



Association moves headquarters

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**JOURNAL OF THE
IL &
COLOUR
CHEMISTS'
ASSOCIATION**

The influence of finish on colour changes in wood

S. Dombay

A new method for the measurement of ink transfer

P. Birkett and P. H. Woodland

The dynamic mechanical properties of thermosetting acrylic coatings

M. Akay, S. J. Bryan and E. F. T. White

Rheology of model carbon black inks

J. Kollerstrom

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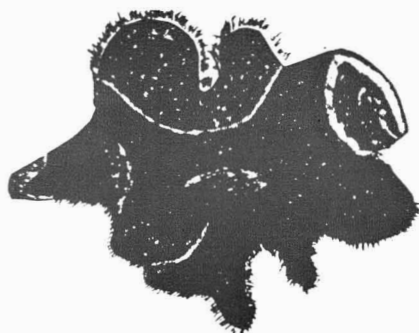


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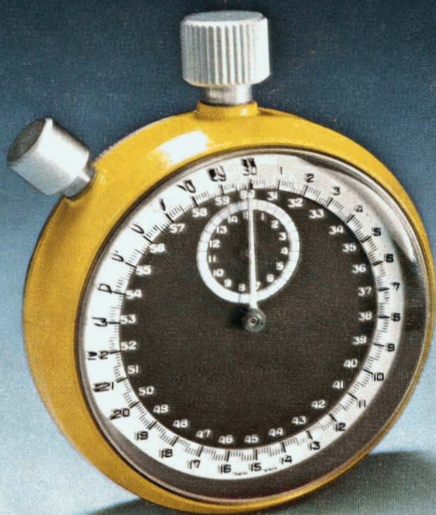
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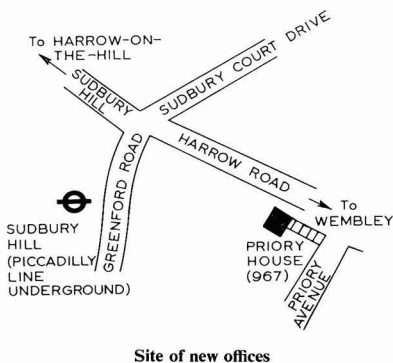
Editorial

The Association's headquarters moves to new offices

After 14 years at Wax Chandlers' Hall in the City of London, it was naturally with considerable reluctance that the Association found itself unable to renew the lease on those offices. When it became apparent that the Association's offices would have to move, Council was faced with the decision of finding alternative accommodation within the Central London area, a very expensive commodity in view of the fact that the Association needs storage as well as office space, or—following the example of many other societies—moving to one of the suburbs in the Greater London area.



Priory House



A search was undertaken in many areas and many properties were viewed before a decision was taken to acquire the lease of Priory House, a self-contained office building in Sudbury, Middlesex. This office block was built approximately twelve years ago and offers the Association office accommodation, a certain amount of storage and a small committee room which will be adequate for the holding of all Committees of Council; however, meetings of the full Council will be held in a Central London venue.

One of the advantages of the new premises is that there is ample car parking space both in front and at the side of the building itself and in the surrounding area, which can easily be reached by road from the M1 and the M4. For those travelling by train, the nearest Underground Station is Sudbury Hill (Piccadilly Line), which can also be reached via the Metropolitan Line (changing at Rayners Lane) and this is of particular help to those travelling from the North to the main line stations in London. The offices are situated half a mile from Sudbury Hill Station and the 92 bus route passes the door. The sketch map shows the situation of Priory House, and the full address of the Association's office is as follows:

Oil and Colour Chemists' Association,
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Telephone: 01-908 1086.
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Correspondence

The levelling of paint films

SIR—I commend Messrs Camina and Howell (*JOCCA*, 1972, 55, 929) for a most interesting article on the levelling of paint films. I am particularly intrigued with their new instrument for the measurement of levelling—I wish I had one!

I will not dispute the conclusions drawn by these authors, since they seem to apply entirely to solvent-based systems. I will question their validity, however, when applied to aqueous systems. Latex paints, as well as latices, are notorious levellers, and usually possess every form of rheology known, except Newtonian. I have made latex paints that were pseudo-plastic, thixotropic, dilatant, etc., and I cannot see these data applied to them. Not only are their rheological properties different from solvent systems, but their drying mechanisms involve much more than the mere evaporation of a solvent. Coalescence of the discrete particles of latex resin accompanied with capillary action present a most complex rheological picture, as all flow virtually has ceased. While solvent systems are basically two phases, latex systems are at best three phases complexed by numerous partially soluble, or insoluble, additives.

I will be interested in having the authors' comments on the above.

Yours faithfully,
J. H. BOATWRIGHT

The Craftint Manufacturing Company,
18501 Euclid Avenue,
Cleveland, Ohio 44112,
USA.
28 November 1972.

SIR—Mr Boatwright's comments on our paper are much appreciated.

We agree with him about the complexity associated with the rheological properties of latex paints, most of which have a high volume fraction of dispersed phase. This high volume fraction of the dispersed phase together with electro-

viscous effects causes their complicated flow behaviour. In addition, the colloid thickener solutions are themselves non-Newtonian. Complicated flow can also occur in solvent systems where there is a high concentration of solid particles.

The theoretical introduction in our paper was intended to promote an understanding of the physics of levelling. The paints we examined had flow behaviour which could be described by relatively simple equations. More complex equations, such as those of Eyring¹, Cross², etc. produce differential equations that are difficult to solve. This is especially true for paints with time dependent flow³. The PRA levelling blade was designed with the aim of giving useful information for a wide range of paints irrespective of their rheological properties, by simulating the shear conditions of brush application.

The work reported was concerned only with solvent-based decorative paints. Our work with latex paints has been less extensive but the indications are that they are in agreement with brush out tests. A number of latex paints we have recently examined with the levelling blade showed a rating of 0 on our scale, very poor flow-out, whereas the glossy type of emulsion showed a rating of 4. We have also found that some emulsion paints follow the power law plus yield value equation initially described by Herschel and Bulkley⁴.

Yours faithfully,
M. CAMINA
D. M. HOWELL

Paint Research Association,
Waldegrave Road,
Teddington, Middx TW11 8LD.
18 December 1972.

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- ¹Eyring, H. and Ree, T. *J. Applied Phys.*, 1955, 26, 793.
- ²Cross, M. M. *J. Colloid Sci.*, 1965, 20, 417.
- ³Camina, M. and Roffey, C. G. *Rheol Acta.*, 1971, 10, 606.
- ⁴Herschel, W. H. and Bulkley, R. *Kolloid-Z.*, 1926, 39, 291.

Corrigenda

The following typographical errors have been noted in the paper by Snuparek published in the November 1972 issue of the *Journal*.

In Fig. 4, page 1014, curve (b) has been designated curve (c) and vice versa.

In Figs. 7 and 8, pages 1017 and 1018, a letter "g" appears instead of the numeral 9 on the abscissas.

In the paper by Moss (*JOCCA* January) the systems A—E are not as indicated in the appendix, which might be the impression given.

Reference to the original will show that the systems are as follows:

Fig. 2

- A = Liquid resin/Aromatic amine adduct
- B = Liquid resin/polyamide
- C = Liquid resin/polyamide adduct
- D = Liquid resin/Aliphatic Amine adduct
- E = Diluent containing liquid resin/solvent-free aromatic amine adduct

Fig. 3

- A = Solid resin/aromatic amine adduct
- B = Solid resin/polyamide
- C = Solid resin/polyamide adduct
- D = Solid resin/liquid aliphatic amine adduct
- E = Solid resin/solid aliphatic amine adduct

The influence of finish on colour changes in wood

By S. Dombay

Furniture Industry Research Association, Maxwell Road, Stevenage, Herts, SG1 2EW

Summary

An investigation has been carried out into the effect on wood colour of different types of finish, representing nitrocellulose, polyurethane, urea-formaldehyde, melamine-formaldehyde and polyester systems on oak, teak, afrormosia, African mahogany and American black walnut veneers, mounted on particleboard. Duplicate samples of coated wood and unlaquered controls were exposed to daylight for six months or kept in the dark for the same period, and their colours were measured with an abridged spectrophotometer, using the blue, yellow and red filters. The reflectance readings were converted to tristimulus values (coefficients) which

were then plotted on graphs similar to the CIE system of colour representation.

The modifying influence of some of the finishes on the colour was to some extent apparent even on the woods stored in the dark, but the effect was much greater on the exposed samples. Although the effects predictably varied from wood to wood, some general pattern has emerged in respect of lacquer types as well as the species of wood studied, though no attempt has been made to relate these in great detail with the natural chemicals present in wood.

Keywords

Types and classes of surface
wood

Types and classes of coating
wood finish

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

L'influence qu'exerce la finition sur les altérations de la couleur du bois

Résumé

On a effectué une investigation sur l'effet provoqué sur la couleur de bois par de différents types de finition, tels que des systèmes à base de nitrocellulose, polyuréthane, urée-formol, mélamine-formol et polyester, appliqués au chêne, teck, afrormosia, acajou d'Afrique, et noyer noir d'Amérique plaqué aux panneaux de particules de bois. Des échantillons en double exemplaire du bois revêtu et des blancs exempt de vernis étaient exposés à la lumière de jour pour 6 mois, soit tenus au noir pour une pareille intervalle, après laquelle leur couleur était mesurée au moyen d'un spectrophotomètre agrégé, en utilisant des filtres bleu, jaune et rouge. Les lectures de réflectance ont été converties aux valeurs tristimulus

(coefficients) qui ont été mises sur des courbes semblables au système CIE de représentation de couleur.

L'influence modificatrice de certaines finitions sur la couleur du bois était à quelque degré apparente même sur les échantillons tenus au noir, mais l'effet était plus important dans le cas de ceux qui ont été exposés. Bien que les effets se variaient, d'une manière qui peut être prédite, d'un bois à un autre, une certaine tendance générale s'était mise en évidence au point de vue des types de finition, ainsi que des espèces de bois que l'on a étudiés. Pourtant on n'a pas tenté de lier ces effets, dans une manière circonstanciée aux agents chimiques naturels qui se trouvent en bois.

Der Einfluss der Lackierung auf Farbwechsel im Holz

Zusammenfassung

Eine Untersuchung über die Auswirkung von Lackschichten verschiedener Zusammensetzung, und zwar Nitrozellulose-, Polyurethan-, Harnstoffaldehyd-, Melaminformaldehyd- und Polyester-systeme wurde über Eich-, Teak-, Afrormosia-, afrikanische Mahogany- und amerikanischem schwarzem Wallnussfurnier, alle auf Spanplatten montiert, durchgeführt. Duplikatmuster lackierter Hölzer und unlackierter Kontrollen wurden 6 Monate lang dem Tageslicht ausgesetzt oder ebenso lange im Dunkeln gelagert. Ihre Färbungen wurden mittels einer verkürzten spektrophotometrischen Methode unter Benutzung blauer, gelber und roter Filter gemessen. Die Rückstrahlungsablesungen wurden in Tristimuluswerte

(Koeffizienten) konvertiert und dann, ähnlich dem CIE System der Farbvorstellung, grafisch dargestellt.

Bis zu einem gewissen Grade war der modifizierende Einfluss mancher der Lackierungen auf die Farbe von sogar im Dunkeln aufbewahrten Hölzern offensichtlich, bei den exponierten Mustern war die Wirkung erheblich grösser. Sowohl bezüglich der Lackarten als auch der Holzsorten kam eine Art allgemeines Schema zutage, obwohl sich die Auswirkungen, wie vorauszusehen war, je nach Holzart unterschieden. Es wurde jedoch nicht versucht, diese Auswirkungen im Einzelnen mit den im Holz auf natürliche Weise anwesenden Chemikalien in Beziehung zu bringen.

Влияние отделки на изменение цвета в дереве

Резюме

Рассматривается влияние на окраску дерева различных типов покрытий, например нитроцеллюлозных, полиуретановых, мочевино-формальдегидных, меламино-формальдегидных и полиэфирных систем на фанерах дуба, тикового дерева, афромозии, африканского красного дерева и американского черного орехового дерева, установленных на панелях. Двойные образцы покрытых деревянных и нелакированных контрольных панелей подвергались влиянию дневного света в течение 6-ти месяцев или хранились в темноте в течение того же периода и их цвета измерялись на спектрофотометре, применяя синий, желтый и красный фильтры. Показания отражаемости преобразовывались в стимулярные значения (коэффициенты),

которые наносились на графики подобно системе С.И.Е. для обозначения цветов.

Модифицирующее влияние некоторых отделок на цвет наблюдалось до известной степени даже на дереве хранимом в темноте, но эффект был гораздо сильнее на образцах подверженных влиянию света. Хотя эффекты, как и надо было ожидать, изменялись от дерева к дереву, все же обнаруживается некоторая общая форма по отношению к типам лака и испытанных деревянных образцов, хотя и не делается попытки связать их с натуральными химическими элементами присутствующими в дереве.

Introduction

The effect of light, natural and artificial, on the colour of wood is to cause it to fade or darken and to bring about changes in tone. Whether light is the primary cause or functions as a catalyst has yet to be decided, and it may be found that its precise role in colour changes in wood may vary with the species.

Extensive studies and observations have shown that most, if not all, species of commercial importance, and in particular those used for the manufacture of furniture, are prone to discolour with age¹. Discoloration occurs both indoors and outdoors and, indeed, changes in colour have been observed by the author in many species even when stored in the dark, though in the presence of air.

The rate of discoloration is usually related to the intensity of light and its wavelength, and also depends on the species of wood. Light of normal intensity tends to promote darkening generally, whilst that of high intensity, e.g. direct sunlight, usually causes fading, though often after an initial period of darkening. Both processes have been observed to occur simultaneously in some veneers when the two sides have been exposed to radiation of uneven intensity. Pale-coloured timbers that are commonly classed as "white", including most pines and some hardwoods, such as oak, birch, beech, sycamore, etc., generally respond² to radiation below 400 μ m, whilst the coloured species that absorb light in the visible spectrum are also sensitive to certain wavebands in the visible region².

In its application in the furniture industry, wood occurs in a variety of forms, the chief being decorative veneer, ply and "solid". The bulk of domestic cabinet furniture is normally finished with clear protective coatings of solvent-based lacquer, although these provide little, if any, protection against light. Such coatings may, however, influence the "natural" colour changes in wood owing to their chemical structure, which reacts with certain constituents of wood, and also through their own tendency to discolour by photochemical action. The Furniture Industry Research Association has made a study of the influence of a number of conventional, clear and initially colourless wood finishes on the "natural" discoloration of several species of wood and a description of this work is given here.

The principal constituents of wood, both hard and soft, are polysaccharides, lignins and a large family of polyphenolic substances (extractives). The polysaccharides have a fair degree of resistance to atmospheric oxidation and are not known to discolour appreciably in ordinary light. Lignin, on the other hand, is more susceptible to oxidation and readily undergoes structural changes (de-methoxylation) in UV light⁴, which are almost invariably accompanied by yellowing, most noticeably in "white" woods.

The extractives, which include tannin-like substances, flavones, flavonols, aurones, anthraquinones, anthocyanins etc., are often brightly coloured and it is mainly to these that wood owes its colour. These and many initially colourless polyphenols (stilbenes, hydroxybenzoic acids, leucoanthocyanins etc.) are the more important constituents involved in photochemical changes^{5, 6}. The initially colourless extractives often yield coloured derivatives, which may be due to formation of quinonoid structures and oxidative polymerisation. Prolonged exposure to intense light eventually results in structural degradation and bleaching of the exposed surface⁷.

Experimental

The species selected for this study comprised five common hardwoods, the aim in the choice being a compromise between uniformity of colour, ease of measurement and the commercial importance of the timber. They were, European oak (*Quercus robur*), American black walnut (*Juglans nigra*), Afrormosia (*A. elata*), Teak (*Tectona grandis*) and African mahogany (*Khaya ivorensis*). The last named is closely related and chemically similar to sapele and utile, which may be more important as decorative veneers, but has a more reliable uniformity of colour. The species selected also provide a fair representation of the photoactive extractives of common occurrence, especially in the heartwood of many timbers, e.g. leucoanthocyanins and catechins (Khaya), tannic acid and quercetin (oak, walnut), anthraquinones (teak), polyhydroxystilbenes and flavonols (afrormosia).

The investigation was carried out with veneers approximately 0.7mm thick, mounted on 20mm particle board with a urea-formaldehyde glue. The test panels were cut into 70mm squares (the size being determined by the sample holder of the colorimeter) and sanded clean for finishing. The lacquers were applied by a brush, producing films of approximately 50 μ m average dry thickness. It was not thought practical or important to standardise film thickness by, for example, diluting lacquers of high solid contents, since each type of finish was to be investigated on its merit under the usual conditions of application, including film thickness. The solids contents, nevertheless, were noted so that allowance could be made for any possible influence of film thickness.

The lacquers were applied singly to each of the five species of wood, as the scope of this work did not cover the effect of combining several types of lacquer on one wood simultaneously. After application of the lacquer, the test pieces were allowed to stand in a dark room at 25°C for three days, and then exposed to the west sky in Stevenage, Hertfordshire, behind 4mm thick window glass for a period of six months from April to October. Although arbitrary, this period of exposure was considered justifiable on the grounds of general observations that the most rapid and significant changes of colour occurred during the first six months of exposure to direct sunlight. To allow the spontaneous yellowing of the lacquers themselves to be distinguished from discoloration of wood, colourless transparent sheets of glass were also coated with the lacquer, to produce films of similar thickness to those on wood, and were exposed alongside the wood specimens. The various finishes investigated were obtained from commercial suppliers and were, at the time, available to the industry. They are described in Table 1.

Measuring the colour of wood and lacquer films

Colour changes after exposure were assessed by reflectance measurements with blue, yellow and red filters of approximate transmission maxima of 470, 580 and 700 μ m respectively, in an abridged spectrophotometer using a tungsten filament light source. The area illuminated was 100mm in diameter and the incident light was diffused by a semi-matt hemispherical reflector to minimise interference due to gloss and thus nullify the possible effect of variation in gloss of lacquered surfaces. The readings were obtained by the selenium photocell/galvanometer method and were referred to a white tile of medium gloss, as standard. The yellow discoloration of the exposed lacquer films on glass was measured with the blue filter only, the standard white tile being placed behind the transparent coated glass plates to reflect the transmitted light to the photocell. The results were expressed in terms of

percentage transmission relative to unexposed, colourless coatings and are summarised in Table 2.

Table 1
List of lacquers

Designation	Type	% solid	pH*
a	Nitrocellulose/alkyd, resin based on soyabean oil. Low resin/nitrocellulose ratio	26.4	5.0
b	Nitrocellulose/alkyd, resin contains natural dammar. High resin/nitrocellulose ratio	31.0	4.5
c	Styrene/polyester alkyd. Resin based on polyol/phtalic/maleic anhydride. Cobalt naphthenate dryer	94.2	5.0
d	Acid-catalysed: urea-formaldehyde/alkyd two-pack system	35.0	3.0
e	Acid-catalysed: melamine-formaldehyde/alkyd two-pack system; alkyd based on castor oil	29.7	1.0
h	Acid-catalysed: urea-formaldehyde/alkyd two-pack system; alkyd based on castor oil	33.1	1.0
j	Polyurethane: aromatic polydiisocyanate/polyol two-pack system	21.0	8.0
k	Soyabean oil-type alkyd	42	4.5

* The pH values were determined colorimetrically to the nearest half unit, using 10% dispersions in acetone/water.

Table 2

Effect of exposure on transmission of lacquers exposed

Lacquer	exposed original transmission %
a	98
b	86
c	98
d	96.5
e	98
h	92
j	88
k	93

Arranging the lacquers in the descending order of yellowing, $b > j > h > k > d > c = a = e$, it is evident that discoloration was greatest in lacquer *b* and the least yellowing occurred in lacquers *c*, *a* and *e*.

The graphical representation of colour

An adaptation of the CIE (Commission Internationale de L'Eclairage) system of colour representation⁸ was found quite suitable for numerical and graphical expression of colour changes, for which the tristimulus coefficients were calculated from reflectance values through the three filters. Only the yellow and red coefficients (*y* and *r*) were used for the colour plots as measures of yellowness and redness respectively; the

degree of brightness was related to the reflectance of yellow light and the absolute value (*Y*) was adopted as its measure. This was thought to be justifiable on the grounds that the human eye is most sensitive to yellow light, and by this practice, a reasonable degree of correlation was obtained between subjective perception and numerical expression. Thus two-dimensional colour plots for the five woods, with a brightness scale, were produced and are shown by Figs. 1-6. Figs. 1-5 refer to the species under different finishes, whilst Fig. 6 shows the "natural" changes in uncoated woods before and after exposure. It is to be noted that the uncoated specimens were finished with lacquer (*a*) for "wetting out" before measurements were taken, to eliminate the light scatter and standardise conditions of reflectance measurement.

The colour values of controls 1 are those obtained before exposure; those of controls 2 were obtained after exposure (uncoated). The meaning of the symbols in Fig. 6 are: K, Khaya; A, Afrormosia; T, Teak; W, Walnut; O, Oak.

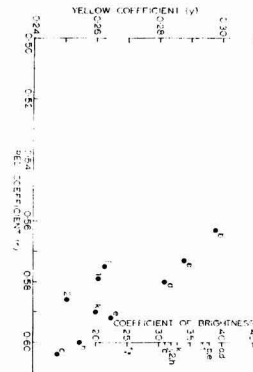


Fig. 1. Colour plot for Khaya (African Mahogany) coated with various finishes, exposed (except Control 1)

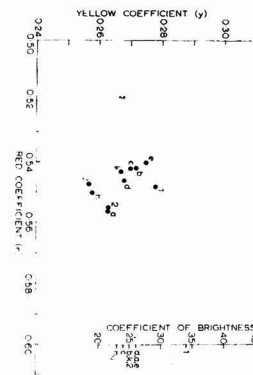


Fig. 2. Colour plot for Afrormosia coated with various finishes, exposed (except Control 1)

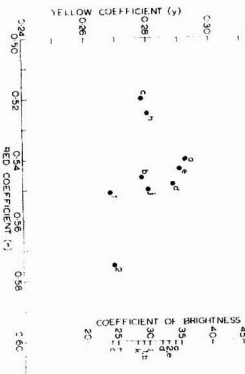


Fig. 3. Colour plot for Teak coated with various finishes, exposed (except Control 1) (For coating k: $y = 0.340$, $r = 0.432$)

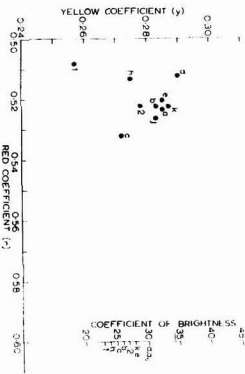


Fig. 4. Colour plot for American Black Walnut coated with different finishes, exposed (except Control 1)

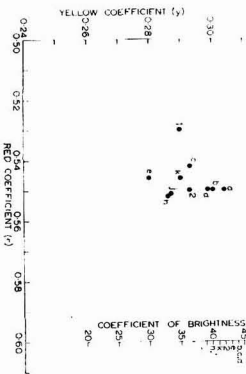


Fig. 5. Colour plot for Oak coated with various finishes, exposed (except Control 1)

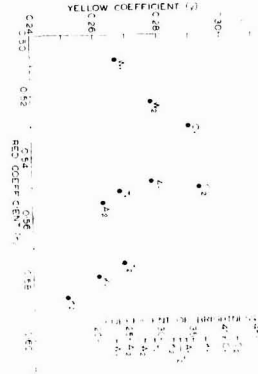


Fig. 6. Colour plot for uncoated Afrormosia, Khaya, Oak, Walnut and Teak. 1—Before exposure 2—After exposure

It is to be noted that, owing partly to the spectral characteristic of tungsten light not being a standard, as stipulated in the official CIE system, and partly to lack of correction factors for the light filters and other variables used, the colour values may be displaced slightly from the "theoretical" positions they would occupy in the true CIE chart. Nevertheless, they will still fall within the same general area.

Summary of results relative to the individual species of wood

African mahogany (Khaya)

The veneer used was of typical "pink" colour before exposure, the tristimulus values in tungsten light being $b = 0.160$, $y = 0.261$, $r = 0.579$ and the relative brightness = 37.5. Upon exposure it followed the familiar pattern of colour change characteristic of this species: an immediate reddening and darkening noticeable within a few days of exposure to strong light, followed by a slower phase of bleaching (yellowing) which is not normally complete even after six months in British daylight conditions.

Though the effects of some of the finishes on the colour after six months were obvious, they consisted of tonal variations of the same general colour characteristic of the species, with yellow or red bias depending on the finish. The least apparent colour change in terms of the yellow and red coefficients occurred under the polyurethane (*j*), but the least change in the sense of overall fading (or darkening) took place with the nitrocellulose (*b*) and melamine—formaldehyde (*e*). The reddest and darkest colours were under the polyester (*c*) and urea-formaldehyde (*h*).

Afrormosia

The veneer used was of the usual yellow-green shade, the tristimulus values in tungsten light being $b = 0.174$, $y = 0.278$, $r = 0.548$ and the relative brightness = 34.

Afrormosia darkens rapidly in strong light and the process may continue for several months, depending on the intensity of light. The dark brown colour thus formed is held fairly well and photochemical bleaching does not normally occur in service.

Only very small tonal variation in the test pieces could be distinguished at the end of the six-month period; the changes

under all the finishes were in the same general direction, differing little from the uncoated control.

The main common feature was a reduction in the yellow component in all, consistent with the overall darkening.

The least change of colour occurred under the melamine-formaldehyde (*e*) and the greatest changes in the sense of darkening occurred under urea-formaldehyde (*h*) and the polyurethane (*j*).

Teak

The wood used could be described as of the medium brown colour that is common in this species before exposure to air and light. The tristimulus values for the fresh surface in tungsten light were: $b = 0.181$, $y = 0.288$, $r = 0.551$ and the relative brightness = 29.5.

Light has a bleaching effect on the colour, resulting in "golden yellow" or pale "reddish brown" shades which are held quite well by the wood. The relative reddening of the uncoated surface was stronger than in the lacquered specimens, which, however, were richer in the yellow component than either control—illustrating, perhaps, the independent actions of light and atmospheric oxygen on the colour of this wood.

The least apparent change occurred under the nitrocellulose (*b*) but yellowing proceeded furthest under the nitrocellulose lacquer (*a*). Losses in the red component were greatest under the polyester (*c*) and urea-formaldehyde (*h*) lacquers, both of which also enhanced general darkening, the more severe being under lacquer (*c*).

American black walnut

The colour of the veneer was characteristic of the species, which can be described as grey-purple. It is relatively rich in the blue component, poor in the red and the overall reflectance (brightness) is quite low. The tristimulus values in tungsten light were: $b = 0.225$, $y = 0.267$, $r = 0.508$, and the relative brightness (Y) = 23.

The unfinished wood has a strong tendency to take on a light brown colour on exposure, owing to partial destruction of the blue component by light and a shift of reflectance towards the yellow and red. This tendency was influenced only to a small extent by most finishes and it was not fully inhibited by any, but to the greatest extent by polyester (*c*). The fading of the original colour proceeded farthest under the mildly acid finish (*d*) and the mildly alkaline polyurethane (*j*). The yellowing was apparently low under urea-formaldehyde (pH 1) and it tended to take on a reddish tone under the polyester.

Oak

The veneer used was of the usual dull off-white shade, characteristic of the fresh surface of European species of *Quercus*. The tristimulus values in tungsten light were: $b = 0.180$, $y = 0.290$, $r = 0.530$ and the relative brightness = 40.

The yellowing and reddening of this wood in light was not appreciably affected by the finishes and with the exception of the test piece under the polyurethane (*j*), all ended up with increased overall brightness, in spite of the positive shift in the red coefficient under all the lacquers. The maximum brightness (yellowing) was obtained under the nitro-

cellulose lacquer (*a*) and the least overall colour change occurred under the polyester finish (*c*).

Discussion

Although the finishes employed in this study were initially clear and colourless in the thin films used, it is by no means certain that they were entirely transparent to ultraviolet radiation and some degree of protection against influences leading to colour changes may be supposed to have been provided by the coatings. By inhibiting the access of atmospheric oxygen and moisture, both of which are believed to promote discoloration, the physical barrier may be expected to have had a general retarding effect on natural colour changes. Thus, the observed and measured changes must be the net product of the degree of protection on the one hand and the chemical reactions between wood and lacquer constituents, in addition to the yellowing of some finishes, on the other. The precise role of the above factors has not been investigated independently, apart from the discoloration of the free lacquer films, though some of the features in the observed changes may be explained by a general knowledge of wood chemistry and the behaviour of certain lacquer components. Judging by the reflectance values, an apparent accentuation of yellowing of all five species occurred under both nitrocellulose/alkyd systems (*a* and *b*), although by no means in a uniform or consistent manner. Since lacquer (*b*) on an inert glass substrate has proved to be strongly discolouring, this behaviour must have contributed to the overall yellowing of the wood surfaces.

A retarding effect on the natural increase in the red component of the uncoated wood was shown by nearly all the finishes on teak and afrormosia and, with three exceptions in afrormosia, yellowing, on the other hand, has been enhanced in both species.

With the exception of polyester (lacquer *c*), the finishes on African mahogany accentuated the yellow component and the red in this wood was promoted by the polyester and the acid-catalysed UF finishes (*e* and *h*), the last two types would no doubt favour the formation of anthocyanidins. This conclusion is supported by the observation that the effect was more pronounced under the more strongly acid lacquer (*h*). The acidity, on the other hand, seems to have had some inhibiting influence on yellowing, presumably through suppression of the dissociation of weak acids, e.g. coloured polyphenols.

The apparent difference in the behaviour between melamine formaldehyde and urea-formaldehyde types of similar degree of acidity (pH 1) was that yellowing was inhibited to a lesser extent under the MF, though the reason for this is not quite clear.

General darkening i.e. decrease in reflectance, as shown by the brightness index Y , was evident under the more strongly acid UF lacquer (*h*), than under UF lacquer (*d*). The role of acidity here could be catalytic on the polymerisation (oxidative or otherwise) of extractives into darker derivatives.

Whilst accelerating the fading of American black walnut, the aromatic polyisocyanate-based polyurethane (lacquer *j*), seems to have promoted general darkening in the other four woods. This effect could be due in part to the alkalinity of the finish, to its own discoloration and in part to possible interaction of isocyanate residues with polyphenols. The influence of polyester was to enhance darkening, with the

exception of oak, which in fact remained lighter than the control, the darkening being most pronounced in teak.

This behaviour may suggest possible protection of the "white" wood against UV radiation on the one hand and interaction with coloured extractives on the other.

No clear trend owing to a coating of the neat alkyd resin (*k*) could be recognised, though the difference in the performance of nitrocellulose lacquers (*a* and *b*) has provided an indication that the dammar type is more prone to yellowing than the soya bean oil modified resins alone.

Conclusion

Clear finishes appear to influence the colour of wood exposed to light in three ways: by yellowing of the finish itself due to oxidation and photochemical action; by chemical interaction of lacquer components with reactive constituents of wood; and by partial inhibition of the "natural" colour changes of the wood by reducing both the access of atmospheric oxygen and the ultraviolet light reaching the wood surface. The resultant effect is the net product of these factors, which are independent of each other and may not all occur together in the same system.

The first factor is of importance only on light coloured woods, such as, for example, "white" oak, which shows up the yellowing of some finishes more than do the coloured woods. The second factor is exemplified by the acid-catalysed and polyurethane finishes on some woods, and the apparent inhibitory effect of polyester was indicated on oak and American black walnut. When two or all of the above factors operate simultaneously, the results can be complex and unpredictable. Such a condition may be the case with teak under polyester (*c*), which not only stopped the wood from

bleaching (the natural tendency) but caused a considerable darkening of the surface apparently through chemical interaction with the wood.

In view of the different woods' responding to the various finishes in different ways, the behaviour of any one species must be assessed individually and, if generalisations are to be extended to species not investigated, they must be based on chemical similarities between them. For example Khaya, sapele and utile, which are characterised by the presence of anthocyanidins and belong to the family *Meliaceae*, may be expected to respond in similar ways to the different finishes.

Although the lacquers used were a fairly representative selection of those currently available, there must be significant variations of behaviour within each type according to formulation, as illustrated by the two nitrocellulose lacquers (*a*) and (*b*), and a caution similar to that in respect of wood species must be exercised when attempting to apply the observations made on one finish to another of similar type.

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A new method for the measurement of ink transfer

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Summary

A rapid method of measuring the amount of ink transferred during impression, which is independent of the printing process used and employs X-ray emission analysis, is described. It is, however, necessary for labelled atoms of reasonably high atomic weight to be present in the ink film.

Since X-ray emission spectra are independent of the outer shell electronic configurations, the appropriate atoms may be in any state of combination. They can, for example, be added in the form of an inorganic salt or complex, organic soap or simply as finely

divided metal. Many laked pigments, meta toners and complexes are suitable carriers.

Providing the substrate does not contain a high proportion of the detectable element, it does not interfere with the analysis.

In the experiment described, gravure prints containing a copper phthalocyanine pigment were printed on paper in the form of a continuous tone step-wedge. Calibration of the X-ray count was made by using known ink film weights on a polypropylene base.

Keywords

Processes and methods primarily associated with: application of coatings

ink transfer

Analysis, measurement and testing

X-ray emission analysis

Une nouvelle méthode pour mesurer le transfert d'encre d'imprimerie

Résumé

On discute une méthode rapide au moyens de l'analyse d'émission de rayons X, qui est indépendante du procédé d'impression, pour mesurer la quantité d'encre transfert lors de l'impression. Cependant il exige la présence, dans le feuil d'encre, des atomes marqués d'un poids atomique assez élevé.

Puisque les spectres d'émission de rayons X sont indépendants de la couche extérieure des configurations électroniques, les atomes convenables peuvent être en aucun état de combinaison. Ils peuvent être introduits sous forme, par exemple, d'un sel ou d'un complexe inorganique, d'un savon organique ou simplement du métal finement pulvérisé. Beaucoup de laques, toners ou complexes

métalliques sont des agents-porteurs convenables.

Pourvu que le support ne contienne pas de quantité élevée de l'élément cherché, il ne provoque pas de perturbation de l'analyse.

Dans l'expérience décrite, des encres pour gravure contenant du pigment de phtalocyanine de cuivre ont été imprimés sur papier sous forme d'un ton en gradins continus. L'étalonnage de la numération des rayons X était effectuée au moyens des feuil d'encre d'un poids déterminé que l'on avait appliqués sur un support de polypropylène.

Eine neue Methode zur Messung des Transfers von Druckfarben

Zusammenfassung

Beschreibung einer schnellen Methode zur Messung der Druckfarbenmenge, welche im Zuge des Abdrucks übertragen wird. Die Methode ist vom benutzten Druckverfahren unabhängig und verwendet Röntgenstrahlenemissionsanalyse. Allerdings müssen im Druckfarbenfilm indizierte Atome von einigermaßen hohem Atomgewicht zugegen sein.

Da Röntgenstrahlenemissionsspektren von der äusseren Elektronenschalenkonfiguration unabhängig sind, können die entsprechenden Atome in irgendwelchem Kombinationszustand sein. Sie können z.B. in Form eines Salzes oder Komplexes, als organische Seife oder einfach als feinverteiltes Metall zugegeben werden. Viele

verlackte Pigmente, Metalltoner und Komplexe eignen sich als Träger.

Das Substrat beeinflusst die Analyse solange nicht, als es nicht selbst einen hohen Prozentsatz der zu entdeckenden Elemente enthält.

In dem beschriebenen Experiment wurden Kupferphthalocyanin-pigment enthaltende Tiefdrucke in Form eines unendlichen Ton-Ätzstreifens auf Papier gedruckt. Kalibrierung der Röntgen-Auszählung wurde unter Benutzung bekannter Druckfarbenfilmgewichte auf einer Polypropylenunterlage vorgenommen.

Новый метод измерения переноса чернильной краски

Резюме

Описывается быстрый метод измерения количества чернильной краски перенесенной во время отпечатка, который не зависит от применяемого печатного процесса и применяет анализ рентгеновского излучения. Однако необходимо присутствие определенных атомов достаточно высокого атомного веса в пленке чернильной краски.

Так как спектры рентгеновского излучения не зависят от электронных конфигураций наружной оболочки, соответствующие атомы могут быть в любом состоянии соединения. Они могут, например, прибавляться в форме неорганической соли или комплекса, органического мыла или просто в форме мелко

измельченного металла. Многие лаковые пигменты, металлические тонеры и комплексы являются подходящими носителями.

Если субстрат не содержит высокой пропорции обнаруживаемого элемента, то он не служит препятствием анализу.

В описываемом опыте гравюрные отпечатки, содержащие пигмент фталоцианина меди, печатались на бумаге в форме непрерывного клинового тона. Калибрация счета рентгеновского излучения проводилась применением известных весов чернильной пленки на основе полипропилена.

Introduction

One early method of ink transfer measurement was the weighed shell technique employed by Mill and Colquhoun¹ in 1939. This technique has continued to be used for letterpress transfer analysis² and has even been adapted for gravure transfer by printing special non-volatile inks from an intaglio plate mounted on a Vandercook proofing press³.

Buchdahl⁴ has described two tracer methods which avoid repetitive weighings either by using a radioactive isotope added to the ink or by addition of a suitable dyestuff. The former method requires analysis by a Geiger-Muller counter, whilst in the latter the dye must be determined colorimetrically after elution from the print. Both methods have certain disadvantages: whilst the radioactive technique is hazardous and requires frequent re-calibration, the use of dyestuffs is limited owing to the variable effects of ink components occluding the dye, or possible absorption on to cellulose fibres during leaching.

To overcome the disadvantage of dyestuffs, work on colorimetric analysis of washings was carried out by Rupp⁵ and Joyce and Fuchs⁶ using pigmented gravure inks.

More recently, Tukahashi *et al.*⁷ have used a spectrofluorimeter to measure gravure ink transfer, incorporating a fluorescent dye into the ink. It would seem that this technique is open to the same criticism as Buchdahl's method. Moreover, due to the common occurrence of fluorescing agents in paper, or the possible presence of quenching agents, highly erratic results may be obtained.

In the work described below, a transferred ink containing a heavy metal atom is examined *in situ* by X-ray emission analysis. This method of analysis has been used for analysis and measurement of thin metal films on various substrates⁸. It has also been used for the inspection of paint films, and trace metal determinations of printed films⁹.

Theoretical

X-ray emission (fluorescence) spectroscopy depends on the phenomenon of large energy emissions of atoms in certain excited states. The excitation is achieved by irradiation with primary X-rays of short wavelength. This results in a K or L electron being ejected followed by a characteristic energy emission as an outer electron fills a vacant inner shell. The transitions K_{α} , K_{β} etc. represent the spectral lines produced by electronic transitions to the K state.

Lighter elements give lower energy transitions to inner shells, emitting longer wavelengths which are largely absorbed in the atom. Thus elements below magnesium are not detectable by this means.

Since inner and not valency electrons are involved, the state of combination of the atom is immaterial in the formation of the spectrum.

Experimental

In order to calibrate the X-ray emission (XRE) spectra, samples of a polypropylene film were printed on a Strachan and Henshaw pilot gravure press, using a commercial ink containing copper phthalocyanine pigment. Different ink film thicknesses were applied by means of a cylinder etched with a step-wedge, and the dried film weights were determined gravimetrically after solvent removal.

The K_{α} line for copper was selected by means of a goniometer in a Phillips PW 1410 spectrometer, using a block of copper as the sample.

The goniometer, shown in Fig. 1, consisted of a crystal which acted as a diffraction grating and a detector which was essentially a scintillation counter. Collimators ensured parallelism in the X-rays.

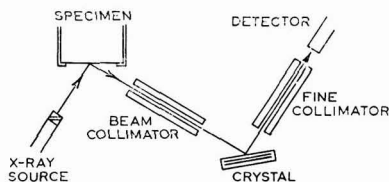


Fig. 1. A schematic diagram of an X-ray emission spectrometer

Results

The reproducibility of the XRE method was not affected by drift; repeated measurements on the same print sample over a 3-hour period showed hardly any difference between means or standard deviations. The precision of the analysis increased with increased amounts of copper present, and generally the coefficient of variation was better than 1 per cent.

Using the X-ray goniometer to scan between 40° and 50° , a large peak due to the tungsten target was shown to overlap slightly the K_{α} line of copper (see Fig. 2). This effect was partly responsible for background count (noise).

With an angle of 44.93° , an adequate count rate was obtained for an input of 50kV and 20mA. Counts were recorded for 10 seconds (later 5) and repeated five times for each sample, to obtain a mean value.

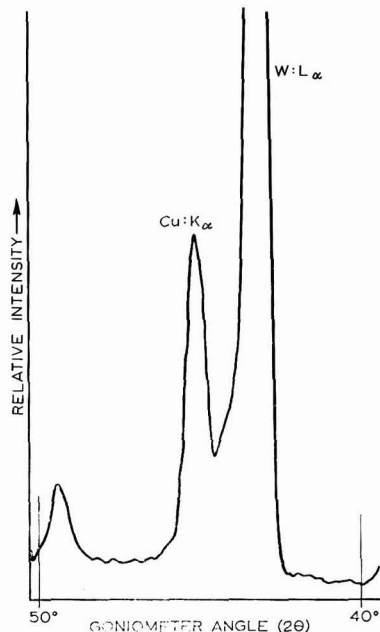


Fig. 2. Goniometer scan, showing tungsten overlap on $Cu:K_{\alpha}$ peak

A further cause of background noise was metallic compounds present in the paper substrate substituted for polypropylene. In the former case, the signal : noise ratio was lowered from 1.15 : 1 to 0.4 : 1 (Step 1) and 5.65 : 1 to 3.95 : 1 (Step 7) when the sample thickness was increased to five sheets.

A corrected calibration curve allowing for background noise (2,014 counts in 10 seconds) showed a linear relationship between ink volume transferred and the XRE count, see Fig. 3.

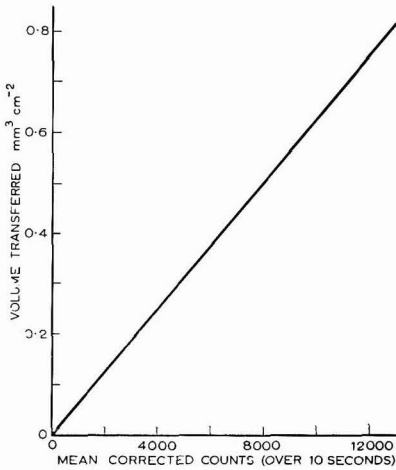


Fig. 3. Calibration curve

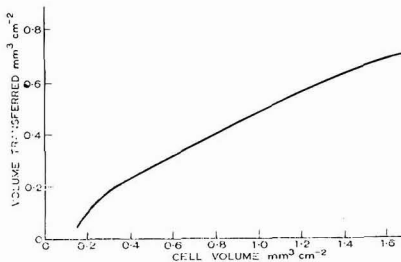


Fig. 4. Typical ink transfer curve

The transferred ink volume was calculated using the measured non-volatile content of the wet ink (23 per cent). With a running speed of one ms^{-1} and a linear pressure of $1,780\text{kgf m}^{-2}$, the typical transfer curve shown in Fig. 4 was obtained on a blade-coated paper with an ink of 260 cP running viscosity.

The cell volume was obtained by calculation, since continuous inking on this type of press prevented analysis of the cell contents.

Conclusions

The technique of XRE analysis provides a quick, accurate, reproducible and non-destructive method of measuring ink transferred to any substrate. The "labelled" atom can be a structural part of the pigment or resin molecule or can be in the form of an ink additive, providing it is uniformly dispersed.

The method should be equally adaptable to other printing processes. It can also be used for detecting changes in pigment : resin ratio during transfer, by suitable labelling of pigment and resin¹⁰.

Acknowledgments

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The dynamic mechanical properties of thermosetting acrylic coatings

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Summary

An experiment to facilitate the development of appliance finishes which takes account of their viscoelastic properties is described. The systems studied were based on thermosetting acrylic resin systems of the hydroxyl type, cross-linked with hexamethoxymethylmelamine.

The dynamic mechanical properties of free resin films were measured over a wide temperature range using a forced vibration technique and the results compared and correlated with conventional physical test results obtained on finishes applied to metal substrates. The effects of varying acrylic copolymer composition, level of cross-linking agent and level and type of titanium dioxide

pigmentation have also been studied.

It was found that the glass transition temperature was raised by modifications which lead to an increase in the degree of cross-linking. The conventional physical tests were relatively insensitive to quite marked changes in composition.

Certain types of titanium dioxide, notably those having a surface treatment of alumina, have the unexpected effect of lowering the glass transition temperature. This behaviour is explained in terms of a mechanism of localisation of cross-links arising from specific interactions between the resin and the pigment surface.

Keywords

Types and classes of coating
thermosetting coating

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

Binders, resins etc
acrylic resin

Properties, characteristics and conditions primarily associated with materials in general
glass transition temperature

Les caractéristiques dynamiques et mécaniques des revêtements à base de résines acryliques thermodurcissables

Résumé

On décrit une expérience destinée à faciliter la mise au point des finitions pour articles ménagers et où l'on tient compte des caractéristiques viscoélastiques de ces finitions. Les systèmes étudiés étaient basés sur des systèmes de résines acryliques thermodurcissables du type hydroxyle, réticulées par hexaméthoxyméthylmelamine.

Les caractéristiques dynamiques et mécaniques des feuillets de résine libre ont été mesurées au moyen d'une technique de vibration forcée, sur une gamme étendue de températures, et l'on fait comparer les résultats auprès de ceux à partir des essais classiques de physique effectués sur des finitions appliquées aux supports métalliques. On a étudié les effets de la variation de la composition du copolymère acrylique, de la teneur en agent de pontage, et de

la teneur et du type de pigment de dioxyde de titane.

On a trouvé que la température de transition à l'état vitreux était augmentée par les modifications qui provoquent une augmentation du degré de réticulation. Les essais classiques de physique étaient relativement insensibles aux variations tout à fait notoires dans la composition de la finition.

Certains types de dioxyde de titane, notamment ceux qui entraînent un traitement superficiel par l'alumine, ont l'effet insolite de diminuer la température de transition à l'état vitreux. On explique ce comportement en termes d'un mécanisme de liaisons de réticulation localisées, provoquées par les interactions spécifiques de la résine et de la surface pigmentaire.

Die Dynamisch Mechanischen Eigenschaften von Wärmehärtenden Akrylharzlacken

Zusammenfassung

Beschreibung eines Experiments, um die Anwendung von Lacken für Haushaltgeräte unter Berücksichtigung der viskoelastischen Eigenschaften zu erleichtern. Die untersuchten Systeme beruhen auf wärmehärtenden Akrylharzsystemen vom Hydroxyltyp, vernetzt mit Hexamethoxymethylmelamin.

Unter Benutzung einer forcierten Vibrationstechnik wurden die dynamisch mechanischen Eigenschaften abgehobener Harzfilme bei vielerlei Temperaturstufen gemessen, und die Resultate mit konventionellen physikalischen Prüfungsergebnissen verglichen und in Wechselbeziehung mit auf Metallsubstraten aufgetragenen Lackierungen gesetzt. Ebenfalls wurden die Auswirkungen von Verschiedenheiten in der Zusammensetzung von Akrylharzkopolymeren, Zusatzmenge des Vernetzungsmittels und Höhe und Type

der Titandioxidpigmentierung unter die Lupe genommen.

Es wurde festgestellt, dass die Glasübergangstemperatur durch Modifizierungen, welche zu stärkerer Vernetzung führten, erhöht worden war. Die üblichen physikalischen Prüfungen waren gegen ziemlich erhebliche Veränderungen in der Zusammensetzung relativ unempfindlich.

Gewisse Titandioxidtypen, vor allem solche, deren Oberfläche mit Aluminiumoxid behandelt worden war, zeigten die unerwartete Wirkung, dass die Glasübergangstemperatur erniedrigt worden war. Dieses Verhalten wird als ein Mechanismus der Lokalisierung von Vernetzungen als Folge spezifischer Reaktionen zwischen dem Harz und der Pigmentoberfläche erklärt.

Динамические и механические свойства термореактивных акриловых покрытий

Резюме

Описывается испытание для облегчения нанесения покрытий, учитывающее их вязко-упругие свойства. Рассматриваемые системы основаны на термореактивных акриловых, смольных системах гидроксильного типа, перекрещенных гексаметоксиметилмеламином.

Динамические и механические свойства свободных смольных пленок измерялись в широком диапазоне температур, применяя технологию вынужденных колебаний и результаты сравнивались и коррелировались с результатами традиционных физических испытаний, полученных для покрытий наложенных

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на металлические субстраты. Изучались также эффекты вариации состава акрилового сополимера, уровня реагента перекрещения и уровня и типа пигментации двуокиси титана.

Найдено что температура стеклового перехода повышалась модификациями вызывающими увеличение в степени перекрещения. Традиционные физические испытания оказались сравнительно нечувствительными по отношению к значитель-

ным изменениям в составе.

Некоторые типы двуокиси титана, в особенности типы с поверхностным покрытием окиси алюминия, обладают неожиданным эффектом понижения температуры стеклового перехода. Такое поведение объясняется механизмом локализации перекрещений в результате специфических взаимодействий между смолой и поверхностью пигмента.

Introduction

Considerable effort has been made in recent years to obtain a better understanding of the viscoelastic properties of surface coatings and their relationships to conventional empirical paint tests.^{1, 2, 3, 4} This understanding should enable coating performance to be more readily interpreted in structural and molecular terms. Molecular properties such as monomer types, copolymer character, composition, sequence length and sequence distribution, molecular weight and distribution, cross-linking density and network arrangement are among the features that can influence the viscoelastic behaviour of resin materials. It is possible to modify these various features within broad limits and to produce materials having different relaxation time spectra. Additionally, the other components in a successful paint formulation, such as solvents, flow modifiers, plasticisers, pigments etc., all exert an influence on the relaxation times with consequent effect on mechanical behaviour.

In the surface coating industry, technical and economic considerations point to the merit of tailoring resin systems to meet coating specifications at an economic cost. However, the currently accepted industrial methods of test are not sufficiently discriminating to distinguish the subtlety of variations.

In principle, studies of the viscoelastic response of a coating resin can give much added information to aid the paint technologist,^{1, 3, 4, 5} but there are serious deficiencies in the state of knowledge on the correlation of these properties with the conventionally-used empirical tests. For reasons of economy in resin development time, it is necessary to establish that these more sophisticated test methods can be carried out rapidly, routinely and the results interpreted in terms of traditional test procedures.

Dynamic mechanical properties of surface coatings

The acceptability of a coating for a given application is judged by the results of tests which are designed to reproduce the service hazards to which the coating is exposed. Generally, the important properties measured on a finished coating are those of hardness, flexibility, impact resistance, stain resistance, and tolerance to attack by solvents. These tests do not depend on a simple fundamental property, such as tensile or shear strength, modulus of elasticity in shear, compression or tension, viscoelastic functions, bulk properties or substrate adhesion, but instead they more often appear to be a composite of these several properties in varying proportions. For example, hardness tests that are designed to simulate the scratch resistance, mar resistance or surface indentation in service are composite property tests in which initial compressive modulus, tensile strength, shear properties and the viscoelastic response all contribute. These conventional empirical test methods, widely used throughout the paint industry, are the basis for all material specifications. However, in the formative stages of development leading to a new formulation, more precise quantitative information, leading to a readier interpretation in terms of fundamental material properties, is required than can be supplied by empirical test methods.

Previous attempts to use stress-relaxation³ and low frequency dynamic data^{4, 5} to correlate with paint performance have achieved some success, but there have been few positive attempts to obtain usable data over wide frequency and temperature ranges that could be studied by a conventional viscoelastic analysis.⁶

In general, when a polymeric material is subjected to a strain ϵ , the stress response, σ , of the material is delayed due to the viscoelastic character of the sample. For a sinusoidally oscillating strain, $\epsilon \exp \omega t$, where ω is the angular frequency and ϵ_0 is the maximum strain,

$$\epsilon = \epsilon_0 \sin \omega t \dots \dots \dots (1)$$

and the corresponding periodic stress is given by

$$\sigma = \sigma_0 \sin (\omega t + \delta) \dots \dots \dots (2)$$

where δ is a phase angle difference between stress and strain and σ_0 is the maximum sample stress amplitude.

Equation (2) can be re-written as

$$\sigma = \sigma_0 (\cos \delta \sin \omega t + \sin \delta \cos \omega t) \dots \dots \dots (3)$$

implying that the stress can be resolved into two components one in phase with the strain and the other $\pi/2$ out of phase. If the real component of the modulus E' is now defined as the ratio of the amplitude of the in-phase component of stress to the strain amplitude and the loss modulus E'' as a similar ratio for the out-of-phase stress, then:

$$E' = \frac{\sigma_0 \cos \delta}{\epsilon_0} \dots \dots \dots (4)$$

$$\text{and } E'' = \frac{\sigma_0 \sin \delta}{\epsilon_0} \dots \dots \dots (5)$$

If the complex modulus E^* is defined as the ratio of maximum stress to maximum strain amplitude:

$$\text{then } E^* = \frac{\sigma_0}{\epsilon_0} \dots \dots \dots (6)$$

$$\text{and } E^* = E' + i E'' \dots \dots \dots (7)$$

A useful parameter in describing the energy loss/energy stored ratio is $\tan \delta$ which is given by:

$$\tan \delta = E''/E' \dots \dots \dots (8)$$

Measurements of E' , E'' and $\tan \delta$ can be made on either resonance or forced vibration instruments and, if the experiments are conducted over a sufficiently wide range of frequency and temperature, may give considerable information on the viscoelastic character of the materials.

Generally, however, it is necessary to use free, i.e. detached, films for measurements of this kind and it is often argued that the behaviour of a surface coating attached to a substrate differs from that of the free film. This is certainly true for tests involving large deformations, such as impact or conical

mandrel flexibility tests, in which adhesion between substrate and film is an important variable. However, determination of viscoelastic data from free films has led to the development of new resin formulations based on a much greater awareness of the influence of structural changes on the coating properties than would otherwise have been the case.

In the field of industrial finishes, thermosetting acrylic systems are widely used, in particular for coating domestic appliances. The mechanical property requirements of paints used in this area are stringent, calling for high flexibility and resistance to impact at a level of cure that ensures resistance to scratching, to attack by chemicals and to penetration by stains. A broad range of monomers having varied functional groupings that may be copolymerised under a variety of conditions and finally cured with different cross-linking compounds under a range of stoving conditions is available, making an almost infinite number of resin systems possible. In such a highly technical and competitive area of business, it is of considerable importance to the manufacturer that high quality should be achieved and maintained at minimum cost. Two main components of the cost of a finish are raw materials and development work. Both of these factors could be reduced if the stages of development between paint specification and acceptable formulation could be reduced, by a method exploiting the connection between the versatility of the acrylic system and the viscoelasticity of the derived coatings. The work reported here concerns a study of the viscoelasticity of a thermosetting acrylic system suitable for domestic appliance finishes. The influence of the functional monomer composition of the copolymer and the concentration of cross-linking agent on the viscoelasticity of the cured clear coating have been examined. In addition, the role of pigments in modifying the viscoelasticity has been studied, with some unexpected results.

Experimental

A conventional acrylic copolymer of styrene, ethyl acrylate, hydroxyethyl acrylate and a minor proportion of methacrylic acid as adhesion promoter was used in this work. A typical resin was prepared in the following manner using the components listed in Table 1, but with variation of monomer proportions to provide alternative copolymers as required.

Table 1
Composition of a typical resin preparation

Material	Charge weight (g)	Wt. % monomer
Styrene	720	40
Ethyl acrylate	720	40
Hydroxyethyl acrylate	306	17
Methacrylic acid	54	3
Xylene (1)	540	—
Xylene (2)	432	—
Xylene (3)	354	—
<i>n</i> -Butanol	150	—
Azobisisobutyronitrile	36	—

A part of the solvent xylene (1) was heated to 100–110°C, and the monomers and initiator dissolved in xylene (2) introduced into the reaction vessel in six aliquot parts at 20 minute intervals whilst the reaction temperature was held at 80–85°C. Polymerisation was allowed to continue until the non-volatile content was 65 per cent by weight, when the solution was diluted by the addition of xylene (3) and *n*-butanol to reduce the non-volatile content to 55 per cent. The resin obtained in this way was used either as a clear coating medium or compounded with pigment as a paint.

Pigment dispersion was carried out in a ball mill or a miniature sand mill to provide a millbase with a fineness of grind greater than 7 on a Hegman gauge. Calculated proportions of the cross-linking reagent, hexamethoxymethyl melamine (HMMM: BE 670 from BIP Chemicals Ltd.) and *p*-toluene sulphonic acid as catalyst (usually 0.5 per cent by weight based on the total resin) were stirred into the paint prior to film casting.

For the preparation of free films, clear and pigmented films with a dry thickness of about 25 microns were cast on tin-foil using a cube film applicator (Ref. 1104 by Sheen Instruments Ltd.) with a 100 micron slot. After stoving at 150°C for 30 minutes, the films were detached by amalgamating the tin substrate with mercury.

Conventional paint tests were performed on Gold Seal Steel test panels (152mm × 101mm; from The Pyrene Company Ltd.) prepared with a polished finish or Bonderite 97T phosphated pretreatment. Application of the wet film in this case was made with an ICI spinner (Sheen Instruments Ltd.) followed by stoving at 150°C as above.

The following empirical paint tests were carried out on the coated Gold Seal panels.

Conical mandrel flexibility

This test was performed following the procedure given in ASTM D522/60 (Amendment No. 2, June 1966). Flexibility was rated on a scale from 10 down to 0 in order of diminishing performance. The number given indicates that diameter of the cone where cracks were first observed in the coating under 5× magnification.

Number	10	9	8	7	6	5	4	3	2	1	0
Diameter (in)	$\frac{1}{8}$	$\frac{3}{16}$	$\frac{1}{4}$	$\frac{5}{16}$	$\frac{3}{8}$	$\frac{7}{16}$	$\frac{1}{2}$	$\frac{9}{16}$	$\frac{5}{8}$	$\frac{11}{16}$	$\frac{3}{4}$

Reverse impact test

The procedure and apparatus (Crown Pat 18998/46) described in BS 1391/1952 were employed. Performance was rated on a scale from 1 to 6 in order of increasing resistance to impact as follows.

6—unmarked	3—more severe cracking
5—very slight marking	2—partial film detachment
4—slight cracking	1—complete film detachment

(Assessments were made at three impact energy levels:

10lb force in, 20lb force in, and 40lb force in, which correspond respectively to 1.1298, 2.2596 and 4.5192 joules.)

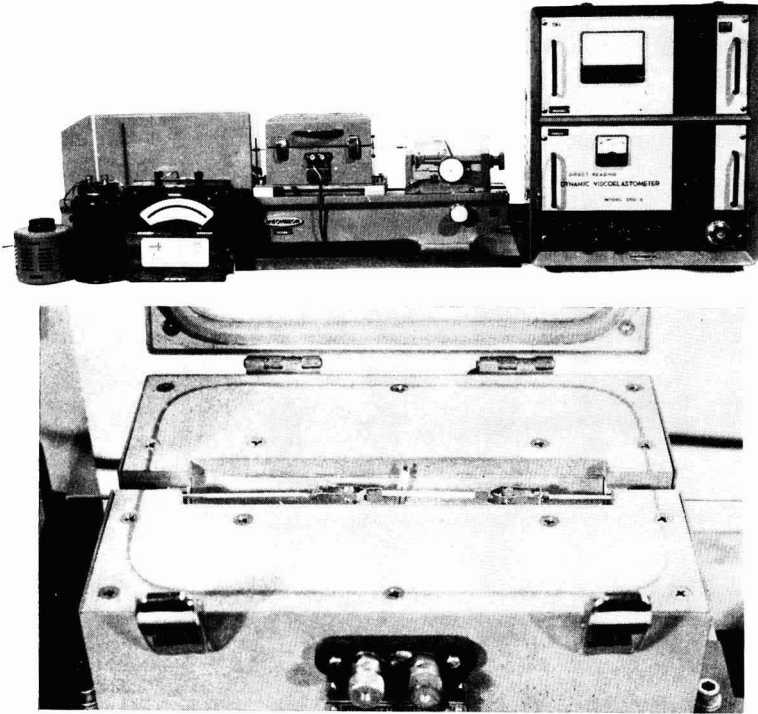
Methyl ethyl ketone (MEK) resistance

The appearance after rubbing 30 times with a cotton rag soaked in MEK was noted and rated using the following scale.

6—no attack	3—slight removal of paint
5—slight marking	2—partial removal of paint
4—loss of gloss	1—complete removal of paint

Pencil hardness test

Graded Faber-Castell brand pencils with cylindrical ends were used, applied at an angle of about 30° to the panel. The grade of pencil which just failed to remove the coating was recorded as the pencil hardness.



Figs. 1 and 2. Stress—strain equipment used for dynamic mechanical measurements of the samples

Dynamic mechanical measurements

These were made using the Rheovibron equipment (Sangamo Controls Ltd.) shown in Fig. 1. This instrument and its mode of operation have been described in detail by Takayanagi⁷.

Briefly, the instrument functions by applying an oscillating longitudinal strain to a rectangular film or to a fibre specimen and the stress developed is measured, together with a measure of the phase angle between stress and strain that results from mechanical damping.

Two transducers are used in these measurements: a strain transducer and a stress transducer. They are provided with

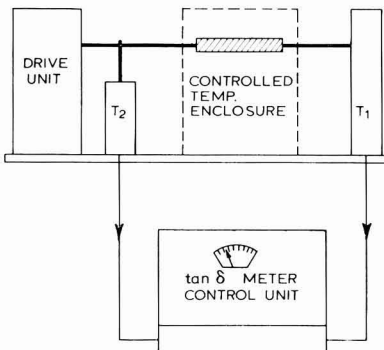


Fig. 3. Block diagram of the equipment shown in Figures 1 and 2

extension rods terminating in clamps which are used to secure the sample between them (see Figs 2 and 3).

The mounted specimen is enclosed in a temperature-controlled chamber capable of operating between -140°C and 200°C . A sinusoidal strain is applied to the specimen by the drive rod, which is activated electromagnetically by a coil producing frequencies of 3.5, 11, 35 or 110 Hz. The applied strain is monitored by the strain transducer T_2 and transformed into a proportional electrical quantity. The resulting stress is similarly transformed into a stress-proportional electrical quantity by the stress transducer T_1 . These two outputs are fed to the main control unit and processed electrically to give a direct reading of $\tan \delta$, where δ is the phase angle between stress and strain. $|E^*|$ the complex modulus is obtained from a calculation involving the instrument settings required in $\tan \delta$ derivations.

Readings of $\tan \delta$ and $|E^*|$ are recorded at intervals of 5°C over the appropriate temperature range. The real component E' and the loss component E'' of the complex modulus may then be calculated using the two equations:—

$$E' = |E^*| \cos \delta$$

$$E'' = |E^*| \sin \delta$$

Rectangular films with accurately known dimensions of approximately $30 \times 2 \times 0.03\text{mm}$ were used in this work. Sample lengths were determined using the micrometer/dial gauge arrangement on the Rheovibron to an accuracy of 0.01mm, widths with a vernier travelling microscope to an accuracy of 0.01mm and thicknesses with a micro comparator (Ferranti Ltd.) to an accuracy of 10^{-3}mm . All dynamic

measurements were made at a frequency of 110 Hz. A semi-automated vibrating reed described elsewhere⁸ was also used in some aspects of this work.

Results and discussion

Generally, measurements of the dynamic mechanical properties of detached films were made on both clear and pigmented systems in order to separate the effect on film properties of the pigment from that of the resin. Empirical tests were carried on pigmented systems only.

Effect of monomer composition on the dynamic mechanical behaviour of clear and pigmented coatings

With the type of thermosetting acrylic resin used in this work, the extent of the reaction of hydroxyl sites in the copolymer with hexamethoxymethylmelamine (HMMM) in the presence of *p*-toluene sulphonic acid will determine the level of cross-linking of the cured coating. Using a constant quantity of HMMM and varying the hydroxyethyl acrylate content of the copolymer, the dynamic properties obtained at 110 Hz are shown in Fig. 4.

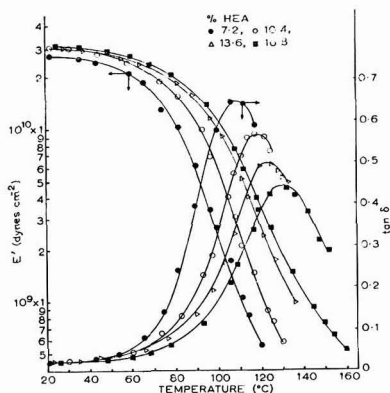


Fig. 4. Plot of elastic modulus (E') and loss tangent ($\tan \delta$) at 110 Hz against temperature for clear films with varying hydroxyethyl acrylate contents. Cross-linked using hexamethoxymethylmelamine (20 wt.% based on resin) and 0.5 wt.% *p*-toluene sulphonic acid

As anticipated, increasing hydroxyl content leads to cured films with increasing hardness, as demonstrated by the modulus against temperature curves. The modulus at 100°C increases from 2×10^9 dyn cm^{-2} to 10^{10} dyn cm^{-2} as the hydroxyethyl

acrylate content is raised from 7.2 per cent to 16.8 per cent. There are also decreases in the peak values of $\tan \delta$ associated with a broadening of the curves and a shift of the peak to higher temperatures with increasing cross-linking.

The same resins were pigmented with rutile titanium dioxide (Kronos RA 45) at 20 per cent pigment volume concentration for the purposes of paint testing. Typical test results obtained on steel panels are shown in Table 2.

The flexibilities and reverse impact properties of coatings based on copolymers with 7.2 per cent, 10.4 per cent and 13.6 per cent hydroxyethyl acrylate content are consistently quite good but the coating with 16.8 per cent hydroxyethyl acrylate content shows a considerable deterioration owing to the brittleness introduced by the increased cross-linking density. As suspected, pencil hardness values do not follow any meaningful pattern, but nevertheless indicate that the resin with the highest content of functional group containing monomer gives the hardest paint. Resistance of the paints to methyl ethyl ketone is on the whole good and increases with increasing hydroxyethyl acrylate content.

The conclusions that increased cross-linking above the optimum level leads to poor flexibility and reverse impact properties, as well as improved hardness and MEK-resistance, are in accord with those of Earhart⁹ and Koral and Petropoulos¹⁰.

When the results of Fig. 4 from dynamic mechanical tests are compared with those from conventional tests, one first and important deduction is the greater sensitivity of the dynamic data. This is particularly true of the region near to optimum cross-linking efficiency, where the conventional tests show little difference between the various formulations. The shifts to higher temperatures of the damping peak and of the high to low modulus transition region of the coatings with increasing cross-linking are manifestations of increasing glass transition temperature.

Similar changes in viscoelastic properties have also been observed by Bender,⁴ who noted the associated deteriorations in impact resistance and flexibility in automotive finishes.

Effect of cross-linking agent (HMMM) on the dynamic mechanical properties

In order to study the effect of this cross-linking agent on the resin behaviour, a typical resin copolymer containing 17.0 per cent hydroxyethyl acrylate was compounded with HMMM in weight ratios of 95/5, 90/10, 80/20 and 70/30.

Table 2

Conventional paint test results for flexibility, hardness, solvent resistance and reverse impact Coatings based on pigmented resins (20% PVC : Kronos RA45) having various hydroxyethyl acrylate (HEA) concentrations and cross-linked using a resin/HMMM ratio of 4 : 1 by weight. Average paint film thickness = 0.033mm

Weight, % HEA	Conical mandrel flexibility		Pencil hardness		MEK resistance	Reverse impact						
	a	b	a	b		10lbf in (1.1298 J)	20lbf in (2.2596 J)	40lbf in (4.5192 J)				
					a	b	a	b				
7.2	9	9-	2H	1H	5	5-	6	6	5	5	5	5
10.4	9-	9-	3H	2H	5+	6	6	6	6-	5	5	5
13.6	9-	9+	1H	1H	5	5	6	6	6	5	5	5
16.8	5+	5	3H	3H	6	6	4	1	2	1	2	1

FAT-FAX 10

FAT-FAX... in which Price's Chemicals Ltd – Britain's largest oleochemical manufacturer – talks a bit about its raw materials, its processes, its products and their applications. FAT-FAX 10 is the second in a series of FAT-FAXes devoted entirely to SURFACE-COATING applications. Price's might prove relatively immodest when it comes to a knowledge of oleochemicals; on second thought, read 'does' for 'might', and 'thoroughly' for 'relatively'. But when it comes to oleochemical applications, Price's modesty is real, and fully justified. You, gentle reader, are the expert here – and we'll not forget it. Yet we dare to hope that the information in this series will prove useful, thought provoking, readable or (with luck) all three.

Frankincense speaking, myrrh's not everybody's cup of resin.

St Matthew's implication that these two secretions of *Boswellia carteri* and *Commiphora abyssinica* (respectively) were

as good as gold, shows that resins have a long and honourable history. Nowadays of course natural resins have been succeeded by the much more flexible and adaptable synthetics, the alkyds, polyesters, epoxys, formaldehydes, and so on that are the basis of the modern surface-coatings industry. But natural resins – those sticky substances exuded by certain trees when their bark has been damaged – were basic raw materials of lacquers and varnishes for thousands of years, going back to the Incas, the ancient Egyptians, the Carthaginians, the Phoenicians and a lot of other old people whom one no longer sees about. There was once a queen of Cyrene, we are told, much given to the wearing of amber (a fossil resin). Her name was Berenice, whence we are led via the usual etymological degradations to *pheronice*, *verenice*, *vernix* (Old French) and eventually, *varnish*. Meanwhile, on the other side of the earth, the ancient Japanese were making lacquer by secret processes from the resin of *Rhus vernicifera*; this coating dries only in the dark, and can produce serious skin irritation not unlike poison ivy. Just two more reasons why surface-coatings people are grateful for synthetic resins (and the Price's chemicals that help make them).

Now we all appreciate polymerisation quite kienle

Making big molecules out of little ones is pretty basic to the surface-coatings business. Before 1930, however, the rules governing polymerisation were little understood, even among those paint and varnish people who'd been successfully practising it for years. Then, writing in *Industrial and Engineering Chemistry's* June issue (Vol. 22, No. 6), 34-year-old Ray Kienle (Ph.D., M.I.T. 1928) cleared up a lot of the confusion with his concept of 'functionality'. An organic molecule, said Kienle in his 'Observations as to the Formulation of Synthetic Resins' can have one or more reactive groups – such as hydroxyl, carboxyl, amino, epoxy, or unsaturation as represented by a double bond. The molecule's functionality, then, equals the number of these reactive groups it contains. Now for Dr Kienle's famous postulates:

1. In polymerisation, the reacting molecules must each have a functionality of at least 2.
2. Polymerisation takes place through random contact of activated reactive groups.
3. The resulting polymer's physical properties are determined by the size and shape of the reacting molecules.

Some molecules of functionality 2: glycols, amino acids, ethylene. Pentaerythritol's functionality is 4, but butadiene's is either 2 or 4, depending on whether one or both of its double bonds react. A splendid polyol of functionality 2.8 is, as it happens, Price's Glycerine – of which (much) more later.

Put backbone in your bookcase with our TP 103 —and it's free!

Let's face it: these FAT-FAXes can only skim the cream off the milk of Price's surface-coatings know-how, and man cannot live by cream alone if the anticholesterol lobby is to be believed. Get the whole pinta, or as much of it as suits your own personal needs, in Price's Technical Publication No. 103. Your copy of this splendid treatise entitled 'Price's Products and the Surface Coating Industry' is available from Price's Chemicals Ltd, Bebbington, Wirral, Cheshire L62 4UF; telephone 051-645 2020; telex 62408.

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Typical curves for the real component of the tensile dynamic modulus (E') at 110Hz and for $\tan \delta$ at the same frequency as functions of temperature are shown in Fig. 5. These results, obtained on unpigmented detached films, show results typical of increasing cross-linking, analogous to those reported by Nielson¹¹ and Zorll.¹²

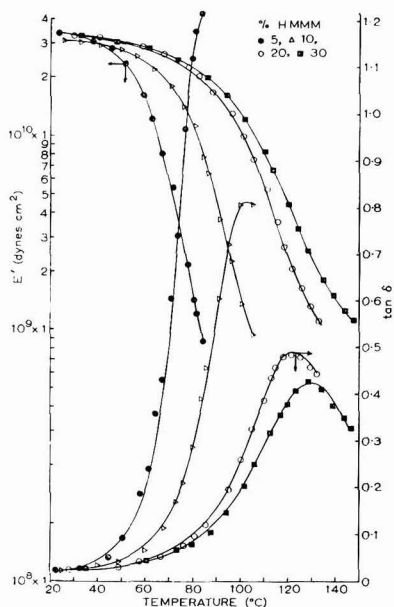


Fig. 5. Plot of elastic modulus (E') and loss tangent ($\tan \delta$) at 110 Hz against temperature for clear films cross-linked with varying hexamethoxymethylmelamine concentrations. Hydroxyethyl acrylate content 17 wt.%, *p*-toluene sulphonic acid 0.5 wt. %

Increasing the HMMM concentration from 5 per cent to 30 per cent brings about an increase in glass transition temperature of about 45°C, a decrease in the associated energy loss peak, and a general broadening of the transition region, as previously noticed for increasing hydroxyl content. At temperatures above 50°C, there is also a pronounced increase in the elastic moduli.

Dynamic mechanical moduli/temperature relationships were also evaluated for similar resin formulations pigmented with 20 per cent pigment volume concentration of titanium

dioxide (RA45), in order to compare with conventional empirical paint tests. As seen in Fig. 6, there is a similar behaviour to that observed for clear films. There is an increase in the T_g from about 70°C to 90°C with increasing HMMM content, which is less pronounced than that obtained with the clear films. As would be anticipated, increasing the HMMM concentration reduces the $\tan \delta$ peak value and increases the value of the elastic modulus at any given temperature. At low temperatures, the elastic modulus for the pigmented material is greater than that for the clear film, owing to the reinforcing effect of filler.

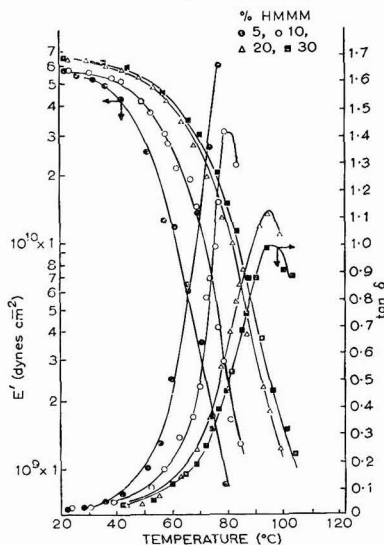


Fig. 6. Plot of elastic modulus (E') and loss tangent ($\tan \delta$) at 110 Hz against temperature for pigmented films with varying hexamethoxymethylmelamine concentrations. Pigment volume concentration 20% or Kronos RA45; hydroxyethyl acrylate concentration 17% based on resin, 0.5 wt. % *p*-toluene sulphonic acid

It should be noticed at this point that, for equivalent resins, the pigmented materials surprisingly exhibited lower glass transition temperatures than the clear films. This observation will be amplified later in the discussion.

The results of conventional paint acceptance tests are shown in Table 3; apart from the poor impact strength and poor flexibility of the least cross-linked paint (which may be

Table 3

Conventional paint test results for flexibility, hardness, solvent resistance and reverse impact on pigmented resins (20% PVC Kronos RA45)

Resins prepared with 17% hydroxyethyl acrylate and having varying concentrations of hexamethoxymethylmelamine (HMMM). Average paint film thickness = 0.027mm, prepared on polished steel panels

Weight, % HMMM, based on wt. of resin	Conical mandrel flexibility	Pencil hardness	MEK resistance	Reverse impact		
				10lbf in (1.1298 J)	20lbf in (2.2597 J)	40lbf in (4.5192 J)
5	0	2H	3	3	3	3
10	10	2H	4	4	3	3
20	10	2H	4	6	6	5
30	9+	2H	4	6	6	5

related to poor cohesion) the data are remarkable in showing the inability of these tests to distinguish satisfactorily between materials of widely differing compositions. The reverse impact tests show a gradual improvement with increasing HMMM content which seems to level off above 20 per cent HMMM. Clearly, there is an optimum cross-link density associated with this property, above which the impact properties do not improve further and may even deteriorate.

Koral and Petropoulos,¹⁰ in studying the effect of HMMM level in an acrylic emulsion coating on some paint properties (hardness, reverse impact and chemical resistance), found that increasing the HMMM content to 12 per cent resulted in improved film properties, but that further increases had adverse effects. Similar effects were noticed for epoxy resin coatings in which the HMMM content exceeded 15 per cent.

In comparison, the paint properties observed by the authors show a levelling off at about 20 per cent HMMM, but no adverse effects associated with a further increase in HMMM content. The difference in the optimum HMMM content is obviously due to the differing coating systems being studied. Koral and Petropoulos attribute the adverse effect to unreacted HMMM which is possibly blocking the effective use of cross-linking sites.

Effect of pigment volume concentration on dynamic properties

Generally, the effect of introducing an inert filler into a polymeric material is to raise the modulus in the glassy region and, in some cases, to increase the glass transition temperature. The viscoelastic properties of titanium dioxide filled epoxy resin¹³ and polyvinyl acetate¹⁴ have been studied by Galperin, whose findings were in accord with general expectations. However, the results obtained in the present study indicate quite clearly (see Figs. 5 and 6) that the presence of pigment in the resins studied reduces the glass transition temperature whilst increasing the modulus at lower temperatures. The decrease in glass transition temperature is clearly greatest for those resins with a higher cross-linking capability. It is of interest to see whether this remarkable feature is related to the pigment volume concentration. Dynamic modulus measured at 110Hz, together with $\tan \delta$, is plotted over a wide temperature range in Fig. 7 for a single resin containing 17 per cent hydroxyethyl acrylate, 20 per cent HMMM and pigmented with varying amounts of rutile titania (RA45).

Clearly, over about 10 per cent PVC, further increases in pigment concentration bring about marked reductions in the glass transition temperature of the paint films. Decreases of some 40°C are observed for the increase of pigment to 30 per cent volume concentration. This is quite a dramatic effect, since this improvement in the flexibility is achieved at

the same time as an increase in the room temperature modulus, or hardness, of the paint. Similar conclusions can be drawn from the $\tan \delta$ temperature relationships, the energy dissipated in the highly pigmented material being considerably greater—a factor that will result in improved impact and high-speed deformation characteristics. These findings are supported by conventional paint test results, the 20 per cent and 30 per cent pigmented systems having an ideal combination of properties (see Table 4).

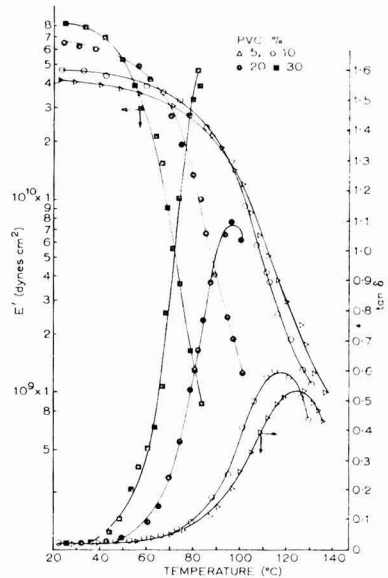


Fig. 7. Plot of elastic modulus (E') and loss tangent ($\tan \delta$) at 110 Hz against temperature for pigmented films with varying pigment volume concentrations (PVC). Hydroxyethyl acrylate content 17% and 20% HMMM based on resin Kronos RA45

Pigmented surface treatment effects on dynamic performance

The particular titanium dioxide pigment (RA45) chosen for the previous work was of a type conventionally used in many fields of industrial paint manufacture. It was of interest to establish if other grades of titania with different or no surface treatments gave results in any way comparable with the RA45 pigment which has an alumina treatment. Dynamic data obtained for pigmented films similar to those used previously, having 20 per cent PVC and made from a variety of treated pigments, are shown in Fig. 8. Data obtained with untreated rutile titania (Ti oxide R—SM) and micronised

Table 4

Conventional paint test results on pigmented resins (Kronos RA 45) with varying pigment volume concentrations.

Hydroxyethyl acrylate content 17% and 20% HMMM based on resin. Average paint film thickness = 0.030mm

Pigment volume concentration	Conical mandrel flexibility	Pencil hardness	MEK resistance	Reverse Impact		
				10lbf in (1.1298 J)	20lbf in (2.2597 J)	40lbf in (4.5192 J)
5	0	H	10	5	5	5
10	8	2H	9	5	5	5
20	9+	2H	10	10	10	5
30	10	2H	9	8	7	7

barytes (Colin Stewart Minerals Ltd.) are shown in Figs. 9 and 10 respectively, with corresponding paint test results in Tables 5 and 6.

The effect of the different pigments varies considerably. Those without surface treatments act as anticipated from

Table 5

Conventional paint test results for flexibility, hardness, solvent resistance and reverse impact

20% PVC barytes pigmented resin of 17% hydroxyethyl acrylate content, cross-linked using a resin/HMMM ratio of 4:1 by weight. Average paint film thickness = 0.030mm

Conical mandrel flexibility a b	Pencil hardness a b	MEK resistance a b	Reverse impact	
			20lbf in (2.2596 J) a b	40lbf in (4.5192 J) a b
8+ 6	4H 4H	6 6	3 1	1 1

a—Results using polished steel panels.
b—Results using "Bondrite" treated steel panels.

Table 6

Conventional paint test results on untreated rutile (R-SM) pigmented resin

17% hydroxyethyl acrylate content and cross-linked using a resin/HMMM ratio of 4:1 by weight. Average paint film thickness = 0.033mm

Pigment volume concentration %	Conical mandrel flexibility	Pencil hardness	MEK resistance	Reverse impact	
				10lbf in (1.1298 J)	20lbf in (2.2596 J)
10	0	3H	6-	3-	3-
20	0	3H	6	3	3-
30	0	3H	6	3	3-

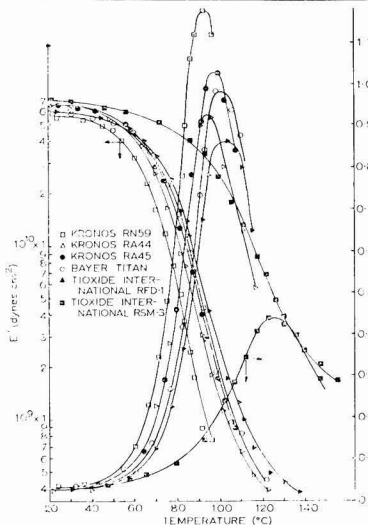


Fig. 8. Plot of elastic modulus (E') and loss tangent ($\tan \delta$) at 110 Hz against temperature for paint films containing differently surface coated rutiles. In each case a pigment volume concentration of 20% was used. Hydroxyethyl acrylate concentration 17 wt.%; hexamethoxymethylmelamine 20 wt.% based on resin

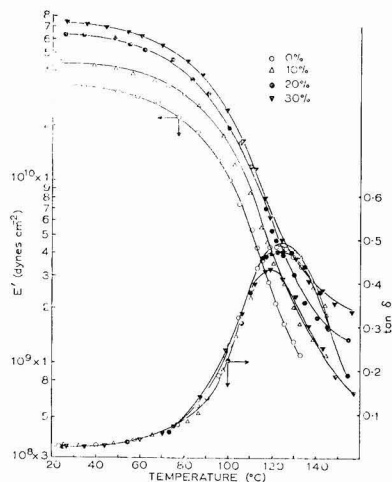


Fig. 9. Plots of elastic modulus (E') and loss tangent ($\tan \delta$) at 110 Hz against temperature for pigmented films with varying pigment volume concentrations. Hydroxyethyl acrylate content 17% and 20% HMMM based on resin. Tioxide R-SM

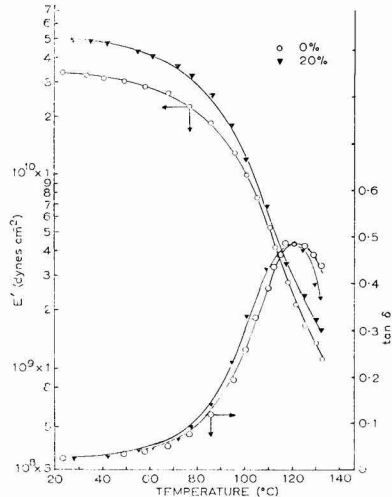


Fig. 10. Plot of elastic modulus (E') and loss tangent ($\tan \delta$) at 110 Hz against temperature for barium sulphate pigmented films. Hydroxyethyl acrylate content 17% and 20% HMMM based on resin

reported studies on pigmented and filled polymers—there is an increase in modulus in the glassy region and the glass transition temperature is unaffected. This is also the case for rutiles that have an undisclosed, light, organic treatment, e.g. Tioxide R-SM3. Those materials that have had some inorganic surface treatment, particularly with alumina, show substantial changes in their dynamic behaviour. It is to be inferred that such changes can be exploited beneficially in the development of thermosetting acrylic paints with better flexibility and hardness properties.

Mechanism of pigment surface treatments in altering dynamic mechanical behaviour

Various theories could be suggested to account for the remarkable behaviour of treated rutiles in altering the dynamic

behaviour of cross-linked materials. Any theory must explain why the transition temperature is lowered although the overall extent of cross-linking, as measured by swelling techniques and indicated by the high MEK solvent resistance, remains the same. Further, it must explain why the change in T_g is greatest when the degree of cross-linking is increased and when the pigment volume concentration is increased above 10 per cent. These latter effects are contrary to what would be expected. It must be remembered that, in this particular thermosetting acrylic resin formulation, the effective cross-linking reaction is between hydroxyl groups—incorporated in the molecule by copolymerisation of hydroxyethyl acrylate with styrene—and hexamethoxymethylmelamine under the catalytic influence of *p*-toluene sulphonic acid. Since the overall extent of cross-linking with treated or untreated rutiles is similar, the explanations for the phenomena must be sought in the distribution of cross-links in the material. It is proposed that there is a preferential adsorption of either the hydroxyl groups or HMMM on to the surface of the Al_2O_3 treated rutile surface and that, because of the high local concentration of cross-linkable sites on the pigment surface, preferential cross-linking takes place there. Fig. 11

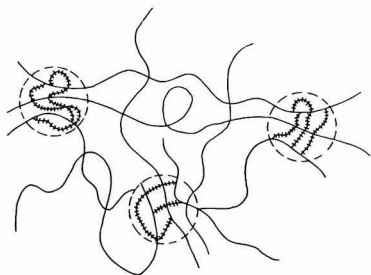


Fig. 11. Diagrammatic representation of increased cross-link density at pigment surface

gives a schematic idea of the cross-linking topology proposed. Although the total number of cross-links remains essentially unchanged, there exist flexible linkages between neighbouring pigment particles but with a high concentration of network sites on the surface of the particles. It is possible that *p*-toluene sulphonic acid could be the material preferentially adsorbed on the treated rutile surface, resulting in improved catalytic activity at the pigment surface. However, the results of specific adsorption measurements have indicated that there is no particularly preferred adsorption of *p*-toluene sulphonic acid on the treated rutile.¹⁵ Localisation of cross-linking in network systems with differences in the material behaviour have been previously observed in block copolymer systems of the styrene-butadiene-styrene type and in some types of rubber system, particularly those with carboxy-terminated butadiene systems.¹⁶

Whatever the cause of the phenomena, there is little doubt that the effect can be exploited, and possibly extended, by choice of suitable cross-linking systems.

Conclusions

The conclusions to be drawn from the work described are self-evident, but the more important observations are briefly summarised here. Increases in cross-link density, whether brought about by modification of the copolymer or by

increased concentration of cross-linking agent, have the effect of raising the glass transition temperature and lowering the damping capability of the cured resin system. The derived paints exhibit increased hardness and reduced flexibility and impact resistance as consequences of the changes in resin structure.

Study of the effects of pigmentation on properties has disclosed some unexpected results. Normal rutile titanium dioxide and micronised barium sulphate have the classical filler effect on the dynamic mechanical properties of paints. Alumina-treated titanium dioxides in common use have the striking effect of reducing glass transition temperature and raising the $\tan \delta$ peak of the clear acrylic resin, particularly for the more highly cross-linked systems.

Paints made with treated titanium dioxide perform far better than those pigmented with a pure rutile type. Although all have comparable solvent resistance, their mechanical properties differ considerably; the treated pigments impart relatively higher flexibility and impact resistance whilst retaining the hardness found with the unmodified rutile pigmentation.

Dynamic mechanical measurements have been found to react more positively to changes in polymer structure than do empirical paint tests. Whereas the latter tests must remain as the final arbiters of satisfactory practical performance, dynamic tests clearly have a strong supporting role to play in the development of synthetic resins for industrial surface coatings.

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Rheology of model carbon black inks

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Summary

Measurements of the plastic viscosity of a series of simple, model carbon black inks has been carried out using a Ferranti-Shirley viscometer, varying the concentration, temperature, diameter of particles and the composition of the dispersion medium individually, in an attempt to relate these factors by a single equation

Using a medium of hydrocarbon oil: oleic acid (9:1), the effects of concentration of carbon, of temperature and of dispersion medium were found to fit the equation $U = \eta_0 e^{kc/T}$ where U = plastic

viscosity of the model ink, η_0 = Newtonian viscosity of the medium, c = concentration, T = temperature (kelvin) and k is a constant dependent on the nature of the carbon black. The viscosity decreased as the particle diameter increased, but no equation has as yet been established relating viscosity to particle size.

The Bingham equation relating U to rate of shear has been confirmed. No correlation was observed between yield value (f) and concentration except that f increased with increasing c .

Keywords

Properties, characteristics and conditions primarily associated with materials in general

plastic viscosity
rheological property

Types and classes of coating

ink

Prime pigments and dyes

carbon black

La rhéologie des encres d'imprimerie à base des noirs de carbone

Résumé

Au moyens d'un viscosimètre Ferranti-Shirley, on a effectué des mesures de la viscosité plastique d'une gamme d'encres types d'une composition simple à base de noir de carbone où l'on fait varier, tour à tour, la concentration, la température, le diamètre particulaire et la composition du milieu de dispersion, en vue de lier tous ces facteurs par une équation unique.

A l'aide d'un milieu composé de 90% d'huile hydrocarbure et de 10% d'acide oléique, on a démontré que les effets de la concentration de noir de carbone, de la température et du milieu de dispersion cadrent avec l'équation $U = \eta_0 e^{kc/T}$ ou U = la viscosité

plastique de l'encre type, η_0 = la viscosité newtonienne du milieu, c = la concentration, T = la température (kelvin), et k est une constante qui dépend de la nature du noir de carbone. La viscosité se diminue à mesure que le diamètre particulaire s'augmente, mais on n'a pas déjà établi une équation faisant un rapport entre viscosité et grandeur particulaire.

On a confirmé l'équation de Bingham où un rapport entre U et la vitesse de cisaillement est prévu. On n'a pas constaté une corrélation entre la limite d'écoulement (f) et la concentration, sauf que (f) s'augmente en même temps que c .

Die Rheologie von Carbon Black Druckfarben

Zusammenfassung

In einem Versuch, alle Faktoren in einer einzigen Gleichung zusammenzufassen, wurden Messungen der plastischen Viskosität einer Reihe einfacher Modell-Carbon Black Druckfarben unter Verwendung eines Ferranti-Shirley Viskosimeters vorgenommen, wobei die Konzentration, Temperatur, Durchmesser der Teilchen und die Zusammensetzung des Dispersionsmediums individuell variiert wurden. Es wurde gefunden, dass, wenn ein Bindemittel aus Kohlenwasserstoff: Ölsäure (9:1) benutzt wird, die Wirkung der Konzentration von Kohlenstoff, Temperatur und Dispersionsbindemittel passt in die Gleichung $U = \eta_0 e^{kc/T}$, wobei U = plastische Viskosität der Modelldruckfarbe, η_0 = Newtonische Viskosität des Bindemittels, c = Konzentration, T = Temperatur

(Kelvin) und K eine von der Art des Carbon Blacks abhängige Konstante ist. Die Viskosität verringerte sich im gleichen Masse, in welchem sich der Partikeldurchmesser vergrößerte; jedoch wurde bisher noch keine Gleichung, die sich auf das Verhältnis der Viskosität zur Teilchengröße bezieht, geschaffen.

Die Binghamgleichung, die sich auf das Verhältnis von U zur Schergeschwindigkeit bezieht, wurde bestätigt. Zwischen Ausbeutewert (yield value) (f) und Konzentration wurde keine Korrelation beobachtet, ausser dass f sich entsprechend der Erhöhung von c vergrößerte.

Реология печатных чернильных красок

Резюме

Произведены измерения пластической вязкости ряда простых модельных печатных чернильных красок, применяя вискозиметр Ферранти-Ширлей и варьируя концентрацию, температуру, диаметр частиц и состав дисперсионной среды отдельно, в попытке выразить эти факторы одним уравнением.

Применяя среду углеводородного масла: олеиновой кислоты (9:1), найдено что эффекты концентрации углерода, температуры и дисперсионной среды выражаются уравнением

$$U = \eta_0 e^{kc/T},$$

где U — пластическая вязкость модельной краски, η_0 = ньютонской вязкости среды, c = концентрации, T = температуре (по Кельвину), а k константа зависящая от природы сажи. Вязкость понижалась с увеличением диаметра частиц, но пока еще не установлено уравнение связывающее вязкость с размером частицы.

Подтверждается уравнение Бингхама связывающее U со скоростью сдвига. Корреляции между значением ползучести (f) и концентрацией не наблюдались, кроме того факта что f увеличивается с увеличением c .

Introduction

The rheology of inks and similar dispersions has been the subject of much investigation. Many different equations have been proposed for the relationship between viscosity and the properties of the disperse phase and of the dispersion medium in inks. It was therefore thought desirable to carry out a series of measurements on the simplest possible model inks, varying one factor at a time (such as concentration of the disperse phase, nature of the dispersion medium, temperature, and diameter of the particles of the disperse phase), in an attempt to arrive at a simple equation which might in future be modified to fit more complex dispersions in line with inks in industrial use. Dispersions of various carbon blacks, in several different media of liquid hydrocarbon oil plus 10 per cent v/v of oleic acid to retard settling, were used.

The earliest equation, suggested by Arrhenius in 1887, was the exponential one: $\eta = \eta_0 e^{kc}$ where η is the viscosity of the suspension, η_0 that of the dispersion medium, c is the concentration of the disperse phase and k is a constant dependent on the nature of both the disperse phase and the dispersion medium, and also on the temperature. The most thorough investigation of the application of this equation to colloidal pigment suspensions was undertaken by Weltmann and Green¹, who worked with dispersions of various pigments in linseed oil. The equation arrived at was of the Arrhenius type, viz: $U = (\eta_0 + A)e^{Bc}$ where U is the plastic viscosity of the pigment dispersion, η_0 is the Newtonian viscosity of the dispersion medium, c is the concentration of the pigment, and A and B are constants, probably dependent on particle size and the top rate of shear. With regard to particle size, these workers claimed to have found a logarithmic relationship between particle diameter and the constant (i.e. reciprocal of particle diameter plotted against e^B was linear). For a selection of other work confirming the exponential relationship, see references 2 to 5. More recently, Rosted⁶ proposed the equation $D = a\tau + b\tau^n$ to describe rheological properties of inks, where D = shear rate, τ = shearing stress and n is a constant of value 1.5.

Einstein⁷ proposed the simple equation: $\eta_{sp} = KV$ where η_{sp} is the specific viscosity of the suspension, K is a proportionality constant (= 2.5 for spherical particles) and v is the volume fraction of the disperse phase. Zettlemoyer and Lower⁸, working with dispersions of calcium carbonate in polybutene oil, extended this equation to: $\eta_{sp} = K(1 + kA)V$ where K is a constant for a system of given chemical constitution, k is another constant, V is the volume fraction of the pigment, and A is the surface area of the pigment, so that kA represents the volume of the adsorbed layer on the pigment particles. They found, as would be expected, that viscosity increased as particle size decreased, and attributed this to immobilisation of the dispersion medium, resulting in a corresponding increase in the volume fraction of the pigment.

Ward and Whitmore⁹ studied the effect of particle size on the viscosity of suspensions of methacrylate polymers, using irregularly shaped particles. They concluded that viscosity increased with decreasing size of particles, and, further, that it increased with increasing asymmetry of the particles, presumably due to the dispersion medium being held within the irregularities on the surface of the disperse phase.

Cross¹⁰, working with aqueous suspensions of various polymers, using a Ferranti-Shirley cone and plate viscometer, at 298°K, arrived at the more complex relationship:

$$U = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + \alpha D^{2/3}}$$

where η_0 is the limiting viscosity at zero rate of shear, η_{∞} is the limiting viscosity at infinite rate of shear, α is a constant associated with the rupture of linkages and D is the rate of shear. Good linearity was obtained for graphs of $\log(\eta_0 - \eta_{\infty})$ against $\log D$, giving a slope of $\frac{2}{3}$, but no explanation was available for the significance of this fractional value.

Garret¹¹ has recently published a study of the relationship between carbon black particle size and various properties of inks, including viscosity. It was shown that viscosity increased markedly with decrease in particle diameter, but no mathematical relationship was put forward.

Experimental

Technique for producing a dispersion of a simplified model ink

The first problem was to evolve a technique for making reproducible small quantities of model carbon black inks. A ball mill was chosen in preference to a roller mill, in order to avoid any possibility of evaporation of solvent. The following procedure was shown to be capable of making 50ml of a model ink, of reproducible viscosity.

A screw-capped polythene bottle of 250ml capacity was used, and to this was added a constant weight of steel balls (diameter $\frac{1}{2}$ in and $\frac{3}{4}$ in) such that the bottle was about half full. A 50ml portion of a dispersion medium (9:1 liquid hydrocarbon oil:oleic acid) was added, which just covered the balls. For preliminary experiments 3 w/v per cent of Philblack 1 carbon black was added. The bottle was sealed with Parafilm tape to prevent leakage or evaporation, and was fitted centrally into a cylindrical tin on the rotating rollers. Rotation was at constant speed for one hour. Under these conditions a dispersion was produced, the viscosity of which was unchanged after a further two hours in the mill.

All subsequent dispersions were made under identical conditions; in particular, the size of the tin, the weight and diameter of the steel balls and the volume of dispersion medium and the grinding time on the rollers were identical.

The liquid hydrocarbon oil used for most of the measurements was either Edelex 11 or Catenex, from Shell. (These are both hydrocarbon mixtures of mean molecular weight 220, Catenex having a higher viscosity). The 10 per cent oleic acid was necessary to retard settling. Without it, all mixtures settled out immediately. All measurements of viscosity were made within ten minutes of removal from the rollers, although no settling of the dispersions was noticeable after several hours.

After any run, the balls, container and lid were thoroughly washed in hot water and detergent to remove carbon and medium, were then transferred to a perforated zinc tray, washed in running cold water for 20 minutes, dried in an oven at 80°C, and were finally allowed to cool in a dust-free environment. This ensured that no detergent contaminated subsequent runs.

Measurement of viscosity

All measurements were made using a Ferranti-Shirley cone and plate viscometer, with the large cone.

For this instrument: viscosity = $1.5 \times 100 \times$ Scale reading/rpm (in centipoises).

Since only comparative values were required, these were not converted to SI units.

Results

Using Catenex oil:oleic acid 9:1 as dispersion medium, a series of experiments was carried out, with Philblack I carbon black in concentrations varying from 1 to 18 w/v per cent. All factors other than concentration were kept constant.

In every case, viscometer readings were taken for increasing and decreasing rpm. Results are plotted in Fig. 1. Only the 1 and 3 per cent dispersions show good linearity of scale reading against rpm between 50 and 500 rpm. At 15 per cent, thixotropy is apparent, i.e. the viscosity decreases with time for the same applied stress. For concentrations of 15 per cent and 18 per cent, when the top rate of shear (500 rpm) was reached, it was held steady until a constant reading was obtained.

In calculating the relative plastic viscosities, the values between 300 and 500rpm were compared throughout this whole series of dispersions. Where thixotropy appeared (as at 15 per cent and 18 per cent in Fig. 1) mean values were taken. The plastic viscosity in centipoises was therefore taken as $1.5 \times 100 \times \text{scale reading}/\text{rpm}$ in Fig. 1 in the range between 300 and 500rpm.

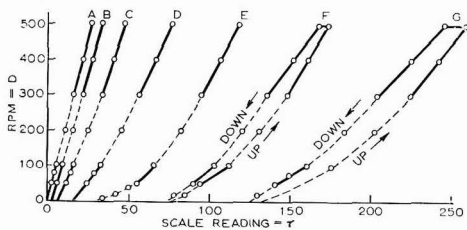


Fig. 1. Plastic viscosity = $1.5 \times 100 \times \text{scale reading}/\text{rpm}$ for various dispersions of Philblack I in Catenex oil:oleic acid, 9:1

A = 1%; B = 3%; C = 6%; D = 9%; E = 12%; F = 15%; G = 18%

The results for the relationship between the plastic viscosity of a dispersion of Philblack I carbon black and concentration are given in Table 1 and Fig. 2, where $\log U$ is plotted against

Table 1
Viscosities of Philblack I dispersions in Catenex:oleic acid, 9:1

w/v % C	0	1	3	6	9	12	15	18
U (300 to 500rpm) cP	6.94	7.65	9.0	11.25	14.6	17.25	23.6	27.5

c , giving a straight line. (It is perhaps worthy of note that, in connection with the plastic viscosity values calculated from mean values for the 15 per cent and 18 per cent dispersions shown in Fig. 1, only the 15 per cent value shows an appreciable positive deviation from linearity in Fig. 2. A slightly lower value of U would have been obtained in this case had the ascending τ/D slope been used rather than the mean, but there appears to be no clear reason for adopting this value. In the case of the 18 per cent dispersion, the value of U is hardly altered by change from mean values to either ascending or descending values of the τ/D slope.) Hence a relationship of the Arrhenius type, $U = Ae^{kc}$ is suggested, where A is a constant depending on the dispersion medium, k is a constant depending on the nature of the carbon

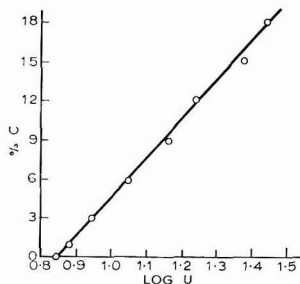


Fig. 2. Relationship between % C (w/v) and plastic viscosity, for Philblack I, in Catenex:oleic acid 9:1

black, and c is the concentration in w/v per cent of carbon black, at constant temperature.

This Arrhenius-type relationship has been confirmed, using similar series of model inks with different carbon blacks, in concentrations ranging from 1 to 9 per cent. The results are summarised in Table 2 and graphs are shown in Fig. 3 (a to d). All confirm the relationship $U = Ae^{kc}$.

Table 2

Variation of plastic viscosity with concentration of various types of carbon black. (Edelex:oleic acid, 9:1)

Type of C black	Plastic viscosity (cp)					
	% w/v 1	2	3	4	5	9
Columbia 999 ..	5.48	6.15	6.90	8.0	9.0	14.2
Molacca ..	5.25	—	5.70	—	6.30	7.58
Philblack I ..	5.17	5.7	6.30	—	7.50	14.6
Raven 35 ..	5.40	—	5.92	—	6.67	8.4
Regal 300 ..	4.68	—	5.49	—	6.03	8.32

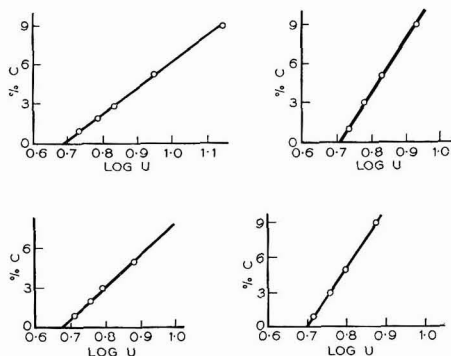


Fig. 3. Relationship between % C and $\log U$

(a) Columbia 999 (c) Philblack I
(b) Raven 35 (d) Molacca

The constant A is, of course, to be identified with η_{00} , the Newtonian viscosity of the medium alone, when $c = 0$, since if $U = Ae^{kc}$, then $\log U = \log A + kc/2.303$. When $c = 0$, $\log A = \log \eta_{00}$. This was checked by measuring the plastic viscosity of carbon black dispersions in five different dispersion media.

In the equation $U = \eta_{00} e^{kc}$, it is to be expected that k will be a constant for a given carbon black, and will vary with particle size. (This latter factor will be discussed later).

That this is the case has been shown by measuring the slope of graphs for log U against c for the same carbon black in various dispersion media. Results are given in Table 3. It will be seen that the values for k are fairly constant, despite a wide range of dispersion media.

Table 3

Plastic viscosity of dispersions of Philblack I in various media

Dispersion Medium (all contained 10% oleic acid)	η_0 (cP)	Slope (=k)
Edelex (Shell)	4.72	0.038
Ethyl benzene	0.92	0.039
Olive oil: Edelex, 1:1	17.5	0.033
Hexadecane	4.20	0.034
Tetradecane	3.00	0.040

Effect of shear rate on plastic viscosity

Bingham¹² put forward his well-known equation which may be expressed as: $D = 1/U (\tau - f)$ where f = yield value. A mathematically equivalent equation was put forward by Goodeve and Arnold¹³ in the form $\tau/D (= \eta) = U + (f/D)$. To test whether the results obtained with these carbon black dispersions agreed with the Bingham equation, graphs were plotted of τ/D against $1/D$ for four dispersions of different carbon blacks. The results are shown in Fig. 4. (Only three are plotted here, since the graph for 9 per cent Raven black overlapped that for 9 per cent Molacca very closely.) All four graphs were linear and the intercept value (at $1/D=0$, corresponding to U at maximum shear rate) agreed well with the observed value of U (at 300 to 500rpm, beyond which no change in slope was observed) as shown in Table 4.

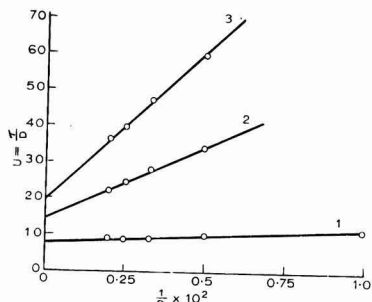


Fig. 4. Relationship between U and D (To test the Bingham equation $D = 1/U (\tau - f)$)

- ⊙ is 9% Molacca in Edelex oil
- ⊙ is 9% Philblack I in Catenex oil
- ⊙ is 12% Philblack I in Catenex oil

Hence these results confirm the Bingham (and Goodeve) equations.

Table 4
Intercept values from Fig. 4

Dispersion	Intercept	U (observed)
9% Molacca in Edelex oil	7.8	7.6
9% Raven in Edelex oil	8.4	8.4
9% Philblack I in Catenex oil	14.6	14.6
12% Philblack I in Catenex oil	19.2	17.3

Effect of temperature on plastic viscosity

For a pure liquid, the effect of temperature on the viscosity is known to follow an exponential relationship of the type given by the standard Arrhenius equation: $k = Ae^{E/T}$ where E = activation energy, T = temperature in degrees kelvin. The variation in plastic viscosity of emulsion inks with

temperature was studied by Lenk¹⁴ who found a linear relationship between $\ln U$ and $1/T$ for temperatures ranging from 273.5 to 313°K. From his results he calculated the activation energy values at different shear rates, and concluded that some relationship existed between the "limiting activation energy of viscoelastic flow" and the yield value.

In the present work, the viscosity of two dispersions was measured at temperatures between 298°K and 328°K. The viscometer was connected to a thermostat and water at temperatures over this range was passed through the plate. At least 15 minutes was allowed for temperature equilibration in each case. (The temperature variation was less than $\frac{1}{2}^\circ$.) In all, 82 sets of readings were taken for two different carbon blacks, Regal 300 and Regal 600, and also for the dispersion medium alone (since its viscosity also varies with temperature). Results are shown in Figs. 5 and 6. Good linearity is shown for all graphs of log U against $1/T$. (T in degrees kelvin.)

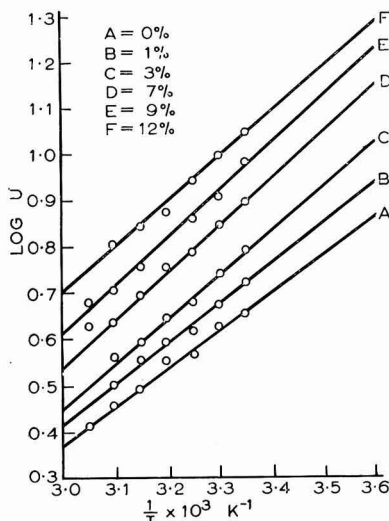


Fig. 5. Relationship between plastic viscosity and temperature (Regal 300 in Edelex oil:oleic acid, 9:1)

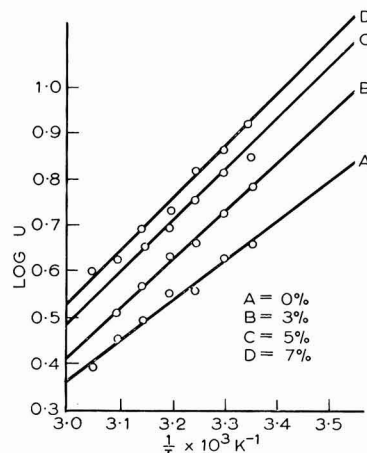


Fig. 6. Relationship between plastic viscosity and temperature (Regal 600 in Edelex oil:oleic acid, 9:1)

Hence an equation of the type $U \propto e^{1/T}$ is supported by the data. Thus an equation of the form: $U = \eta_0 e^{k_c/T}$ may now be put forward to represent the variation of plastic viscosity with concentration of carbon black disperse phase and with temperature, where k is a constant for any given carbon black. (It may be pointed out that the viscosity of the dispersion medium when $c = 0$ also varies with temperature; this has been shown in Figs. 5 and 6, curve A. Thus the value of k may also vary with different media if the slope of η_0 vs $1/T$ varies.)

Effect of particle diameter on viscosity

In an attempt to relate viscosity to particle diameter, twelve carbon blacks of different diameters were used in 3 per cent w/v and nine in 5 per cent w/v, in the standard dispersion medium. Results are shown in Table 5 and Fig. 7. It is clear that the plastic viscosity increases as the particle diameter decreases.

Table 5

Viscosity of 3% and 5% dispersions of various carbon blacks of differing particle diameters

C = channel black, F = furnace black

Type of C black	d (nm)	U (3%)	U (5%)
C Royal Spectra	10	11.7	16.7
C Neo Spectra	11	12.0	14.0
C 999	16	6.95	9.5
C Philblack E	17	7.2	8.2
F Raven 35	27	5.9	6.7
F Regal 600	23	6.15	7.07
F Regal 300	27	6.1	6.7
F Philblack I	22	5.85	7.4
F Statex B12	33	6.22	—
F Statex	54	6.18	—
F Molacca LS	60	5.8	6.5
F Molacca H	70	6.0	—

Further, there would appear to be a marked difference in the effect of particle diameter on viscosity between channel

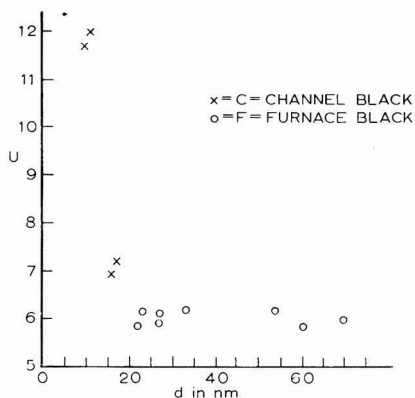


Fig. 7. Variation of plastic viscosity with diameter (3% carbon black dispersions)

and furnace blacks. In the case of channel blacks, small variations in diameter appear to cause large changes in plastic viscosity, whereas the latter hardly varies for the whole range of furnace black (from 22 to 70nm). It is to be expected that channel and furnace blacks would show markedly

varying results in this study, owing to their different surface properties. (A detailed account of the properties of carbon black surfaces is given by Dollimore¹⁵.)

A graph of $\log U$ against $1/d$ (Fig. 8) showed no linearity; hence no support has been found for the type of equation suggested by Weltmann and Green¹.

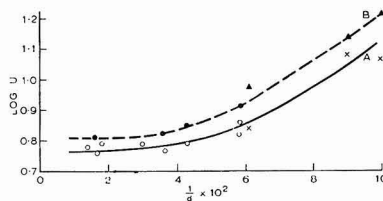


Fig. 8. Relationship between plastic viscosity and particle diameter (in nm)

A 3% carbon black in Edelex oil:oleic acid 9:1

⊗ = channel black; ○ = furnace black

B 5% as above. ▲ = channel black; ● = furnace black

Further, a graph of $\log U$ against $\log d$ was also non-linear (Fig. 9). It has therefore not been possible so far to suggest an equation relating plastic viscosity to particle diameter.

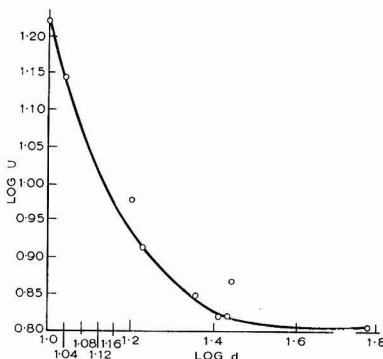


Fig. 9. Graph of $\log U$ against $\log d$ (d = particle diameter) (3% dispersions)

Relationship between yield value and concentration

Using a Ferranti-Shirley viscometer, the yield value (f) would be defined as the intercept on the axis (scale reading) when rpm = 0. Fig. 10 shows the yield values obtained for a series of dispersions of Philblack I carbon black, from 1 to 18 per cent in Edelex:oleic acid. In all cases the yield values have been obtained by extrapolating from the linear part of the curve at the top rates of shear, viz 300 to 500rpm to zero rpm. A graph of $\log f$ against c was plotted (Table 6 and Fig. 11); linearity was not observed but a curve was obtained. Similar results were obtained for Philblack I in a medium of Catenex:oleic acid.

The only effect which can be deduced is that the yield value increases as the concentration of the disperse phase increases.

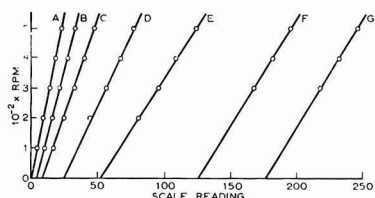


Fig. 10. Yield value (intercept at 0 rpm) for various concentrations of Philblack I in Edelex oil (Shell): Oleic acid, 9:1

A = 1%; B = 3%; C = 6%; D = 9%; E = 12%; F = 15%; G = 18%

Table 6

Relationship between yield value and concentration (see Fig. 5)

w/v % carbon	Yield value (f)
1	—
3	4
6	8
9	21
12	52
15	126
18	176

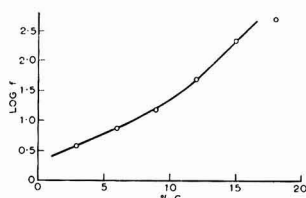


Fig. 11. Relationship between log f (yield value) and concentration

Conclusions

Several points have emerged from this work, and are shown below.

The plastic viscosity (U) of dispersions of various carbon blacks in a medium of liquid hydrocarbon:oleic acid (9:1) appears to vary with concentration c (expressed as g/100 ml) exponentially, according to the equation $U = \eta_0 c^{kc}$ where U = plastic viscosity of the dispersion, η_0 = Newtonian viscosity of the dispersion medium, and k is a constant for a given carbon black at constant temperature. This equation has been found to hold for concentrations from 0.5 per cent to 18 per cent. So far, more concentrated dispersions have not been investigated. (In all cases where the graphs of τ/D were non-linear, the slopes at 300 to 500rpm were compared.) The equation has also been found to hold for such dispersions in five different dispersion media.

Unidentified Journals at binders

The company with which the association has an agreement to supply the service of binding volumes of the *Journal*, W. Heffer & Son Ltd., has reported that a complete set of *Journals* for the years 1971-72, together with Resins Reports, has been received without identification. The parcel containing the *Journals* was damaged in the post and rewrapped by the Post Office, finally arriving at Heffers without any indication of the source. Any member who despatched

The Bingham (Goodeve and Arnold) equation relating plastic viscosity to rate of shear, [$D = 1/U (\tau - f)$] has been confirmed for four different sets of dispersions, using four types of carbon blacks.

The plastic viscosity of the model inks examined was found to vary exponentially with the reciprocal of the temperature (in degrees kelvin).

The effect of particle diameter on the plastic viscosity of the dispersion has been studied for twelve different particle sizes. No equation has been established from the results, although the plastic viscosity clearly tends to increase as particle diameter decreases. With furnace blacks, the viscosity appears to change hardly at all with change in particle diameter, whereas with channel blacks, a marked variation of plastic viscosity has been observed with fairly small changes in particle size. The results do not seem to confirm any of the existing suggested relationships between particle diameter and viscosity.

No apparent correlation was observed between yield value (f) and concentration (c) of the dispersion, measured for mixtures of from 3 to 18 per cent for Philblack I in two different dispersion media, except that f increased as c increased.

Acknowledgments

The author is most grateful to Shell-Mex for generous supplies of Edelex 11 and Catenex oil, and to Columbian International, for supplies of various types of carbon black, also to Cabot Carbon Ltd., Philblack Ltd., Mr J. D. Cohen of Sun Printers Ltd., and to Dr C. Butler, Mr J. Ames and Mr N. Moore, all of this College, for much helpful information and advice.

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Journals in Autumn 1972 and who has not yet received bound copies should contact the binder as soon as possible.

Heffers' have pointed out that all parcels should be bound securely with string, and that a slip giving the sender's name and address should be enclosed. Members are reminded that the cost of binding the 1972 volume is £2.50 and that the address for despatch is; W. M. Heffer & Son Limited, Hills Road, Cambridge.

Reviews

Chemsyn organic chemistry revision cards

London: Heyden & Son Ltd., 1972. Price 95p

Chemsyn is an interesting and useful aid to learning the basic reactions and preparations of organic compounds. It is a system consisting of a pack of 50 playing-type cards describing 50 compounds taken from a wide range of chemical classes. The examples have been chosen with care to give a considerable degree of interrelationship so that the subject is presented as an integrated whole rather than a collection of isolated facts.

The front of the cards shows the linear and shorthand formulae of the compound as well as a photograph of the Catalin molecular model. The reverse side gives the methods of preparation and properties of the class of compound.

Involving a "game" that can be played by 1-4 people, the system is intended to supplement rather than replace lectures and textbooks and offers a novel and effective aid to learning and revision for pre-university and first year students. The cards are well produced and packed in a neat plastic cassette. At the price quoted, Chemsyn appears to be a good investment.

W. M. MORGANS

Particle size measurement and surface area determination

By T. Allen (Editor)

**Published by Bradford University,
September 1972**

Bradford University, 1972, pp 34. Price £2.00

In his bibliography of literature published between 1969 and 1972, Dr Allen recognises the problem facing everyone

involved in experimental science, that of keeping up with the ever increasing volume of literature. In his normal search he locates annually over 400 papers on topics of concern to the powder technologist, and those for the years 1969, 1970 and 1971, plus a few from the 1972 literature, are reviewed in his bibliography.

For each year the papers are listed in author alphabetical order, with title and location. There is a general index under subjects and the whole field is reviewed under the appropriate headings. Included are review papers, and original papers on characterisation of powders, sampling and sizing aerosols, classification, particle size analysis by sieving, sedimentation, hindered settling, microscopic examination, radiation scattering, holography etc., and surface area determination by adsorption of gases and vapours, adsorption from solution, gas chromatography, porosimetry, permeametry and gas diffusion. The review contains only a short statement on the content of each paper, mostly without comment (1,130 papers are reviewed in 9,000 to 10,000 words).

Although this bibliography cannot be complete, and the author accepts that omissions are inevitable, nevertheless anyone attempting to keep abreast of developments in those aspects of powder technology covered by the review is well advised to invest the modest sum involved. They might even be encouraged to take up the author's invitation to bring omissions to his attention so that future issues will be even more comprehensive.

G. D. PARFITT

Note—This book is available from Dr Allen, Postgraduate School of Powder Technology, University of Bradford, Bradford DD7 1DP.

Next month's issue

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

"Comparison of Continental and British practice in the manufacture and use of emulsion paints on buildings," by H. Lehmann

"Some factors affecting the opacity, colour and gloss of thermosetting powder coatings," by J. K. Rankin

"The ANLAB colour system," by A. Cooper and K. S. McLaren

"An investigation into the durability characteristics of masonry finishes," by J. Boxall

"Some physical properties of pigments. 1: Compaction under pressure," by M. J. Smith

Information Received

Derby depot for Silexine

A new 5,000sq ft distribution depot and office in Derby has been opened by Silexine Paints Ltd. The full range of *Silexine* products, including speciality paints, will be available from stock, and the depot will serve the whole of the Midlands, and will provide counter service for local customers.

Beaver buys Hinshelwood

The Beaver Group Limited has recently announced that it has reached agreement to acquire from Scotcrocs Limited the whole of the issued share capital of Thos. Hinshelwood & Co. Ltd., together with Hinshelwood's Glasgow factory.

The move is in accordance with Beaver's stated policy of acquiring companies operating in markets that fit into the existing pattern of group trading activities. A close co-operation between Hinshelwood and Arnold Hamilton & Co. Ltd., another group subsidiary in the Glasgow area, is foreseen.

Bayer in Mexico

Bayer AG has announced that it is to have a 40 per cent participation in the Mexican group belonging to Polieteres SA, a Mexican industrial concern operating in the polyether and polyurethane market. Polieteres will construct a 4 million Dmark plant for the production of polyether and polyurethane products, building on the basis of Bayer plans. The plant, which will have a capacity of 7,000 tonnes per year, will operate by the latest Bayer process, and is scheduled for start-up in 1974.

Bayer has also announced that the joint company Bayer-Shell Isocyanates NV has started production of toluene diisocyanate and methane diphenylene diisocyanate. This first stage has a capacity of 30,000 tons TDI and 24,000 tons MDI; a total of 60,000 tons of each product is planned for the complete venture.

M and B to market French chemicals

A selected range of chemicals manufactured in France by Societe de Usines Chimiques Rhone Poulenc and "Sifrance," is to be marketed in the UK by May & Baker Ltd., a member of the Rhone-Poulenc Group. The range will cover polymers, including polyvinyls—and include the Rhone-Poulenc products previously handled in the UK by R. W. Greef & Co. Ltd.

ICI Dispersymer for Ford and British Leyland

Large scale manufacture of non-aqueous dispersion paints for car finishing is now under way at the Paints Division of ICI Ltd. Thermosetting acrylic paints produced by the *Dispersymer* process are now being used on some models in the current British Leyland and Ford ranges, reportedly with favourable customer reaction. As the formulations are dispersions rather than solutions, lower solvent concentrations are required to achieve a suitable viscosity, and thus drying times are shorter and atmospheric pollution is reduced. Both

Ford and British Leyland are claimed to have reduced finishing times and speeded production, and to have achieved consistently higher quality of finish with the new paints.

Nopco Hess acquired by Diamond Shamrock

The Diamond Shamrock Corporation of Cleveland, USA has recently increased its holding (from 50 per cent), and thus acquired a majority interest in Nopco Hess Ltd.

The acquisition is seen as a move to further accelerate the excellent growth record achieved by Nopco Hess since its formation in 1963. The current range of speciality chemicals for the paint industry will continue to be marketed, and will be expanded to incorporate allied specialities developed and distributed throughout the world by Diamond Shamrock.

The existing UK management team and key personnel remain unchanged.

New Products

Colorguard Sensor Series III

Colorguard Sensor Series III, recently introduced by Gardner Laboratory Incorporated, is an additional accessory for the Gardner digitized photometric unit system. This system is based on a main unit into which instruments measuring various properties can be connected. The new sensor incorporates the same optical system as the Gardner *XL-10* colorimeter, and can be supplied to measure colour to CIE XYZ co-ordinates or to Gardner's own G,A,B. The system can now measure gloss, haze, opacity, hiding power, brightness, luminous reflectance or colour on the same basic instrument.

Two new paints from Crown

Crown Paints has recently extended its range of trade emulsion paints by the addition of *Crown Sheen* and *Crown Covermatt*.

Crown Sheen Emulsion is a vinyl emulsion for use where a finish of higher gloss than conventional matt emulsions is required. A range of twelve colours, white and brilliant white is available, and the paints' quick drying properties are stressed.

Crown Covermatt Emulsion is a new high opacity formulation for the initial decoration of interior walls and ceilings. Maximum covering power, even over minor flaws, is claimed, and as the final coating is porous it allows newly plastered surfaces to breathe and dry out.

High-build chlorinated rubber paint from Hadfields

A new high-build paint system for use on steel structures, including marine application, has been introduced by Hadfields (Merton) Ltd. Based on chlorinated rubber, the two-coat system can produce a total dry film thickness of 300 microns, made up of 225 microns of rust inhibitive primer and 75 microns of semi-gloss finish.

The system is fire retardant, and can be supplied in red, grey or (finish only) buff.

Literature

BS4849 1972 1,1,2-Trichlorotrifluorethane

The British Standard specification for 1,1,2-Trichlorotrifluorethane, in the preparation of which the Association was pleased to be of assistance, has now been published, and copies are available from the BST.

Carless brochure

A new brochure describing its full range of aliphatic and aromatic hydrocarbons has been published by Carless, Capel and Leonard Limited. A full description of each product is given, together with chemical and physical properties, and test methods, temperature conversions and other relevant data are included.

Raman reference spectra from Sadtler

A new continuing collection of Raman Standard reference spectra has been published by Sadtler Research Laboratories Inc. The initial publication is in three volumes, covering 1,200 compounds; Raman and infra-red spectra of each compound are given, with information about the compound and the instrument parameters. The collection is comprehensively indexed for ease of retrieval.

Additional spectra will be published at the rate of 2,000 compounds per year and will be available on an annual subscription basis.

Tin chemicals for industry

The Tin Research Institute has published "Tin chemicals for industry," a 31-page booklet summarising the salient properties of the commercially important tin chemicals and outlines their scope in the major areas of use, including packaging, building, furniture, electronics, agriculture and metal finishing.

Cementone product guide

A new pocket-sized product guide has been issued by Cementone Ltd., showing details of all the company's standard lines.

Conferences and symposia

Rheology conference

The 1973 Autumn conference of the British Society of Rheology is to be held at the University of East Anglia, Norwich, from 18-21 September. The title of the conference will be "Modern developments in rheology" and it is hoped, within this general theme, that specific sessions on elongational flow and on multiphase systems will be arranged.

Offers of papers are invited; prospective authors should get in touch with the organisers immediately and must submit a title and abstract by 30 April.

All correspondence to: Dr M. M. Beazley, 44 Brockstone Road, Boscoppa, St. Austell, Cornwall.

Section Proceedings

Irish

Printing ink developments

On Friday 17 November, Mr G. A. Hutchinson, Technical Director of the Ink Division of Croda Polymers, gave a lecture on "Printing ink developments".

His main theme was the fact that, in the field of letterpress and sheet fed offset printing, there was a demand for higher production combined with quality. One of the delaying factors was the drying time of inks and the necessity in some cases of applying a spray powder at the delivery end of a press to prevent set-off.

Mr Hutchinson dealt with the well-known methods of drying inks, and his ideas on what happened when inks based on drying oil/resin complexes were converted from a wet to dry state by polymerisation were admirably and ingeniously illustrated by structures made from wire and coloured pipe cleaners.

Midlands

Trent Valley Branch

Wallpaper manufacture

Under the chairmanship of Mr J. R. Bourne, the Trent Valley Branch met on Thursday 7 December, at the British Rail School of Transport, Derby, to hear a talk by Mr S. Duckworth on the subject of wallpaper manufacture. Mr Duckworth, chairman of the Manchester Section, is deputy research director of the Wallcoverings Division of Wallpaper Manufacturers Ltd.

Invitations were extended to members of the Derby and Nottingham branches of the Federation of Master Painters and Decorators, and the audience totalled 23 OCCA members and guests.

Mr Duckworth opened with a rather remarkable statement, in which he indicated that conventional wallpaper still represented approximately 75 per cent of the market despite the advent of vinyls, etc.

The original method of printing wallpaper had been block printing and this was still used in certain spheres. Although it catered for individual design, it proved to be rather too expensive for normal use. Screen printing was another method that had proved popular in the past but this, too, was now being phased out, again for reasons of economy.

The basic paper used for wallpaper production was 75 per cent mechanical pulp and 25 per cent chemical pulp.

Mr Duckworth went on to describe the various processes involved on the production side. The ground coating method was widely used. The conventional method of wallpaper printing by surface printing machines—gravure, flexographic, etc., did not give the same softness of print.

He estimated that the W.P.M. factory maintained a range of 3,000 to 3,500 patterns, each involving the use, on average, of eight different colours. There were something like 40,000 different colours involved in the pattern card.

Mr Duckworth then went on to describe briefly the work involved after a certain design had been selected. Printing rollers were prepared by a number of methods—for instance, the coppering method, still used where the design included very fine details. In the case of embossed rollers, the pattern

He detailed the various methods of radiation cross-linking that were being examined with a view to instantaneous drying: ultra-violet radiation, microwave drying and electron beam curing; and outlined the part that inks developed to be used with these drying methods would play in limiting atmospheric pollution.

Whilst on the subject of ink toxicity and pollution of the atmosphere, Mr Hutchinson thought that greater use would be made of water-in-ink formulations. In the field of flexography, he forecast that water reducible inks would eventually be printed at high speeds on film, and instant drying achieved by the microwave technique.

A vote of thanks to Mr Hutchinson on behalf of the 25 members present was given by Mr P. Jones.

A.R.

was engraved by hand. This type of roller was operated at extremely high pressure.

After the printing operation the wallpaper was then fed into steam-heated dryers which were in wide use, although festoon drying was a method still used, but, of course, this tended to take up a large amount of floor space. In the case of gravure printing there was an inter-stage drying process.

Mr Duckworth outlined the main design functions of wallpaper printing, as shown below.

Ground coating. Protection from uv light; good print acceptability (screen printing, gravure, flexo, ink emboss, pick resistance); adequate binding and adhesion; flexibility; water resistance; opacity.

Printing. Design and colour; good print quality; cleanliness of colours; light and heat fastness; economics.

Mr Duckworth emphasised that the choice of binder and pigment was very important for clean, bright colours. As far as light fastness was concerned, the rating of 4 to the BS specification was usually more than adequate and, as far as heat stability was concerned, products should be capable of withstanding 100°C for 100 hrs.

As far as application of wallpaper coatings was concerned, the most important requirements for both ground coating (application by air knife) and printing (application by screen printing or surface screen printing) were considered to be mechanical stability, long pot-life, freedom from settling, compatibility, non-foaming, colour stability, and high pigment solids.

Binders used include casein (gives good print quality), soya protein, polyvinyl alcohol, cellulose derivatives, glue, emulsions, and starch.

Most systems were either emulsions or colloidal; the former offered water resistance, flexibility and uniform pigment solids, while the latter provided easy sieve cleaning and colour stability but increased raw materials costs and colour usage.

A comprehensive selection of slides was shown, illustrating all the facets of wallpaper production covered in Mr Duckworth's talk.

A lively discussion followed, and although this brought to light a number of very interesting aspects not covered in the lecture, Mr Duckworth was able to deal very thoroughly with each new topic raised.

Thames Valley

Adhesives and adhesion

The first meeting of the winter session was held at the Beech Tree Hotel, Beaconsfield, on 28 September, when Dr Fletcher of Croda Chemicals Ltd. spoke on adhesives and adhesion.

Dr Fletcher began by outlining the basic principles of adhesion. Good adhesion depended on molecular forces and intimate close contact, and an adhesive, to be ideal, must fill all the voids on a molecular scale. Mathematical treatment indicated that much higher bond strengths ought to be possible than were realisable in practice. This was because contamination reduced the wetting efficiency and adhesives were inconsistent and changed composition during setting.

Because adhesive strength was so important, few low molecular weight materials were satisfactory and natural and synthetic polymers were the rule, with natural polymers having a diminishing market share.

The most commonly used polymers were synthetic rubbers, melamine/formaldehyde, polyesters, polyamide, polyolefin, polyacrylate, polycyanoacrylate, vinyl acetate, copolymers with styrene, and urea/formaldehyde, which had the highest sales, consumption for chipboard amounting to 40,000 tons per annum. Dr Fletcher then considered three main categories of polymer for adhesives in more detail.

A vote of thanks for this most intriguing and absorbing talk was given by Mr H. F. Clay and the audience showed their appreciation by hearty applause.

D.F.G.

Cyanoacrylates were unique in undergoing polymerisation after catalysation by weak bases, including water. A good bond was given between a wide variety of surfaces.

Pva emulsions were used to a large extent. To overcome their limitations, such as poor moisture resistance and plasticiser migration, it was usual to copolymerise them with acrylates or maleic esters. Ethylene modified polymers (eva) were assuming increasing importance; because the amount of ethylene could be as high as 50 to 85 per cent, they were economically attractive, and they were becoming widely accepted for use with furniture, laminating/packaging, bookbinding (pvc covers), and textile lamination.

Styrene/butadiene or styrene/isoprene block copolymers found significant usage, offering high tack.

Finally Dr Fletcher discussed the overall formulation of adhesives, in particular the hot-melt types.

During the discussion period a number of questions emerged, ranging from the possibility of using pva emulsions as gap fillers to the use of eva as a laminating pvc adhesive.

Mr Bailes gave a vote of thanks to Dr Fletcher which was followed by hearty endorsement from his audience, shown in the usual manner.

R.E.G.

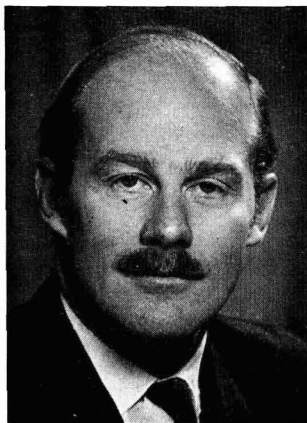


25th Technical Exhibition

21-24 May 1973

Empire Hall, Olympia, London

Lord Limerick to be the Guest of Honour at the Exhibition Dinner



Lord Limerick

The Exhibition Committee is pleased to announce that Lord Limerick, Parliamentary Under Secretary of State for Trade to the Department of Trade and Industry, has accepted its invitation to be the Guest of Honour at the Exhibition Dinner on 21 May at the Savoy Hotel and to reply to the Address of Welcome by the President of the Association, Mr A. W. Blenkinsop.

Additional Exhibitors

The Exhibition Committee has now allocated space to Elcometer Instruments Limited, and to The Patent Office, which is to exhibit its advanced information retrieval system. This now brings the total number of exhibitors to 96 with 8 who have not appeared at previous OCCA Exhibitions.

The full list of exhibitors is as follows:

Amoco International SA
Anchor Chemical Co. Ltd.
*APV-Osborne Ltd.
Arco Chemical Company
Akzo Chemie NV
*Willy A. Bachofen
Baker Castor Oil Co.
†BASF United Kingdom Ltd.
†Bayer AG
BIP Chemicals Ltd.
Victor Blagden & Co. Ltd.
William Boulton Ltd.

Bowater Industrial Packaging Ltd.
†Buckman Laboratories SA
†Buhler Brothers (England) Ltd.
Cabot Carbon Ltd.
Rex Campbell & Co. Ltd.
CdF Chimie
†Chemische Werke Huls AG
†CIBA-GEIGY (UK) Ltd.
Cornelius Chemical Co. Ltd.
†Croda Chemicals Ltd.
†Croda Processed Oils Ltd.
†Croda Universal Ltd.
Croxton & Garry Ltd.
Daniel Products Co.
Degussa
DH Industries Ltd.
*Diffusion Systems Ltd.
Durham Raw Materials Ltd.
†Dynamit Nobel AG
†Dyno Industrier AS
Eastman Chemical International AG
Elcometer Instruments Ltd.
G. J. Erlich Ltd.
Ferranti Ltd.
†Guest Industrials Ltd.
Henkel & Cie GmbH
Hercules Powder Co. Ltd.
†Harold Heydon & Co. Ltd.
†Hoechst UK Ltd.
Imperial Chemical Industries Ltd.
†Industrial Colours Ltd.
International Colloids Ltd.
*Jacobson Van den Berg (UK) Ltd.
Kemira Oy
Kollmorgen Colour Systems
†Kunsttharsfabrik Synthese NV
Laporte Industries Ltd.
Marchant Brothers Ltd.
Mastermix Engineering Co. Ltd.
†Rudolph Meijer's Inc.
*H. E. Messmer Ltd.
Microscop Ltd.
†Millroom Accessories & Chemicals Ltd.
Montecatini Edison
†A/S Norwegian Talc
*The Patent Office
†Plastanol Ltd.
Polymers, Paint & Colour Journal
†Polyvinyl Chemie Holland NV
Research Equipment (London) Ltd.
Rhône-Poulenc Group
RCK Chemical Co. Ltd.
Rohm & Haas (UK) Ltd.
†Roehm GmbH
Sachtleben Chemie GmbH
†Sandoz Ltd.
Pigment & Resin Technology (Sawell Publications Ltd.)
Schering AG
Sheen Instruments (Sales) Ltd.
†Shell Chemicals UK Ltd.
Peter Silver & Sons (Engineers) Ltd.

*Denotes companies who have not previously shown at an OCCA Exhibition.

†Denotes companies who were not at the 1972 Exhibition.

†Silverson Machines Ltd.
Society of Dyers and Colourists
†Spelthorne Metals Ltd.
†Synres International NV
Tioxide International Ltd.
Titanium Intermediates Ltd.
Torrance & Sons Ltd.
Torsion Balance Co. (GB) Ltd.
Transportmaschinen Export/Import
Ugine Kuhlmann
†Union Carbide Europe SA
†Vebe-Chemie AG
†Wacker-Chemie
†Wentworth Instruments Ltd.
*Westerlins Maskinfabrik AB
Winn & Coales (Denso) Ltd.
Winter Osakeyhtio
Worsdall Chemical Co. Ltd.
*Carl Zeiss (Oberkochen) Ltd.

Aims of the Exhibition

Preparations for the Exhibition are now well advanced and the Exhibition Committee feels that it may be worth reiterating the aim of the Exhibition as laid out in the General Rules for Exhibitors.

The aim of the Exhibition is the presentation of technical advances in those industries supplying the Paint, Varnish, Printing Ink, Colour, Linoleum and other allied industries. The technical advances may relate to: new products, new knowledge relating to existing products and their uses, or in suitable cases, existing knowledge which is not generally available in the consuming industries.

The Committee stipulates that exhibitors present a technical theme—that is display in a technical manner the technical developments in raw materials, plant or apparatus illustrated by experimental evidence. It is essential that a technically or scientifically trained person, who has full knowledge of the products displayed, be available on the stand throughout the official hours of opening.

Whilst the Committee naturally encourages the showing of new products, it does not stipulate that a new product has to be shown each year, since it fully appreciates that there are occasions when this is not possible. Accordingly, the Committee draws attention to the fact that new technical data on existing products are regarded as acceptable subject matter.

Official Guide

The printing of the *Official Guide* is now under way, and it is hoped that copies will be available for circulation at the end of the month. Any company or individual who is not already on the Association's comprehensive mailing list should apply to the Association's offices for a copy of the *Guide* when available.

OCCA Biennial Conference

towards 2000

eastbourne 19-23 June 1973

Conference Brochure

Full details of the Association's Conference were circulated to all Members of the Association and non-members who had made requests to receive these details early in January.

The full programme and summaries of the papers appeared in the December issue of the *Journal*, and biographies of the lecturers appeared in the January issue.

A considerable number of applications has now been received and readers are reminded that the closing date for registrations will be **31 March 1973**. Later applications will still be considered after that date, but those applying from United Kingdom addresses must add Value Added Tax at the standard rate to their remittances.

Preprints

Preprints of the papers are now being prepared, and it is expected that these, together with details of accommodation, badges, programmes, etc., will be sent to those who have registered in May. It is a feature of the Association's Conferences that preprints are sent well in advance of the function, in order to enable delegates to read them before the conference, at which the lecturers illustrate their topics but do not read the papers in their entirety. This allows for a much longer discussion period than at many other conferences, and has proved of immense value to those attending previous Association Conferences.

Register of Members

The following elections to Membership have been approved by Council. The Section to which new Members are attached is given in italics.

Ordinary Members

- HITCHMOUGH, REX HENRY, 35 Croasdaile Road, Stansted, Essex. (*London*)
- KAMAL, ANWAR, Jenson & Nicholson of Bangladesh Ltd., PO Box 353, Chittagong, Bangladesh. (*General Overseas*)
- MCGRATH, ANTHONY HILTON, BSc, Arthur Holden & Sons Ltd., Bordesley Green Road, Birmingham. (*Midlands*)
- MOMAYA, HIDDEN K., BScTech, c/o Shri C. J. Vurdhman, Manek Mahal, 90 Vir Nariman Road, Bombay-20, India. (*General Overseas*)
- PARKIN, MALCOLM HIRST, LRIC, 5 Mildred Avenue, Grotton, Oldham, Lancashire. (*Manchester*)
- POWELL, JEREMY HUGH, LRIC, Ciba-Geigy (UK) Ltd., Plastics Division, Duxford, Cambridge. (*London*)
- ROGOW, STANLEY MAX, c/o Coates Bros. (Pty) Ltd., PO Box 1057, Cape Town, South Africa. (*South African*)
- SJODIN, BERTIL, Dr Eng, Radjursvagen 17, 170 10 Ekero, Sweden. (*General Overseas*)
- THOMPSON, PETER ALEXANDER, 19 Hansons Bridge Road, Walmley, Birmingham B24 OPE. (*Midlands*)
- WATKINS, DAVID CLIVE, 6 Brimtree Drive, Shifnal, Salop. (*Midlands*)

measurement of research output". The number attending each Workshop Session is strictly limited and places will be allocated in order of receipt. Where the total places for a session have been filled, later applicants will be informed and, if possible, offered an alternative session.

Receptions and Dinner

There will be an informal reception for all delegates at lunchtime on Wednesday and a Civic Reception will be held, at which delegates will be welcomed by the Mayor and Mayoress of Eastbourne, on the evening of the same day. The Association's Dinner and Dance will be the closing function of the Conference on the Friday evening. Other social activities, such as coach tours, are being arranged for the benefit of ladies attending the conference.

News of Members

Mr D. C. Wall, an Ordinary Member attached to the Manchester Section and a Fellow in the Professional Grade, has been appointed managing director of the Wallcoverings Division of the Crown Products Group. Mr Wall has been deputy managing director since December 1971.

Mr A. G. North, an Ordinary Member attached to the London Section, has been elected chairman of the British Resin Manufacturers' Association and succeeds Mr C. H. Morris, an Ordinary Member attached to the Newcastle Division. Mr North is joint managing director of Cray Valley Products Ltd.

Dr W. Carr, an Ordinary Member attached to the Manchester Section, presented a paper entitled "Pigment dispersion in publication gravure inks" to a meeting of the Ink Commission of the European Rotogravure Association in Amsterdam last November. Dr Carr has often contributed papers for publication in the *Journal* during his long association with the Pigments Division of CIBA-GEIGY (UK) Ltd.

Programme notes

Attention is drawn to the further information now given in Forthcoming Events for the joint meeting of the West Riding Section and the Northern Section of the Colour Group on Wednesday 21 February at the Colour Chemistry Department of Leeds University, and for the Thames Valley Section on Thursday 22 February. The latter will commence with a tour of the printing department of Pasolds Ltd., makers of "Ladybird" children's clothes; tickets are available from the Section Hon. Secretary, Mr J. D. Horne, c/o ICI Ltd., Wexham Road, Slough, Bucks.

Also, we have been notified that tickets for the Newcastle Section Ladies Night, to be held at the Five Bridges Hotel on Friday 23 February, are now available from Mr H. Fuller, 552 Acklam Road, Middlesbrough, at £3.00 each. Overnight accommodation is available at the hotel at 50 per cent of normal charges.

Forthcoming Events

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

Thursday 1 February

Newcastle Section: "Polyurethane systems in the marine industry" by a speaker from Farbenfabriken Bayer, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle, at 6.30 p.m.

Friday 2 February

Scottish Section—Eastern Branch: Annual Burns Supper, to be held at the Royal Mile Centre, Edinburgh.

Monday 5 February

Hull Section: "Are emulsion paints good enough?" by Mr J. Cruden of Harco Ltd., to be held at the Queens Hotel, George Street, Hull, at 7.00 p.m.

London Section: "Zinc phosphate, its history, development and future" by Mr M. Rendu of Imperial Smelting Corp. (Alloys) Ltd., to be held at the East Ham Technical College at 7.00 p.m.

Wednesday 7 February

Newcastle Section—Student Group: A talk by a member of the staff of Camrex Ltd., to be held at the Newcastle Polytechnic, Ellison Place, Newcastle, at 3.00 p.m.

Thursday 8 February

Midlands Section—Trent Valley Branch: "Vinyl resins" by Mr D. J. Silsby of Bakelite Xylonite Ltd., to be held at the British Rail School of Transport, London Road, Derby, at 7.00 p.m.

Scottish Section: "Powder coatings" by Mr D. W. Brooker of Shell Research Ltd., to be held at the St. Enoch Hotel, Glasgow, at 6.00 p.m.

Thames Valley Section—Student Group: Works visit, to be arranged. Leaving Slough College car park at 1.00 p.m.

Friday 9 February

Manchester Section: "Technological forecasting and its potential in the surface coatings industries" by Mr H. Jones, to be held at the Manchester Literary and Philosophical Society at 6.30 p.m.

Thames Valley Section: Buffet Dance, to be held at "Great Fosters," Egham, at 7.00 p.m.

Saturday 10 February

Scottish Section—Student Group: "Selection of pva emulsions for water based paints" by Mr D. Wallace of Vinyl Products Ltd., to be held at the St. Enoch Hotel, Glasgow, at 10.00 a.m.

Tuesday 13 February

London Section—Southern Branch: "Sealants" by Mr L. D. Hall of Ralil-Bondite Ltd., to be held at the Pendragon Hotel, Southsea, at 7.00 p.m.

West Riding Section: "Functional extenders in emulsion paints" by Mr S. E. Maskery of Crosfield Chemicals Ltd., to be held at the Griffin Hotel, Leeds, at 7.30 p.m.

Wednesday 14 February

Manchester Section—Student Group: "Synthetic stoving finishes" by Mr D. Pountain of WPM Paint Division, to be held at the Manchester Literary and Philosophical Society at 4.30 p.m.

Friday 16 February

Irish Section: "Organic pigments for the paint industry" by H. Biffar of Farbwerke Hoechst AG, to be held at the Clarence Hotel, Dublin, at 8.00 p.m.

Midlands Section: "Dispersymer" by Mr R. L. Baylis of ICI Ltd. Paints Division, to be held at the Birmingham Chamber of Commerce and Industry, 75 Harborne Road, at 6.30 p.m.

Wednesday 21 February

West Riding Section: Joint meeting with the Northern Section of the Colour Group: "Whiteness" by Mr R. Blakey and Dr G. Langdon of Tioxide International Ltd., to be held at Leeds University at 2.30 p.m.

Scottish Section—Eastern Branch: "Testing of raw materials for paint and varnish" by a speaker from ICI Ltd., to be held at the Carlton Hotel, North Bridge, Edinburgh.

Thursday 22 February

Thames Valley Section: "Recent developments in vapour phase transfer printing" by Dr C. E. Vellins of L. B. Holliday & Sons Ltd. A short introductory talk on textile printing in general will be given by Mr M. Roberts of Pasolds Ltd. To be held at Pasolds Ltd., at 5.30 p.m.

Friday 23 February

Bristol Section: "Modern dispersion techniques" by Mr I. Berg of Berger Paints Ltd., to be held at the Angel Hotel, Cardiff, at 7.15 p.m.

Newcastle Section: Ladies Night, to be held at the Five Bridges Hotel, Gateshead.

March

London Section: Preliminary Details—Joint Symposium with the Organic Finishing Group of the Institute of Metal Finishing on "The future of motor car coatings" date to be arranged.

Thursday 1 March

Newcastle Section: "The evolution of alkyd resins" by Mr T. I. Price of BP Chemicals, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle at 6.30 p.m.

Monday 5 March

Hull Section: Ladies Evening "Contemporary textiles" by Professor C. S. Whewell, Department of Textile Industries, University of Leeds, to be held at the Queens Hotel, George Street, Hull at 7.00 p.m.

Wednesday 7 March

London Section: "Some aspects of colorimetry, particularly fibre optics" by Mr D. Irish of the PRA, to be held at the South Bank Polytechnic at 7.00 p.m.

Manchester Section: "Recent trends in the development of organic pigments" by Dr E. R. Inman of Ciba-Geigy (UK)

Limited, to be held at the Royal Institution, Liverpool at 6.30 p.m.

Newcastle Section—Student Group: "The use of water in paints" by Mr B. Ridley, of the International Paint Co. Limited, to be held at the Newcastle Polytechnic, Ellison Place, Newcastle at 3.00 p.m.

Thursday 8 March

Midlands Section—Trent Valley Branch: "The origin and extraction of natural colours and minerals" by Mr E. Hare of Via Gellia Colour Co. Limited to be held at the British Rail School of Transport, London Road, Derby at 7.00 p.m.

Scottish Section: "Research and innovation at the Paint Research Association" by Dr S. H. Bell, to be held at the St. Enoch Hotel, Glasgow at 6.00 p.m.

Thames Valley Section—Student Group: "Glass reinforced plastics" by a speaker to be arranged, to be held at the Main Lecture Theatre, Slough College at 4.00 p.m.

Saturday 10 March

Scottish Section—Student Group: Short talk and film on pollution by Mr Alwyn Jones of the Scottish Council Development and Industry, to be held at the St. Enoch Hotel, Glasgow at 10.00 a.m. followed by the AGM.

Tuesday 13 March

London Section—Southern Branch: "Medicines for coatings" by a speaker from Byk-Mallinckrodt, to be held at the Pendragon Hotel, Southsea at 7.00 p.m.

West Riding Section: "Microbiology" by Mr W. R. Springale of the Paint Research Association, to be held at the Griffin Hotel, Leeds at 7.30 p.m.

Wednesday 14 March

Manchester Section—Student Group: "Pigment dispersion" by Mr G. R. Robson of ICI Limited Organics Division, to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester at 4.30 p.m.

Friday 16 March

Irish Section: "Modern developments in packaging" by Mr E. G. O. Ridgewell, of the Irish Packaging Institute, to be held at the Clarence Hotel, Dublin at 8.00 p.m.

Midlands Section: Annual J. Newton Friend Lecture "Some Great English Potters" by Mr C. E. L. Franklin of Royal Dalton Tableware Limited, to be held at the Birmingham Chamber of Commerce and Industry, 75 Harborne Road, Birmingham at 7.30 p.m.

Wednesday 21 March

Scottish Section—Eastern Branch: AGM followed by films (ICI Limited) to be held at the Carlton Hotel, North Bridge, Edinburgh at 7.30 p.m.

Thursday 22 March

Thames Valley Section: "Recent developments in the painting and decoration of metal containers" by Mr A. D. Lott of the Metal Box Co., to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks at 7.00 p.m.

Friday 30 March

Bristol Section: Informal Debate "The customer is always right" to be held at the Royal Hotel, Bristol at 7.15 p.m.



Oil and Colour Chemists' Association

President: A. W. BLENKINSOP, F.T.S.C.

General

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

Sections

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 (I.I.68) the Oil and Colour Chemists' Association Australia, having the same aims and activities as, and working in close liaison with, the parent body.

Membership

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. An optional Professional Grade, conferring designatory letters, is open to Ordinary Members. Student membership 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 £5.25, except for registered Students, whose subscription is £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.

Professional Grade

The Association recently introduced (1971) an *optional* professional grade for its Ordinary Members, giving the designatory letters FTSC (Fellow in the Technology of Surface Coatings), ATSC (Associate in the Technology of Surface Coatings), and LTSC (Licentiate in the Technology of Surface Coatings). Full details are available upon request from the Association. Where Membership has lapsed, previous periods of Ordinary Membership count towards the total required under the regulations, as set out in the January 1973 issue of *JOCCA*.

Exhibitions

A technical exhibition is held annually at Olympia; Members are sent copies of the *Official Guide* several weeks in advance, in order to plan their itineraries. Non-members should apply, in writing, to the Director and Secretary for copies of the *Official Guide*.

Conferences and Symposia

The Association organises large, biennial technical conferences, the papers for which (together with discussions) are published in the *Journal*. Sections of the Association, in the UK and abroad, hold symposia and these, too, are reported in *JOCCA*.

Publications

Journal of the Oil and Colour Chemists' Association (JOCCA) is published monthly and includes a yearly index in the December issue. The subscription rate to non-members is £10.00 p.a. in the United Kingdom and £12.00 p.a. (£31) abroad (post free; payable in advance). Single copies may be purchased for £1.00 (£1.25 abroad).

Introduction to Paint Technology (Second Edition with additional chapter). With illustrations, 187 pages and index £1.00 (including postage).

Paint Technology Manuals (Parts 1, 2, 4, 5 at present out of print).

Part 1 "Non-convertible Coatings"

Part 2 "Solvents, Oils, Resins and Driers"

Part 3 "Convertible Coatings," Second Edition, pp. 350, £2.80

Part 4 "The Application of Surface Coatings"

Part 5 "The Testing of Paints"

Part 6 "Pigments, Dyestuffs and Lakes, pp. 340, £2.00

Part 7 "Works Practice," available shortly, £2.40

Director & Secretary: R. H. Hamblin, MA, FCIS, Priory House, 967 Harrow Road, Wembley, Middlesex, England HA0 2SF.

Tel. 01-908 1086; Telex 922670 (OCCA WEMBLEY)

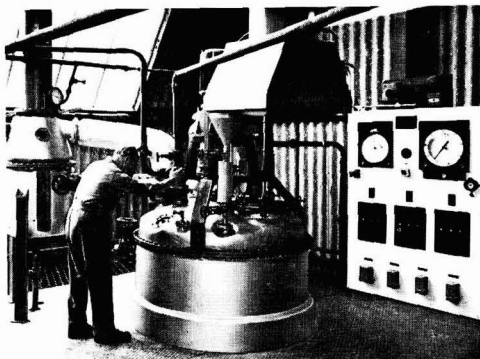
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(List of representative clients given upon request)

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Paint Technology Manuals



Part Seven : Works Practice

The seventh volume of the Association's series of Paint Technology Manuals, entitled "Works Practice," is now being collated, bound and offered for sale.

The articles which have appeared under Student Reviews each month have been so designed that the bound volume will form a complete, coherent book with full continuity. Apart from the necessary typographical changes in maintaining consistency in the *Journal*, "Works Practice" will be exactly the same as those parts of the Paint Technology Manuals already published by Chapman & Hall Ltd.

It is anticipated that the book will be available towards the end of January 1973; orders can now be accepted.

Contents include:

- Chapter 1—The factory. Siting and layout*
Chapter 2—Raw materials. Storage and handling
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Chapter 5—Factory organisation and personnel
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To: Oil and Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middx. England HA0 2SF.

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