respect to its breakdown on grinding, and that it is impossible to generalise about organic pigments in terms of their dispersion behaviour.

This is not altogether surprising. The texture of pigments is known from experience to vary considerably, even though it has not been possible to measure it.

It has been shown that both techniques, in the laboratory, are inefficient in an absolute sense. In industrial use, the absolute efficiency of the two grinding processes is likely to be even lower, because the grinding times used are considerably shorter.

Their efficiency, on a practical scale (disregarding economics) may be much better, but to determine this, one would have to know the relationship between the colour strength of the stainers and their particle size distributions. In both grinding processes, the particle size is still being reduced with further grinding for all three pigments. If, therefore, colour strength was directly proportional to particle size, the colour strength would not have reached a maximum after 72 hours' ball milling or 8 hours' sand grinding.

If colour strength increased as the particle size was reduced, to a certain point only, and then levelled off or even went through a maximum, it would be impractical and unnecessary to grind below that particular point. The practical point to which grinding should be taken, therefore, is dependent on the relationship between colour strength and particle size for the particular pigment. This relationship will vary from pigment to pigment, as it is a function of the optical constants of the pigment.

If economic factors are taken into account, the position becomes more complex. The cost of extra grinding can be offset in part by increases in colour strength achieved by it. If the pigment is cheap, e.g. the pigment green B, the extra colour strength may not be worth while, but if it is dear, as in the case of the dioxazine violet, the opposite may be the case.

Other factors may enter into the picture, grouped under the general heading of performance. The gloss will increase with dispersion, and if maximum gloss is required, then the extra grinding must be used. There is also a possibility that better dispersion of the pigment may substantially improve the weathering properties of paint films, and if this is important then the extra grinding may be worth while.

The actual dispersion required to give the requisite properties at the lowest price is therefore dependent on many external factors in a way not yet determined. Now that the degree of dispersion can be measured, in decorative paint stainers at least, it should be possible to determine the relationship between dispersion and these various factors.

What has clearly emerged from the results is:

each pigment will have to be examined separately, and

current practice in ball milling and sand grinding, especially the latter, only achieves low degrees of dispersion.

Of the three organic pigments examined, the colour strengths of the blue and violet stainers have been found to be highly dependent on the size distribution. Even after 72 hours of ball milling and 8 hours of sand grinding, the colour strength has not reached a maximum.

In the case of the green, a different picture is obtained. This pigment breaks down rapidly on ball milling, and after 12 hours the 50 per cent diameter is approximately 0.11μ. Coupled with this rapid breakdown is the observed fact that the colour strength of the pigment green B is found to increase only very slowly as the 50 per cent diameter is reduced from 0.5μ down to 0.1μ. In terms of colour strength, therefore, there is little to be gained by ball milling this pigment for periods greater than 12 hours.

From the author's experience and the general consistency of the results, it is believed that the technique described for measuring the size distribution of organic pigments in decorative paint stainers is satisfactory, subject to the limitations already mentioned.

Analysis of the size distribution curves

Apart from the comparisons of sand grinding and ball milling already discussed, further interesting information can be obtained from the size distribution curves if they are examined or analysed in a different way.

In this approach, the percentage by weight of particles under a specific size is plotted against time of grinding, the data being read off from the individual size distribution curves. The data obtained in this way for the ball milled green, blue and violet stainers are shown graphically in Figs. 12, 13 and 14. The data from grinding times greater than 36 hours has been omitted from the graphs in Figs. 12 and 13 to keep the scale reasonable.

It can be seen from these graphs that, as the ball milling proceeds, the percentage by weight of particles under 2 microns increases rapidly. The percentage by weight under 1 micron increases a little less rapidly, and so on. At low particle sizes, the weight percentage undersize no longer increases.

For the green, in Fig. 12, the percentage of particles under 0.05 microns is virtually independent of the time of ball milling.

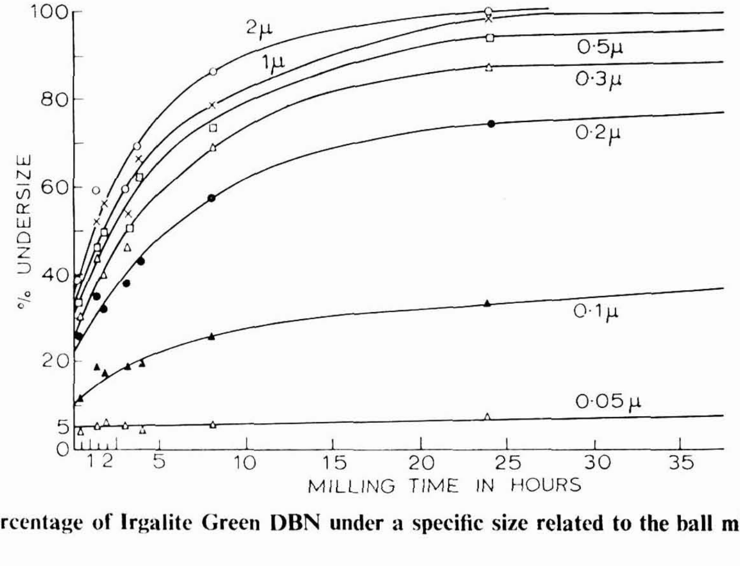

Fig. 12. Percentage of Irgalite Green DBN under a specific size related to the ball milling time

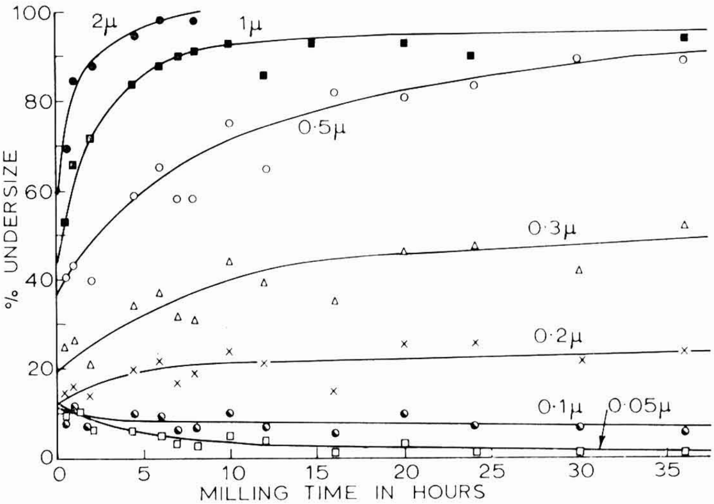

Fig. 13. Percentage of Irgalite Blue GLS under a specific size related to the ball milling time

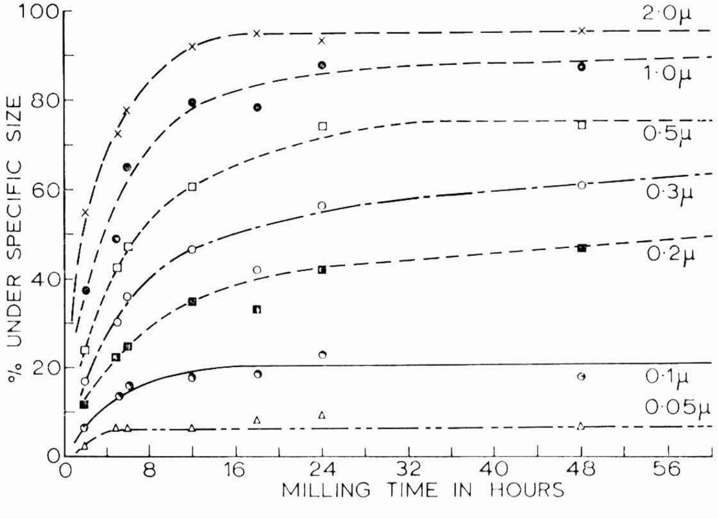

Fig. 14. Percentage of Irgazin Violet 6RLT under a specific size related to the ball milling time

For the blue, in Fig. 13, with particles of 0.1 micron, the weight percentage *decreases* very slowly with time of milling. With particles of 0.05 microns, the decrease in weight percentage with time is more noticeable.

For the violet, the percentage of particles under 0.05 microns is virtually independent of time of milling.

The author believes that these results provide experimental proof of the dynamic nature of grinding. The shearing conditions in the mill provide the energy to break down the large aggregates of pigment particles, but they also provide smaller particles with opportunities to collide with, and possibly unite with, other small particles to form aggregates. In the case of the ball milled blue paint stainers, the forces of attraction between two particles which, on contact, are big enough to form an aggregate of 0.1 micron in size, are roughly equal to the kinetic energy required to break down aggregates of 0.1 micron size. In the case of the green and violet stainers, the equilibrium is reached at sizes of 0.05 microns.

The corresponding data for the sand ground green and violet stainers is given in Figs. 15 and 16 in graphical form and the data for the sand ground blue stainers in Figs. 17 and 18.

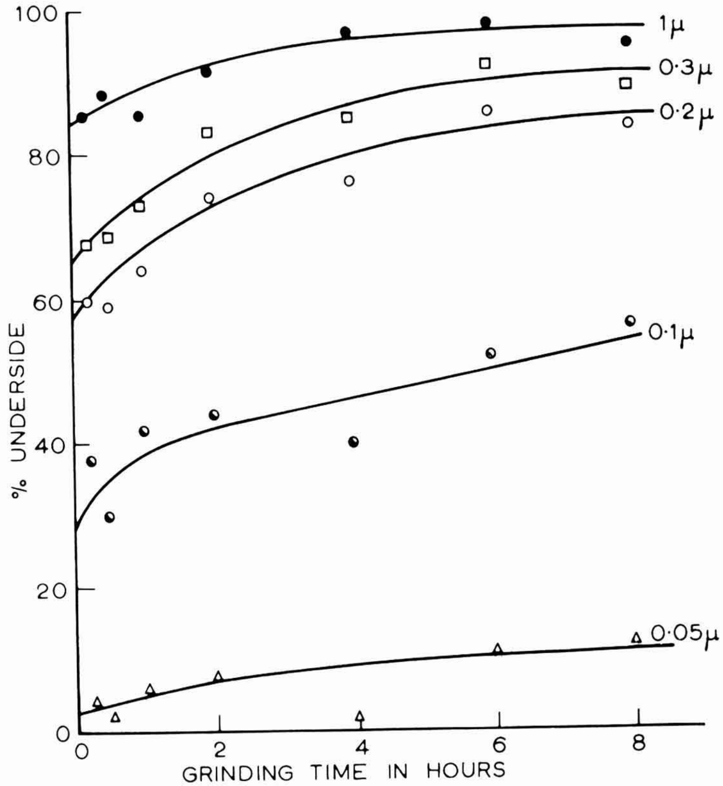

Fig. 15. Percentage of Irgalite Green DBN under a specific size related to the sand grinding time

In the case of the green and violet, the curves follow the expected pattern. The percentage by weight of particles under a specific size increases with time of grinding, but the rate of increase slows down as the size in question gets smaller. The amount of pigment under 0.05 microns only rises very slowly with time of sand grinding.

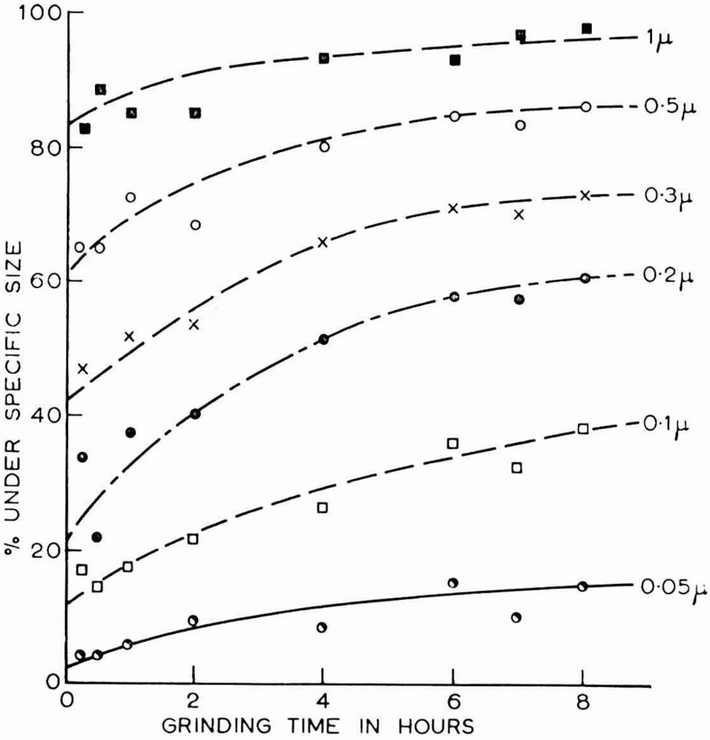

Fig. 16. Percentage of Irgazin Violet 6RLT under a specific size related to the sand grinding time

The curves for the blue are somewhat different. They follow the expected pattern down to sizes of 0.3 microns but the curves for the small particles such as 0.2, 0.1 and 0.05 microns are very different. They appear to be independent of time of milling up to 4 hours' sand grinding. In the fifth hour of sand grinding, they show a definite change, the amounts under these sizes increasing.

Experimentally, a considerable increase in viscosity was noted in this period. If the speed of agitation was maintained, this would mean that greater shearing or disruptive energy would be applied to the aggregates of particles and the number of smaller particles would consequently increase.

This aspect of sand grinding should be investigated further.

Storage trials

The size distributions of a number of stainers were repeated after they had been standing in the laboratory for a period of 6-7 months. The results for some of the GLS stainers are given in Figs. 19, 20 and 21. There appears to be a slight, but definite, coarsening of the stainers. In the three examples given, the 50 per cent particle size increases by 0.03μ, 0.07μ and 0.08μ.

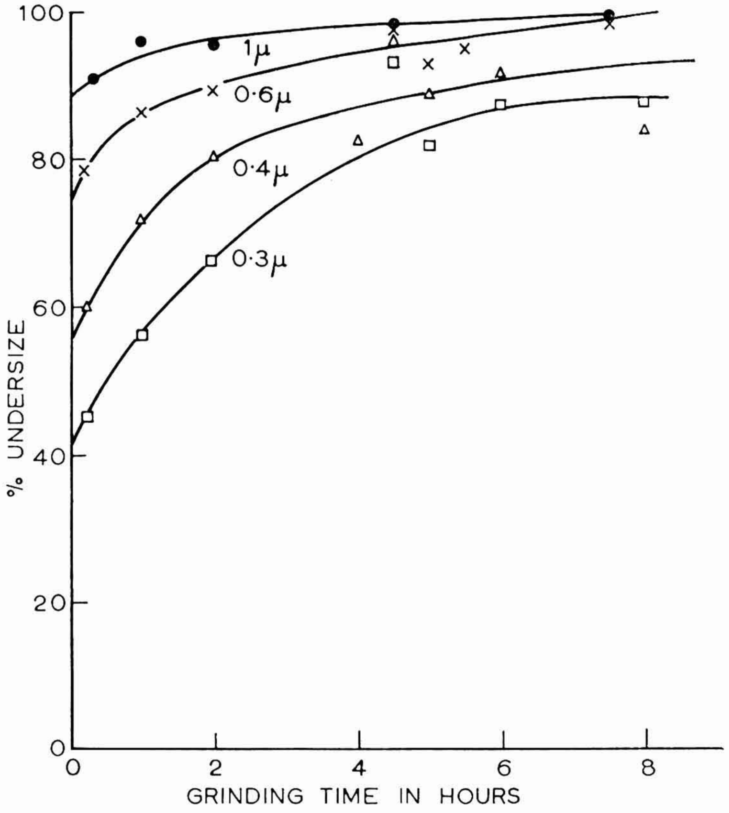

Fig. 17. Percentage of Irgalite Blue GLS under a specific size related to the sand grinding time

Conclusion

The author believes that the Joyce Loebl—I.C.I. disc centrifuge can be used to measure pigment particle size distribution accurately in decorative paint stainers if the pigments are non-bleeding.

Using this instrument, the size reduction achieved in stainers based on three organic pigments by laboratory ball milling and sand grinding techniques has been followed.

The results obtained have been discussed and analysed in detail. Two main facts have emerged, namely that pigments react differently from each other, and that conventional grinding techniques only achieve a limited degree of dispersion.

As to the future, the author feels that if this or similar techniques for the accurate measurement of dispersion can be extended to other pigments, and to a wider range of vehicles, it should be possible to get a much more basic knowledge

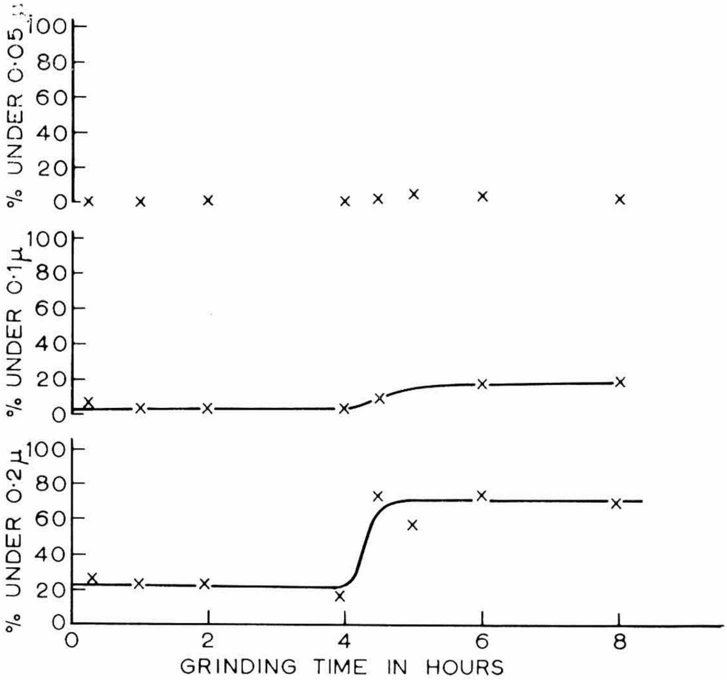

Fig.18. Percentage of Irgalite Blue GLS under a specific size related to sand grinding time

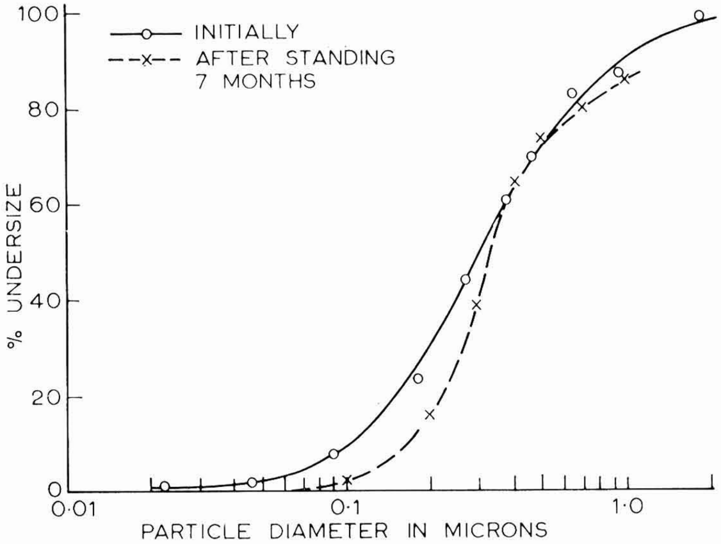

Fig. 19. Particle size distribution of Irgalite Blue GLS after 15 minutes' sand grinding

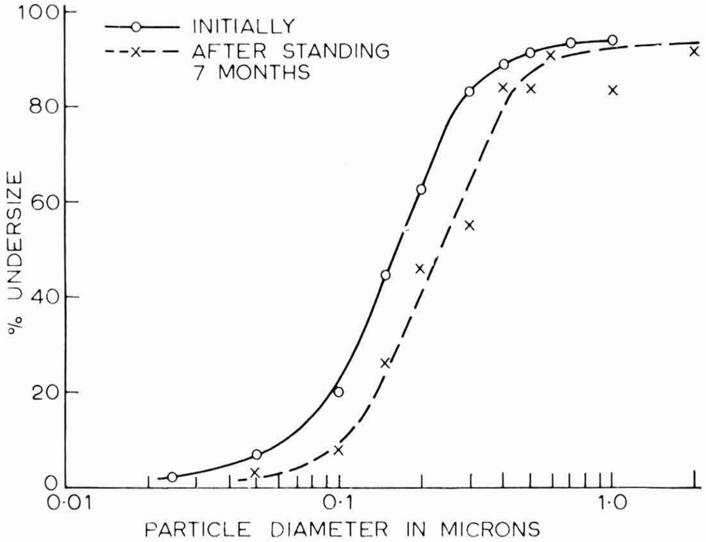

Fig. 20. Particle size distribution of Irgalite Blue GLS after 5 hours' sand grinding

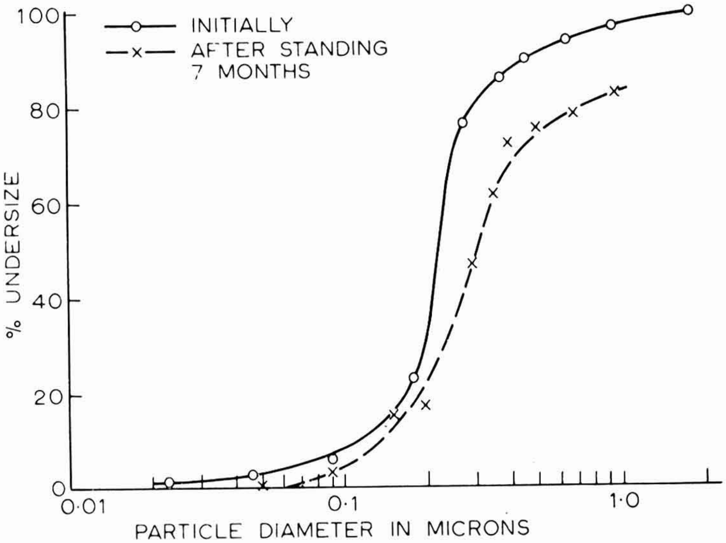

Fig. 21. Particle size distribution of Irgalite Blue GLS after 48 hours' ball milling

of the physics of paints and inks. This in turn should help the formulator to obtain the application properties required in a rational manner.

[*Received 2 April 1970*

References

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2. Beresford, J., *JOCCA*, 1967, **50,** 594.

Discussion at the Manchester Section

Dr J. Toole noted that it was concluded that ball milling was less efficient than sand milling in laboratory operations, taking size reduction achieved as a measure of efficiency. He wondered if the same relationship held for bulk operations.

Dr W. Carr could not provide the answer, and hoped that paint makers might be able to provide the information.

Dr Toole further commented that Dr Carr had found a change of size distribution on storage after ball milling. He had observed in similar experiments with phthalocyanine blue that the coarser the dispersion, the greater the flocculation as judged by brush/pour tests. He wondered if the coarsening on storage observed by Dr Carr was due to flocculation.

Dr Carr pointed out that the slight coarsening which took place on storage appeared to be independent of the fineness or coarseness of the original dispersion. He did not think that this slight coarsening was due to the flocculation of the blue, but he did not want to get drawn into a discussion on flocculation at this stage.

Mr Lakin asked if there was any possibility that flocculation occurred during dilution to spin concentrations, and if the increase in viscosity noted on sand milling phthalocyanine blue for eight hours was due to further particle size reduction and surface area increase.

Dr Carr replied first, that comparisons of dilutions to different levels, eg 1:20 and 1:200, by giving similar size distributions, gave fairly good evidence for the absence of solvent shock, and secondly he had thought originally that particle size reduction was the cause of viscosity rise, but had later concluded that solvent loss was more likely to be the factor. With the green and violet pigments, where care was taken to ensure no solvent loss, viscosity increase after long milling was small.

Mr W. A. Allman asked if particle size and tinting strength could be correlated, and if there was any risk of contamination from the grinding medium, especially in long sand grinds.

Dr Carr pointed out that only a portion of the results had been presented; other parameters examined had been colour strength, viscosity, gloss, and opacity, and weathering tests were in progress; in fact, colour value had been plotted against size distribution. The possible presence of comminuted sand in the various size fractions existed, but was eliminated when the pigment was dissolved for optical density measurements and so would not be registered as part of the size distribution.

Mr E. Alston enquired if the mill base formulations used were optimal.

Dr Carr considered that they were typical, but not necessarily optimum.

Mr G. R. Robson asked if any connection had been found between particle size and light, or weathering, fastness by comparing the extremes of dispersion time by a given method.

Dr Carr replied that he had made some observations in the case of the green, which was fugitive. After three months exposure, there appeared to be differences in extent of visual fades, but spectrophotometric curves showed little difference in strength loss.

Mr Hanning asked if the use of surface active agents in producing shorter milling times to a given level of dispersion had been investigated.

Dr Carr said he had not examined this aspect, and confessed to being disillusioned with surfactants in solvent systems; he would not expect any dramatic effect.

Discussion at the London Section

Mr I. Berg asked whether one could assume that there was no change in the state of dispersion when the millbase was diluted considerably with white spirit.

Dr W. Carr said that there were three stages in the size analysis, dilution, centrifuging, and analysis of the pigment content of the withdrawn sample, and all three stages had been checked. The effect of dilution had been examined at several different levels of dilution.

Mr A. H. Soane said that a small laboratory ball mill was very inefficient because it would only handle a free-flowing mixture, whereas the large machine in the factory would handle a thick paste. The sand mill, on the other hand, worked better on free-flowing substances.

Dr Carr said that this was one of the problems that occurred frequently, namely relating laboratory to works practice.

Mr N. M. Sheppard said that he had obtained good correlation between laboratory scale ball milling and factory manufacture, but a significant variation in the results could occur with varied ball charge dimensions.

Dr Carr said that the size analysis technique could be used with any type of mill, to determine its optimum grinding conditions.

Mr Berg said that on the basis that each pigment should be treated individually, then ideally the millbases should be tailor-made to fit the pigment.

Dr Carr said that one had to make a compromise in practice.

Mr K. W. Green said that a change in pigment coarseness on storage had been observed. Had any conclusions been drawn on the influence of dispersion time and efficiency on the change in storage, bearing in mind that this might affect the colour match of a tinted material.

Dr Carr said that to check this point, storage trials had been carried out on three different blue stainers; one was ball-milled and the other two sand ground for different times. The slight coarsening of the dispersion on standing was of the same order in each case.

Dr G. L. Fuchs, referring to the previous question, asked what effect the particle size growth during storage had on colour strength. Also, what method was used to measure and compare colour strength?

Dr Carr said that an increase in particle size on storage would result in a decrease in tinting strength. This was measured using a standard white base paint and the strength of the resulting tint was measured with a spectrophotometer.

Next month's issue

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

"New resin systems for coil coating applications," *by W. J. Lanigan and L. A. Tysall.*

"An assessment of some commercial insecticidal paints," *by L. A. Hill and J. R. Elliot.*

"The aluminium vinyl system for ships' bottoms," *by W. A. Anderton.*

"Solvent retention in phenolic varnish films," *by M. Yaseen and H. E. Ashton.*

"Determination of the phosphoric acid content of the acid component of etch primer paint by flame emission spectrophotometry," *by W. N. Elliot and K. A. Mostyn.*

Reviews

AN INTRODUCTION TO THERMOGRAVIMETRY.

By C. KEATTCH. London: Heyden & Son Ltd., 1969. Pp. vii+59. Price 38s.

This book gives a concise, easily readable, account of the technique. The first half deals with the history, apparatus, principles and interpretation, and the last with applications. The inorganic examples cover studies of analytical procedures, structures and chemical processes. The organic examples are rather sparse and subjects dealt with include wood, coal and ion-exchange resins, but there is little on polymer chemistry. There is an adequate number of literature references and a useful final chapter on commercially available equipment. Although no aspects of direct interest to the paint industry are covered, this work enables an overall picture of the subject to be obtained in a very short time.

L. A. O'NEILL

POLYMER CONFORMATION AND CONFIGURATION.

By FRANK A. BOVEY. New York: Academic Press, 1969. Pp. x + 177. Price 89s.

This is not a book for the reader who is only interested in his job and its immediate foundations. Indeed, it contains practically nothing of direct consequence for the coatings technologist. It is largely devoted to the work of a brilliant group of scientists, led by the author, at the famous Bell Telephone Laboratories, an unlikely site, one may think, for researches on polypeptides or even on polymer stereochemistry in general. As such it will be enjoyed by those with a sufficient academic background to enable them to appreciate the elegance of the theory and techniques employed in a specialised field, remote perhaps from their own. It is based on a series of lectures given by Dr. Bovey in 1967 when he was visiting professor to the Polytechnic Institute of Brooklyn. The emphasis is on his work on high resolution nuclear magnetic resonance spectroscopy, optical rotatory dispersion and circular dichroism in the study of the stereochemistry and conformation of polymers.

The book opens with a deep discussion of molecular symmetry and conformation, the probabilities of various types of structure sequences in polymers, and a comparison of 60, 100 and 220 M Hz NMR spectra as tools for the elucidation of microstructure in some simple vinyl polymers. This is followed by an equally erudite presentation of propagation mechanisms in terms of Bernoulli & Markov statistics. This first part of the book is concluded by a chapter on the observation of polymer chain conformation by NMR spectroscopy with the accent on the interpretation of the spectra in fundamental terms.

The second half comprises two chapters on optical and NMR studies of the α-helix and the helix-coil transition, and on the conformations of N-disubstituted polypeptide chains. Here the reader discovers where circular birefringence and circular dichroism have their origins and how observations of such optical properties can be correlated with NMR results to clarify the stereochemical

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picture. There is also an interesting discussion of the still unanswered question—what causes the helix-coil transition?

It is likely that only a minority of our readers will possess the understanding of statistics, NMR theory and physicochemical optics needed to appreciate this book. Others may find it well worth the trouble to brush up first on Bovey's monograph "Nuclear Magnetic Resonance Spectroscopy—principles and applications in organic chemistry." Whatever their background, most will find it hard going—but the intellectual satisfaction will be worth the effort, for those who like that sort of thing.

A. R. H. TAWN

Information Received

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

The Association was represented at the recent premiere of the film "Research for building" which outlines the work of the **Building Research Station.** The film, which was produced by the Central Office of Information and made by Rayant Pictures Ltd in full colour, was introduced by Sir Michael Carey, Permanent Secretary to the Ministry of Public Building and Works, and Mr J. Dick, Director of the BRS.

It has recently been announced that **ICI Ltd** has reached agreement to acquire a 25 per cent shareholding in **Nippon Polyurethane Industry** of Japan, a private company of which, at present, 80 per cent is owned by **Hodogoya Chemical Co. Ltd.** and 20 per cent by **Toyo Soda Manufacturing Co. Ltd.** The ICI shares will be purchased from Hodogoya, and Toyo's shareholding will remain unchanged.

ICI and Nippon Polyurethane will enter into an agreement for exchange of technical information related to the manufacture and use of certain polyurethane chemicals, particularly methylene diphenyl di-isocyanate (MDI) and its derivatives.

Although agreement has been reached between the companies involved, the investment is still subject to the approval of the Bank of England and Japanese Ministry of International Trade and Industry.

ICI has also announced that it is to market urethane chemicals throughout the world as coatings for leather products.

Over 200 high purity inorganic chemicals are listed in a new publication available from **Johnson Matthey Chemicals Limited.** In most cases, chemicals are available in more than one grade of purity, and each grade is defined in terms of parts per million of metallic impurity content.

Edwards High Vacuum (Plant) Ltd. has introduced centrifugal vacuum evaporation equipment which is claimed to give fast and efficient removal of organic solvents. Based on the Edwards centrifugal freeze dryer, the machine can handle up to 6 × 50ml liquid samples (or more samples of smaller volume) and, by spinning the tubes of liquid while vacuum is applied, eliminates frothing and splashing of the solvent. It is claimed that this method is quicker and less likely to cause contamination than thermal evaporation or nitrogen bubbling techniques.

Acrylic Stoving Texture Finish is a new product produced by **Hadfields (Merton) Limited.** It is claimed that the semi-gloss, medium-grain texture finish, which simulates natural leather, is uniform and reproducible, an attractive appearance which also hides minor defects in a metal surface being obtainable without the necessity for expertise in the application. It is also claimed that a single coat of 1.5 to 2 mil on metal will provide an abrasion-resistant coating which will resist cutting oils, detergents, humidity and chemicals.

A range of colours is available, in one and five gallon packs.

Edacs Data Limited have recently published "Edacs 70", a new reference manual of process plant for the chemical and allied industries. Process equipment is catalogued by design, using sketches and descriptive notes to make the type of plant and application clear. Copies of the manual are available direct from Edacs at £2 10s., and a back-up enquiry service can also be supplied at £30 p.a.

The Under-21 Lawn Tennis Championships of Great Britain, held in Manchester in August, were once again sponsored by the **Anchor Chemical Company Ltd.** It will be recalled that the company, which has been Manchester-based since its birth 78 years ago, stepped in last year with financial aid so that the championships could continue to be held in the city.

A 50-page booklet has been published by **A. Gilby and Sons Ltd.** to describe the new range of *Coronet* offset process inks. These inks have been matched to the most frequently used standards, all colours being interchangeable to give a wide selection of four-colour inks from a limited range. The booklet gives colour illustrations of 65 to 150 line reproduction together with graduated density charts from 5 to 90 per cent, and copies are available from Gilby on request.

What will be the world's largest plant for the manufacture of polyvinyl alcohol is to be constructed at La Porte, Texas, the **Du Pont Company** has recently announced. This move follows the completion of the expansion of Du Pont's Niagara Falls *Elvanol* polyvinyl alcohol plant. The new plant is scheduled to come on stream in 1972.

Bergviks Hartsprodukter Aktiebolag, the Swedish producer of tall oil derivatives, has recently published a 16-page booklet giving details of its main products. Copies of the booklet can be obtained from the company's UK agents, **The White Sea & Baltic Company.**

The availability of *t*-butyl peroctoate (*Trigonox* 21) with a purity of at least 97 per cent has recently been announced by **Novadel Limited.** It is claimed that *Trigonox* 21 is ideally suited as a curing agent for high temperature applications of unsaturated polyester resins, and that unsaturated polyesters so cured have extremely good colour.

Novadel has also announced that it has by-product phosphorous acid surplus to requirements, and welcomes enquiries.

Arnold Services has recently announced the availability of a new multi-client innovation study, entitled "Unusual cyclisations". Copies of the study, which deals with over 140 homo- and heterocyclic reactions, can be obtained from Arnold Services at £400 per copy.

The first stage of a long term plan for increasing production capacity and flexibility has been completed at the No. 1 plant of the Minerva Works, announce **Pinchin Johnson Paints.** The 1,000 gallon ball mills which used to be contained in this plant have been replaced by a continuous process utilising a 50hp *Morehouse-Cowles* high speed disperser operating in 400 gallon pots, the premix from which is fed to a *Sussmeyer S.P.*60 sandmill, said to be the largest used by any paint manufacturer in the world. The sandmill is said to effect considerable time savings, as it can operate at 400 gallons an hour, which quantity would take at least 16 hours in a ball mill. Automatic mixing and cleaning facilities are also incorporated in the production line.

PJP has also produced a new booklet entitled "Aircraft finishes", giving finishing schemes for aircraft in the range of DTD and BS specifications, as well as detailed information on application and preparation, with trouble-shooting advice.

A new brilliant white high-quality vinyl-based emulsion is being produced by **Carson-Paripan Ltd.** The new product will replace all white emulsions in the company's range but, say Carson-Paripan, it will sell at a lower price than competitive brilliant whites. Improvements claimed include additional set, opacity and whiteness, improved wash resistance, reduced dirt retention and easier surface cleaning.

Kronos Titanium Pigments Ltd. has issued "Kronos Laboratory Report 11", entitled "Determination of the opacity of films of differing thickness and pigmentation level". The report, which runs to 36 pages, describes experimental work in evaluating how a method described in "Laboratory Report 8" for determinating the opacity of a pvc sheet by plotting the contrast ratio against the concentration and thickness on log/probability scales can be applied to thicker sheets of other polymers. Copies are available from Kronos.

A new paint stripper in paste form, which, it is claimed, can cut labour cost by up to 50 per cent, has been introduced by the **Inter-strip Company Limited.** It is said that the new product, *Inter-strip*, is odourless, non-inflammable, non-toxic, and virtually harmless to the skin, and that it can dissolve up to 11 layers of old paint in one application. The paste is applied, left for 1-2 hours, and the surface then wiped clean with a sponge or scrubbing brush and cold water.

A new high performance colorimeter-spectrophotometer, the *KCS-40*, has been introduced by the Colour Systems Division of **Kollmorgen Corporation.** The first of a series of Kollmorgen colour instrumentation systems for the 70's, the *KCS-40* is claimed to be the first colour measuring system designed to take full advantage of the integration of digital computer technology with colour measuring instrumentation, and thus to have greater flexibility and inherent accuracy than the union of conventional instruments with a computer. Output is by typewriter print-out, perforated tape for transfer to off-line computers, e.g. for formulation, or direct graphical display.

Kollmorgen states that the system was designed specifically for solution of colour problems where human vision is the ultimate judge of colour match and, as such, represents a great advance in the performance and usefulness of colour instrumentation.

Two new resins based on solution and emulsion polymers of vinyl acetate have been developed by **Resinous Chemicals Limited.** The resins are intended for use in high gloss water based paints, and it is claimed that they impart superior application properties, flow characteristics and colour stability compared to other currently available materials of this type. Low odour, elimination of fire hazard, and easy water cleaning of brushes are said to be other advantages of formulations based on these resins.

A new laboratory for detergent research has recently been opened by **Unilever Research** at Port Sunlight. The new building adjoins Bromborough Road outside the Port Sunlight complex, and is linked to the other laboratories by a 500ft covered footbridge, which crosses the road and a railway.

Berk Limited has recently announced that it now has available a number of accessories for the basic range of *Karr Pneumatic Volumetric* filling machines. These include special nozzles for higher throughput or prevention of dripping, and hopper heating equipment.

Association Conference, 4-8 May 1971

Surface properties and appearance

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

Ten papers have been arranged, and summaries of these are given below.

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

Conference papers

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

Having established a technique for measuring the pigment particle size distribution of non-bleeding organic pigments in an alkyd resin system, paint stainers were made from six well known types of paint pigments by ball milling and sand grinding for various times. The pigments used were commercial brands of a β-form phthalocyanine blue, a phthalocyanine green, a carbazole violet, a dioxazine violet, a pigment green B and a diarylide yellow. Paint stainers that differed in degree of pigment dispersion were obtained from each pigment. The particle size distribution of each of the stainers was determined on a disc centrifuge.

The stainers were also complete paints in themselves. Films were made from the stainers and from reductions of them with a white base paint made from the same resin. The resultant films were critically examined for the following properties:

colour strength, changes in shade, brightness, flocculation, flotation and flooding, gloss (using a Zeiss goniophotometer), light fastness, weathering, bronzing, opacity and transparency.

The relationship between these properties and pigment dispersion in the stainer was examined for the alkyd resin system used.

In many of these properties, but not all, the degree of dispersion of the pigment, as expected, plays an important part. The present work has shown that its role becomes more and more important in the region of high levels of dispersion, i.e. at very much small particle sizes. At lower levels of dispersion, small changes are much less significant.

The relationships between colour strength, flocculation and stainer particle size are particularly interesting in that they open up a completely new approach to the phenomenon of flocculation of phthalocyanine blues.

Dr W. Carr is a native of Liverpool and took chemistry at Liverpool University to honours B.Sc. level, followed by a doctorate in physical chemistry at the same University. He joined Geigy (U.K.) Limited in 1939 at their old Belsize Laboratory in Manchester. Dr Carr has had wide experience in technical service to the ink, paint and paper industries concerning dyes and pigments. He is now technical manager of the special section concerned with the study of all aspects of the physical properties of pigments in relation to their performance, and is also the visiting lecturer on pigment physics in the Colour Chemistry Department of Leeds University.

Dr W. Carr

Opacity of roller coatings by D. G. Dowling and D. F. Tunstall.

Part I—Practical aspects

A statistical study of the influence of seven factors (grade of TiO_2, pigment volume concentration, resin, solvent system, film thickness, substrate, and the effect of sizing) on the opacity of a series of roller coating enamels showed the powerful influence on film opacity of the substrate reflectance, substrate sizing, and film thickness in comparison with the other factors. Furthermore, some quite complex interactions were revealed, indicating that the precise formulation of roller coatings varies with the surface characteristics of the substrate. The practical implications of the results will be discussed.

Part II—Theoretical analysis

A fundamental study of the influence of internal and external surface reflections on the opacity of thin paint films has been made, and an equation relating opacity to the reflectance characteristics of the film surfaces (the upper surface and the substrate) has been derived. It is shown how the true Kubelka-Munk back-scattering coefficient is obtained from the experimental data and the effect of sizing a metal surface is examined on a quantitative basis.

Mr D. G. Dowling was educated at West Hartlepool Grammar School, and then Kings College, Newcastle on Tyne (University of Durham), from which he graduated with Honours in chemistry in 1952. After seven years industrial research experience in heavy inorganic chemicals and laminated plastics, he joined the technical service department of British Titan Products Co. Ltd. in 1959. After a brief period in the decorative paints section, he assumed responsibility for technical service of industrial paints and printing inks in 1962. Mr Dowling has specialised particularly in pigment dispersion and utilisation, and has published a number of papers on these subjects.

Mr D. G. Dowling

Mr D. F. Tunstall graduated from Cambridge in 1961 with an Honours Degree in physics. He was employed from 1962-5 on general process research and development work at Australian Titan Products in Tasmania. He then transferred to British Titan Products Co. Ltd., where he now holds the position of section manager in the mathematics and physics research division at the company's central laboratories, Stockton on Tees. His main interest lies in the optical properties of pigmented systems but he is also actively engaged on research into the physical degradation of paint films.

Mr D. F. Tunstall

Colour specification by visual means by K. McLaren.

A collection of colour samples representing the whole gamut of surface-colour space with near-perfect replicas widely available is a desirable means of communication even at a time when colorimetry is a practical alternative. The best known collections are those of Munsell and Ostwald, which contain about 1,200 samples but both have one major defect which has prevented their use by the textile industry: the number of samples is far too small to represent adequately the total number of discriminable surface colours, which has been reliably estimated as 10 million. Interpolation is theoretically possible but not practical in view of the three-dimensional nature of colour space.

To overcome this defect by conventional means requires the preparation of at least 10 thousand colour samples systematically arranged and evenly spaced, and such a task is quite impracticable and probably impossible. However, the technique of colour photography known as dye transfer has been successfully used to produce about 1,300 colour samples, each being a combination of not more than two subtractive primaries. The gamut is extended to about 26,000 shades by the simple expedient of providing 20 neutral grey filters of increasing depth, each of which can be super-imposed on any of the colour samples.

The 1,300 colour samples were then matched by conventional pigments dispersed in nitro-cellulose and thousands of copies printed by a patented colour-depositing process which guaranteed that there was no significant difference between any two samples nominally the same. The neutral grey filters were produced photographically to the same high standards.

A simple colour coding, employing no more than three of the letters R Y B N and X and three numbers from 0-26, identifies each shade, which can then be found by anybody possessing a copy within seconds.

Mr K. McLaren graduated in colour chemistry at Leeds University in 1943, and since then has been in the technical service department of ICI Dyestuffs Division; he is currently manager of the identification and colour measurement section. The author of more than 20 papers, mainly concerned with colour fastness, abnormal colour vision, lighting for colour matching and more recently, colour measurement, Mr McLaren is chairman of both the Fastness Tests Co-ordinating Committee and the Colour Measurement Committee of the Society of Dyers and Colourists and was a co-chairman of the joint SDC/OCCA Light Fastness Committee. He is the recipient of the SDC Silver (1955) and Gold (1962) Medals and of the Research Medal of the Worshipful Company of Dyers (1956-57) for his work on the fading of dyes.

Mr K. McLaren

Gas chromatographic investigations of interaction forces between binder and solvent in paint films by K. H. Reichert.

From gas chromatographic measurements of solvent retention data on several binder columns, indices for the basic distribution equilibria of the solvents between binder and carrier gas have been obtained. On binders with different chemical structure, specific dependencies of retention values with solvent polarity were found and these are probably due to a different participation of the distinct types of interaction forces in different binder/solvent systems. In the case of vinyl chloride/vinyl acetate copolymers with increasing vinyl acetate content, increasing retention data for ester type solvents were obtained.

The advantage of the interaction data from gas chromatographic experiments is, that these values are obtained from direct measurements on concentrated binder-solvent systems. Previously found values for aromatics and esters are in good agreement with the solubility parameters obtained by Hansen and with other polarity indices, whereas corresponding data for alcohols differ remarkably from the Hansen concept. With regard to the different types of interaction forces, especially to the hydrogen bonding, an overall scheme should be developed that could possibly be suitable for predictions of the unknown interaction forces affecting the film-forming process.

Dr K. H. Reichert graduated in chemistry from the Technical University of Stuttgart in 1958, and went on at this university to attain his doctorate under Professor Hamann, specialising in macromolecular chemistry.

Since 1961, he has both continued work in the university, and evolved an instrumental analysis at the Forschungsinstitut für Pigmente und Lacke e.V. in Stuttgart. At present, the main topics of his work are irradiation and light-ageing of paint films, surface analysis of polymer films, molecular interaction in paint systems, and cationic polymerisation.

Dr K. H. Reichert

Film appearance and its dependence on solvent formulation; a systematic approach by L. A. Tysall and D. H. Schärer.

The film appearance given by a coatings system is very much dependent upon the solvent composition used. Badly chosen solvents will give poor flow or gloss, or even more serious defects such as blushing or pinholing. Multi-component mixtures are attractive both for performance and from the point of view of cost reduction, but the number of possible variations is usually so large that a systematic approach appears impracticable and is abandoned in favour of traditional rules of thumb. A further limitation is that data cannot normally be carried over from one experimental programme to another; for example, film appearance is judged solely on a comparative basis and no general bank of information is built up for future use.

The paper deals with two methods of tackling these difficulties. The first is a completely general approach which generates starting-point formulations from basic solvent data such as solubility parameters, evaporation rates and prices. This is useful where there is only limited data available on the system being studied. This limited data is used to establish suitable constraints on the values of the basic properties; for example a limit of 300 seconds might be placed on the 90 per cent evaporation time. Solvent compositions within these constraints are then examined. An aspect of particular interest is the ability to calculate the cheapest possible mixture of chosen components within the constraints; here computer assistance is desirable. Some compositions will be judged to be unsuitable on grounds of general experience. This is not surprising considering the nature of the approach. Other constraints may be imposed at this stage until an apparently acceptable composition is obtained. This is then tested experimentally. The method therefore makes use of the accumulated experience which forms the basis of traditional formulating techniques, together with more modern developments.

The second technique is more narrow in its application, making use of an accumulated store of data for a particular coating system. It is useful where problems continually arise with that system. With a satisfactory store of data it is possible to predict the performance of selected solvent compositions by interpolation. Such a store can be built up if test methods used give quantitative results related to some fixed standard. For example, the usual methods of assessing flow give only an order of merit for the compositions studied in one single programme and thus no data suitable for storage. The authors have developed a quantitative method of flow assessment for this type of work whose results are related to geometrical patterns of fixed dimensions; the same patterns can be used for all programmes and the data therefore accumulated to form a store for future reference. In this situation it is naturally desirable that each programme is systematically planned and that, as far as possible, the plans of the various programmes are of similar type. Although it is not essential to use a computer, there are advantages in doing so. Apart from the obvious economy of effort, more accurate predictions can be obtained and their reliability readily calculated. Moreover, as before, optimisation of cost or other properties is possible. This second technique gives, over a period of time, a much higher yield of information from a given amount of experimental work than traditional methods. It also offers other possibilities, for example it could be used to calculate composition adjustments required to maintain high cost/efficiency in a changing price structure.

Mr L. A. Tysall is a principal scientist in charge of laboratory work on solvents at the Egham Research Laboratories of Shell Research Limited, near London. After graduating at Queen Mary College, University of London he began his working life as a teacher. During World War II he moved into industry, working successively on explosives, fine chemicals and paints and lacquers. In 1946 he joined the Shell group and became involved in the laboratory work supporting Shell's entry into the solvents and epoxy resins fields. He has since been associated with all aspects of this work, principally on the surface coatings side, and has tended to specialise on solvent topics.

Mr L. A. Tysall

Dr D. H. Schärer graduated from St. Edmund Hall, Oxford, in 1965 and obtained his D.Phil. from Oxford for research on the magnetic properties of inorganic complexes. Since joining Shell Research Ltd. in 1968, he has worked as a chemist in the resins and surface coatings division at Egham Research Laboratories, and is currently concerned with research and development on the use of solvents in surface coatings applications.

Dr D. H. Schärer

Appearance and performance factors in coatings for buildings by P. Whiteley and G. W Rothwell.

The requirements of coatings for building surfaces, particularly for exterior walls, their evaluation and testing, and the influence of physical and mechanical properties on the behaviour and change in appearance during ageing, are discussed. As coatings become more durable, capable of maintaining an intact and protective film for periods of over 10 years, greater emphasis has to be put on the retention of the original or an acceptable appearance for the greater part of their lifetime.

The more durable the coating, however, the more difficult becomes the task of predicting, from short-term tests and artificial ageing, the probable life in a variety of circumstances. Colour change, dirt and algal resistance of coatings are obviously important factors in assessing appearance, but because of their subjective nature, difficult to quantify. Other properties such as hardness, flexibility, adhesion and permeability also affect the eventual appearance as well as the film integrity. Some specially devised tests of extensibility and the measurement of the effective permeability of coatings during exposure tests are described.

Mr P. Whiteley grew up in the paint industry, and with only a brief spell outside it, spent 20 years on the research and development side of various companies before taking up a research fellowship on tropical paint problems for the Colonial Office and later the Department of Technical Co-operation. Working from the Building Research Station as a base, he travelled extensively in the developing countries of the tropics, advising on the use of paint, and carried out field trials in West Africa on durability, corrosion and mould growth. He was appointed to his present post as principal scientific officer in charge of the surface coatings section at BRS in 1964.

Mr P. Whiteley

Mr G. W. Rothwell started his working life in steel and later, for British Rail, worked on corrosion problems, paints, and protective coatings, at Derby and in the chemical research division at Muswell Hill. He joined the surface coating section of BRS in 1965 and has been studying durability and the physical properties of paint films.

Mr G. W. Rothwell

Several factors affecting appearance and properties of thermosetting acrylic enamel films by J. R. Taylor and H. Foster.

The surface properties and appearance of thermosetting acrylic enamel films may be defined by many well known properties, such as gloss, colour, surface texture, and hardness. These properties are influenced by various factors including pigmentation, cross-linking resins, oven flow, solvent release, and environmental effects resulting from weathering and abrasion.

The effect of the compatibility of the acrylic and melamine resins on the viscosity, flow properties and gloss of the enamel films was examined.

Using the concept of centre line average height, curves were obtained and used to give limits of acceptable reflow in terms of acrylic and melamine resin proportions and the pigment:binder ratio. The resulting tri co-ordinate graph had two significant peaks, one of which appeared to coincide with the acrylic:melamine ratio that gave the optimum cure. The other peak was explained in terms of poor compatibility at a low acrylic-melamine ratio.

The work was then extended to the use of two pigments, in which systems the acrylic:melamine ratio was fixed at 7:3. The type of pigment and pigment:binder ratio were found to be important factors in the degree of reflow obtained. A method is proposed of measuring oven flow of the film by following the change in viscosity during a stoving cycle.

The difficulties associated with reflow of metallic finishes were examined and a process suggested to minimise colour change of these finishes when reflowed.

The effect of two repair-in-process techniques on the outside durability of enamels based on hydroxylated acrylic resins was reported. Enamel films before and after weathering were also examined by means of the Stereoscan electron microscope and a comparison made with alkyd/melamine based finishes.

The present interest in the over lacquering technique in the motor car industry was discussed and various requirements relating to the base and lacquer coats were considered.

A novel method of assessing mar resistance was proposed utilising a Talysurf instrument for measuring surface texture of marred and abraded film surfaces.

Mr J. R. Taylor is a B.Sc. of London University and Fellow of Royal Institute of Chemistry, a member of the Plastics Institute, the British Society of Rheology, and the South Wales Chemical Club and is an overseas member of the Association Francaises des Techniciens des Peintures et Vernis, Ile de France Section.

He has been associated with the paint industry for many years, as a chemist with Sissons Bros. Ltd. in Hull, the Chemical Inspectorate, and as the technical manager of Goodlass Wall & Co. Ltd., Speke, Liverpool. His present post as technical service manager, resins, BP Chemicals (UK) Ltd. at Barry, South Wales, has brought him in contact with members of the plastics and paint industries, both in the U.K. and Europe, and other parts of the world giving insight into a broad range of paints, plastics and resin technology in industry.

Mr H. Foster is a graduate of the University of Wales (Cardiff) with a B.Sc. degree in chemistry and mathematics. He joined British Resin Products in 1957 as a development chemist in surface coating resins and later became a section leader in the research and development laboratories. During the period 1963-65, he spent two and a half years in Australia with Spartan Paints Pty. Ltd. in Melbourne (Victoria) and later with the Australian Mineral Development Laboratories in Adelaide (S.A.).

His present position is with BP Chemicals (UK) Ltd., plastics department, in Barry, Glamorgan, where he is in charge of the paint evaluation section of the resins technical service.

Mr J. R. Taylor

Mr H. Foster

Basic lead silicochromate pigments—facts about them by R. P. Bates

The history of silica core furnaced pigments as exemplified by National Lead Company's basic lead silico chromate is reviewed.

The procedure for preparing a lightweight, active basic lead compound useful as a pigment for paint coatings was first described in 1948. Since that time the technique has been found useful in preparing the very versatile basic lead silicochromates (fine and regular grades). The chemical compositions and physical characteristics are reviewed. The use of the scanning electron microscope has been most useful in showing that the pigment particles are well coated and indeed finer in size than had been considered to be the case in the past.

The paper describes in detail the corrosion-resistance performance of basic lead silicochromate indicating concentrations to provide optimum performance in solvent-base and latex coatings.

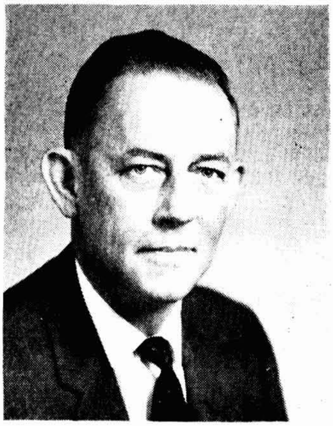
The use of basic lead silicochromate, particularly the fine grade, in electrodeposition coatings is discussed, with reference to concentration required and the properties which the pigment offers.

One of the most important properties of basic lead silicochromate, which has given it wide acceptance by the bridge divisions of state and provincial governments throughout North America, is the colour-retention characteristics it provides. Because of its low-tinting strength, the characteristic dull-orange colour of basic lead silicochromate can be masked to develop an extensive range of hues.

Without question it has been demonstrated in practice that basic lead silicochromate-containing finishes, when properly formulated by choosing the correct auxiliary pigments, have provided improved appearance for countless bridge structures. This is due to the nature of the product, a low-tinting strength material which must be used in some substantial quantity to achieve the colour and hiding desired and a furnaced rather than a precipitated compound which has resulted in a more stable system.

Mr R. P. Bates received a B.Sc. degree in chemistry from the Polytechnic Institute of Brooklyn and joined National Lead Company's Brooklyn research laboratory upon graduation. His activities have included colour pigment control and development, the formulation and evaluation of metal protective and exterior wood house paints utilising lead pigments, and technical service and field work in connection with structural metal painting. Mr. Bates served as an associate department head concerned with pigment technical service in the pigments and coatings department of the laboratory prior to his appointment as assistant to the ONCOR pigments product manager. Since 1967 Mr Bates has been product manager of ONCOR pigments in the pigments and chemicals division of National Lead Company.

Mr Bates is chairman of Subcommittee 46 of ASTM Committee D-1 (Industrial protective painting) and a member of the New York Society for Paint Technology.



Mr R. P. Bates

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

Earlier publications have related subjective and objective gloss assessments of paint films and, by means of a spectrogoniophotometer, interpreted gloss in terms of micro and macro surface defects.

This has been investigated further by introducing different sizes of surface defects into a 15 per cent PVC high gloss acrylic paint. Various sizes and concentrations of a silica flatting agent were used to produce these defects. The resulting paint surfaces were examined by conventional gloss measurements, S.G.P. examinations and interference microscopy. It was found that the gloss reduction was caused by the relatively low quantity of material, with diameter in the region of 1 micron, which was present in the flatting agent. On the other hand, the distortion of the S.G.P. peaks was related to the amount of large material which was present. Pre-milling of the flatting agent had little effect on the gloss, even though it appreciably reduced the mean particle size from the region of 8 microns to the region of 3 microns and did reduce peak distortion. These observations confirm the earlier work.

Approximate calculations based on the population densities of various size fractions of particulate material present in the paint film further confirmed that it is the smaller particles which are most detrimental to gloss.

Using a range of TiO_2 pigments at a standard milling time, and a base pigment at a wide range of milling times and two PVCs, acrylic paints with widely different gloss values were produced. The gloss was investigated by S.G.P. and it was shown that only micro defects were present. The state of dispersion of the pigment particles in these films was examined by thin section studies using the electron microscope. It was shown that the gloss of the paint film surface was related to the degree of grouping of the pigment particles within the paint film. Increased grouping, regardless of whether it was an intrinsic property of the pigment or whether it was a result of milling procedure, always leads to a reduction in the observed gloss. In this acrylic media, the overall size of the groups of particles involved in gloss reduction is in the region of 0.5 microns.

(It is hoped that biographical notes on the authors of this paper will appear in the November issue.)

Management session

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

In the past, in industries in which particular specialist technologies are employed e.g. paint and printing ink manufacture, technologists have often "served an apprenticeship" in the technician ranks. This, often unplanned, approach meant that informally and slowly over a number of years the future technologist gained a wide knowledge of the industry which he could later apply in developing new and improving existing products. With the increased opportunities for full-time higher education, the number of potential technologists entering directly from school is decreasing and the present entrants are often less academically capable. Fewer are therefore likely to reach Grad. R.I.C. or specialist endorsement (to H.N.C.) levels. On the other hand recruitment of science graduates has increased and these new entrants, who have probably little or no direct knowledge of the technology they will use, must be given "the experience of years" and become fully effective in the shortest possible time. The Chemical and Allied Products Industry Training Board has produced an interim recommendation—"Recommendations for the immediate postgraduate training of engineers, scientists and technologists" which details an approach to this training. Currently, the recommendation is being expanded by two Board working parties to include examples from a wider range of initial appointments and it is hoped thereby to increase the value of the recommendation to our industries.

As the technology alters the technologists will need updating to keep abreast of the latest developments and with increasing managerial responsibilities will need help in assimilating appropriate management techniques. Firms will need to appraise their staffs regularly to discover these needs and find means to satisfy them adequately.

At the technician level, often due to recruitment difficulties, youngsters from a wider spectrum of abilities are now being recruited and in some cases these entrants have no formal academic qualifications. As a result there is an increasing awareness of the need for a more systematic approach to the training of these new technicians, including the need to analyse carefully the jobs which they will be performing to disclose the knowledge and skills required. From this analysis a meaningful training programme is drawn up, which can be modified for entrants of differing ages and initial experience. Again one of the C.A.P. I.T.B. working parties will be offering advice on this training in due course.

The present pattern of further education courses for technicians is likely to change particularly as there is a need for some rationalisation of the specialist technicians courses and indeed some movement has already occurred. Further more radical alterations could occur if in due course the recommendations of the "Haslegrave" Committee are implemented. The pattern of release of technicians for further education courses may also alter with a movement towards block release courses in a smaller number of centres for specialist technologies where there is insufficient demand on a local basis.

The technician will need, as he develops, to be given opportunities to update his technical knowledge and skills and to acquire the appropriate supervisory and other skills (e.g. instructional techniques) necessary for his work.

The mechanism of discovery and innovation by R. R. Davidson.

The process of choice occurs in the individual brain by a cerebral computation of probabilities which closely parallels the scientific method: observation, classification, hypothesis, and check by experiment. Generalised, all human progress, whether political, economic, industrial, or scientific, depends on the right operation of this unconscious mechanism in producing useful new ideas and syntheses. The process of scientific discovery will be taken as a specific example of the coming of original individual thought, followed by confirmation, communication and rediscovery by individuals in a small group, the end-result being unthinking use of the practical results by many.

The factors conducive to true operation of the process of individual discovery are discussed: the will to know, to solve and to clarify; availability of and attitude to information; personal interactions; effective operation of all the four Jungian personality functions; the overcoming of preconception-blocks; the use of chance. The time-sequence of discovery is outlined: confusion; the silence of the deep mind (recognition of problem); the implosion; the fecund image; the explosion; critical analysis and exposition; team development. Examples, ranging from the simple and concrete to the abstract and complex are given.

A personal discipline to promote discovery is suggested, together with some useful aids.

Financial evaluation of research projects by A. G. North.

While research projects should never be justified or rejected solely on financial terms, it is always advisable in major projects to carry out financial analysis. A research investigation is no different from any other financial investment in that one expends money in the hope of future profit, and judges whether the return is sufficient. Financial evaluation of investments has been studied in the past by the traditional method of calculating payback time, and then judging subsequent profitability on the basis of criteria such as percentage of sales, or return on investment. Such methods may still be applicable in the case of relatively short term projects, but for any major project, one must take into account the time scale of the investment and return. This has led to the almost universal use of the method known as discounted cash flow which compensates for the time element. Essentially this method is one in which one calculates the cash flow at yearly intervals for the life of the project and then discounts these to arrive at zero present value.

The big difference between a research project and many other investments is that one must accept that research projects incorporate a major risk, that objectives will not be achieved, or that external influences, such as change in potential requirements or the issuance of a competitive patent, may invalidate the whole operation. The risk element is best included by endeavouring to assign probabilities to the various outcomes based on both decisions and chance results. The use of such a decision tree can then be combined with D.C.F. calculations to arrive at an expected average return for the project.

When one is dealing with research projects where the chance of success is low but the ultimate rewards in the case of success are high, one must also be concerned with both the magnitude of the investment and the effect of failure on other events within the company. Attitude to risk varies both with the individual and the company, and must depend in both cases on the financial situation at the time the decision is made. These attitudes are best examined by utility theory which can be combined with D.C.F. and decision tree analysis to present a final answer.

These methods will be used to investigate the potentiality of a project for investigation of electron beam curing.

Technical Exhibition

21-25 June 1971

As previously announced, copies of the Invitation to Exhibit for the Twenty-Third Technical Exhibition, to be held at the Empire Hall, Olympia, London, W14 from 21-25 June 1971, were despatched early in July.

Resulting from the success of OCCA-22, many companies, both from the U.K. and overseas, have already applied for stand space. Any company, therefore, wishing to exhibit is urged to contact the Director and Secretary immediately at the address shown on the front cover as the closing date for applications is **1 December 1970**.

The Committee is pleased to announce that it is now possible to revert to the practice of keeping the Exhibition open on the Friday and that the hours of opening will remain as for the 1970 Exhibition to allow for an earlier start and later closing during the days of the Exhibition, since it proved that overseas visitors staying in London hotels welcomed these additional hours. The days and hours when the Exhibition will be open are given below:

Monday	15.00–18.30
Tuesday	09.30–18.30
Wednesday	09.30–18.30
Thursday	09.30–18.30
Friday	09.30–16.00

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

The Association is making arrangements with various hotel groups for hotel accommodation for visitors to the Exhibition and information will be published in the *Official Guide*.

Programme Liaison Committee

This committee comprises representatives of each of the following societies:

Institution of the Rubber Industry (IRI)

Oil and Colour Chemists' Association (OCCA)

Plastics Institute (PI)

Plastics and Polymer Group, Society of Chemical Industry (SCI)

Society of Dyers and Colourists (SDC)

Royal Institute of Chemistry (RIC)

Major meetings or conferences on polymer or related subjects and other functions planned by these societies are given below and will be in London except where otherwise stated.

1970

8 Oct	Autumn symposium, joining of plastics and assembly of plastics components, at Mid Gloucestershire Technical College, Stroud (PI)
8 Oct	Institute's Annual Dinner—Dorchester Hotel (RIC)
8 Oct	Foundation lecture and dinner at Painter-Stainers Hall in evening (OCCA)
13–14 Oct	Conference "Reinforced thermoplastics" in Solihull (PI)
20–22 Oct	7th International reinforced plastics conference at Brighton (BPF)
27 Oct	Half day symposium "Computers and polymer information" (SCI)
4 Nov	Symposium—Status and prospects of the UK mould making industry (PI)
4 Nov and 6 Nov	Bradford and London respectively. First CATCC evenings in UK. Lecture on "Scientists, society and sympathy" by Dr L. Sheps (SDC)
9–13 Nov	The Scottish plastics, packaging and printing exhibition at Glasgow
13 Nov	Meldola medal lecture—Queen Elizabeth College University of London (RIC)
19–20 Nov	Conference "Plastics in furniture" (PI)
4 Dec	Annual symposium at John Dalton College "Structural foams" (PI)

1971

4–6 Jan	Conference "Designing for plastics—the integrated approach" at Cranfield (PI)
12 Jan	Eighteenth London lecture (SDC)
27 Jan	Symposium—Extrusion processing (PI)
2–4 Feb	Conference "Carbon fibres, their composites and applications" (PI)
11 Feb	Spring symposium—"Plastics in the building industry" at the Grand Hotel, Bristol at (PI)

16 Feb	One day symposium—"Natural and synthetic polymers; structure and biodegradation" (SCI)
17 Feb	Thermosetting injection moulding 1971 Half day symposium at UMIST (PI)
23 Feb	Half day symposium—"Techniques for polymer examination" (SCI)
3 Mar	Bradford—Presentation of diplomas and medals (SDC)
10 Mar	All day symposium at Royal Hotel, Cardiff "Newer engineering plastics" (PI)
10 Mar	Symposium—"Decoration of plastics" (PI)
10 Mar	Conference "Plastics in fire: building" (PI/Agrément Board)
11–12 Mar	Conference "Plastics in fire: transport and materials" (PI)
25–27 Mar	The exploitation of polymer research at Loughborough (IRI/PI)
30 Mar–3 Apr	Joint AGM (RIC/CS)
2 Apr	One day symposium "Polymers in water and waste treatment" (SCI)
22–23 Apr	Industrial conference at Leamington Spa (IRI)
23 Apr	AGM and Annual Dinner, London (SDC)
4–8 May	Biennial conference, Palace Hotel, Torquay "Surface properties and appearance" (OCCA)
20 May	AGM, Foundation lecture, Jubilee dinner (IRI)
21–25 June	23rd Annual Technical Exhibition, Olympia (OCCA)
25–31 July	23rd International congress of pure and applied chemistry at Boston, Mass. (IUPAC)
16–23 Sep	6th International plastics trade fair "K-71" at Dusseldorf.
15–17 Sep	Aviemore: Symposium on "Colour processing challenges in the 'seventies" (SDC)

1972

15–19 May	International rubber conference in Brighton (IRI)

News of Members

Mr L. Bottomley, an Ordinary Member attached to the London Section, has become group technical director of Croxton and Garry Limited following the group's reorganisation. Mr Bottomley was previously director and manager, rubber division.

Mr A. Nutton, an Ordinary Member attached to the London Section, has retired from the board of Novadel Limited. During his 33 years' service with the firm, Mr Nutton served in many capacities, and was managing director until he ceased full time employment in the company in 1967.

Mr V. C. Thompson, an Ordinary Member attached to the Bristol Section has been appointed deputy managing director of Berger J & N Paints Ltd. Mr Thompson, who will also continue in his present position as managing director of John Hall & Sons (Bristol & London) Ltd., will have special responsibility for industrial surface coatings manufactured by the UK paint companies in the group.

Paint technology course

The East Ham Technical College is to organise a course on "Essentials of paint technology", primarily intended for those indirectly concerned with the technology related to the paint and allied industries. The course, which is said to be particularly suitable for technical representatives, customer service clerks, and similar staff, is based on attendance for one half day a week over a period of 30 weeks, although other arrangements may be possible.

International chemistry symposia

The International Union of Pure and Applied Chemistry has recently announced several symposia to be held in the course of the next two years. A list of those after October 1970 is given below.

2-6 November 1970—
International Congress on industrial waste water. Stockholm.

16-21 August 1970—
Vth International Conference on organometallic chemistry. Moscow.

30 August-3 September 1971—
International symposium on chemical education. Sao Paulo, Brazil.

5-8 August 1972—
Symposium on man-made polymers in papermaking. Helsinki.

The main lectures from the first three meetings will be published in *Pure and Applied Chemistry* in due course.

Anti-corrosion coatings congress

An international congress on "New trends in anti-corrosion coatings" is to be held in Milan on 22-23 October 1970. Papers on allied topics will be delivered by speakers from several countries. The congress is sponsored by Colorificio Italiano Max Meyer SpA, and will be held at the Federation of Scientific and Technical Associations building. The congress secretariat is at Via Visconti Venosta 7, 20122 Milan.

Surface Coating Resins Index

The preparation of a new edition of the "Surface coating resins index" has recently been announced by the British Resin Manufacturers' Association. The new edition is intended for publication in spring 1971, and will have the same format as the 1968 edition. The possibility of publication of indices of resins for other purposes is also being considered.

Register of Members

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

Ordinary Members

BUCKLEY, DOUGLAS, 172, Stonelow Road, Dronfield, Sheffield, S18 6EQ. (*Manchester*)

FRAZER, ROBERT HICKS, 6, Cawood Haven, Buttershaw, Bradford, Yorks. (*Newcastle*)

STRETTON, ELIZABETH, 81, Dewsnap Lane, Dukinfield, Cheshire. (*Manchester*)

Associate Members

SMITH, PETER LEONARD, 48, Linden Avenue, Thornton Heath, CR4 7DW, Surrey. (*London*)

Student Members

UNWIN, MARTIN JOHN, "Watersplash", 116, Marine Crescent, Goring-by-Sea, Sussex. (*West Riding*)

Forthcoming Events

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

Thursday 1 October

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

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

Monday 5 October

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

Tuesday 6 October

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

Wednesday 7 October

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

Thursday 8 October

Foundation Lecture: by Sir Paul Chambers, to be held at the Painter-Stainers Hall at 7.00 p.m.

Friday 9 October

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

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

Tuesday 13 October

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

Wednesday 14 October

Manchester Section—Student Group: "Some aspects of paint formulation" by Mr T. W. Wilkinson of Laporte Industries Limited, to be held at the Manchester Literary and Philosophical Society at 4.30 p.m.

Thursday 15 October

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

Friday 16 October

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

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

Wednesday 21 October

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

Thursday 22 October

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

Friday 23 October

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

Tuesday 27 October

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

Friday 30 October

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

Monday 2 November

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

Wednesday 4 November

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

Tuesday 10 November

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

West Riding Section: "Zinc rich paints" by Mr B. Jones of Amalgamated Oxides Limited, to be held at the Griffin Hotel, Boar Lane, Leeds, 1, at 7.30 p.m.

Wednesday 11 November

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

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

Thursday 12 November

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

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

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

Friday 13 November

Manchester Section: "Olefine route to new paint latices" by Mr J. A. Wall of BP Chemicals Limited, to be held at the Bolton Institute of Technology, Deane Road, Bolton at 6.30 p.m.

Thursday 19 November

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

Friday 20 November

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

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

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

Monday 23 November

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

Wednesday 25 November

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

Friday 27 November

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

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

CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of 10s per line. Advertisements for Situations Wanted are charged at 2s 6d per line. A box number is charged at 1s 0d. They should be sent to the Director & Secretary, Oil & Colour Chemists' Association, Wax Chandlers' Hall, Gresham Street, London EC2V 7AB. Telephone: 01-606 1439.

SITUATIONS VACANT

Industrial Paint Technologist required by progressive Scottish Paint Company. Applicants, preferably aged 25-35 years, should have had some experience in quality control and/or development of convertible coatings. Salary commensurate with qualifications and experience. Superannuation. Assistance with removal. Apply Technical Director. Box No. 318.

CONSULTANT WANTED

A foreign company wants a Consultant to advise the manufacture of Cadmium Pigments and Fluorescent, Phosphorescent, Perlescent and such specialized type of pigments. Apply in confidence Box 320.

CONSULTANT WANTED

A foreign company wants a Technician to advise the manufacture of Reflex Blue (Alkali Blue) Pigment. Experienced Technicians please apply in confidence. Box 321.

CONSULTANT WANTED

A foreign manufacturing company wants a Consultant to advise the manufacture of Phthalocyanine Blues (particularly non-crystallizing and non-flocculating types) and Phthalocyanine Green. Experienced Technicians apply in confidence. Box 322.

Technical Exhibition

OCCA 23

21-25 JUNE 1971

EMPIRE HALL, OLYMPIA, LONDON

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