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Papers from the Torquay Conference

Film appearance and its dependence on solvent formulation; a more systematic approach D, H. Scharer and L. A. Tysall

Basic lead silochromate

R. P. Bates

Opacity of roller coatings: Part 1—Practical Aspects D. G. Dowling and D. F. Turnstall

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Transactions and Communications

Film appearance and its dependence on solvent formulation: A more systematic approach*

By D. H. Schärer and L. A. Tysall

Shell Research Ltd., Egham Research Laboratories, PO Box 11, Whitehall Lane, Egham, Surrey.

Summary

Quantitative information relating solvent composition to coating performance is available for only one-, two-, and occasionally three-component solvent mixtures. None of the data refers directly to film appearance. A systematic approach to the formulation of multicomponent blends is not possible and general rules of thumb based on experience have to be used. Two approaches to this problem are described.

The first deals with the experimental determination and use of systematic performance data. A technique is described for assessing the flow of paint films on a numerical scale using standard geometrical patterns. This enables large series of panels to be examined and a store of useful data to be built up. A planned statistical programme to determine flow and viscosity trends with a multi-component solvent mixture is outlined, and methods of using the results discussed. Simple formulating problems can be solved graphically, but a computer optimisation technique is needed when three or more variables are involved.

The second approach describes the use of basic solvent properties such as solubility parameters and evaporation times in formulating solvent blends, and is of use when specific performance data are unavailable. Some limitations of the method are demonstrated and ways of improving the mathematical model to include factors such as solvent balance are considered.

Keywords

Properties characteristics and conditions primarily associated with dried or cured films

appearance

Miscellaneous solvent formulation Equipment primarily associated with analysis measurement or testing computer

L'apparence du feuil et sa dépendance sur la composition du solvant utilisé. Un abordement plus rationel

Résumé

Les données quantitatives sur le rapport entre la composition du solvant et le rendement du revêtement qui le contient, est disponible seulement dans le cas des mélanges de solvants à deux ou rarement à trois composants. Aucune des données ne rapportent à l'apparence du feuil. Un abord rationel à la mise au jour des mélanges à plusieurs composants n'est pas possible, et l'on doit utiliser des généralisations empiriques basées sur expérience. On décrit deux abords à ce problème.

Le premier se traite de la détermination expérimentale et de l'utilisation des données rationnelles à l'égard du comportement. On décrit une technique pour apprécier l'écoulement

^{*}Presented to the Torquay Conference on 6 May 1971.

des feuils de peinture en fonction d'une échelle numérique en utilisant des modèles géometriques étalonnés. Ainsi on peut examiner une série nombreuse d'épprouvettes et d'y accumuler un fonds de données utiles. On trace les grandes lignes d'un programme, rédigé sur une base statistique, pour la détermination des variations de viscosité et d'écoulement dans le cas d'un mélange de plusieurs solvants. On peut resoudre graphiquement de simples problèmes de la mise au point des formules, mais on a besoin d'un ordinateur pour mettre en évidence la technique optimale, dans le cas où il s'agit de trois variables ou de plus. Dans le deuxième abord on décrit l'emploi des caractéristiques fondamentales du solvant, telles que les paramètres de solubilité, et les vitesses d'évaporation, à la mise au point des mélanges de solvants qui est utile où les données spécifiques sur le comportement n'existe pas. On démontre certaines contraintes de la méthode et l'on considère quelques moyens pour perfectionner le modèle mathématique afin de tenir compte des facteurs, tels que la balance des solvants.

Aussehen eines Filmes und Abhängigkeit desselben von der Rezeptur der Lösungsmittel

Zusammenfassung

Nur für aus ein, zwei und gelegentlich drei Lösungsmittelkomponenten bestehende Mischungen liegt quantitative Information hinsichtlich des Einflusses der Lösungsmittelzusammensetzung auf das Verhalten von Anstrichmitteln vor. Keine davon bezieht sich direkt auf das Aussehen von Filmen. Zur Rezeptierung von aus vielerlei Bestandteilen bestehenden Mischungen kann keine systematische Methode benutzt werden, es müssen auf Erfahrungen beruhende Faustregeln allgemeiner Art angewandt werden. Zweierlei Wege werden zur Lösung dieses Problems beschrieben.

Der erste befasst sich mit der experimentallen Bestimmung und Anwendung systematischer Angaben hinsichtlich Leistungsfähigkeit. Es wird eine Methode zur Beurteilung des Verlaufes eines Lackfilmes mittels einter Nummernskala mit genormten geometrischen Mustern beschrieben. Auf diese Weise können viele Serien von Tafeln geprüft und zahlreiche nützliche Beobachtungen angesammelt werden. Ein planmässiges statistisches Programm zur Bestimmung von Verlauf und Viskositätstrend bei Anwendung einer Mehrkomponenten-Lösungsmittelmischung wird skizziert, und Methoden zur Auswertung des Ergebnisses werden besprochen. Einfache Rezeptprobleme können graphisch gelöst werden, wenn es sich aber um 3 oder 4 Variablen handelt, braucht man eine optimale Komputertechnik.

Der zweite Weg beschreibt die Anwendung der hauptsächlichen Eigenschaften von Lösungsmitteln, z.B. die Löslichkeitsparameter und Verdunstungszeiten bei der Zusammenstellung von Lösungsmittelmischungen; er ist von Nutzen, wenn keine spezifischen Leistungswerte vorliegen. Einige Begrenzungen der Methode werden aufgezeigt, und Wege um das mathematische Modell durch Einschluss von Faktoren wie Lösungsmittelgleichgewicht zu verbessern, werden in Betracht gezogen.

Внешний вид пленки и его зависимость от формуляции растворителя: Более систематический подход

Резюме

Количественные данные связывающие строение растворителя с характеристикой покрытия имеются только для однокомпонентных, двухкомпонентных и иногда трехкомпонентных растворительных смесей. Ни одни из этих данных не ссылаются непосредственно на наружный вид пленки. Систематический подход к формуляции многокомпонентных смесей невозможен и необходимо прибегать к эмпирическим правилам основанным на опыте. Описывается два возможных подхода к этой проблеме.

Первый заключается в экспериментальном определении и применении систематических данных эксплуатационных качеств. Описывается техника применяемая для оценки потока красочных пленок на цифровой шкале, с использованием стандартных геометрических шаблонов. Таким образом можно исследовать многочисленные серии панелей и обеспечить запас полезных данных. Предлагается план статистической программы для определения направлений потока и вязкости в случае многокомпонентной смеси и обсуждаются методы использования результатов. Простые формуляционные проблемы могут быть решены графически, но требуется технология оптимизации вычислительной машины когда вопрос касается трех или более переменных.

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Второй подход описывает применение основных свойств растворителя, как например параметров растворимости и периодов испарения в формуляции растворительных смесей, который может быть использован когда нет специфических данных касающихся эксплуатационных качеств. Упоминаются некоторые ограничения этого метода и обсуждаются способы улучшения математической модели, включая такие факторы как например равновесие растворителя.

Introduction

Solvent based formulations are still the most widely used type of surface coating system, and the selection of suitable solvent mixtures is a subject of continuing interest and importance. The volatile components play a vital role during the application and drying of this type of coating, and have a marked effect on final film appearance. Badly chosen solvents will lead to poor flow or loss of gloss, or in more serious cases to defects such as blushing and pinholing. Better appearance can often be obtained by modifying application techniques, but no amount of practical expertise will give good results if the solvents are poorly formulated.

In most coating systems, multi-component solvent blends are used so that, for example, volatility and viscosity can be suitably adjusted, and advantage taken of synergistic effects such as "latent solvency". Non-solvents may also be included to modify "solvent power" and reduce attack on previous coats, though a more compelling reason for their use is the economic incentive of cost reduction. Non-solvents are generally cheap, and it is usually possible to include them in the mixture while maintaining adequate performance. In most situations, the object when formulating is not to produce the solvent mixture with the best overall technical performance, but rather to produce the cheapest mixture that just meets minimum acceptable requirements. But how is a formulator to select a suitable solvent mixture? Most of the quantitative information available on evaporation rates, resin solubilities, and solution viscosities refers to single solvents. There are limited data on binary mixtures and a little on ternary mixtures, the latter mainly concerned with diluent tolerances and solubility limits. Systematic data on more complex mixtures are virtually non-existent. Moreover, none of the information available refers directly to film appearance. The formulator must therefore rely on traditional rules of thumb, such as "slow evaporating solvents are good for flow", and "too much non-solvent is bad for flow". At the same time, volatility must be kept high to ensure acceptable drying time, and the maximum amount of cheap non-solvent used to give acceptable cost. At present, the only guide to achieving a sound compromise between these conflicting factors is general experience. In practice, this process is used to produce a number of possible solvent blends which are then submitted to testing in the laboratory. If none is acceptable, the results may indicate the direction in which adjustments should be made. The skill of the formulator is judged by the cost-performance of the mixture finally selected, and by the amount of experimental work needed to locate it.

It seems basically unsatisfactory that such an arbitrary procedure still has to be adopted even for coating systems that have been available for many years and have been the subject of a great deal of experimental work. The desirable alternative is to be able to make use of systematic quantitative information in place of general experience. For simple solvent blends of two or three components, it is not difficult to plan a short experimental programme to provide some systematic performance data, nor would such a programme involve a large amount of experimental work. In addition, the relationship between properties and blend composition can easily be visualised using simple graphs, triangular diagrams etc., and a suitable blend located.

When more complex mixtures of five, six or more components are being considered, then the number of variations open to the formulator rapidly becomes very large. It becomes essential to use a planned statistical programme to determine adequately the influence of composition on performance. This type of exercise can involve considerable experimental effort, but the expense is more easily justified if the results can be carried over and coupled with those of other programmes to form a general bank of information suitable for future use. Too often the results of experimental programmes are applicable solely to one problem. There is no carry over of quantitative data and a great deal of potentially useful information is lost. This is particularly true with properties such as film appearance, which do not lend themselves readily to numerical assessment. Even with easily measurable properties, such as viscosity and drying time, there has been virtually no build-up of data because procedures have not been adequately standardised. In this paper several quantitative techniques for dealing with some of these difficulties are discussed.

The assessment of flow in lacquers

A common problem when formulating low cost solvent blends, particularly for cheap non-convertible coatings, is to balance the low viscosity needed for spray application with acceptable film appearance. Reasonably successful solvent blends should not, of course, cause serious film defects such as pinholing or blushing to be developed, but will certainly give rise to some degree of bad flow (usually called "orange peel" because this describes well the appearance of the film). Frequently a choice between blends comes down to a comparison of their effects on the flow of the formulation. It is soon found that, when a series of trial panels are sprayed out, an assessment of their flow involves a good deal of personal preference. As a first step in making the assessments quantitative, the opinions of a panel of assessors should be obtained and their overall rankings analysed for significance by a statistical method. It is the authors' experience that results are often influenced by spraying techniques, and it is desirable to standardise the method of application as far as possible and to have the coatings applied by more than one operator. Alternatively, an automatic spraying machine can be used, although it is important to be satisfied that the machine applies the coating in the same general way as a spray-hand.

As an example of the type of ranking procedure which can be used, suppose that a trial lacquer formulation has been made up using five different solvent blends (I to V), and the lacquers sprayed out in duplicate by three operators (A, B and C). Each group of five panels is then examined by three assessors (α , β and γ), who are each asked to rank them in order of flow, scoring 4 points for the best down to 0 points for the worst. Within each group, the numbering of the panels should be random, so that no preconceived ideas of performance can be carried over from one series to the next. Equal rankings are not allowed and an opinion must be given even in cases of uncertainty. The results

are given in Table	1, where t denotes	the total	score per	panel, and	T the total
score per lacquer.					

	1											Spra	ayer												Total
Lacquer			A		A	(du	plic	ate)			В		В	(du	plic	ate)			С		C	(dı	upli	cate)	points
	As a	ses β	sor γ	1	A: a	ses ß	sor Y	t	A: a	sses ß	sor Ƴ	t	As a	ses B	sor γ	1	A: a	sses β	sor γ	t	As a	sses β	sor γ	t	T T
1	0	2	2	4	1	3	2	6	2	3	1	6	3	2	2	7	2	2	1	5	1	1	1	3	31
п	3	3	0	6	2	1	0	3	0	1	4	5	1	1	1	3	0	0	0	0	3	2	0	5	22
Ш	1	0	1	2	0	0	1	1	1	0	0	1	0	0	0	0	1	1	2	4	0	0	2	2	10
IV	2	1	3	6	3	2	4	9	3	2	3	8	2	3	3	8	3	3	3	9	2	3	3	8	48
v	4	4	4	12	4	4	3	11	4	4	2	10	4	4	4	12	4	4	4	12	4	4	4	12	69

Table 1Typical set of ranking assessments

The overall points scores for each lacquer (T) indicate an average assessment of flow, but there is obviously uncertainty in the results, shown up by a lack of unanimity between assessors. It is vital to know whether the differences in these scores could have arisen purely by chance owing to variation caused by other factors, or correspond to a genuine difference in flow. A statistical analysis can be used to estimate the minimum difference in scores needed for the variation to be considered significant with any chosen degree of confidence. The following simplified calculation is based on a two-way analysis of variance, details of which can be found in standard statistical texts, and uses the mean square for the lacquers \times sprayers interaction to estimate the required variance. The steps involved are shown below.

Let N_A = number of assessors

 N_S = number of sprayers (including duplicates)

 N_L = number of lacquers

Calculate a sum of squares for the total points scores per lacquer (T),

$$SS(1) = \frac{\Sigma(T^2)}{N_A N_S} = \frac{(31^2 + 22^2 + 10^2 + 48^2 + 69^2)}{3 \times 6} = 478$$

Calculate a sum of squares for the total points scores per panel (t),

$$SS(2) = \frac{\Sigma(t^2)}{N_A} = \frac{(4^2 + 6^2 + 6^2 \dots + 12^2 + 12^2)}{3} = 496$$

Calculate the mean sum of squares for the lacquers \times sprayers interaction,

$$M = \frac{SS(1) - SS(2)}{(N_L^{-1})(N_S^{-1})} = \frac{496 - 478}{4 \times 5} = 0.9$$

Calculate the variance of a points total (T)

$$V = N_A \cdot N_S \cdot M = 3 \times 6 \times 0.9 = 16.2$$

As an approximation, any pair of points totals must differ by more than $3 \times$ standard error or $3\sqrt{V}$ for the difference to be considered significant at the 95 per cent confidence level. In this example, the difference must be greater

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than $3\sqrt{16.2}$ or approximately 12 points. This means that the assessments have failed to show a convincing difference in flow between lacquers I and II, whilst that between II and III is borderline. The results can thus be summarised:

Lacquer	Points score (T)	Order of flow performance
V	69	1
IV	48	2
I	31	3 =
11	22 }	5
Ш	10	5

This type of analysis can thus lead to firm conclusions in a field of personal preference. More sophisticated analyses than the one illustrated above can be used to examine the variations between sprayers, assessors, etc., but will not eliminate one serious drawback of this approach. The results for any set are not tied to a fixed standard, so although complete within themselves they cannot be related to those of another set of assessments. There is thus no accumulation to form a general store of data. Even if it is established for one set of lacquers that solvent A gives better flow than solvent B, it is not valid to assume that it will do so when used with other components, or even with the same components in different proportions.

The ranking method of assessment is also unsatisfactory when a large number of panels is involved. (Note that, although 30 panels were involved in the above example, they were assessed in groups of five.) When asked to arrange a series of panels in order of performance, the assessor should in principle examine all possible pairs within the set. In practice, some of the less likely comparisons will be omitted. For example, if panel 1 > panel 2, and 2 > 3 and 3 > 4, he will not usually bother to compare 1 with 4. In a 5-panel set, there are 10 possible pairs, of which about 6 are likely to be examined in order to produce a ranking. For a 12-panel set, there are 66 possible pairs, and the assessor easily becomes confused. In the authors' experience the practical limit for ranking assessments is about 8 panels per set. This is hardly sufficient for the large experimental programmes needed to examine the performance of complex solvent mixtures. Some alternative method is needed.

Assessment of flow against fixed standards

Some of the difficulties discussed above can be overcome by assessing flow against a series of fixed standards and expressing the results on a numerical scale. The simplest approach is to select a range of panels illustrating suitably different levels of flow and use them as standards. These are given arbitrary numerical ratings, say 1, 2, 3, 4 up to 10, and the flow of a test panel obtained by comparison with this standard range. This method is convenient and easy to apply in practice, but suffers from a number of drawbacks. It is difficult to reproduce the standard panels when new standards of the same performance are required, and there is no firm basis for assigning ratings to the standards in the first place.

When asked to compare flow, many assessors find it helpful to use the reflected or transmitted image of some convenient bright object such as a

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striplight or window frame as a guide. The principle is that images transmitted or reflected by a film are distorted by the flow pattern, and the clarity of the image may be used to judge performance. This approach can be made the basis of a quantitative method of flow assessment by introducing a series of standard geometrical patterns as an aid to the assessor.

The transmission technique is currently being used in the authors' laboratory for assessing the flow of clear lacquers sprayed on glass panels. As a further development, it is intended to examine the use of reflection techniques with pigmented systems where transmission of images is impossible. Although the transmission method is capable of further refinement it is already proving useful. One convenient arrangement is to use an overhead projector. Standard patterns are placed on the projector and the image passed through the test panel and focused on a screen. The test panel is mounted at a fixed point in the light path, as shown in Fig. 1.



Fig. 1. Projection scheme for flow assessment

A series of geometrical standards progressively decreasing in pattern size is projected on to the screen until the pattern becomes too blurred to be distinguished. A panel of assessors is asked to record the finest pattern just visible under these conditions. The size of this pattern is taken as a quantitative measure of the flow of the film, coarse patterns indicating poor flow and fine patterns good flow. As the panel of assessors views the projected images simultaneously, a large series of panels can be examined fairly quickly. The numerical results recorded by the assessors are averaged for each panel and for each lacquer to give an overall rating of flow. The values can be analysed for significance by statistical methods, as described in the previous section.

In the early stages of development, a set of wire mesh grids was used as standard patterns. While the wire grids were convenient, being readily available,

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it was found that mesh size was not a suitable measure of their relative sizes. Close inspection showed that the ratio of wire diameter to the aperture size varied for different meshes. Whilst this can be allowed for by calculating suitable size factors for the grids, it seemed a basically unsatisfactory approach, and the wire meshes have now been replaced by a series of photographically reproduced standards. These were obtained as a series of ten black and white transparencies from a photograph of a 50 mesh wire grid by using magnifications ranging from \times 0.5 to \times 2.5. These grids maintain a constant ratio between line width and aperture size. The magnification size of the smallest grid visible to an assessor through a lacquer is taken as a numerical rating of its flow.

The method is basically satisfactory but is capable of a number of refinements. For example, the Institute of Ophthalmology has suggested that patterns of parallel bars would produce less eye fatigue than the present grid designs, and should therefore give improved consistency. The optimum relation between the sizes of successive patterns and whether it should be based on an arithmetic or a geometric progression is also being studied. A further source of variation is that, owing to differences in eyesight and in judgment of the end-point, some assessors consistently record finer grids than others. Some variation in results is to be expected in a subjective test such as this and can be taken into account by using a panel of assessors. However, consistent variations should be eliminated, and methods for incorporating a test of end-point decision into the procedure are being examined so that results can be scaled accordingly.

These improvements are only refinements and do not alter the basic philosophy of the approach. The most important point is that each panel is examined separately and given an independent rating for flow on a numerical scale. The method does not involve comparisons within a series and, unlike the assessment by ranking, is suitable for large series of panels. The results are no longer purely relative, but can be carried over and compared quantitatively with those from other programmes.

The systematic determination and use of data

The development of a numerical assessment method allows flow data on coatings to be accumulated. However, it is essential to ally the method to a systematic approach if the influence of solvent composition on performance is to be adequately determined. In general, the effect of any one solvent on flow, viscosity, or other performance factors will not be a simple function of its concentration, but will depend on the levels of the other components. In order to detect non-linear relationships and interactions between components, it is essential to examine the effect of each component at several different levels.

For example, as part of a continuing programme to generate data on solvent effects that can be used in solving future formulation problems, a five-component solvent blend intended for use in a nitrocellulose lacquer has recently been examined. The object was to take a standard nitrocellulose resin system and determine, within the useful composition range, the effect of each solvent on the viscosity and flow of the system. The components were selected so that the

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relation between true solvent, latent solvent, and diluents could be examined, as well as the effect of varying the aromatic content of the hydrocarbon diluent and the volatility of the true solvent. The five solvents used were:

- (1) MEK, methyl ethyl ketone, low boiling true solvent
- (2) MIBK, methyl isobutyl ketone, medium boiling true solvent
- (3) IPA, isopropanol, latent solvent
- (4) TOL, toluene, aromatic hydrocarbon
- (5) SBP, SBP 100/120, aliphatic hydrocarbon

Composition variations in the blend were described by four variables:

x(1) = Alcohol in total mixture	IPA/Total
x(2) = Ketone in the remainder	KET/(KET + HC)
x(3) = Aromatic in hydrocarbon	TOL/HC
x(4) = Medium boiler in ketone	MIBK/KET

The effect of solvent composition on performance was determined using an RCC (Rotatable Central Composite) design for the experiment. The general method of use of RCC designs in surface coating work has been described elsewhere and need not be discussed here^{1, 2, 3}. Lacquers based on the 31 different solvent blends required by the design were made up and tested, including seven replicates of the centre point composition to determine the experimental error of the test methods. Each variable was examined at a total of five levels, denoted -2, -1, 0, +1, and +2 in design units as given in Table 2.

Composition variable				Levels		
Composition variable		-2	-1	0	+1	+2
x(1) = % vol. alcohol in total		0	6	12	18	24
$x(2) = \frac{9}{6}$ vol. ketone in remainder		45	50	55	60	65
$x(3) = \frac{9}{6}$ vol. toluene in hydrocarbon		30	40	50	60	70
x(4) = % vol. MIBK in ketone	••	45	55	65	75	85

 Table 2

 Levels selected for composition variables

The experimental effort of examining all the possible combinations of these levels would be out of the question. In an RCC design, only certain specified combinations need to be examined, as set out in Table 3. After the lacquers had been prepared, sprayed out, and tested, the experimental results were processed by computer using a multiple regression programme. A general regression equation was used, and a best fit equation derived relating each property to solvent composition. Linear, quadratic, and two-way interaction terms were included for each composition variable and non-significant terms discarded.

	RCC programme
Table 3	Combinations of levels used in a 4-variable

																						L	L	İ.	
										, ,	Exp	erim	ent r	lmur	Der										
Variable	1-7	8	6	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
<i>x</i> (1)	0	1	-	-	1	1	1	-	-	-	1	ī	-	ī	-	I	-	+2	-2	0	0	0	0	0	0
x(2)	0	-	Г	1	1	1	ī	1	ī	1	1	1	1	T	1	T	-	0	0	+ 2 $+$	-2	0	0	0	0
x(3)	0	Г	1	ī	1	1	-	ī	ī	1	1	ī	1	Г	_	T	Ξ	0	0	0	0	± 2	-2	0	0
x(4)	0	-	T	-	-	-	Ī	-	ī	-	ī	-	Ŧ	-	I	-	1	0	0	0	0	0	0	+	2
																		_			I		İ		1

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These equations relating performance to solvent composition can be used in several ways. First, it is possible to interpolate multi-dimensionally and estimate the performance expected for any blend of the five components. These estimates will be most accurate for points near the central composition and will become progressively less well defined as the distance from the centre increases.

Whilst this type of information can be useful, the formulator usually requires some sort of visual impression of performance trends. There is an insuperable problem here in that the human mind cannot visualise variations in more than three dimensions simultaneously, and in practice can only deal conveniently with two-dimensional plots. The computer programme used to analyse the results of this experiment can also be used to plot out diagrams showing the dependence of any performance factor on any pair of composition variables. Figs. 2, 3, and 4 are examples of these plots and show the flow and viscosity of the lacquer, and the cost of the solvent blend as functions of alcohol content and the proportion of ketone in the remainder of the solvent. Variables x(3)and x(4) are held constant at the +1 and -1 levels respectively, so that each diagram refers to a hydrocarbon containing 60 per cent TOL/40 per cent SBP, and to a ketone of composition 55 per cent MIBK/45 per cent MEK.



Fig. 2. Flow

The flow results are derived from measurements using standard grids and have been put on a scale from 0 (bad) to 10 (good) for the purposes of this exercise. Fig. 2 shows that the lacquer gives the best flow with solvents containing no alcohol and the maximum amount of ketone. However, it is interesting to note that, although alcohol adversely affects the flow of mixtures rich in ketone, it has little effect on flow with lean mixtures. Fig. 3 shows the viscosity in poise at 25 per cent wt/vol solids. In this case there is an optimum alcohol content for the lowest viscosity, but again the situation is not straightforward. The optimum shifts from about 12 per cent alcohol in the richest mixtures. The



cost of the solvent mixtures in shillings/gallon is shown in Fig. 4. It is obvious here that the best area for cost does not correspond with those for flow or viscosity, and any practical system will have to be a compromise between these opposing trends. It must be stressed, however, that these conclusions may not hold for other values of the two variables x(3) and x(4) which were held constant in this example.

Two-variable plots such as these can be used to solve simple formulating problems graphically. For example, within the limited range of compositions represented by Figs. 2-4, it is simple to locate the minimum cost blend giving a viscosity say of ≤ 2.4 poise and a flow of ≥ 7 . The problem is not so simple when none of the composition variables is fixed and an optimum is being sought in more than three dimensions. In some cases it may be possible to print out

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enough plots of this type to locate the required composition graphically. However, it is much easier to let a computer find the optimum composition using a standard non-linear optimisation programme. As an example, the centre point blend examined in the RCC experiment gave a flow of 6.1, viscosity of 2.8 poise and cost 5.4 shillings/gallon. The optimisation programme can be used to answer the question, "What is the cheapest blend of these components giving the same or better flow and viscosity?" The computer located a blend meeting these requirements and showing a 5 per cent cost saving. The composition variables and the actual compositions of the centre point and optimum cost blends are given in Table 4. As the proportion of every solvent has been changed to some extent it is doubtful if any other method could have located this minimum cost composition in a reasonable time.

The procedure is quite general in application and can be used to optimise any property within a set of constraints provided these can be expressed by an equation in solvent composition.

							Centre point blend % vol.	Optimum cost blend* % vol.
x(1) Alc	cohol	in total					12	18
x(2) Ke	tone i	n rema	inder				55	47.5
x(3) Are	omatio	in hy	frocart	on			60	70
x(4) Me	edium	boiler	in keto	ne	• •	• •	65	74.5
MEK							17	10
MIBK							31	29
IPA			• •				12	18
TOL							20	30
SBP	• •	•••	••	• •	••		20	13
Cost (sł	nilling	s/gallor	n)				5.4	5.1

		Tab	le 4		
Solvent	blends givin	g equal	lacquer	viscosit y	and flow

*Within the area examined experimentally.

With consistent information of this type available, the formulator would be in a much better position to tackle practical problems. Provided test methods are adequately standardised, further data can be added to the store from subsequent experimental programmes, and a still more general picture of performance trends built up. An aspect of particular interest is the ability to make a quick response to a sudden shortage of a component or a change in price structure. Although it would no doubt be prudent to carry out some check tests on the calculated formulations, the amount of work involved should be small.

The selection of solvent blends using basic solvent properties

The drawback of the formulating approach outlined in the previous section is that it provides no basic understanding of the factors that influence the performance of a coatings system. Whilst data on solvent effects can be steadily built up from experimental programmes and accurate predictions made within the range of compositions examined, there is no firm basis for projecting those predictions to include other solvent components and behaviour with other resins.

It should be possible to make use of the basic properties of the solvents themselves to estimate the performance of a mixture. It is known, for example, that the solubility parameter and measures of polarity and hydrogen bonding give a guide to which solvents will dissolve a resin, that solvent viscosity correlates to some extent with solution viscosity, and that evaporation rates give some indication of drying time and flow performance. These basic properties can be used as a first step towards setting up a quantitative formulating method. For example, consider the following problem. A solvent blend performing satisfactorily in a nitrocellulose lacquer is calculated to have properties as shown below.

Solubility parameter	δ	8.75
Fractional polarity ⁴	Р	0.16
H-bond acceptor index ⁵	HB	6.22
Solvent viscosity (cP)	Visc.	0.61
90 [%] wt evaporated time (sec)	Ev. time	440
Cost/unit volume (relative cost)	Cost	23.7

These properties were calculated assuming a linear dependence on composition, that is by weighting according to volume fraction. This is known to be a poor approximation in many cases, but there is little alternative unless a specific non-linear relationship is known to apply. In this calculation mixture viscosities were obtained by linear combination of log values.

The object is to produce a blend with properties at least as good as those of the control at lowest cost, using the six components shown below.

		Relative price/unit volume
Acetone	DMK	19.0
Methyl isobutyl ketone	MIBK	37.7
"Oxitol" acetate*	OXAC	83.8
<i>n</i> -Butanol	NBA	36.4
Xylene	XYL	12.1
SBP 120-140	SBP	9.6

The constraints defining an acceptable blend are set up as follows. It is known from the solvency parameters of true solvents and non-solvents for nitrocellulose that any reduction in the δ , P, and HB values from those of the control blend will give reduced performance. However, it is tempting to make such a reduction because of the need to maximise the hydrocarbon content to obtain minimum cost. Thus, any blend matching the control should

^{*}Mono-ethylene glycol mono-ethyl ether acetate. Shell trade mark.

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have $\delta \ge 8.75$, P ≥ 0.16 , and HB ≥ 6.22 . It is unnecessary to set maximum limits on the values of these parameters as those of the cheapest solvents tend to be lower than those of the control. For mixtures of similar solubility characteristics, solvent viscosity is likely to be a guide to the viscosity of the resin solution. A limit of ≤ 0.61 cP is thus appropriate for the blend viscosity, so that mixtures more viscous than the control are ruled out. Lastly, fast evaporating blends might be expected to be bad for flow. As the cheap solvents, in general, evaporate very quickly, a minimum limit on the 90 per cent wt evaporated time is necessary. The 440 seconds value for the control was used as a guide.

The cheapest blend of the six components which meets all these requirements was located using a linear optimisation programme.¹⁰ The blend composition is shown in Table 5 as "first attempt," together with its calculated properties and the limits set on them.

Solvent					First attempt composition % v/v		Second attempt composition % v/v	
DMK MIBK OXAC NBA XYL SBP	 		··· ·· ··	 	2.7	3.0 0.0 0.0 0.0 4.5 2.5	10.0 25.9 5.0 0.0 51.8 7.3	
Blend price per unit volume				e	13.6		22.7	
Properties					Limit set	Value found	Limit set	Value found
δ P HB Viscosi Evap. t Volum Volum	ty (cP) time (se e fracti e fracti	 ec) on Di on O	 мк кас	 		9.08 0.16 6.22 0.55 550		8.75 0.16 6.85 0.59 575 0.10 0.05

 Table 5

 Examples of cost optimised blends

The blend is borderline as a solvent for nitrocellulose but is definitely unacceptable from the point of view of volatility balance. The true solvent, acetone, evaporates too fast compared with the diluents, and the blend would rapidly become a non-solvent for the resin. This is perhaps not surprising, as none of the constraints applied have any influence on solvent balance.

Two approaches are possible at this stage. The first is to fall back on general formulating experience and use this to set additional constraints until an acceptable blend is obtained. For example, the proportion of fast evaporating true solvent could be limited to a maximum of 10 per cent, and a minimum of 5 per cent of slow evaporating true solvent could be required in the blend. The result is shown in Table 5 as "second attempt." This appears to be an acceptable blend and might be a reasonable starting point formulation for an

experimental programme. The most convenient way of using this approach is to set up the optimisation programme so that it can be used through a conversational computer terminal. The formulator can then set constraints defining the properties required and obtain a minimum cost blend in a matter of seconds. The effect of changing or adding constraints can be judged and an acceptable blend located by a stepwise procedure.

However, it is evident that the formulator's experience plays a vital role in the above procedure and a second and more satisfactory approach would be to extend the mathematical model to include further solvent effects. The question of solvent balance is perhaps the most important. Methods of calculating composition changes during the evaporation of mixed solvents are now available that take into account non-additive effects⁶, ⁷, ⁸. These can be used to estimate the way in which the properties of the solvent mixture change during evaporation⁹. This type of calculation could be used to set further constraints on properties, so that only blends maintaining adequate solvency throughout the evaporation process would be considered acceptable. There is thus room for considerable further development of the method.

The methods described in this paper are in a fairly early stage of development. Nevertheless, it is believed that they show promise of improved efficiency in dealing with the problem of formulating solvent mixtures for coatings so that film appearance coupled with other required properties can be obtained.

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Discussion at the Torquay Conference

MR G. W. ROTHWELL referred to the technique of using a panel of assessors to compare experimental paints with a standard. Obviously some acceptance limits must have been set, but was it not possible that the subjective judgments of the assessors would vary, for a number of reasons? Discussions between assessors could influence their decisions.

MR L. A. TYSALL agreed that this was possible, but said that it could be allowed for. It was really a question of designing the method. When the earlier work on assessment of flow had been carried out, an investigation of the method had been included, by





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performing the work almost in reverse: the assessors had been assessed using specially prepared samples. This gave a guide to the efficiency of the method.

A similar problem arose in testing in the food industry, and there was a British Standard Method for the screening procedure in choosing the panel. Similar procedures could be carried out for the flow assessments—in general, inconsistent assessors were discarded, and the individual tendencies of each assessor discovered and, if necessary, allowed for mathematically.

MR F. ARMITAGE remarked that it had been stated that in setting up the observation experiments it had been necessary to prepare as many as seven different resin solutions to allow for variations in raw materials. Differences between batches of the same raw material were a constant problem in the paint industry; did this mean that different batches of each of the seven resins had also to be made up, to allow for batch-to-batch variation?

MR TYSALL said that the emphasis had not been intended to be on batch variation; in fact, he would not expect much variation in flow between formulations based on two deliveries of the same resin, and the reason for the seven-fold replication of the centre point blend was to estimate general experimental variations, for instance, the consistency of the operator in preparing the blend.

MR ARMITAGE said that he did not think it should be necessary to allow for operator error in this sort of experimental work.

DR E. E. LONGHURST said that Mr Tysall had adopted a truly statistical approach to this problem, and had, no doubt, taken into account several factors which had not been specifically mentioned. In particular, would he comment on the order of presentation of the grids—had these been presented in random fashion—and the differences in eye fatigue at different times of day? If such factors were not taken into account, the usefulness of the technique would be diminished.

MR TYSALL agreed with the last remark. They had been aware of the large number of factors to be considered, but as this had been rather a tentative investigation, not all were allowed for. In fact, the grids were presented in order of decreasing mesh size, so that the first one whose pattern could not be distinguished could be decided; this had proved to be the easiest method in practice.

In respect of variations in eye fatigue at varying times of day, no work had been carried out. Dr Wheale, of the Institute of Ophthalmology, had been invited to see the test and give a specialist opinion, and he had approved the procedure in general. With the procedure used so far, it was felt that there was little danger of eye strain to the assessors.

An operation that might be affected by the time of day when it was performed was the spraying. It was suspected that the flow of the sprayed paint was strongly influenced by the humidity at the time of spraying, and this was being investigated.

MR S. L. DAVIDSON mentioned work that had been carried out in California in connection with humidity effects. Specimen traffic paints had been tested in Sacramento, where the summer conditions were in the range of 105°F and 0 per cent humidity. When the paints were applied in San Francisco, where the conditions were 60°F and 70 per cent humidity, the paint did not dry satisfactorily. This was eventually traced to the fact that there was 5 per cent of isobutyl carbinol in the formulation. When this was replaced by mineral spirits, the paint dried quickly. Was it possible to incorporate this type of practical experience in a computer programme of the type Mr Tysall had described?

MR TYSALL said that, in principle, any factor could be included. The results of tests on the evaporation rate or drying rate of the coatings over a range of temperatures and humidities could be used to correct for these properties, although he felt that the

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humidity had a negligible effect on evaporation, mainly affecting water pick-up by the film.

The work described in the paper had been on nitrocellulose lacquers, where the drying time factor could be covered by including print test results in the programme, but for other types of coating, more than one drying test might have to be used. As long as a test gave consistent results, and could be carried over from one programme to another, there was nothing to prevent its being incorporated in the programme.

MR T. R. BULLETT returned to the variation in component materials. He said that, at the Paint RA, it had been found, in computing colour formulations, that the most economical formulations could be on the edge of possible matching, giving no margin of adjustment if materials varied slightly. Was it possible to incorporate safety factors into optimisation procedure to avoid choosing minimum cost formulations that turned out to be on the edge of a cliff and, therefore, impractical?

MR TYSALL replied that, in principle, safety factors were already used. The minimisation of cost was not built in to the experimental programme, but had merely been given as an example of how the results might be used. Acceptable standards were set for all properties but one, and this one property was then optimised. Thus, the cheapest formulation giving a certain level of viscosity and flow could be obtained, but equally well a formulation giving the best possible flow for a set viscosity and price could be determined. If the area within which optimum blends were selected were further restricted by setting minimum acceptable limits on more properties, this was in effect building in a safety factor, and there then seemed little danger of falling over Mr Bullett's hypothetical cliff.

More difficulties would be expected to arise from such aspects as the correspondence of laboratory preparation to full scale production.

MR P. FINK-JENSEN asked if it would be necessary in selecting an optimum blend to evaluate the sensitivity of the properties to changes in composition arising from, say, errors in production.

MR TYSALL said that this was going back to thoughts of safety factors. The setting of the original levels of acceptability would obviously include an allowance for such eventualities.

MR FINK-JENSEN asked if other properties of the film, such as solvent retention and mechanical properties, which were perhaps of more interest to the customer, could be included, and if the choice of solvent could be influenced.

MR TYSALL said that the number of factors included was limited only by the eventual size of the programme involved, and a decision on how much work should be carried out had to be made. The simple programme he had outlined had been based on appearance merely to illustrate the general technique.

DR S. H. BELL commented that Mr Tysall had shown how to assess the sprayers and the assessors, but what was emerging from the discussion was the difficulty of assessing the customers. It was the definition of "acceptable" tolerances that was in question, which perhaps Mr Bullett had had in mind in drawing his cliff-edge analogy. The tolerances aimed at might be too fine. Perhaps the customer's tolerances were less exacting. Had the authors gone into this aspect of acceptable tolerances?

MR TYSALL agreed that this was a very important point, but said that it was difficult to design a laboratory programme to measure such tolerances. The problem of persuading the customer what level he required was a psychological one, and it was hard to see how to allow for it. In a sense, it could be argued that it was not the immediate customer who should be satisfied, but his customer's customer, i.e. the individual buying the finished paint in the shop. For this reason a panel representing the public who bought the paint had been used to assess the properties, rather than one representing the companies buying the solvent.

Basic lead silicochromate*

N. L. Industries Inc., 111 Broadway, New York, NY 10006

Summary

This paper describes in brief the properties and uses of basic lead silicochromate. The composition, dispersing characteristics, corrosion-inhibition to be expected and versatility of the pigments when used with a wide selection of types of binder for protection of steel under many conditions of exposure, are outlined.

Keywords

Types and classes of substrate steel

Prime pigments and dyes basic lead silicochromate

Types and classes of coating corrosion resistant coating

Le silicochromate de plomb basique

Résumé

Cette communication décrit brièvement les propriétés et les applications du silicochromate de plomb basique.

On délinée la composition, les caractéristiques de dispersion, l'inhibition de corrosion que l'on doit s'y attendre, et la polyvalence de ce pigment lors de son utilisation avec une gamme étendue de types de liants pour la protection de l'acier sous plusieurs conditions d'exposition aux intempéries.

Basisches Bleisilicochromat

Zusammenfassung

Die Eigenschaften und Anwendungsmöglichkeiten von basischem Bleisilicochromat werden beschrieben. Zusammensetzung, Dispergierungscharakteristika, zu erwartende Korrosionsinhibierung und Vielseitigkeit der Pigmente in Verbindung mit einer grossen Auswahl von Bindemitteln für den Stahlschutz, unter vielerlei Beanspruchungen angewandt, werden dargelegt.

Основной кремнистый хромат свинца

Резюме

Статья кратко описывает свойства и применения основного кремнистого хромата свинца.

Рассматриваются состав, дисперсные характеристики, ожидаемое ингибирование коррозии и многосторонность пигментов в применении с широким выбором крепителей для предохранения стали в различных условиях выветривания.

Introduction

The use of basic lead silicochromate in coatings has been thoroughly investigated over a long period by paint chemists and those concerned with the protection of steel. It has gradually gained acceptance and now has found a permanent place amongst the anti-corrosive pigments of the paint industry.

In the Western Hemisphere alone, basic lead silicochromate primers, undercoats and finishes for bridges, tanks and other structural steel surfaces are specified by over 60 city, county, state and provincial highway departments, toll roads and bridge authorities. A number of paint manufacturers formulate coatings based on basic lead silicochromate. Both the Canadian and United States governments have specifications for paints containing the pigment.

^{*}Presented to the Torquay Conference on 6 May 1971.

It may be very conservatively estimated that a minimum of fourteen million tons of steel have been coated and protected by basic lead silicochromate paints in the past five years alone. The true figure may be twice that.

Basic lead silicochromate, as sold by NL Industries, for example, under the trade name Oncor M50, is one of a family of light-weight active pigments which have been developed primarily for use in paint compositions. The techniques of preparing compounds of this type were first disclosed by National Lead Company in 1948 in connection with basic silicate white lead.¹ The further development and properties of basic lead silicochromate have also been described 2,3

Basic lead silicochromate is a complex monobasic lead chromate/y-tribasic lead silicate compound formed by calcination on to a silica core. The allowable range of chemical composition for the product under discussion is described in: "Standard specifications for basic lead silicochromate: ASTM designation: D1648," and is as follows:

Composition of basic	Table 1 lead silicochromate pigment
PbO	46.0-49.0%
CrO ₃	5.1-5.7%
The molar rational technology	io of PbO to CrO_3 is 4:1.

In 1970 a new basic lead silicochromate pigment was introduced; the fine grade of this material, Oncor F31, is a finer particle size product and has the following composition:

PbO	42.0-45.7%
CrO ₃	6.3- 7.1%
SiO_2	47.5-50.5%
The molar ratio	of PbO to CrO_3 is 3:1.

Table 2	2 outlin	es som	e physical	propertie	s of	both	basic	lead	silicoch	romate
pigments	which	are of	importanc	to the	pain	t forn	nulato	r.		

Table of properties	—Basic	lead si	ilicochr	omate	
Specific Gravity	 cm ⁻¹) e hidin	 g, con	 ntrast	Regular grade 4.1 0.08 %* 0.002 %* 0.005 %* 120000 99.7 % 13-18 390 sq.ft., 9.7	Fine grade 3.95 0.21%* 0.003%* 0.017%* 0.008%* 61000 99.9% 13-19

Table 2

*Average analysis.

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Spectrophotometric analysis of basic lead silicochromate shows that its dominant wavelength lies in the red-orange part of the spectrum. Its colour is dull orange.

Fig. 1 shows the particle size distribution of the basic lead silicochromate pigments.



Fig. 1. Particle size distribution of basic lead silicochromate

Behaviour toward infra-red light

Basic lead silicochromate tends to transmit light in the near infra-red region of the spectrum (700-900nM). The data indicates low values of absorption, diffuse reflection and hiding power under this condition.

The percent reflection does not vary markedly over the 700-900nM range.

Basic lead silicochromate, therefore, should be useful in camouflage colours for one-coat metal protection. The tinting colours used will mask the characteristic dull orange colour in the visible range.

Toxicity of basic lead silicochromate

The toxicity of lead silicochromate is an important factor when considering personnel applying paints formulated with it. Since it is a compound of lead, obviously the pigment can be toxic. However, it is interesting to note that, because of its unique structure (a thin shell of lead compound on a silica core which represents 50 per cent by weight of the pigment particle) and chemical composition—in which about half the lead is present as acid insoluble non-

toxic compounds (lead chromate and lead silicate), that only about one-quarter of the weight of the pigment can be considered dangerous (basic PbO). By comparison, the lead in red lead is completely available as a toxic agent, and half the lead in monobasic lead chromate is soluble in acid.

With any normal precautions, basic lead silicochromate paints can be handled without danger. It should be borne in mind that the solvents used in paints are more immediately hazardous and must be handled accordingly.

Dispersion

Basic lead silicochromate is easy to disperse with all customarily used equipment. Some care must be taken when using a roller mill, otherwise discolouration from the abrasive action of the silicate pigment on the rolls will take place. Intimate premixing, and adjustment of the grinding paste to have considerable tack, will eliminate this potential problem. Of course, some wear of the mill blade is to be expected.

Steel ball mills should not be used because of the discolouration problem. Even here, it has been found that by careful formulation of the mill charge—low solids and low viscosity—a reasonable dispersion can be obtained in a short time. Time, of course, is most important, since the longer the milling period, the worse the discolouration.

Regular grade basic lead silicochromate has been evaluated for speed and degree of dispersion in four types of equipment: sand mill, high speed dissolvers (Kady, Cowles), pebble mill, and roller mill. Table 3 presents some of the data obtained.

			Hegman fineness of grind gauge reading
High-speed dissolvers*			
2 minutes	÷.	 	 4.5
35 minutes		 	 5.0
Sand mill*			
5 minutes		 	 4.5
10 minutes			 5.0
20 minutes		 	 5.5
Pebble mill**			
24 hours		 	 5.5

Table 3 Dispersion data Standard grade basic lead silicochromate

*Single pigment basic lead silicochromate/long oil alkyd formula at 33.4 per cent PVC. Dispersing charge varied for equipment used, whether a dissolver or sand mill.

**Mixed pigment formulation: 4 parts basic lead silicochromate, 1 part titanium dioxide, 1 part chromium oxide green, long oil alkyd at 33.4 per cent PVC: Complete formula ground with the exception of the driers.

A properly formulated paste for a roller mill dispersion will result in a paint fineness of grind of from 4 to 5.

Fine grade basic lead silicochromate pigment has been evaluated for ease of dispersion by two laboratory control methods.

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Pebble mill

Pigment and alkyd resin solution are inserted in a glass jar containing flint pebbles and shaken for intervals up to 15 minutes on a paint shaker. The finenesses of grind obtained were, for example:

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Grind	Regular grade	Fine grade
2 minutes .	4.5	4.0
5 minutes .	4.5	5.0
5 minutes .	. 5.0	6.0

High-speed dissolver

Pigment and alkyd resin solution are mixed by hand to a uniform, wetted, paste condition. An air-driven stirrer is inserted into the mix and operated at 2500—3500 RPM for three minutes, after which the paste is reduced and checked for fineness of grind.

Regular and fine grades of basic lead silicochromate show an equal ease of dispersion by this test.

Colour and gloss characteristics

When comparing regular grade and fine grade basic lead silicochromate pigments as replacements for one another in solvent based formulations, two marked differences arise.

If the regular grade is replaced on an equal volume basis with the fine grade in a structural steel primer (US Federal Specification TT-P-615d, Type II, a basic lead silicochromate, iron oxide, 1:1 linseed oil: medium-oil alkyd) an approximately twofold increase in measured 60° gloss is noted. The figures range from 22-31 per cent for the regular grade to 45-57 per cent for the fine grade, based on several determinations. This must be considered when formulating primers and undercoats. This property is of greatest interest for high-gloss anti-corrosive finishes.

If the fine grade is substituted for the regular grade on an equal volume basis in a medium depth blue-grey coloured coating, for example, the fine grade will produce a much yellower colour. It will be tan rather than grey, and there will be little resemblance in colour. If the fine grade is substituted on an equal *cost* basis (approximately 90 per cent as much as on a volume basis) the resulting colour will be comparable.

The reasons for these colour differences are the finer particle size and higher chromium content of the fine grade.

Despite the finer particle size of the newer pigment, when compared on an equal volume basis with the regular grade in an alkyd resin primer, for example, little increase in paint viscosity has been noted, values from 0 to 10 per cent higher being obtained.

Formulating and paint characteristics

There is not sufficient space available to discuss in depth the variety of compositions in which regular grade basic lead silicochromate has been used. Table 4 gives a partial list of end-uses for which paint manufacturers are known to have adopted the pigment. It may be said, as a generalisation, that basic lead silicochromate is much more versatile than red lead in its ability to be used with a wide variety of vehicle types. Such coatings perform well, are canstable and free of drastic viscosity changes.

 Table 4

 Uses of basic lead silicochromate coatings

Salt water immersion Fresh water immersion Severe chemical exposure General chemical & industrial Shop & maintenance Agricultural chemical Zinc rich barrier Specification paints Marine atmosphere Electrodeposited coatings

Table 5 gives a partial list of types of binder with which basic lead silicochromate may be used.

 Table 5

 Useful binders for basic lead silicochromate

		Epoxy resins (esters, amine-cured)
	••	Water-soluble resins (convertible)
		Water-emulsion resins (latex)
rnishes		Chlorinated rubber
		Petroleum resins
	 Irnishes	

Settlement problems may occur with basic lead silicochromate, as with many other pigments. It has been found that the usual suspension aids, particularly an organo-montmorillonite (Bentone* 34, 38 and 27) solve the settling problems, provided, of course, that these agents are used properly.

The fine grade basic lead silicochromate, which to date has found commercial acceptance in electrocoating and dipping primers, shows superior suspension properties in water reducible vehicles. Instances are reported where no suspending agents have been required.

Experimental work has been done to determine the effect on corrosion inhibition of the concentration of regular grade basic lead silicochromate present in a formula. In Fig. 2 a series of curves is shown, in which the per-

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^{*}Bentone is the registered trade mark of NL Industries Inc. for viscosity control and pigment suspending agents.

formance (corrosion ratings with 10 being perfect) of paints with different concentrations of anti-corrosive pigment is plotted against time. The basic lead silicochromate/iron oxide primers were formulated at 39 per cent PVC in a long-oil alkyd. The surfaces were sandblasted to white metal followed by complete rusting. Loose rust was then gently brushed off and the paints applied by brush. The ratings are performance of one coat of primer applied at 50μ dry film thickness and exposed in a rural environment inclined at 45° facing south.



Fig. 2. Effect of basic lead silicochromate on corrosion resistance

These data may be useful in the development of a competitive, modestly priced anti-corrosive primer or finish, or a first-class, long-term durability type paint for the protection of major structures.

Because of its colour, hiding, and raw materials cost, regular grade basic lead silicochromate is usually diluted with one or more auxiliary pigments. Those auxiliary pigments that have been found most suitable are listed in Table 6. It should be understood that other pigments which have not been explored in depth may be equally good.

Table 6 Auxiliary pigments for basic lead silicochromate

Siliceous red iron oxide	Barium sulphate
Pure (98%) iron oxide	Magnesium silicate
Titanium dioxide	Mica (Max. 10% of pigmentation)
Graphite	Aluminum flake
Titanium dioxide	Mica (Max. 10% of pigmentation)
Graphite	Aluminum flake

Barium sulphate is of particular interest because it may be used in greater amounts than magnesium silicate, for example, to extend the useful PVC protective range.

In one test of alkyd primers for structural steel containing a constant amount of basic lead silicochromate, the addition of barium sulphate allowed an increase in the PVC from 45 to 55 per cent, without adversely affecting corrosion protection. Aluminum pigment and basic lead silicochromate mutually assist each other. Aluminum is particularly effective in marine primers. Basic lead silicochromate, when present in an aluminum bridge finish, retards erosion of the aluminum paint, thus delaying an expensive repainting cycle.

It should be pointed out that zinc chromate, an anti-corrosive pigment, does not perform as well when used in combination with basic lead silico-chromate as it does when used with red lead. This is demonstrated in Fig. 3. Paints T-8881 and T-8877 both contained basic lead silicochromate and were identical in composition except that T-8881 also contained zinc chromate. After 500 hours' 5 per cent salt-fog exposure, the panels were stripped. Pitting is evident in the sample marked T-8881.

In addition to accelerated tests of this type, experience has shown that this also occurs with paints atmospherically exposed where varying ratios of basic lead silicochromate to zinc chromate have been used.



Basic lead silicochromate and zinc chromate Basic lead silicochromate Fig. 3. Effect of intermixing pigments

In general the presence of other anti-corrosive pigments has not been found to improve the performance of basic lead silicochromate.

Basic lead silicochromate pigmented coatings are designed for use on steel. They will usually outperform red lead or zinc chromate when applied on rusted surfaces. This is shown by the following corrosion ratings of mill scale carrying specimens, with some rust present, some protected by single pigment shop primers of standard grade basic lead silicochromate and others protected by primers based on red lead, the panels being exposed at an inclination of 45° in a rural environment, facing south.

Table 7	
Comparison of corrosion-resistance of basic lead	l silicochromate and red lead primers

						1	Mont			
					12	19	31	47	69	
Basic lead silicochromate		•••	••						10	corrosion rating
Red lead (non setting)	••	••		••	10	9	8	6	1	

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Part of the failure of red lead can, of course, be attributed to carbonation and eventual erosion. The excellent weathering characteristics of basic lead silicochromate are evident. This is an advantage when shop-primed steel is exposed for periods up to 18 months.

The specific anti-corrosion characteristics of fine grade basic lead silicochromate in a conventional solvent-based type primer may be recorded. In two examples containing two pounds and six pounds of anti-corrosion pigment per US gallon, using a medium-oil alkyd, the fine grade basic lead silicochromate showed slightly better corrosion resistance in 5 per cent salt-fog box and high humidity box exposures than the standard grade.

Basic lead silicochromate primers have no adverse effect when applied on aluminum metal. They are not, however, suggested for use on galvanised surfaces, unless those surfaces have been well weathered or coated first with a vinyl butyral primer.

Basic lead silicochromate-containing paints are satisfactory when applied over zinc-rich coatings, but when inorganic types are used, it is as well to use an alkaline-resistant barrier coat, otherwise the alkalinity will attack the conventional oil and alkyd vehicles.

Marine exposure tests (alternate immersion) have shown that considerably less system failure results when a vinyl butyral metal primer is used over either organic or inorganic zinc-rich primers, despite the fact that alkali-resistant finishes (vinyl or epoxy) may be used.

Resistance to erosion

It has been found that coatings pigmented with standard grade basic lead silicochromate show outstanding colour retention and resistance to erosion and chalking whether used as undercoats or finishes. It is obvious, of course, that if free chalking pigments are used they will reduce the resistance to colour change and erosion.

Several years ago erosion exposure tests were carried out at locations having dissimilar environments, (marine, rural and industrial atmospheres). The coatings used were simple oil/alkyd undercoats and finishes pigmented with basic lead silicochromate (standard grade). Comparison was made with coatings of the types which were standard at that time in specifications for protecting structural steel work.

In order to demonstrate the resistance to erosion, it is only necessary to quote the results with single coats of paint. The loss in film weight makes it obvious what would happen over a period of time with systems combining several of the coatings.

It should be noted that the industrial environment, which is quite corrosive, did not produce the degree of erosion experienced in the rural environment. This is because of the protective layer of soil and dirt which prevented the sun from attacking binders to the same extent as in the clean rural environment.

The data conclusively show the resistance of basic lead silicochromate paints to erosion.

R. P. BATES

Table 8

Percentage loss in film thickness after 62 month's exposure at an inclination of 45° facing south

Composition	on				Envir Rural % loss	onment Industrial s of film
Red lead/linseed oil			 		80	33
White lead/leaded zinc/extenders/linsee	ed oi	1	 		100	33
Leaded zinc tinted with chromium oxi	de gi	reen	 		30	20
*BLSC/4:1/linseed oil:alkyd			 		11	0-5
BLSC/TiO ₂ /extender/2:1 oil:alkyd gre	ev	••	 		10	0
BLSC/TiO ₂ /chromium oxide green/2:	i oil	alkyd	 		0	0
BLSC/iron oxide/2:1 oil:alkyd					0	0-5
Red lead/linseed oil			 		100	40
Aluminum/phenolic resin varnish				• •	100	66
				,		

*BLSC = Basic lead silicochromate.

Use in emulsion paints

There is an ever increasing interest on the part of paint manufacturers in the development of effective anti-corrosive primers and finishes for steel surfaces, using water-emulsion or water-dispersible resins.

There are a few obvious reasons that make such coatings interesting, among which are the growing need to comply with anti-smog regulations, elimination of toxic organic solvents, the relative ease of handling and water clean-up, and the possibility of having available coatings which may be used satisfactorily on damp surfaces without the attendant failures associated with solvent coatings which may trap moisture.

Emulsion paints have their disadvantages, for example, porous films which necessitate multiple coats, inability to be applied in freezing weather, the presence of water sensitive or soluble ingredients, and fast setting time which prevents satisfactory penetration into rusted surfaces.

Pigmentation

A variety of water-based primers have been formulated and exposed. Most of the work has been with formulations containing from 50 to 80 per cent standard grade basic lead silicochromate based on the pigmentation.

Pigment volume concentration: Two PVC ladder series of exposures were made to determine the optimum level. An acrylic resin latex was used.

In general, it was found that good protective primers can be made up to a PVC of 36 per cent, providing the substrate is rust-free. Where conditions are less perfect, and rust is present, a PVC between 25 and 30 per cent is preferred.

It is interesting to observe that the presence of basic lead silicochromate in coatings formulated in the preferred range improves corrosion resistance. This is shown in Table 9.

				0						
			5	1 coat				2 coats		
				Weathering Months	12	19	33	19	33	
Iron oxide	•••	 	 	PVC %	10	8	1	10	9	
*BLSC/iron oxide		 	 	20	10	10	7	10	10	
Iron oxide		 	 	30	4	1	1	10	10	
BLSC/iron oxide		 	 	30	10	10	10	10	10	
Iron oxide		 	 	36	1	1	1	8	3	
BLSC/iron oxide		 	 	36	10	10	10	10	10	

	1	able 9					
Emulsion	primers-corrosion	ratings:	cold	rolled	steel	surfaces	

*BLSC = basic lead silicochromate. (300 g, l^{-1}).

Vehicle formulation

Experience has shown that, to obtain better performance over the wide variety of surface conditions that a paint is expected to protect, the use of some modifying oil or resin is of value.

At the expense of some drying speed, up to 40 per cent of linseed oil or chinawood oil, based on the non-volatile content of the vehicle, might, for example, be added to an acrylic latex. This aids surface wetting characteristics and renders the paint film less permeable. Alkyd and epoxy esters may be used, not particularly for wetting, but to enhance impermeability.

The choice of other vehicle ingredients, i.e. wetting agents and pigment suspending aids, is important to performance.

Anticipated use growth

The obvious and immediate use for basic lead silicochromate water-base primers is in trade sales. As the technology improves to make such primers comparable in performance to solvent-base types, they will gain acceptance with fabricators and maintenance engineers followed later by bridge departments concerned with new construction.

It is believed that initial large-scale usage of basic lead silicochromate waterbased coatings on structural steelwork will be in undercoats and finishes applied on site, where the versatility of such paints under adverse conditions is desirable. These will probably be applied over conventional primers so as to provide impervious films. The gloss of the finishes will have to be improved to make them initially more acceptable and to reduce dirt accumulation. The colour retention characteristics should satisfy the engineers.

Use in electro-deposition coatings

Standard grade basic lead silicochromate has been found useful in electrodeposited coatings. Its principal advantages in this application are ease of dispersion, excellent throwing power (as measured by the tube method), good suspension properties, ability to be used in low- and high-voltage systems, compatibility with a variety of vehicle types, good static paint tank stability, and superior corrosion inhibitive properties. The fine grade pigment is particularly useful, owing to its suspension and corrosion inhibition properties.

Use in electron-beam cured coatings

Some preliminary work with basic lead silicochromate has shown that it does not inhibit electron-beam curing of the film, in spite of its lead content. On the contrary, it appears to enhance the toughness and adhesion of radiationcured polymers. Pot life with some commercial vehicles is very satisfactory. Development work has indicated that it is possible to cure films at a speed of 60 metres per minute, corresponding to exposure of the film for one second in the electron beam.

[Received 10 September 1970]

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Discussion at the Torquay Conference

MR E. L. FRENCH referred to the preparation of the steel test panels. Mr Bates had quoted sand-blasting the panels. This tended to give a very fine texture to the surface. Had any work been carried out on surfaces shot-blasted to SA $2\frac{1}{2}$ or 3 standard?

MR R. P. BATES replied that sand-blasting had been used throughout so as to eliminate any effects of variation in the surface. The panels were either sand-blasted to white metal and then coated, or sand-blasted to white metal and then left to allow complete surface rusting before final coating. If any further preparations were carried out, this would increase the number of variables, and thus reduce the number of paints that could be evaluated within the limits of the experimental scheme.

MR D. J. SILSBY said that Mr Bates had stated that basic lead silicochromate pigmented coatings performed better than those with red lead or zinc chromate pigments when applied to rusty steel. Had the performances of these coatings been compared applied to steel immediately after sand blasting and, if so, did the lead silicochromate still have the edge in performance?

MR BATES replied that, on a clean surface, the differences between the types of formulations would be less noticeable. Rusted surfaces were more common in practice, and this was where the basic lead silicochromate would have the greatest advantage. On a well blasted surface, formulations containing basic lead silicochromate performed better than those containing red lead, but, in most media, zinc chromate based primers were about equal.

DR M. ELLINGER remarked that no mention had been made of toxicity. It appeared from the data given that the toxicity level was much less with lead silicochromate than other lead pigments, by reason of its structure. This fact should be stressed, particularly to industrial paint users such as motor manufacturers, since it was often necessary for the manufacturer to compromise in his formulation between the optimum for performance and the maximum lead content limits laid down by the user.

MR BATES agreed.

DR J. E. O. MAYNE said that he thought that the idea of combining the inhibitive material, in this case lead compounds, on to an inert base, and thus extending it

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without reducing its activity was very good. However, he did not think that the chromate part of these pigments would cause any inhibition. In the presence of lead, chromate was very insoluble, and thus no inhibitive chromate ions would be formed. It seemed likely that the inhibitive effect was due entirely to the formation of lead soaps or even soluble lead compounds. Was there any experience of pigments containing only lead and silica, and their performance compared to the lead silicochromate?

MR BATES pointed out that basic silicate white lead pigment performed poorly, possibly because of the sulphate present. Some work had been carried out along the lines Dr Mayne had suggested and, although he could not quote the actual figures, the performance of a range of lead silicate pigments had not been as good as when chromate was present. A number of so called Oncor pigments had been prepared, but even with different cores, the chromate had been found to impart better inhibition.

DR W. FUNKE (Chairman) asked if it was not important to define on what basis different films were compared. Was it possible to do this on the basis of lead content, or the basicity of the pigment?

MR BATES replied that if the comparison were made on lead content, the PVC of the formulations would be very different. The paints had been evaluated on an equal volume basis; for instance, a solid gallon of lead silicochromate weighed 34lb, and of red lead weighed 74lb, so 34lb of silicochromate would be replaced by 74lb of red lead. This was felt to be a fair comparison. The pigments could also be compared on a cost basis, on the same principle.

What was very important was to control closely the film thicknesses applied, otherwise any comparison was invalidated.

MR R. L. J. MORRIS enquired as to how the standard rusted panels had been prepared. Was it a light, even, surface rust, or a pitting corrosion?

MR BATES said that it was the former. The company had had 20 or 25 years experience in achieving a standard rusted panel, the procedure being to sand-blast to a fairly smooth surface without much profile, and to stand exposed to the atmosphere for three or four weeks, spraying with fresh water daily. When an even rust film had developed, the surface was wire bushed to remove loose particles, and then painted.

MR T. R. BULLETT said that, based on experience at the Paint Research Association, this procedure was perhaps not ideal. Rusting in an industrial atmosphere gave a much more severe test than the rust obtained in a comparatively rural area. This would explain the remarkably good performance of even the red lead/linseed oil paints shown by Mr Bates, compared with what one would expect in a heavily polluted site such as, say, Middlesbrough.

He would also like to mention zinc phosphate, in which there was increasing interest in the UK for anticorrosive paints. Had this pigment been compared with basic lead silicochromate, particularly in combination with red lead?

MR BATES said that this comparison had not been made. Comparisons had been made between zinc phosphate and other white anti-corrosive pigments, but not with lead silicochromate. In this respect, it had not been felt that the two pigments were in direct competition, since zinc phosphate was white.

Returning to the first part of Mr Bullett's question, panels had been pre-rusted in both semi-rural and industrial environments, but little difference in the final results had been found. In some cases the deposited soot and other particles in the industrial environment had actually protected the steel, and it had corroded quicker in the semirural areas. However it had been noticed that the type of corrosion in the two sites was different; in the industrial environment it was more of a mushrooming corrosion.

Opacity of roller coatings : Part I. Practical aspects^{*}

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Summary

The results of an empirical study of the influence of seven factors—substrate, sizing of the substrate, film thickness, pigment, pigment volume concentration, resin and solvent—on the opacity of roller coatings are reported, and the contribution of each of these factors is quantified. Statistical analysis of the results has revealed a number of interesting interrelationships.

Opacity was found to depend more on the substrate, sizing, resin, film thickness, and pigment content, than grade of pigment. Pigment performance was found to be complexly interrelated with resin and solvent. While the physical optics of the coated panel, dealt with in part II of this paper, largely seem to control opacity, there is some evidence that physico-chemical effects at the paint substrate interface also have some influence.

Keywords

Types and classes of coating roller coating

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

Processes and methods primarily associated with analysis, measurement and testing statistical analysis

L'opacité d'émaux couchés. Première partie : Les aspects pratiques

Résumé

On rend compte des résultats d'une étude empirique sur l'influence qu'exercent, sur l'opacité d'émaux couchés, les sept facteurs suivants: l'épaisseur de feuil, le pigment, la concentration pigmentaire en volume, la résine, le solvant, et l'on chiffre l'effet relatif de chaqu'un de ces facteurs. L'analyse statistique a mis en évidence quelques rapports interéssants entre eux.

On a trouvé que l'opacité se dépend plutôt du subjectile, de la présence d'un feuil de vernis clair de la résine, de l'épaisseur de feuil, de la teneur en pigment que du type de pigment. On a trouvé que le rendement du pigment est entre-lié dans une manière complexe avec la résine et le pigment. Bien que les optiques physiques, que l'on traite dans la deuxième partie, aient l'air de maîtriser l'opacité en général, il y a de l'évidence indiquant que des effets physico-chimiques à l'interface exercent une influence également.

Opazität von durch Bandlackierung Aufgetragenen Beschichtungen Teil I. Praktische Gesichtspunkte

Zusammenfassung

Bericht der Resultate einer empirischen Umtersuchung des Einflusses von sieben Faktoren-Substrat, Absiegeln des Substrates, Filmdicke, Pigment, Pigmentvolumenkonzentration, Harz und Lösungsmittel-auf die Opazität von Bandlacken. Der Beitrag von jedem dieser Faktoren wird quantitativ festgtellt; Analyse dieser Resultate zeigte eine Anzahl interessanter gegenseitiger Beziehungen.

Es wurde gefunden, dass Opazität mehr vom Substrat, Versiegelung, Harz, Filmdicke und Pigmentgehalt, als von der Pigmentqualität abhängt. Das Pigmentverhalten steht, wie gefunden wurde, auf komplizierte Weise in Wechselbeziehur gen zum Harz und Lösungsmittel. Während

^{*}Presented to the Torquay Conference on 6 May 1971.



introduction to paint technology



second edition with additional chapter

The sales of this Association publication now exceed 13,000, and because of continuing high sales of the second edition, and the need for a work of reference to be constantly abreast of the latest developments in its field, the Council of the Oil and Colour Chemists' Association has authorised the addition of an eleventh chapter to the "Introduction to Paint Technology." Entitled "Recent Developments," the Chapter incorporates up-to-date information on the latest advances in the technology of the paint and allied industries.

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

new chapter

The new chapter is subdivided into three sections

resins and media

Including polyester, epoxy, polyurethane resins and developments in water based paints, vinylics, etc.

application techniques

Including electrodeposition, powder coatings, strip-coating, aerosol spraying.

instrumental testing and control methods

Including colour measurement, viscometers, brushability, hardness, film thickness, weatherometers, and use of computers.

The book contains 204 pages including 11 line diagrams, 8 photographs of common paint defects, and comprehensive index. Copies can be obtained from the Oil and Colour Chemists' **Association**, Wax Chandlers' Hall, Gresham Street, London E.C.2, price £1 (post free).

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das physikalisch-optische Verhalten der gestrichenen Tafeln, wovon in Teil II die Rede ist, grossenteils die Opazität zu kontrollieren scheint, so liegt einiges Beweismaterial dafür vor, dass auch physikalisch-chemische Wirkungen an der Grenzfläche Anstrich/Substrat einen Einfluss ausüben.

Непрозрачность валиковых покрытий

Часть І. Практические соображения

Резюме

Даются результаты эмпирического анализа влияния семи факторов – субстрата, проклейки субстрата, толщины пленки, пигмента, объемной пигментной концентрации, смолы и растворителя – на непрозрачность валиковых покрытий и количественно определяется контрибуция каждого из этих факторов. Статистический анализ результатов обнаружил ряд интересных соотношений.

Найдено что непрозрачность зависит больше от субстрата, проклейки, смолы, толщины пленки и содержания пигмента чем от сорта или качества пигмента. Показано что рабочие характеристики пигмента сложным образом взаимосвязаны со смолой и растворителем. В то время как физическая оптика покрытой панели, описанная в части II, повидимому в значительной степени обуславливает непрозрачность, все же есть некоторые основания полагать что физико-химические эффекты на поверхности раздела краски и субстрата также проявляют некоторое влияние.

Introduction

The origin of this work does not seem to have any direct precedent but can be traced back some 8-9 years to the introduction of the so-called "premium" grades of TiO_2 pigments.

Considering, very briefly, the fundamental optics of pigments, there is an optimum particle size for maximum light scattering for any pigmentary substance, which depends upon the refractive index of the substance and of the surrounding medium, and the wavelength of the incident light. Thus, the perfect pigment should consist entirely of single particles of this optimum size to give the maximum possible light scattering (opacity).

In practice, some aggregation of primary pigment particles always occurs and, consequently, practical pigment performance is always below that which is theoretically possible. With the manufacture of the so-called premium types of pigment, the extent of this aggregation was significantly reduced, and hence better opacity and tinting strength should have been obtained from their use than with the older types. In practice this was not always so, and the reason for this would be of interest.

The present study of roller coatings evolved from general attempts to answer this question for all types of industrial coatings and inks. Quite obviously, factors other than pigment properties were influencing the effective opacity (hiding power) of paint and ink films, and hence previous concepts of opaqueness and of its cause needed to be revised and expanded to take these factors into account. Consequently, the term opacity within the context of this paper refers to the total scattered light reflected by the paint film under the conditions of test, and not merely to simple hiding power under specified test conditions. (Academic physicists might well have preferred the term "brightness" or "reflectance" but the definition used seems to correspond with the concept of opacity used in the metal decorating industry.) As a preliminary to the paper, the factors other than pigment properties that may be influencing opacity may be considered.

The role of the film surfaces

It soon became evident from qualitative work following the introduction of the "premium" qualities of TiO_2 pigment that the new grades most often failed to show the anticipated opacity improvement in printing inks (that is, in very thin films). Often the older types continued to give the more opaque films. Moreover, apparent differences between inks depended very much on the particular stock to which they were applied. It seemed that factors other than merely the pigment, or the individual ink composition, were influencing results. The vital importance of the optics of the film surfaces finally became evident about six years ago when an ink failed to adhere properly to its stock: the free film showed enhanced opacity in comparison with the adjoining film, which was still adhering to the stock, and dramatically demonstrated the role of the lower film surface, see Fig. 1. Tunstall² has already discussed the implications of this effect theoretically.



Fig. 1. Enhancement of opacity with loss of adhesion

Craker and Robinson³ and Bruehlman and Ross⁴ have since drawn attention to surface effects, and in a recent publication Corless, Dowling and Dupuv⁵

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demonstrated that, in thin ink films, the relief of the upper surface of a print is an important factor, as well as the lower surface.

The role of pigment dispersion

Although the instances where the premium pigments failed to show advantages over the previous types were noticed most frequently in thin films, they were by no means restricted to them. Even in thicker paint films, where the surface effects would be expected to be small and generally insignificant, discrepancies were observed, and some further cause of the apparent anomalies had therefore to be sought. One of the authors was concurrently studying factors influencing pigment dispersion and had shown⁶ that resins and solvents significantly affected the dispersion/flocculation effects of pigments in flowpoint pastes. It seemed that the state of dispersion/flocculation of the pigment in the final film might also be a factor influencing opacity.

A literature search was not very rewarding. As long ago as 1942, Lightbody and Dawson⁷ had concluded that the medium influenced opacity and had attributed their results to differences in dispersion in the dry film. However, their attempts to demonstrate differences in opacity in the same medium by varying the grinding time were unsuccessful. So were their attempts to relate differences in opacity to choice of solvent (white spirit or toluene). Yet, in retrospect, it would appear that these authors' ideas were correct, albeit far ahead of their time, and perhaps it was simply the lack of the tools to do the job (which will be discussed later in this paper) that was responsible for their inconclusive results in this aspect of their investigations.

More recently, results obtained by Bruehlman, Thomas and Gonick⁸ show differences in opacity for the same pigments in different media at the same pigment content but, although these workers wrote of "highly dispersing melamine/alkyd" and "a flocculation-inducing vehicle, unbodied linseed oil," they do not specifically draw attention to differences in opacity arising from the different vehicles. Thus, there was little positive published evidence to support a view that opacity differences could arise from differences in dispersion-reflocculation of the pigment arising from the resin system and/or solvent, though many experienced workers in the field must have been aware of the circumstantial evidence supporting the idea. Consequently, the present authors had to carry out their own pilot investigation to confirm, in advance of this study, the probable influence of resin and solvent on the opacity of coatings pigmented with TiO₂. Some of these results have been published very recently⁹.

The pigment content

It has been well known for many years¹⁰ that film reflectance (at a constant film thickness) increases with an increase in the pigment volume concentration of a dry film (hereinafter abbreviated to PVC(d)) up to a pigment content of about 25 per cent, and that beyond 30 per cent an increase in the pigment content usually gives a decrease in reflectance until the critical pigment volume concentration is reached. However, it seems to have been largely overlooked that there is nothing absolute about this 25-30 per cent figure, and that the minimum PVC(d) giving maximum film reflectance varies with the film thick-

ness. Since the fact that this relationship exists does not seem to have been published previously, it will probably be useful to present the evidence now (Fig. 2), although it is slightly out of the context of the main study.



Fig. 2. Variation in opacity with PVC(d) at various film thicknesses

Consequently, it was quite clear that pigment volume concentration would have to be an essential part of any study of factors influencing the opacity of roller coatings, particularly since its influence may depend upon the nature of the substrate and film thickness.

The film thickness (film weight)

The last, but by no means the least of the factors to consider was the film thickness and the problem of how it should be measured.

Traditionally, the coverage of paint films is measured by weight, and then expressed as weight/unit area, or area covered per unit volume (gallon or litre) of wet paint. For most practical purposes, weighing paint films may be accurate enough, but the authors' experience indicated that, when dealing with thin films, it is not. This conclusion is implied also by the results of Craker and Robinson³, exactly in the regions in which precise figures were needed. An improved and more reliable method of measuring film thickness (or film weight) than merely weighing was therefore found to be essential, otherwise the opacity

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differences which had almost certainly been observed could not be quantified within sufficiently close limits. This is quite likely to be the reason that Lightbody and Dawson⁷ failed to demonstrate the influences they sought so many years ago.

Fortunately, and quite independently, Smith¹¹ largely solved this problem by means of X-ray fluorescence, just when it appeared as if it might become a major obstacle. His method is based on an absolute measurement of the titanium oxide in a unit area of sample by means of a scintillation count. As long as the PVC(d) of the dry film under test is known, the film thickness can be calculated. The method is the more accurate, the less the $TiO_2/unit$ area. It is necessary to run a blank on the substrate to correct, if necessary, for interference. (It is interesting, in retrospect, to note that Bruehlman and Ross⁴ resorted to X-ray absorption, in preference to film weight, in their recent work.)

The experimental plan

Film thickness, the paint/substrate boundary (the substrate reflectivity, and whether it is sized or not), the pigment content, the resin system, the solvent system, and the grade of pigment were therefore known, or suspected, to influence the opacity of roller coatings to some extent. This being so, what was the purpose of the current study? Although the importance of the factors was known, the weighting of their influence was not. The purpose of this study was to quantify the influence of these various factors, so that each could be placed in perspective, and at the same time to try to confirm an impression that the various influences were interrelated.

The possibilities arising from the decision to investigate as many as seven factors were rather daunting, and it was necessary in practice to prune the experimental plan to a manageable scale. There were various ways of doing this, and the method finally chosen will perhaps not appeal to the academic statistician. Nevertheless, it was decided to study the seven factors in two full factorial experiments¹², one full factorial of five factors and one full factorial of six factors, with a group of individual observations common to both the factorials. This method reduced the amount of work while retaining precise identification of all the main factors and of most low-order interactions, and was preferred to the alternative of fractionating the full seven-factor experiment.

The method chosen does not confuse main effects with high-order interactions, and it is possible to cross-reference the two factorials for the common main factors and low-order interactions. It follows, inevitably, that certain interactions are lost completely, but this would equally have been the consequence of fractionating a full factorial experiment—some loss of data for interpretation inevitably follows the pruning of any experimental plan. The plan finally adopted is given in Table 1.

Experimental design

Treatments studied in Experiment 1 Treatments studied in Experiment 2 Treatments common to both experiments

			Discont	T1 Sized T2 Unsized																							
esin	Solvent	Volume Concentration PVC (d)		Matt Bright Hitop Hitop S1 S2		nt)	Tin- plate S3		Steel S4		1	Matt Hitop S1		t p	Brigh Hitop S2		ht p 2	ך p	in- late S:	- e 3	1	Steel S4					
R		Ч		FI	F2	F3	FI	F2	F3	FI	F2	F3	FI	F2	F3	Fl	F2	F3	F1	F2	F3	F1	F2	F3	F1	F2 F	_
			C1													/	/	1	/	/	/	/	1	/			
		P1	C2													1	1	/	1	/	/	1	/	1		_	
			C3													1	/	1	/	/	/	1	/	1			
			C4													1	/	/	1	/	/	/	1	/		1	
			Cl				/	/	1	/	/	/	/	/	/	/	/	/	\times	X	×	X	\times	X	/	7	
	D1 Aromasol H	P2	C2				/	/	/	/	/	/	/	/	/	/	/	/	X	×	\times	X	X	X	/	7]	
	7 Homasor H	12	C3				/	/	/	/	/	/	/	/	/	/	1	1	X	\times	X	X	X	\times	/	/	
			C4				/	/	/	/	/	/	/	/	/	/	1	/	\times	\times	X	X	X	\times	/	2]	
			C1				/	/	/	/	/	/	/	/	/	_			/	/	/	/	/	/	/	1	
		P3	C2				/	/	/	/	/	/	/	/	/			_	/	/	/	/	/	/	/		
			C3				/	/	/	/	/	/	/	/	/				/	1	/	/	/	/	/	11	
R 1		-	C4				/	/	/	/	/	/	/	/	/				/	1	/	/	/	/	/	14	R
		P1	Cl													/	$\overline{\ }$	/	/	\geq	1	/	1	/			
			C2		_		_									1	/	1	/	1	/	/	1	$\overline{\ }$			
			C3	_	L		_									/	/	/	/	1	/	1	$\overline{\ }$	/			
			C4			_	_	_		_	_			_		/	1	/	/	/	1	/	/	1			
	D2		Cl		_	_							_			/	/	1	/	/	/	/	/	/			
	Aromasol H: Cyclohexanone	P2	C2		_	_	_								_	1	/	/	/	1	/	/	/	/	_	1	
			C3		_										_	/	/	/	1	/	1	/	1	/	_		
			C4		_								_			/	1	1	>	1	/	1	/	1	_		
			Cl				_							_					_		_						
		P 3	C2																								
			C3																	_						_	
			C4																			1				1	

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Table 1—Continued

Experimental design

Treatments studied in Experiment 1 Treatments studied in Experiment 2

Treatments common to both experiments

			Diamont	T1 Sized									T2 Unsized														
esin	Solvent	igment	Volume Concentration PVC (d)	Matt Hitop S1		Bright Hitop S2		Tin- plate S3		Steel S4		Matt Hitop S1		tt op	B H	rig lito S2	ht p	F	Fin blat S3	e	Steel S4		:l				
×		Р		F1	F2	F3	FI	F2	F3	F1	F2	F3	Fl	F2	F3	F1	F2	F3	F1	F2	F3	FI	F2	F3	F1	F2	F3
			Cl													/	/	/	/	1	1	/	1	1	_		_
		P1	C2													/	1	/	/	1	1	1	1	/			
			C3													/	/	1	/	/	/	1	/	~			
			C4													/	/	/	/	1	/	1	1	1			
			C1													/	/	/	/	/	1	/	/	1			
	D1 Aromasol H	P2	C2													/	/	/	/	1	/	/	/	/			
	P3	12	C3													/	/	/	/	1	1	/	/	1			
			C4													/	/	/	/	/	$\overline{\ }$	/	1	1			
			C1																								
		P3	C2																								
			C3																								
R2			C4																								
			C1													/	/	/	/	1	/	/	>	/		_	
		PI	C2													/	$\overline{\ }$	/	/	\mathbf{i}	$\overline{\ }$	1	/	1			
			C3													/	/	>	/	/	$\overline{\ }$	1	1	1		_	
			C4													/	/	1	1	1	/	1	1	1			
	D2		C1													/	/	/	/	\mathbf{i}	1	/	1	1			
	Aromasol H: Cyclohexanone	P2	C2													/	/	/	/	1	\mathbf{i}	/	/	/			
			C3		_			_								1	>	/	1	1	/	1	1	>			
		_	C4		_											/	/	/	/	/	/	/	1	1			
			Cl										_										_				
		P3	C2																								
			C3															_									
-			C4)]																	

(144)

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(24)

Experimental

Materials (with symbols as used in the statistical analysis).

Substrate, S

- SI Matt "Hitop" (British Steel Corporation)
- S2 Bright "Hitop" (British Steel Corporation)
- S3 Electrolytic tinplate (Metal Box Co. Ltd.)
- S4 Burnished mild steel (origin unknown)

Sizing, T

- T1 Sized with $1\mu m$ film of a vinyl lacquer (Vinylite VMCH, Bakelite Xylonite Ltd.)
- T2 Unsized

Pigments, P

- P1 Type III premium, high-durability, after-treated rutile (Tioxide R-CR6)
- P2 Type III premium, durable, after-treated rutile (Tioxide R-HD6)
- P3 Type II non-premium, durable, after-treated rutile (Tioxide R-HD2)

All pigments manufactured by Tioxide International Ltd.

Resins, R

- RI An acrylic modified alkyd resin supplied at 55 per cent non-volatile (Acrysol 2AH, Plastanol Ltd.)
- R2 A modified polyester resin supplied at 55 per cent solids (Amberlac 292G, Rohm and Haas Co.)

Solvents, D

- D1 A petroleum-derived aromatic solvent, distillation range 165°-208°C ("Aromasol H," Imperial Chemical Industries Ltd.)
- D2 50:50 w:w, "Aromasol H":cyclohexanone

Additional factors:

Pigment volume concentration, PVC(d) per cent, C

Cl	18.5 per cent	(0.9:1 P:B)
<i>C2</i>	23.8 per cent	(1.2:1 P:B)
<i>C3</i>	27.5 per cent	(1.5:1 P:B)
<i>C</i> 4	31.5 per cent	(1.8:1 P:B)

Film thickness, F

Results interpolated to

- *F1* 10µm
- F2 12.5µm
- F3 15.0µm

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Paint manufacture

The pigments were dispersed by ballmilling for 16 hours in the appropriate resin, each resin being diluted with each one of the two solvent systems, as dictated by the experimental design, to 20 per cent non-volatile. After milling, the millbases were stabilised by adding a further proportion of the resin and trundling for 30 minutes more before discharging from the mill. Each millbase was then used to prepare four paints, at each of the four pigment volume concentrations under test. The various paints were adjusted to final composition by adding more solvent, so that each paint, irrespective of the resin or PVC(d), was of the same non-volatile content by volume. (When any two of the paints are then applied side by side using a wire-wound applicator they will, within close experimental limits, dry naturally to the same film thickness. In this way, quick qualitative assessments of performance can be made.)

Film application

Each paint was applied at each of four film thicknesses to the various substrates (sized and unsized) by means of wire-wound applicators (Nos. 3, 4, 5, and 6 K hand coaters, R. K. Chemical Co. Ltd.). The method is quick and reliable when a good quality of plate is used, free from burred edges.

The films were allowed to flash off, after application, for 10 minutes, and then stoved for 15 minutes at 150°C.

Measurement of film reflectance

The reflectance of the films was measured on a Harrison colorimeter with a green filter. This instrument is a tristimulus colorimeter, designed to measure reflectance in terms of C.I.E. illuminant C.

Measurement of film thickness

The thickness of each film was measured on precisely the same area of film as the reflectance, using X-ray fluorescence as earlier described.

Interpolation of results

The reflectance values were plotted against film thickness for each of the substrates under test, and the best curve was drawn through the points. Using this method, there is no prejudgment of the relationship between film thickness and reflectance, and PVC(d). Reflectance values corresponding to 10, 12.5, and 15μ m film thickness were read from the graphs. The results are tabulated in Table 2 (experiment 1) and Table 3 (experiment 2).

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Table 2

Harrison reflectance readings, experiment 1

Standardised on a standard tile at galvanometer reading of 510 = 83% absolute reflectance

				Sized T	1	Unsized T2					
Pigment	PVC (d)	Film thickness µm	Bright Hitop S2	Tinplate S3	Burnished steel S4	Bright Hitop S2	Tinplate S3	Burnished steel S4			
		F1	437	479	421	433	456	418			
	C1	F2	458	494	448	457	478	448			
		F3	477	508	471	474	494	469			
		F1	453 492		438	445	474	443			
P2	C2	F2	477	508	469	471	494	472			
		F3	495	519	488	491	509	495			
		F1	452	489	440	440	473	440			
	C3	F2	478	508	467	469	494	468			
		F3	497	520	487	493	508	487			
		F1	451	492	440	443	473	434			
	C4	F2	478	508	468	472	494	464			
		F3	497	519	487	492	508	485			
		F1	440	479	429	430	459	420			
	C1	F2	466	496	454	457	481	452			
		F3	483	508	473	473	497	475			
		F1	451	490	444	447	470	443			
	C2	F2	478	505	470	470	492	468			
D2		F3	493	517	490	490	507	487			
13		F1	452	485	439	443	469	437			
	C3	F2	475	502	466	468	491	465			
		F3	495	515	486	485	506	482			
		F1	441	483	428	439	466	430			
	C4	F2	465	501	456	464	485	461			
		F3	483	513	477	483	500	482			

Table 3

Harrison reflectance readings, experiment 2

Standardised on a standard tile at galvanometer reading of 510 = 83% absolute reflectance

		M	att Hite S1	Br	ight Hitc S2	р	Tinplate S3					
		1		F1 10µm	F2 12.5µm	F3 15µm	F1 10μm	F2 12.5µm	F3 15µm	F1 10μm	F2 12.5µm	F3 15µm
	D1	D1 Aromasol H	C1 C2 C3 C4	450 474 466 471	475 502 491 501	494 518 514 521	439 477 467 478	467 503 493 504	491 517 515 522	472 495 492 487	497 519 515 511	514 538 527 534
D1	KI	D2 Aromasol H cyclohexanone	C1 C2 C3 C4	430 455 458 453	459 480 487 481	479 501 504 502	434 447 457 458	466 479 485 487	485 501 504 509	466 483 480 485	485 501 501 506	500 514 517 518
FI	DJ	D1 Aromasol H	C1 C2 C3 C4	445 452 440 448	465 471 471 448	482 488 492 503	434 453 457 450	462 477 485 480	485 498 504 502	469 481 481 473	490 501 501 495	508 514 515 513
	K2	D2 Aromasol H cyclohexanone	C1 C2 C3 C4	431 449 436 445	454 472 465 481	473 489 485 500	. 437 451 441 440	458 475 469 459	476 493 489 475	468 466 470 468	491 487 496 491	506 504 512 509
	DI	D1 Aromasol H	C1 C2 C3 C4	436 449 444 442	457 477 479 469	478 495 500 490	431 444 446 449	454 470 471 473	474 493 492 494	458 477 470 473	479 499 493 496	497 513 509 511
P2	KI	D2 Aromasol H cyclohexanone	C1 C2 C3 C4	431 458 464 455	459 479 486 483	481 498 503 504	435 458 456 458	463 485 482 485	484 506 503 504	470 481 478 469	491 501 500 490	504 517 515 503
P2	D 2	Dl Aromasol H	C1 C2 C3 C4	400 406 441 447	450 463 465 469	481 492 484 485	429 444 463 431	468 470 483 459	489 482 499 478	465 476 466 468	487 499 486 489	503 511 502 507
		D2 Aromasol H cyclohexanone	C1 C2 C3 C4	425 456 441 441	456 473 469 469	480 491 489 491	436 443 443 445	461 469 473 473	481 489 495 494	463 473 473 468	485 494 496 493	504 509 516 510

Analysis of the results

The two factorial experiments were analysed for variance¹². Breakdowns of the variance analysis for the two experiments are given in Tables 4 and 5. A comparison of the significant factors in the two experiments (Table 6) indicates that those common to both series are significant in both, the only exception being $P \times C \times S$, which is significant in the second factorial but not in the first. As different pigments were being compared in the two different series, there is no discrepancy here.

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Factors	Designation of factors	Sum of squares	Degrees of freedom	Mean square	Variance ratio	Signifi- cance level (%)
Р	TiO ₂ pigment	184	1	184	36	0.1
C	PVC(d), %	5063	3	1688	331	0.1
Т	Sized or unsized	1647	1	1647	323	0.1
S	Substrate	30600	2	15300	3000	0.1
F	Film thickness	42981	2	21491	4214	0.1
$\mathbf{S} \times \mathbf{F}$	Substrate \times film thickness	1075	4	269	53	0.1
$\mathbf{T} \times \mathbf{S}$	Sizing \times substrate	1138	2	579	113	0.1
$\mathbf{C} \times \mathbf{S}$	$PVC(d) \times substrate$	213	6	36	7.1	0.1
$\mathbf{P} \times \mathbf{C}$	Pigment \times PVC(d)	655	3	218	43	0.1
$\mathbf{P} \times \mathbf{C} \times \mathbf{T}$	$\begin{array}{l} \text{Pigment} \times \text{PVC(d)} \\ \times \text{sizing} \end{array}$	94	3	31	6.1	0.1
Residual	Unaccounted variation	589	116	5.1		

Table 4 Abbreviated analysis of variance, experiment 1

Table 5	
Abbreviated analysis of variance,	experiment 2

Factors	Designation of factors	Sum of squares	Degrees of freedom	Mean square	Variance ratio	Signifi- cance level (%)
P*	TiO ₂ pigment	3902	1	3902	284	0.1
S*	Substrate	32249	2	16125	1177	0.1
F*	Film thickness	94846	2	47423	3462	0.1
R*	Resin	6309	1	6309	461	0.1
D*	Solvent	455	1	455	33	0.1
C*	PVC(d)	11747	3	3916	286	0.1
$\mathbf{R} \times \mathbf{C}$	Resin \times PVC(d)	1199	3	400	28	0.1
S×C	Substrate \times PVC(d)	935	6	156	12	0.1
$S \times R^*$	Substrate \times resin	476	2	238	17	0.1
$S \times F^*$	Substrate \times film	1035	4	259	19	0.1
	thickness			1000	-	
$\mathbf{P} \times \mathbf{C}$	Pigment \times PVC(d)	297	3	99	7.2	0.1
$\mathbf{P} \times \mathbf{D}^*$	Pigment \times solvent	4480	1	4480	327	0.1
$P \times R^*$	Pigment \times resin	917	1	917	67	0.1
$\mathbf{S} \times \mathbf{C} \times \mathbf{D}$	_	429	6	72	5.3	0.1
$\mathbf{S} \times \mathbf{R} \times \mathbf{C}$		850	6	142	10.4	0.1
$S \times R \times D^*$		271	2	135	9.9	0.1
$\mathbf{R} \times \mathbf{C} \times \mathbf{D}$		271	3	90	6.6	0.1
$\mathbf{P} \times \mathbf{D} \times \mathbf{C}$		151	3	50	3.6	1.0
$\mathbf{P} \times \mathbf{R} \times \mathbf{C}$		140	3	47	3.4	1.0
$\mathbf{P} \times \mathbf{R} \times \mathbf{D}^*$		466	1	466	34	0.1
$\mathbf{P} \times \mathbf{C} \times \mathbf{S}$		284	6	44	3.2	1.0
$P \times D \times S^*$		133	2	67	4.9	10
$S \times R \times$		392	6	65	4.8	01
$\mathbf{D} \times \mathbf{C}$						
$\mathbf{P} \times \mathbf{C} \times$		583	6	97	7.1	0.1
$S \times D$				2.2		
$\mathbf{P} \times \mathbf{S} \times \mathbf{R} \times$		638	6	106	7.7	0.1
$\mathbf{D} \times \mathbf{C}$						
Residual	Unaccounted variation	2568	188	13.7		

* These factors remain significant when all second order interactions involving C are removed (see interpretation of results)

Factors an	nd interactions	Experiment 1	Experiment 2
Main effects T S* F* C* P* D* R*	Sizing Substrate Film thickness PVC (d) % Pigment Solvent Resin		
$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	2		

 Table 6

 Comparison of factors significant in experiments 1 and 2

*retain significance after combining all C-interactions with residual error.

- □ indicates significant
- × indicates non significant
- means not studied

Interpretation of the results

On occasion, statistics are unfortunately misused for propaganda or political purposes, and consequently, even in legitimate use in scientific work, they remain misunderstood, and even mistrusted. Therefore, before proceeding to interpret the results it is proposed to say something about the statistical analysis used and its implications, since standard texts on the subject seem to be submerged in a specialised terminology which is not readily understood. The principles really are exceptionally simple.

The basic idea of the theory of probability (now commonly described as statistics) was described by Laplace as "Commonsense, reduced to calculation." Elaborating, Laplace continued "... it makes one appreciate exactly, what reasonable minds feel by a sort of instinct."

In an "analysis of variance," such as the assessment carried out herein, the average of all the results is calculated. The individual results are then comintuitively and not by conscious measurement.

pared with this average, and those which differ appreciably from it are noted, together with the extent of the difference. Having done this, it is decided, by reference to tables, whether the difference is likely to be due to pure chance, or whether it is more likely to be a real difference. Normally, exactly the same judgment of the data is made in any experiment, only the judgment is made

In practice, differences are not calculated from a simple average, but the "variances" (σ^2) are computed instead. (The variance is proportional to the square of the differences between a single result and the average of all the results.) Any variance can be identified with any single factor (substrate, pigment, etc.), or any combination of factors studied, by the nature of the experimental design and, by reference to the theoretical tables, the probability (the significance level) that the variance (our measure of difference) is real, and not merely due to chance, can be determined. This, in outline, constitutes an analysis of variance as tabulated in Tables 4 and 5: high variance ratios indicate "real" differences (significant factors), while the "significance level" indicates the likelihood of this difference being due to chance (as a percentage, in Tables 4 and 5).

The results are interpreted entirely from the original data (but having calculated in advance the individual factors and results which are relevant). Without the analysis of variance the results would be interpreted in exactly the same way, using commonsense alone. The merit of an analysis of variance is that it frequently reveals minor yet important influences, especially where there are interrelationships between main factors, which are likely to be overlooked by simple inspection. Several such interrelationships ("interactions" to the statistician) have been revealed in the present study. Furthermore, an analysis of variance quantifies the risk of misconstruing any results, and gives a measure of experimental error.

Experiment 1

All five factors studied, grade of pigment, pigment volume concentration, sizing of the substrate, the substrate itself, and the film thickness, affect opacity. However, none of this information can be considered original. What is perhaps revealing from this study is the relative importance of these factors.

Adopting as a standard for comparison the average increase in opacity obtained by increasing the film thickness by 1μ m from 10μ m to 11μ m, then the factor with the biggest single influence on the film reflectance (the practical opacity) is the substrate, or, to be more precise, its reflectivity, and this will be discussed in more detail in the second part of the paper. Thus, roller coatings applied to electrolytic tinplate (unsized reflectivity approximately 71 per cent) are far brighter than the same coatings applied to bright "Hitop" (unsized reflectivity approximately 47 per cent), which in turn are far brighter than the same coatings applied to the rather dull burnished steel (unsized reflectivity approximately 36 per cent). (The concept of approximate reflectivity is preferred because the actual reflectivity of the substrate may vary with the refractive index of any film applied thereon, from which it follows that the substrate reflectivity might vary with the pigment volume concentration of a roller coating.)

Following in order of influence is pigment volume concentration (between 18.5 and 23.8 per cent), film thickness, then sizing, with, in this series, choice of pigment a relatively unimportant factor.

However, discussing main effects in isolation is a little irrelevant, because the analysis of variance indicates that four first-order interactions (namely the interdependence of opacity on substrate/film thickness, sizing/substrate, PVC(d)/substrate, and PVC(d)/pigment) and one second-order interaction (the interdependence of opacity on sizing/PVC(d)/pigment) need to be considered. The final assessment must therefore be based on the interrelationship between all factors and not simply on their main effects. These interrelationships must be considered.

Substrate/film thickness (the $S \times F$ interaction): After plotting reflectance against film thickness (Fig. 3), it is noted that the slope of the curves decreases with increasing film thickness on all three substrates. Put another way, the influence of the substrate on the realised opacity decreases with the film weight applied. It should also be noted that this effect is rather small, and it might





have been overlooked by simple inspection of the data. The "analysis of variance" helps to avoid this risk.

The points in Fig. 3, and all subsequent graphs, are relative. Each point is a sum of a number of reflectance readings and is a sort of intermediate average, for example, any single point on Fig. 3 represents the total of all the Harrison colorimeter readings at the four values of PVC(d) studied for each of the two pigments, that is the sum $(4 \times 2) = 8$ Harrison Colorimeter readings. The actual points also have a factor of $(8 \times 475) = 3,800$ subtracted, which explains the negative values in certain cases. This may seem a very complicated way of calculating points but in practice it is not, since the figures plotted are obtained as a routine step towards the analysis of variance. A similar method of grouping of readings is also used in the various histograms, e.g. Figs. 5, 7, 8, 9, and 12.

Incidentally, plotting the data as in Fig. 9 illustrates very well the simple concept of measuring differences from the total average which was discussed earlier. The actual average for all readings in this experiment is -1.45, which is not significantly different from zero on the reflectance scale. It can be seen that the total areas of the six curves above and below the zero line are approximately equal.

Sizing/substrate: This interrelationship is also plotted in Fig. 3, where it can very easily be seen that sizing makes a dramatic contribution to opacity on the very reflective tinplate: this fact might usefully be more often exploited in practical metal decorating. However, sizing a very dull substrate such as the burnished steel makes only a trivial difference, and is virtually of no commercial value. This was predicted earlier by one of the authors.²

PVC(d)/substrate: This interrelationship, which is relatively minor, is plotted in Fig. 4. It appears from the data that the location, peak, and slope of the curve of reflectance against PVC(d) varies with the substrate. However, anticipating the results of experiment 2, where some rather random variations between opacity and PVC(d) were found, it is proposed to reserve judgment on this matter.

PVC(d)/pigment: In this experiment (refer again to Fig. 4) there is little doubt that the two pigments tested (in one resin only) give different curves for PVC(d) against opacity, particularly at the higher values of PVC(d) examined, and that, on the whole, P2 is slightly the better. However, it would be unwise in view of the results of experiment 2 and more general experience to judge this effect outside the rather narrow limits of this experiment.

PVC(d)/pigment/sizing: This interrelationship, the weakest of all the influences revealed by the analysis, defies explanation, particularly as it is also difficult fully to explain the PVC(d)/pigment interrelationship as mentioned in the previous paragraph.

Summary of experiment 1

All the five factors studied were found to influence opacity. The substrate had the greatest effect, followed by pigment volume concentration (between C1 and C2), film thickness, sizing, and finally the particular TiO₂ pigment.

The influence of the substrate seems to be a function of its reflectivity and decreases with an increase in film thickness. The influence of sizing decreases

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with a decrease in substrate reflectivity. The influence of pigment volume concentration appears to be interrelated with the pigment and with the substrate, but it is preferred to defer judgment on this. The combined effects of pigment, pigment volume concentration, substrate, and sizing are shown in the histogram, Fig. 5. Side by side on the same figure, and on the same scale, a bar chart shows the average influence of each factor, in comparison with the standard, namely, the average increase in reflectance arising from an increase in film thickness from 10 to 11μ m. This figure is a little complex, but it seems the best way to demonstrate the combined influences in a condensed yet understandable form.

Experiment 2

In this experiment, 25 factors and interactions were initially found to be significant—the 6 main factors, 7 first-order interactions, 9 second-order interactions, 2 third-order interactions, and 1 fourth-order interaction. It follows that full interpretation of the results is bound to be complex, and it is made all the more so by random variations in reflectance with PVC(d) in the region 23.8-31.5 per cent, as already intimated in the discussion of experiment 1 (for example, see Fig. 6).



Fig. 6. Experiment 2. $S \times C$ interaction

In view of these variations, it might well be asked "Are the data precise enough?", and this question must be very carefully considered before proceeding to discuss the results. It was because such a possibility had been foreseen that the statistical design was adopted, and it is in just such a situation as this that the ability to handle the data mathematically is invaluable. 1971 (10) OPACITY OF ROLLER COATINGS: PART I

Calculation of the standard deviation from the factorial analysis gave a figure of ± 1.53 . Although this standard deviation appears to rank with the very best claimed for similar work in the literature⁴, and is far better than most, by itself it gives no justification for interpreting the results at face value. Something more is needed.

Two further statistical checks were therefore used to strengthen confidence in the assessment of the data. First, since random variation between C2, C3, and C4 was the main source of doubt, all interactions involving C, despite the fact that they had been shown to be significant at the first analysis, were grouped with the original estimate of error (the unaccounted variation) and a new measure of error calculated. This almost doubled the apparent error. Nevertheless, comparison of the remaining results with this new measure of error still indicated that all the main factors, and the $S \times F$, $P \times R$, $P \times D$, $S \times R$, $P \times R \times D$, $S \times R \times D$, and $P \times D \times S$ interactions, were significant. Consequently, these interactions can be confidently interpreted as real, even if the variations involving C within the limits C2 to C4 are difficult to interpret. The factors retaining significance after this recalculation are marked with an asterisk in Table 5.

Such a conclusion then poses other questions. Are the random variations in C which inhibit assessment real? Is there any other means of handling the data that would decide this question? It was as much to answer these questions as to obtain a second check on the earlier query about precision that a further statistical analysis was carried out. This required recalculation of the data of experiment 2, omitting all the figures for C1. The justification for this is simple enough. The significance of C almost certainly arises from the large difference in reflectance between C1 and C2. By eliminating C1 from a new analysis it can be determined whether the much smaller and random variations between C2, C3, and C4 are significant or not. Consequently, experiment 2 was reanalysed for variance using only 216 figures instead of the original 288. The results of this re-analysis are given in Table 7, where all the factors of Table 5 have been included whether they retain significance or not.

Perhaps the first point to mention in this new analysis is the degree of error. The new standard deviation of ± 1.46 is scarcely different from the earlier one. (No large difference would be expected, since the same basic data were used each time, but the point is worth noting.) The second and crucial point arising from the recalculation is the non-significance of C. Thus, while C is nonsignificant within the PVC(d) limits 23.8 per cent and 31.5 per cent, all the other main factors, and most of the interactions revealed by the first analysis. remain significant; hence the variations in C that were causing anxiety can be ascribed to experimental error without prejudicing the status of the other factors in any way. Also, the loss of three interactions $R \times C$, $P \times D \times C$, and $P \times R \times C$, all involving C, is very minor in comparison. However, two first-order and four second-order interactions involving C retain significance, and consequently the influence of C cannot be overlooked altogether. Also, a new first-order interaction, $S \times D$, previously significant at a level of 5-10 per cent, and hence ignored, achieves significance at a level of 1 per cent in the re-analysis.

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Factors	Designation of factors	Sum of squares	Degrees of freedom	Mean square	Variance ratio	Signifi- cance level (%)
$\begin{array}{c} P\\ S\\ F\\ R\\ D\\ C\\ C\\ S \times C\\ S \times D^{*}\\ S \times R\\ S \times F\\ P \times C\\ S \times R\\ S \times R\\ S \times C \times D\\ P \times C \times D\\ S \times R \times D\\ R \times C \times D\\ P \times R \times D\\ P \times C \times S\\ S \times R \times D\\ P \times C \times S\\ S \times R \times D\\ P \times C \times S\\ S \times R \times D\\ P \times C \times S\\ S \times R \times D\\ P \times C \times S\\ S \times R \times D\\ P \times C \times S\\ S \times R \times D\\ P \times C \times S\\ S \times R \times D\\ P \times C \times S\\ S \times R \times D\\ P \times C \times S\\ S \times R \times D\\ P \times C \times S\\ S \times R \times D\\ P \times C \times S\\ P \times C \times S\\ P \times S \times R\\ E \times D \times C\\ R \times C \times D\\ R \times C \times C \times C\\ R \times C \times D\\ R \times C \times C \times C\\ R \times C \times D\\ R \times C \times C \times C \times C\\ R \times C \times C \times C \times C \times C \times C \times C \times C \times C\\ R \times C \times C \times C \times C \times C \times C \times C \times C \times C \times$	TiO ₂ pigment Substrate Film thickness Resin Solvent PVC(d)	3488 20433 69730 7350 400 29 50 296 169 312 703 199 3936 997 247 803 170 267 58 25 367 198 173 368 411 440 1843	$ \begin{array}{c} 1\\ 2\\ 1\\ 1\\ 2\\ 4\\ 2\\ 4\\ 2\\ 4\\ 2\\ 2\\ 1\\ 4\\ 4\\ 2\\ 2\\ 2\\ 1\\ 4\\ 4\\ 4\\ 4\\ 4\\ 4\\ 4\\ 4\\ 4\\ 4\\ 4\\ 4\\ 4\\$	3488 10217 34865 7350 400 15 25 74 85 156 176 100 3936 997 62 201 85 134 29 13 367 50 87 92 103 110 12.6	$\begin{array}{c} 277\\ 810\\ 2767\\ 583\\ 31\\ 1.2\\ 2.0\\ 5.9\\ 6.7\\ 12.4\\ 14.0\\ 7.9\\ 312\\ 79\\ 4.9\\ 16.0\\ 6.7\\ 10.6\\ 2.3\\ 1.0\\ 29.1\\ 4.0\\ 6.9\\ 7.3\\ 8.2\\ 8.7\\ \end{array}$	0.1 0.1
Conduit						

 Table 7

 Re-analysis of variance, experiment 2, omitting C1

* New factor, insignificant in first analysis

Finally, as a result of the re-analysis, it may be concluded that there is full justification for interpreting effects arising from P, S, F, R and D as they lie outside the limits of experimental error. By contrast, variations in C within the limits of C2 and C4 are within experimental error and consequently cannot be positively interpreted. The fact that certain interactions involving C remain significant in the re-analysis indicates that C might still be of some significance between 23.8 per cent and 31.5 per cent, but greater experimental accuracy would be needed to determine whether this is really so or not.

The results of experiment 2 can now be interpreted using the re-analysis of variance omitting CI as a base.

The main factors

When the main factors are interdependent with one, and frequently more than one, other factor, to interpret the main effects in isolation is not good practice. 1971 (10) OPACITY OF ROLLER COATINGS: PART I

Nevertheless, a brief review of the main effects will provide assistance in appreciating the interdependencies which follow.

Grade of pigment: in general, Pl develops better opacity than P2.

Substrate: as in experiment 1, the more reflective substrate gives the better opacity. Order of performance is S3, electrolytic tinplate (approximate reflectivity 71 per cent) better than S2, bright "Hitop" (approximate reflectivity 47 per cent) better than S1, matt "Hitop" (approximate reflectivity 42 per cent).

Film thickness: opacity increases with increasing film thickness.

Resin: R1 develops better opacity than R2.

Solvent: in general DI is the better, but D is involved in some fascinating interactions.

PVC(d): within the limits C2 to C4, 23.8 per cent to 31.5 per cent, any variations in PVC(d) which may exist are masked by experimental error. Consequently, explorations within this range are inconclusive.

Between 18.5 per cent (C1) and 23.8 per cent (C2) opacity increases with increase in PVC(d).

Interactions

Probably the best way to discuss the interactions is to start with one or two of the first-order interactions and then follow these through to the more complex interdependencies. This will inevitably entail some cross-referencing. For example, since $P \times D$ and $P \times R$ are themselves interdependent as the secondorder interaction $P \times R \times D$, conclusions about $P \times D$ or $P \times R$ on their own are not, in the final assessment, relevant. Although a discussion of $P \times D$ or $P \times R$ alone helps to illustrate trends, the final conclusions must be made not on $P \times D$, nor on $P \times R$, but on $P \times R \times D$.

Film thickness/substrate, $F \times S$: This is the only interdependence not further dependent on any other factor. It shows, as in experiment 1, that the contribution to opacity arising from the substrate reflectivity decreases as the film thickness is increased.

Substrate/resin $(S \times R)$, substrate/solvent $(S \times D)$, substrate/resin/solvent $(S \times R \times D)$: In interpreting these three interrelationships, it must also be borne in mind that five additional interrelationships involving $S \times R$ and $S \times D$ (or $R \times D$) are significant also. These are $S \times R \times C$, $R \times C \times D$, $P \times R \times D$, $S \times R \times D \times C$ and $P \times S \times R \times D \times C$.

The substrate/resin interrelationship, the most powerful of the three under consideration, is shown in the histogram, Fig. 7. R1 is better than R2, but the differences in opacity attributable to the choice of resin decrease with the transition of S1 to S3. This resembles the change of opacity with film thickness. The effect might be a function of the substrate reflectivity, but the possibility that it is a surface chemical one at the substrate/paint film interface must also be considered.

The substrate/solvent interrelationship is shown in Fig. 8. On S1 the differences between the two solvents are trivial, but, on S2 and S3, D1 is clearly better than D2.





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Fig. 8. Experiment 2. $S \times D$ interaction

The $S \times R \times D$ interrelationship is illustrated in Fig. 9, and is by no means simple to interpret. *R1* is better than *R2*, and *D1* better than *D2*, as already concluded. However, the advantage of using *R1* and *D1* is more pronounced on tinplate (*S3*) than on the two different "Hitop" surfaces. With the coatings formulated on *R1* in particular, there is very little difference in opacity between those applied to the matt "Hitop" *S1* and the bright "Hitop" *S2*.

No positive trends can be discerned from the more complex $S \times R \times D \times C$, and $P \times S \times R \times D \times C$ interrelationships. It appears that different pigment

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Fig. 9. Experiment 2. S \times R \times D interaction

contents may be preferable to optimise opacity, depending upon the substrate, resin, solvent and even pigment, but more results within the PVC(d) range of 23.8 per cent to 31.5 per cent would be needed to justify a firm conclusion: in retrospect, the number of PVC(d)'s studied was perhaps too small, and the steps between the individual points too wide.

Substrate/PVC(d), $S \times C$, substrate/resin/PVC(d), $S \times R \times C$, substrate/ PVC(d)/solvent, $S \times C \times D$, pigment/PVC(d), $P \times C$, pigment/PVC(d)/substrate, $P \times C \times S$, resin/PVC(d)/solvent, $R \times C \times D$. The $S \times C$ interaction was plotted in Fig. 6, as illustrative of the problem encountered in trying to interpret changes in opacity within the limits C2 to C4. It is quite clear from this that neither C (which is non-significant as a main factor within the PVC(d) limits of 23.8 per cent to 31.5 per cent) nor any interactions involving 1971 (10) OPACITY OF ROLLER COATINGS: PART I

C can be confidently interpreted on the data available. It is safer to conclude that more data are needed for effective interpretation of these effects. The effects might all be real, but the case is not proved.

Pigment/resin, $P \times R$, pigment/solvent, $P \times D$, pigment/resin/solvent, $P \times R \times D$: These three interdependencies are by far the greatest, and rank in their influence with the main effects.

The pigment/solvent interaction, illustrated in Fig. 10, is the most influential, a possibility which had not been expected. Considering this interaction alone, independent of resin, inspection of the results shows that PI gives better results with the hydrocarbon solvent, DI, whereas P2 is better with the ketone/hydrocarbon mixture, D2. However, too much importance must not be attached to this conclusion in isolation and the next step is to consider the pigment/resin interrelationship. Considering the main effect of resin first, it has already been noted that RI gives more opaque coatings than R2. However, when RI and R2 are correlated in relation to the pigment, the basic fact that RI is superior to R2 still holds, but whereas PI is very much better than P2 in RI, the superiority of PI over P2 in R2 is much smaller. But, competing with this are the different solvent compatibilities of PI and P2 already mentioned, and consequently when P, R and D are considered together it is found that the main trend





elaborated at the start of this paragraph is not now entirely correct. This is shown in Fig. 11, which illustrates the eight possible combinations of P, R and D (averaged over all three substrates and the four pigment volume concentrations), in relation to film thickness.

This shows that in general, R1 is superior to R2, P1 to P2, and D1 to D2, but the potential of P2 is more fully realised with D2 than with D1, and so the detailed performance rankings are as follows:

$$\begin{array}{l} P1 \ R1 \ D1 > P1 \ R1 \ D2 = P2 \ R1 \ D2 > P1 \ R2 \ D1 > P2 \ R1 \ D1 > \\ P2 \ R2 \ D2 > P1 \ R2 \ D2 > P2 \ R2 \ D1 \end{array}$$

This is the most complicated example of an interaction between factors that the authors have so far met, and illustrates only too well how it is possible to draw valid conclusions from one experiment and then apply them outside its limits and get the wrong answer. For example, if one carried out a single comparison of P1 and P2 in R2, using D2 as solvent, one would conclude that P2 was the better pigment, and although this would be a correct conclusion





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from the test carried out, with fuller knowledge it would be incorrect. If, on the evidence of this single comparison, one then proceeded to formulate a roller coating, in RI with DI as solvent and pigmented it with P2 one could finish up with a coating 20 per cent inferior in opacity to one in which PI was substituted.

Summary of experiment 2

All six factors studied influenced opacity in the original analysis, but reanalysis showed that pigment volume concentration was of no practical influence between 23.8 per cent and 31.5 per cent.

In general, the substrate had the biggest influence, followed by the resin, film thickness, then choice of pigment, and finally solvent.

Strong interdependencies were revealed between pigment, solvent and resin, and that between pigment and solvent was far more influential than expected. As a result of the interactions between pigment, resin and solvent, the relative performance of the two pigments was reversed in certain conditions.

There is evidence of interrelationships between the substrate and resin and solvent, suggesting that physico-chemical interactions at the paint/substrate boundary may play a part.

Fig. 12 summarises in a bar chart the relative influences of the factors studied.



Fig. 12. Experiment 2. Summary, $P \times S \times R \times D$ interaction, and average effect of all six factors studied, on the same scale

General discussion

The object of the experimental work was to carry out an empirical study of factors influencing the opacity of roller coatings, excluding the bias of preconceived ideas, and to quantify the relative importance of these factors. Three independent lines of discussion emerge from the study. These are:

practical conclusions of interest to the paint technologist and metal coater; theoretical consideration of the effects;

the limitations of the study.

However, before embarking on this discussion, it is perhaps worthwhile to consider the general implications.

In identifying the opacity of roller coatings, it is helpful to consider first the individual optical elements of the system. Initially, there are only two: the dry paint film (consisting of the pigment embedded in the resin), and the substrate (which for all practical purposes acts as a mirror behind the paint film). The opaqueness of the coating depends upon the light scattered by the pigment and is generally accepted as being related to the quality of the pigment dispersion and the volume concentration of the pigment (factors P, C and Fin our empirical study). If this is so, then what is the role of such factors as the resin, R, and the solvent, D? How do they influence opacity? The solvent is not even present as a constituent of the film by the time opacity measurements are made. Because the authors' results show that R and D affect opacity, it must consequently be concluded that these factors also influence pigment dispersion in the dry film, although this fact has received little previous recognition. This being so, the dependence of film opacity on P, C, F, R and D and/or interactions between these components can be explained. Factors S (substrate), and T (the effect of sizing), then combine together as "the mirror behind the film" and the simple picture is complete.

How then can the other interactions revealed by the study, such as the substrate with components of the film $S \times R$, $S \times D$, $S \times C$, $S \times R \times D$ be explained? The simple picture just envisaged does not adequately explain these effects. Consequently the state of affairs must be more complex.

An effect such as $S \times C$ can be explained on the assumption that the refractive index of the pigmented film changes with PVC(d), and there are practical results in one medium to show that such a change does in fact occur. But is it reasonable to expect significant differences in the refractive index of the pigmented films with a change in the resin, when the resins are of very similar composition? Even accepting such differences, why is there an $S \times D$ or $S \times R \times D$ interaction? Two explanations are possible. The substrate reflectivity may change with the resin and solvent, in which case the effect is purely optical. This seems unlikely. Alternatively, some physico-chemical interaction may occur between the substrate and the wet film, affecting the orientation of the resin molecules and/or the pigment particles, and, consequently the opacity of the dry film. Orientation of polymer films at surfaces has been reported in the literature¹³, but, as far as is known to the present authors, the possibility of such an effect influencing pigment behaviour has not. Nevertheless it is quite a reasonable supposition.

Theoretical treatment of the observed effects on the basis of physical optics is dealt with in part II of this paper, but in view of the evidence of interactions between substrate and individual film elements, this treatment may not fully provide for the complexity of all roller-coating systems. It must, however, be recognised that the experimental plan used in this work would not be expected

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to detect effectively differences caused by physico-chemical interactions between the roller-coated film and the substrate due to the chemical similarity of the substrates. Also, such an effect is not conclusively proved; its positive identification would have to be studied separately.

Practical conclusions

Using as a standard for comparison the average increase in opacity secured by increasing the film thickness from 10 to $11\mu m = 10$ per cent, the following practical conclusions can be drawn from the study.

The reflectivity of the substrate has the biggest individual influence on film opacity (see Figs. 5 and 12). Highly reflective substrates, such as tinplate, can amplify the opacity of a given roller coating by as much as 30 per cent in comparison with the same coating applied on a dull steel substrate; 25 per cent is an average figure.

Sizing of the substrate enhances opacity in comparison with the unsized metal. The extent of the improvement depends on the reflectivity of the substrate. With a dull substrate the effect is trivial, about 1 per cent, but with a bright substrate the improvement in opacity is about 20 per cent (see Fig. 5).

The influences of pigment, resin and solvent are interrelated, and in practice each roller coating should be considered against a standard if accurate conclusions are to be drawn.

The influence of choice of resin on opacity was in general greater than that of choice of pigment. The maximum difference in opacity arising from choice of resin was 27 per cent, the minimum 2.5 per cent, and the average 13 per cent (see Fig. 12). The influence of the resin changed with the different pigments and solvents studied.

As a rule, choice of pigment was less important than that of most other factors. The maximum difference found between two pigments was 27 per cent, the same as for the resins, but the minimum difference was very small, and negative (that is, the pigment which was generally the poorer was better in the circumstances that gave rise to the smallest difference between them). The average of about 9 per cent was less than the effect of a $1\mu m$ increase in film thickness.

The two pigments gave different results with the two resins and also with the two solvent systems used.

Opacity differences as large as 19 per cent were obtained between the two solvents investigated (see Fig. 12). The minimum difference was 2 per cent, the average about 3.5 per cent.

The influence of the solvent was more interrelated with the pigment than with the resin.

No significant differences in opacity were confirmed with changes in pigment volume concentration within the limits 23.8 per cent to 31.5 per cent. Between 18.5 per cent and 23.8 per cent PVC(d), opacity increased with increasing PVC(d) by about 15 per cent, or approximately the same as a 1.5μ m increase in film thickness.

Comparisons between formulations sometimes differed on different substrates. No significant reversals in performance were recorded, but significant differences on one substrate were reduced almost to zero on another. It follows that roller coatings (and probably other coatings as well) should wherever possible be compared under the conditions of use, and not by an arbitrary method.

Theoretical considerations

Theoretical interpretation of the results is dealt with in part II of the paper.

Limitations of the study

Definite conclusions concerning the effect of substrate, sizing, film thickness. choice of pigment, resin and solvent can be drawn from the experimental work. but the effect of pigment volume concentration within the limits 23.8 per cent to 31.5 per cent remains uncertain. Theoretically, this PVC(d) region is very interesting, because within it lies the point where crowding of pigment particles commences, with the possibility of optical interference. Also, because "blueness" increases with an increase in PVC(d), pigment volume concentrations within these limits are used, by paint manufacturers, to improve the colour and colour stability of white roller coatings.

On the basis of opacity data obtained previously on black substrates, it had been expected that the PVC(d) points chosen for study would reveal an opacity maximum between the limits of 23.8 per cent and 27.5 per cent. As it is, the results fail to discriminate between 23.8 per cent, 27.5 per cent and 31.5 per cent PVC(d), which means that, in roller coatings at any rate, the maximum is found not at a point but within a broad range, and that for all practical purposes differences within this range are insignificant.

If there are real opacity differences related to PVC(d) in the region 23.8 per cent to 31.5 per cent that are of theoretical interest, greater experimental precision is needed to identify them.

Acknowledgments

The authors wish to thank the Directors of Tioxide International Ltd. for permission to publish this paper. They are also indebted to Mr. D. Corless and Mrs. V. Greggains, who together carried out most of the experimental work and statistical analysis, and to Mr. S. J. Gill for his assistance with the statistical analysis.

[Received 16 October 1970]

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Discussion at the Torquay Conference

MR S. R. FINN, referring to Fig 1, said that the area of greater opacity had been quoted as being due to poor adhesion. Had this been, in fact, due to an air gap, which would imply complete detachment, or did the degree of adhesion affect opacity?

MR D. G. DOWLING replied that it was a simple air gap. The interesting fact was that exactly the same effect was obtained when the substrate was sized.

MR J. BOROKY said that work he had been involved in had led him to suspect different factors for opacity of coatings. Titanium dioxide pigmented coatings, at extreme pigment to binder ratios—in the region of 1 to 6—had been applied to substrates such as aluminium foil at speeds of 100m min⁻¹. Under these conditions, poor adhesion was unlikely. It was found that mixtures of two binders which individually had good adhesion to the substrate and affinity for the pigment, produced very opaque films. It was thought that this phenomenon occurred because the partial incompatibility of the binders caused incipient precipitation of the pigment, i.e. precipitation that was invisible to the eye but could be detected instrumentally. A similar result had been obtained by modifying the solvent formulation; if a coating producing a thin transparent film was reformulated to induce incipient precipitation, opacity resulted.

Also, it had been noted that, in some cases, paints giving a transparent film at lower speeds became opaque when applied at speeds over 175m min^{-1} .

Would Mr Dowling comment on these phenomena?

MR DOWLING remarked that the types of formulation Mr Boroky was discussing, with pigment to binder ratios of 1:6, were very much different to those reported in the paper. Some work had been done on similar coatings, and the results confirmed Mr Boroky's comments. However, the formulations were above the critical PVC, and dry hiding was involved. It was true that excellent adhesion was obtained, but he preferred to regard this as a completely separate branch of technology.

With respect to the question of speed of application, and of drying, it was possible that this had affected the work reported in the paper, and might explain why some of the results had not been as precise as expected.

MR A. R. H. TAWN said that, although he was an advocate of statistical design of experiments, he was always a little suspicious of a statistical programme as large as that reported here, particularly when many results were achieving a level of 0.1 per cent significance in an analysis of variance. When seven factors were included, a vast number of experiments was necessary, and it was usual to carry out a fractional factorial by confounding certain of the variables. However, even before adopting this procedure, the necessity of inclusion of some of the factors should be examined. Where the significance of the first order factors in the analysis of variance was around the 0.1 per cent level, it seemed that the factor need not have been tested in the first place. In other words, if a prime factor was found to have a significance at the 0.1 per cent level, the experimenter should have been aware of it before the multi-factorial experiment was undertaken. A case in point was the effect of film thickness on opacity. It seemed fairly obvious that this would have a finite effect, and the work done in showing a level of significance of 0.1 per cent in the analysis of variance was perhaps unnecessary. He was a little uncertain as to why several such factors had been included, unless it was to investigate interactions, in which case why was not a standard fractional factorial adopted?

Further, if it had been felt necessary to test factors which might be regarded as obvious, and to draw conclusions on the basis of an 0.1 per cent probability, why had the author chosen to accept some results at this level and express doubt about others?

MR DOWLING replied that, in the paper, it had been stated that there was evidence that all the main factors did affect opacity. It had been the interactions which had been felt to be of importance. When working with very thin films, different results were often obtained from experiments nominally involving the same principles, but using different resins, pigments and solvents. Obviously interactions must be involved, and the work had attempted to show this and to investigate the interactions, as well as to put some numerical measure on the individual manifests relative to each other. Anyone using the numbers obtained outside the context of the paper was unwise, but the paper had been intended to show that opacity, or lack thereof, was not merely caused by the pigment used, and in doing so, bringing out the interactions was a positive step forward. The number of experiments carried out had been very large, but this had been necessary because of the difficulties involved in accurately measuring thin films. Statistics had been used as a laboratory tool, and as the laboratory work involved was difficult to perform to precise limits, a large number of determinations had been necessary—even with a large volume of experiments, the results were not always as precise as might have been desirable. An experimenter was surely permitted to reject results as not proved.

MR TAWN said that if statistics were to be used, the significance level produced should be accepted for effects which were originally thought unlikely as well as in support of effects originally expected to occur.

MR DOWLING replied that common sense also played a part in interpreting the results. Some of the points brought out by the statistical analysis did not seem logical from a commonsense point of view. Where this occurred, it was pointed out. As the results were not understood, it might be that the experimental design was at fault. For instance, after the experimental work had been completed, a batch of the tin plate used as the substrate was examined, and variations in its reflectance found. This may have caused erroneous figures. It was this sort of phenomenon that was being borne in mind when certain findings were queried. Also, as had already been mentioned, precise quantitative measurements of films as thin as those investigated were very difficult to obtain, and this should be taken into account in interpreting the results, statistical or otherwise.

Returning to the point about fractionation, a standard fractional design was not the way to approach this investigation: how did one separate the aliases?

DR R. BULT (Chairman) remarked that a problem common to any research work in the paint field was the large number of variables involved, and the increasing use of statistical methods to deal with these was most useful.

MR J. A. L. HAWKEY referred to work he had carried out on the effect of the pigment on the opacity of lithographic ink films. The application of such films, which were of the order of 0.2 microns thick, showed that, as with the thin roller coatings discussed in the paper, the type of pigment was of minor importance compared with other factors influencing opacity. One reason which could be put forward in support of the authors' not taking for granted the relation between film thickness and opacity was that, in both roller coatings and lithographic inks, film splitting occurred on deposition, and with very thin films this tended to cause imperfect levelling and pinholing. On a tinplate substrate, this would add as much as 10 per cent of reflectance from bare tinplate to the reflectance from the film.

In discussing the relative effects of dispersion and reflocculation it should be remembered that a great deal of the lower molecular weight components in the resin would be adsorbed on the pigment, and this could influence the rheological property and thus the levelling and opacity, and even the adhesion.

Finally, he said that he thought that the facts brought out in the paper were most important and useful, and congratulated the authors on their work.

MR DOWLING thanked Mr Hawkey. He had experience of the pinholing effect in lithographic tin-printing. If this phenomenon could be controlled, or made October

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The ties will be supplied from stock; all other items are made to order. Only the tie can be supplied by airmail at an extra cost of 35p. reproducible, it could be advantageous in producing a brighter effect to the ink, owing to the reflection from bare substrate.

MR P. FINK-JENSEN said that when a statistical evaluation produced a fourth order interaction of high significance, it paid to be suspicious, as this would not normally be expected. In this case, he suspected that misinterpretations might be caused by the fact that reflectance was not an additive quantity. The basis of the statistical evaluation of the experiments was that the quantities involved were additive, and in his experience non-additive quantities often produced high order interactions which were not valid. The remedy was to transform the reflectance to a function that was additive in nature.

MR DOWLING replied that he was aware of this. After the results had been calculated, Mr Tunstall had suggested that the reciprocal of the reflectance should have been used.

In a sense this was surely playing with numbers, and was going back to his point about using commonsense interpretation of the results. His own feeling was that it would be more useful not to manipulate the present results yet again, but to start a new experimental design.

DR R. AMBERG pointed out that it had been stated that the opacity of the coating depended on the pigment. However, the binder might have an influence. Was it not possible that the binder caused the differences between the two formulations, the pigments used being similar in their opacity behaviour?

MR DOWLING said that the two pigments had been of different particle size, which would be expected to cause difference in opacity. The authors had deliberately chosen pigments not only of different particle size but also with different coatings for the second series of experiments, and different results had been expected from these pigments.

Erratum

Milling—a printing ink variable

By J. R. Groom, JOCCA 1971, 54, 266-280

It is regretted that an error occurred in the structural formula given by the author for CI Pigment Yellow 85.

We are informed that the correct structure is



Next month's issue

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

"Opacity of roller coatings Part II—Theoretical analysis," by D. F. Tunstall and D. G. Dowling

"Several factors affecting appearance and properties of thermosetting acrylic resin based enamels," by J. R. Taylor and H. Foster

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

Correspondence

Geographical distribution of Transactions and Communications

SIR,—Further to our correspondence on the above subject, let us regard all transactions and communications simply as "papers," and if a paper is presented in two or more parts, let us regard each separate part as a paper in itself, as indeed it is virtually so treated in the *Journal*.

On this basis we notice that in the past three years there have been 10 papers from Paint Research Institute TNO, Delft, and 11 papers from the Division of Building Research, Melbourne, compared for example with eight papers from PRS Teddington and three papers from Building Research Station, Garston. From Holland as a whole there have been 16 papers, and from Australia as a whole, 15 papers; these two countries have contributed between them about 50 per cent of all papers from overseas. What is there about the climate of Holland and Australia which engenders such extraordinary technical and scientific activity? By comparison we have no papers at all from Russia, Japan, Italy or France.

Your answer to my first letter suggests that there is no established policy which might lead us to expect a higher overall representation from British sources, and a more equitable distribution of contributions from overseas countries. Would it not be appropriate to formulate such a policy?

Yours faithfully,

F. Armitage

195 Clarence Gate Gardens, London, NW1 15 May 1971

Water transport through paint films

SIR,—I have followed with interest the series of papers by D. Y. Perera and P. M. Heertjes of Paint Research Institute, TNO, Delft, on "Water transport through paint films"¹⁻⁵. Since the authors have referred to a paper of mine⁶, may I comment on the suggestion they have attributed to me³, "... that, in the presence of a solution of an electrolyte such as sodium chloride, some of the properties of a polar polymer could change, and this consequently might affect the semipermeable characteristics of the membrane" (pp. 553/4).

The results I obtained certainly indicated no significant diffusion of the K^+ cation through the films below pH 6.5, even for oleoresinous and alkyd resins, which to this extent behaved in a semipermeable manner with respect to water transport in agreement with reference 3 above. They did show, however, that electrical resistance of some types of films was affected by exposure to electrolyte solutions and depended on the pH balance. Some films were irreversibly affected as pH increased beyond about 6.5 and the degree of cation exchange or absorption increased with pH.

Ulfvarson, Khullar and Whalin have reported a similar relationship⁷ and Ulfvarson and Khullar in a recent paper⁸ have shown some correlation between

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ion exchange capacity and anti-corrosion efficiency of coatings. I would agree entirely with the authors' conclusions if pH was in the region of 6.0 to 7.0, as would be assumed from the experimental details given, but their results might have been different above this range.

Yours faithfully,

G. W. Rothwell

11 Spring Gardens, Watford, WD2 6JJ 20 August 1971

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SIR—We have been pleased to read that the results with respect to the semipermeability characteristics of the films under our experimental conditions

(namely pH 6.0—7.0) agree with those of Mr Rothwell. Under experimental conditions of pH beyond 7, it might be possible that

the measurements under discussion would lead to different results, as suggested by Mr Rothwell.

Yours faithfully,

D. Y. Perera P. M. Heertjes

Verfinstituut TNO, Schoemakerstraat G7, Delft, Holland. 1 September 1971

Review

THE CHEMISTRY OF SYNTHETIC DYES, VOLUME 3

Edited by K. VENKATARAMAN. New York: Academic Press, Inc., 1970. pp. xix + 485. Price \$27.50.

The publication of Volumes 1 and 2 of "Venkataraman" in 1952 provided what was probably a more comprehensive and scholarly account of dyestuffs chemistry than any hitherto available. Rapid progress in this field in the succeeding 20 years has led to a clear need for a new edition of this classic work. This need is now being met by the publication of four further volumes, Nos. 3-6. These are different from the original two in that they are supplementary rather than complete in themselves; they cover new developments since the appearance of the earlier edition. Further, in the new volumes Professor Venkataraman appears as editor rather than sole author; each specialised area is now dealt with separately by an acknowledged authority in the field concerned.

For the present volume, the editor has assembled a formidable team of experts selected internationally and from both industry and the academic world. Professor Venkataraman himself has contributed an introduction which constitutes a general survey of recent developments in dyestuffs chemistry. This is followed by chapters on raw materials (G. Collin and M. Zander), intermediates (N. N. Vorozhtsov, Jr.), colour and the electronic states of organic molecules (S. F. Mason), diazotisation and coupling (J. M. Tedder), azo dyes (C. V. Stead), the chemistry of metal complex dyestuffs (R. Price), and disperse dyes (J. M. Straley).

Comparison with the relevant portions of the earlier volumes is, of course, unavoidable. Such an exercise reveals straight away the considerable advances which have taken place in the last two decades. For example, the chapter on diazotisation and coupling by Tedder indicates how greatly our understanding of the kinetics and mechanism of these important reactions have increased. Even more remarkable, however, is the section on colour by Mason. We are now clearly very much further on the way to establishing a rational, quantummechanical basis to account for the relations between colour and constitution than we were 20 years ago. The valence bond approach and its attendant resonance theory have been virtually superseded by the conceptually simpler and more widely applicable molecular orbital theory.

To sum up, the arrangement of the material within each chapter and the standard of writing throughout are, as to be expected, excellent. The layout of the text and the presentation of formulae and tables could hardly be improved upon. This book is thus a worthy successor to Volumes 1 and 2 and can be unreservedly recommended to all those interested in dyestuffs chemistry.

A. H. BERRIE

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.)

It has recently been announced that the name of the company **The Yorkshire Dyeware** & Chemical Co. Ltd. has been changed to Yorkshire Chemicals Ltd. In considering the change to a less cumbersome title, it is stated "Yorkshire" was required to maintain the historic links with the county of Yorkshire, and also to maintain continuity, since it is by this word that the company is known abroad. The word "chemicals" embraces its interests in a variety of products for the dyeing, leather, paint and other industries.

Degussa has issued a booklet giving full details of *Special Black 15*, a new fine particle oxidised low structure furnace black for letterpress and offset inks.

The *Ferritector Model 1581*, a new instrument for the measurement of the ferrite content in stainless steels, has been introduced by **Elcometer Instruments Ltd.** Similar to the *Minitector Thickness Gauge*, the new instrument has a dual scale calibrated in ferrite content from 0-10 and 10-25 per cent, and is particularly intended for the control of weld quality and possible degradation of neighbouring regions.

The "Proceedings of the Australasian Vitreous Enamellers' Institute Convention Vol. 2 1970" has recently been published. The volume contains the full texts of 18 papers delivered at the convention, covering subjects from metal preparation for enamelling to furnace tooling and design, and copies are available from the Australasian Vitreous Enamellers' Institute at \$10.00 Australian.

The Paint Division of Atlas Preservative Co. Ltd. is to be merged with Storry Smithson & Co. Ltd., it has recently been announced. This move has been made in order to strengthen the Atlas range of specialised surface coatings, which will continue under the trade name *Storitol*. The sales representation and paint distribution facilities of the Atlas Paint Division will be added to those of Storry, Smithson and, with production, will be based at the latter company's Hull factory. It is claimed that this will create one of the largest, and technically best equipped, specialised coating suppliers in Europe.

Details of the *Russell Camflap* continuous discharge valve, a new valve of particular interest for discharging from vessels maintained above or below atmospheric pressure, are now available from **Russell Finex Ltd.** The valve operates by a motorised double-flap system, in which the inlet flap opens to allow material into the receiving chamber, and then closes before the outlet flap opens to discharge the material. This cycle is repeated 20 times per minute. The flaps are closed by a cam operating against a wedge, ensuring tight closure, and each flap is attached to the cam arm by chain link, so that it cannot remain closed, even when contaminated by a sticky material.

Two models are available, *model 1012* with a cast iron body, inlet size $5in \times 6in$, and capacity 50-70cu ft/hr, and *model 1008*, with a fabricated body, inlet size $8in \times 6in$ and capacity 100-120cu ft/hr.

Oncor anticorrosive pigment will be produced in Europe as from November, it has recently been announced. The two types involved are Oncor M50 and the finer grade F31, the basic lead silicochromates pigments developed by NL Industries Inc.

in the USA. Following the growing demand for the pigments in Europe, production will be carried out by **Kronos SA/NV** (formerly Derives du Titane SA), the Belgian subsidiary of N L Industries.

A new company, **Chemsyn Ltd.**, has recently been set up to manufacture fine organic chemicals. Utilising the production facilities of **Chemical Process Developments Ltd.**, Chemsyn offers a contract chemical manufacturing service, intended for larger chemical groups who find the production of small scale or limited run chemicals uneconomic. The company will also undertake the manufacture of fine organics in quantities from 10 grams to 10 tons.

A new type of coating for metal which is claimed to last at least three times longer than conventional coatings, has been developed by **ICI Ltd.**, Paints Division. The new paint, *Flurolux*, is designed basically for architectural cladding, curtain walling and roofing systems where the metal sheet is precoated and formed before leaving the factory. It is based on *Kynar 500*, a polyvinylidene fluoride resin produced by the **Pennwalt Corporation** in the USA, and is claimed to have outstanding durability and flexibility, being capable of withstanding any likely forming of the metal substrate. Application may be by roller coater or spray on high speed coil coating equipment, to give coatings of 20-25 microns thickness. After extensive market trials over the past two years, the product is now generally available in a range of eight colours, plus black, white and metallic finishes.

ICI has also issued "Pretreatment for metal," a quick reference guide to standard products and processes.

The automated *Co-precipitate* plant commissioned in March is now operating close to its design capacity, announce **Interstab Ltd.** The plant is producing a wide range of co-precipitated heavy metal stabilisers for pvc. These stabilisers are claimed to be more effective and economical than simple lead soaps, since the presence of two metals provides a considerable degree of synergism.

A new low cost modified polyester resin for coil coating enamels, *Cyzac resin 1531*, is available in the UK from **Cyanamid of Great Britain Ltd.** Intended for enamels for non-critical users, *Cyzac resin 1531* is claimed to impart good hardness, impact resistance and fabricating potential, together with reasonably good resistance to colour and gloss change when overbaked.

Also new from Cyanamid are two electrocoating resins. XC 4020 Resin has been developed specifically for use in corrosion-resistant primers and one coat off-white and coloured electrocoating systems. Good bath stability is claimed. The resin can also be used in aqueous and organic based general purpose industrial finishes. XM 1132 is a cross-linking agent for use in electrocoating paints requiring high corrosion and detergent resistance; excellent migration properties are claimed.

Further details of all three products, including suggested formulations, are available from Cyanamid.

Cyanamid International, the above company's American parent, has published a new 24-page catalogue of products: "Cyanamid products for industry." Copies are available from Cyanamid of Great Britain.

Piggy-Bak, a stacker for many types of carton, sack or bundle, has been introduced by the **Newcastle Company Inc.** The *Piggy-Bak* is a fully automatic self-contained

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unit on which a single file line of stackable objects can be placed one on top of another to almost any desired height. The stacked items are then discharged in line on the same level as the intake conveyor. Between 20 and 40 objects can be handled per minute, depending on their type and size.

It has recently been announced that Intracolor Corporation, part of the US operations of CIBA-GEIGY, is to be acquired by Crompton & Knowles as part of the Consent Decree negotiated with the US Department of Justice prior to the merger of CIBA and GEIGY. Intracolor handles the dyestuffs and auxiliary products and the optical brighteners of the former CIBA Chemical & Dye Company. The sale is subject to Department of Justice approval.

Wintermix, a paint tinting scheme claimed to be the most highly developed in the world, is to be marketed in the UK by **Winter Osakeyhtio** of Finland. Winner of an award at the Inventions Exhibition, *Wintermix* is based on a very small number of base paints over the eight available types of formulation. The tinting machine operates by punching a hole in the lid of a tin of base paint, and injecting the appropriate amount of tinter. The hole is then plugged with a plastic stopper, and the tin shaken mechanically until the shade is even. A rack of shade cards is also supplied.

Cabot Carbon Ltd. has recently announced that it has signed the CBI undertaking, with regard to its British-produced carbon black, concerning the limiting of any price increases over a twelve month period.

A new full gloss white decorative paint, said to have been formulated regardless of cost, has been introduced by **International Decorative Paints**, a division of the **International Paint Company Ltd.** Known as *International Luxury White Enamel*, the paint is claimed to be the easiest brushing on the market, being sag free and quick drying. Other properties claimed for the paint, which is formulated on an oil modified alkyd resin and polyurethane reinforced with silicone, are excellent durability, hardness and dirt and scrub resistance.

Several new product developments were recently announced by The Baker Castor Oil Company.

Two new colloidal thixotropic agents for sag control in thick film chlorinated rubber and industrial coatings, *Rheox 46* and 53 are being introduced to the European market. *Rheox 46* is a soft paste, while *Rheox 53* has a stiff paste consistency; superior heat stability and effectiveness in sag control of thick films are claimed for both.

A new aliphatic polyurethane elastomeric polymer, *Alfa 841*, has been developed. Containing no free isocyanate groups, the new product is claimed to have excellent non-yellowing and abrasion resistant properties, and is recommended as a protective coating for leather, natural and synthetic fabrics, upholstery, foams, plastics, over-print lacquers, and inks, and as an adhesive for flexible substrates.

Thixseal A and *Thixseal 435* are two new thixotropic agents for sealants, caulks, and pvc plastisols. Excellent heat and storage stability are claimed for both products; recommended uses are in polybutene, rubbers, drying oil epoxy and polysulfide based systems—*Thixseal 435* is also recommended for pvc plastisols.

A new two-pack polyurethane wood finish, stated to be a breakthrough in lacquer technology, has been developed by **Sonneborn & Rieck Ltd.** The new range, designated

INFORMATION RECEIVED

9049 A and B type, is claimed to eliminate the storage instability common with this type of formulation, to be fast drying, and to combine high resistance properties with a higher standard of finish than previously available with polyurethane coatings. Tests with boiling water, coffee, nail varnish remover, vinegar, lipstick, ink and lemon juice all produced no marking or staining. The new finish is available clear or pigmented, in varying degrees of matt, with suitable base coats and undercoats.

A five day course on "Colour measurement and industrial applications" is to be organised by **Instrumental Colour Systems Limited.** To be held from 15-19 November, the course is orientated towards the practical side of colorimetry, particularly in match prediction, colour control, and tolerance setting. Various instruments will be available for delegates' use, and full details are available from Instrumental Colour Systems.

"Polymer Paint and Colour Journal" is the new title of "Paint, Oil and Colour Journal," it was recently announced. In adopting the new title, the journal will change its frequency from weekly to fortnightly.

Notes and News



At the time of writing, many applications for stand space at OCCA 24, to be held at the Empire Hall, Olympia, 17-21 April 1972, have already been received, including a number from companies that have never before exhibited at an OCCA Exhibition. Although the closing date for applications was 1 October 1971, it may still be possible for interested companies to obtain space if they apply *immediately* to the Director & Secretary at the Association's offices.

The times when the Exhibition will be open are given below:

Monday	15.00-18.30
Tuesday	09.30-18.30

Technical Exhibition

17-21 April 1972

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*.

Paint Technology Manuals— Part VII

In the April issue of the *Journal* (page 391) the attention of members was drawn to the report of the October 1970 Council Meeting, which appeared in the December 1970 issue, concerning the manuscript for the seventh part of the Paint Technology Manuals. By October 1970 the manuscript had been finalised, and it had been hoped that publication would follow in

1971. Unfortunately, however, this did not prove possible and since one of the original reasons for the publication of the Manuals was to be of help to students and younger personnel studying for City and Guilds, and in order to avoid further delays, Council decided that extracts would be taken from the manuscript, by the Hon. Editor (Mr S. R. Finn, BSc, FRIC) and printed in the *Journal* as Student Reviews throughout 1972.

In the previous announcement, it was stated that the list of the proposed extracts would be published in the October 1971 issue of the *Journal*, so that students would be aware of the scope of the scheme well in advance of publication; the proposed topics and dates of issue are as follows:

1972

January-The factory. Siting and layout

February—Raw materials. Storage and handling

March—Varnish and media manufacture: (1) Cold processes

April—(2) Manufacture in open vessels

May-(3) Manufacture in closed vessels

June-Paint manufacture. (1) General

July—(2) Processes involving premixing August—(3) Processes without premixing September—(4) Layouts, maintenance,

London Section

Development in resins for surface coatings As mentioned in the September issue, a special course of six lectures under the above title is being organised by East Ham Technical College in association with the London Section. It will be held on successive Monday evenings from 25 October 1971 to 29 November 1971 inclusive, from 7.00 to 9.00 p.m.

The lectures are aimed primarily at maturer technicians and technologists within the surface coatings and allied industries, and will be concerned with relatively recent developments. The programme is as follows:

25 October—"Alkyd resins," by Mr A. K. Unsworth

Newcastle Section

The British Titan Cup

The tenth annual tournament for the British Titan Cup was played for over the Hexham Golf Course on Saturday 3 July 1971. The competition, a four ball, better ball, against bogey, was won by Mr R. G. Carr of Camrex Ltd. and Mr filling and warehouse

- October—Factory organisation and personnel
- November—Legal requirements and regulations
- December—Factory hazards and safety precautions

Reprints of these extracts will be made at the time of printing and these will be bound together at the end of the series and offered for sale. A special price for the bound version will be available to Student members. Thus, although the Students will already have had the Student Reviews in the *Journal* during the year, they will also be able to obtain a bound version at a reduced rate; this concession being limited, while stocks last, to one copy per Student member.

Further announcements will be made towards the end of 1972 concerning the availability of reprints and their costs.

- 1 November—"Epoxide resins," by Mr L. A. Tysall
- 8 November—"Urethane components," by Mr N. Armstrong
- 15 November—"Emulsion polymers," by Dr C. Bondy
- 22 November—"Thermosetting acrylic resins," by Mr A. G. North
- 29 November—"Water soluble resins," by Mr A. R. H. Tawn

The lectures will be held in a lecture theatre at East Ham Technical College, High Street South, London E6 4ER, and enrolment will be on the first evening. Fee for the course will be £3.50.

D. Ansbro of Tioxide International five up.

This year the trophy was presented to the winners by the Chairman, Mr A. A. Duell, who also took part in the competition.

West Riding Section

Dinner and Dance

The 13th Annual Dinner and Dance of the West Riding Section will be held on Friday 26 November at the Crown Hotel, Harrogate. The ticket charge per person will be £3.50, and special concession prices for those staying the night have been arranged. Members wishing to take

OCCA Australia

1972 Convention

The 1972 Convention of the Oil and Colour Chemists Association Australia is to be held at Terrigal, New South Wales, from 22-25 June.

Details of the Convention and of

advantage of these rates should approach the hotel direct, stating that they are attending the OCCA function. Tickets for the dinner and dance are obtainable from the Hon. Social Secretary of the West Riding Section, Mr M. J. Cochrane, 49 Almsford Drive, Harrogate, Yorks, and applications should be received by Friday 12 November.

registration can be obtained by writing to:

Mr R. A. Bettison, c/o British Paints Ltd., P.O. Box 43, Bankstown, NSW 2200, Australia.

Electro-paint 71 Conference

Final arrangements for the conference on electropaint organised by the Technical Conference Organisation have now been announced. To be held at the Mount Royal Hotel, Marble Arch, London W1, from 13-15 October, the conference will contain six lecture sessions. Dr B. Bard, CBE, the managing director of the National Research Development Corporation, will open the proceedings, and Dr S. Wernick, OBE, the Hon. Secretary General of the Institute of Metal Finishing, will give the Keynote Address.

Register of Members

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

Ordinary Members

AHMED, SYED ANWAR, MSc, 4 Hillbury Road, London SW17. (London) BORGIN, KARL BORGVALD, MSc, DSc, 5 Hendrik Bergh Street, Stellenbosch, South Africa. (South African)

GIBBONS, PETER GEORGE, LRIC, 32 Skelton Road, Forest Gate, London E7 9NJ (London)

- JOHNSON, ROBERT JAMES, Coates Bros. SA Limited, 2 Baltex Road, Isipingo Rail, PO 2150 Durban, South Africa. (South African)
- JOUBERT, THORNTON JEFFREY, 14 Ponsford Crescent, Escombe, Queensburgh, Natal, South Africa. (South African)

NOMANALI, ABDUL KARIM, BSc, PO Box 81163, Mombasa, Kenya, East Africa.

(Overseas)

		JOCCA
Olmstead, Hugh Do	DUGLAS, BS, PhD, 18 Limbrick Court,	
Stockton on	Tees.	(Newcastle)
PRICE, CLIVE JOHN, 8	Greenways, Penkridge, Stafford.	(Midlands)
RIEGMAN , PIETER FRI	DERIK, 5 Janine Place, Howick, New Zealand.	(Auckland)
Standish, Brian, Bev	ALOID (SA) (Pty.) Limited, Box 65, New Germany	, South Africa. South African)
Wendon, Gunter W 36 Fitzjohn	ILLIAM, BSc, PhD, DIC, FRIC, ARCS, Flat 4, s Avenue, London NW3 5NB.	(London)
Associate Members		
BEST, R. A., 21 Millf	eld, Berkhamsted, Herts.	(London)
GLARNER, RENE PIER	RE, 115 Chase Road, Southgate, London N14.	(London)
HARBOUR, GEORGE N	ARTIN, 7 Nassau Road, Barnes, London SW13.	(London)
MOUNTJOY, BRIAN KI	EITH, Freightways Bulk Services Limited, PO Box	30-280. Lower

NOTES AND NEWS

WHITWELL, FRANCIS COLIN, C/O ICI Paints Ltd., Wexham Road, Slough, Bucks. (Thames Valley)

Student Members

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BIGGS, REGINALD PAUL, 30 Clatworthy Drive, Hengrove, Bristol 4.	(Bristol)
JONES, ALAN REGINALD, 39 Vassall Road, Fishponds, Bristol BS16 2LR.	(Bristol)
LEMAISTRE, PAUL FRANCIS, 14 Hanbury Road, Amington, Tamworth, Staffs.	(Midlands)
WATKINS, DAVID PAUL, 100 Northcote Road, Mangotsfield, Nr. Bristol BS17 3DF.	(Bristol)

Forthcoming Events

Hutt, New Zealand.

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.

Friday 1 October

Scottish Section—Student Group: "The properties of anti-corrosive pigments" by Mr J. Bowden of Craig-Hubbuck Ltd., to be held at the St. Enoch Hotel, Glasgow, at 10.00 a.m.

Monday 4 October

Hull Section: "Practical pigment dispersion" by Mr J. R. Groom and Mr M. Baker (Sandoz Products), to be held at the Queen's Hotel at 7.00 p.m.

Tuesday 5 October

Thames Valley Section—Student Group: "Metal pretreatment" by Mr P. Burden of Pyrene Ltd., to be held at the Main Lecture Theatre, Slough College, at 4.00 p.m.

Thursday 7 October

Bristol Section: "The future of plastics." Joint meeting with the Birmingham PVL Club, to be held at the Imperial Hotel, Birmingham.

IOCCA

(Wellington)

Newcastle Section: "The fibre optics colorimeter and its applications for industrial colour control" by Dr I. G. H. Ishak of The Paint Research Association, to be held at Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Friday 8 October

Manchester Section: "The fibre optics colorimeter and its applications for industrial colour control" by Dr I. G. H. Ishak of The Paint Research Association, to be held at the Bolton

Tuesday 12 October

West Riding Section: "Pigmentation of plastics" by Mr J. E. Todd of CIBA-GEIGY (UK) Ltd., to be held at the Griffin Hotel, Boar Lane, Leeds at 7.30 p.m.

Wednesday 13 October

London Section: Chairman's Forum, "Cost effectiveness and profitability in the paint industry" introduced by Mr D. E. Eddowes, to be held at the South Bank Polytechnic from 2.15 p.m. to 5.30 p.m.

Manchester Section—Student Group: "A review of printing inks and printing processes" by Mr F. Lewis of WPM Colour & Adhesives Co. Ltd., to be held at the Manchester Literary and Philosophical Society at 4.30 p.m.

Newcastle Section—Student Group: Visit to Tioxide International Weathering Station at Carlton.

Scottish Section: "Personalised marketing" by Mr W. A. Croom of the International Life Assurance Co. (UK) Ltd., to be held at the St. Enoch Hotel, Glasgow, at 6.00 p.m.

Thursday 14 October

Midlands Section—Trent Valley Branch: "Corrosion and the automobile" by Mr H. L. Quick of Chrysler UK Ltd. Joint meeting with the East Midland Branch of the Institute of Metal Finishing, to be held at the British Rail School of Transport, London Road, Derby, at 7.00 p.m.

Friday 15 October

Irish Section: "Factors which affect the efficiency of ball milling" by Dr W. Carr of CIBA-GEIGY (UK) Ltd., to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

Midlands Section: "The importance of electrokinetics in electrodeposition" by by Professor G. D. Parfitt of Tioxide International Ltd., to be held at the Birmingham Chamber of Commerce

and Industry, 75 Harborne Road, Birmingham, at 6.30 p.m.

Wednesday 20 October

Scottish Section—Eastern Branch: "Developments in water-based surface coatings" by Mr A. J. Becalick of Lennig Chemicals Ltd., to be held at the Carlton Hotel, North Bridge, Edinburgh, at 7.30 p.m.

Thursday 21 October

Thames Valley Section: "Pollution" by Dr R. B. Brown, Scientific Adviser to the Greater London Council, to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks, at 7.00 p.m.

Friday 22 October

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

Monday 25 October

London Section/East Ham Technical College course: "Developments in resins for surface coatings" see page 1000.

Friday 29 October

Bristol Section: Ladies evening. "Paint, art, colour and heraldry" by Dr S. H. Bell of The Paint Research Association, to be held at the Royal Hotel, Bristol, at 7.15 p.m.

Irish Section: Annual Dinner Dance, to be held at the Tara Towers Hotel, Dublin. Reception at 8.00 p.m.

Monday 1 November

Hull Section—"Some aspects of drying oil technology" by Mr G. Hutchinson of A. B. Fleming & Co. Ltd., to be held at the Queen's Hotel at 7.00 p.m.

London Section/East Ham Technical College course: "Developments in resins for surface coatings" see page 1000.

Tuesday 2 November

Thames Valley Section—Student Group. "Acrylic resins" by Mr A. R. H. Tawn of Cray Valley Products Ltd., to be held in the Main Lecture Theatre, Slough College, at 4.00 p.m.

Thursday 4 November

Newcastle Section. "Hazard analysis a quantitative approach to safety" by Mr T. A. Kletz of ICI Ltd., HOC Division, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne, at 6.30 p.m.

Monday 8 November

London Section/East Ham Technical College course: "Developments in surface coatings" see page 1000.

Tuesday 9 November

West Riding Section. "Silicates" by Mr K. Loftman of the Cabot Corporation of Boston, to be held at the Griffin Hotel, Boar Lane, Leeds, at 7.30 p.m.

Wednesday 10 November

London Section. "Changes in the physical characteristics of paint films in differing environments" by Mr R. L. J. Morris of the Quality Assurance Directorate (Materials), to be held at East Ham Technical College, at 7.00 p.m.

Newcastle Section—Student Group. "Paint formulation" by Mr H. Caddell of International Paints Co. Ltd., to be held at the Newcastle Polytechnic, Ellison Place, Newcastle upon Tyne, at 3.00 p.m.

Thursday 11 November

Scottish Section. Joint Meeting with British Paper and Board Makers' Association. "Amino resins—their use in surface coatings and paper industries" by Mr R. McD. Barrett of BIP Chemicals Ltd., to be held at the St. Enoch Hotel, St. Enoch Square, Glasgow, at 6.45 p.m.

Midlands Section—Trent Valley Branch. "Chromate and phosphate pigments in anti-corrosive primers" by Mr H. F. Clay and Mr J. H. Cox of SCC Colours Ltd., to be held at the British Rail School of Transport, London Road, Derby, at 7.00 p.m.

Friday 12 November

Manchester Section. "The management of human resources" by Mr J. Munro-Fraser of the University of Aston-in-Birmingham, to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester, at 6.30 p.m.

Saturday 13 November

Scottish Section—Student Group. "Exploration of the North Sea for fuel" by Mr Junor of BP Chemicals International Ltd., to be held at the St. Enoch Hotel, St. Enoch Square, Glasgow, at 10.00 a.m.

Monday 15 November

London Section/East Ham Technical College course: "Developments in resins for surface coatings" see page 1000.

Wednesday 17 November

Scottish Section—Eastern Branch. "Pollution." Joint meeting with BPBMA in Aberdeen. Further details will be supplied later.

Friday 19 November

Irish Section. "Powder coatings" by Mr Lonsdale of BJN Paints Ltd., to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

London Section: Ladies Night, to be held at the Strand Palace Hotel, London WC2, at 7.00 for 7.30 p.m. *Midlands Section.* "Oil-free alkyds" by Mr A. G. North of Cray Valley Products Ltd., to be held at the Birmingham Chamber of Commerce and Industry, 75 Harborne Road, Birmingham, at 6.30 p.m.

Monday 22 November

London Section/East Ham Technical College course: "Developments in resins for surface coatings" see page 1000.

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Thursday 25 November

Thames Valley Section. "The philosophy of paint testing" by Mr T. R. Bullett of The Paint Research Association, to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks, at 7.00 p.m.

Friday 26 November

Bristol Section. "Quality control." Discussion evening. Panel: Mr W. S. Grainger of Berger Paints, Mr D. S. Newton of British Steel Corporation, and Mr J. R. Taylor of BP Chemicals International Ltd. To be held at the Royal Hotel, Bristol, at 7.15 p.m.

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

Monday 29 November

London Section/East Ham Technical College course: "Developments in resins for surface coatings" see page 1,000.

Oil and Colour Chemists' Association

President: A. W. BLENKINSOP

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

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

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

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. Student Membership, which is intended primarily for students, is open without restriction to persons under the age of 21 and to those up to 25 who are following a course of technical study. The annual subscription in each case is $\pounds 5.25$, except for Student Members whose subscription is $\pounds 1.05$. An entrance fee of 50p is payable by all members. Applications for membership are invited from suitably qualified persons who are engaged or otherwise interested in the industries noted above. Applications, which should be supported by two members of the Association (one of whom must be an Ordinary Member), should be forwarded to the Director & Secretary at the address given below. Application forms and full details of membership may be obtained from the offices of the Association.

PUBLICATIONS

Journal of the Oil and Colour Chemists' Association. Published monthly. Subscription rate to non-members in UK and abroad; £10.00 p.a. post free; payable in advance.

An Introduction to Paint Technology (Second Edition with additional chapter). Pp. 187, illustrated, with index, £1.00 (including postage).

Paint Technology Manuals

Part 1: "Non-convertible Coatings," Second Edition, Pp. 343, £1.80.

Part 2: "Solvents, Oils, Resins and Driers," Second Edition, Pp. 268, £1.80.

Part 3: "Convertible Coatings," Pp. 318, £1.75.

Part 4: "The Application of Surface Coatings," Pp. 345, £1.75.

Part 5: "The Testing of Paints," Pp. 196, £1.75.

Part 6: "Pigments, Dyestuffs and Lakes," Pp. 340, £1.75.

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

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Please Heip The paint trade Benevolent fund

The Fund was established in 1935 to provide assistance by grants or loans to necessitous cases amongst persons engaged in the colour, paint and varnish industries and to the widows and other dependants of persons lately engaged in those industries.

Pension schemes and the "Welfare State" are unfortunately not always adequate to meet difficult circumstances at a given time. It is in such cases that the Fund can be of practical assistance.

Finance is obtained by voluntary gifts from firms and individuals by way of covenanted subscriptions, annual subscriptions and donations, supplemented mainly by money raised by an annual golf competition. The Fund costs very little to administer as all services are given voluntarily.

For many years the income from these sources proved adequate to meet the yearly grants paid. This is no longer so.

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