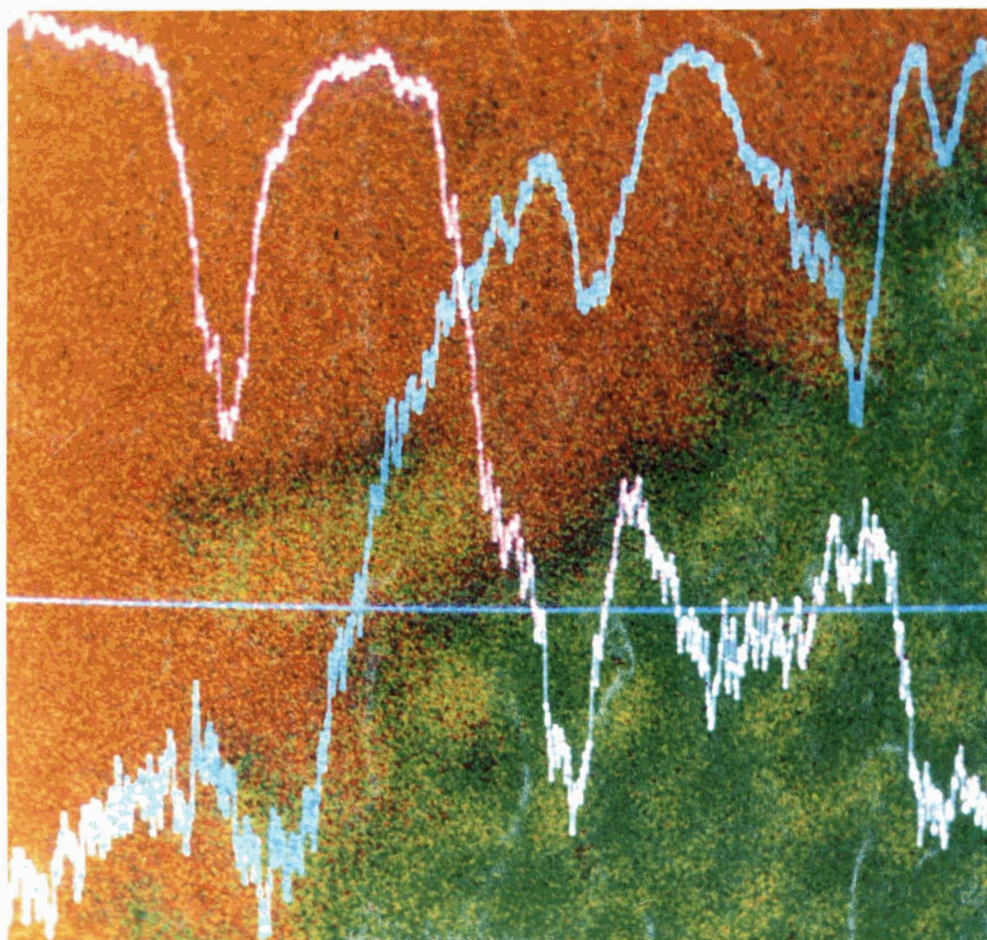




JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION

# JOCCA



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### Contents

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- The Paint Market:** Past-present production, International trade, country consumption, breakdown by type of paint.
- Market Segmentation:** Breakdown by end-usage, decorative finishes, production-line finishes, special purpose coatings.
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- Miscellaneous:** Standards, tariffs and taxes, packaging and labelling, pollution control, energy conservation.
- Companies in the Field:** Number, categorisation, International affiliations, relative importance.
- Trends in Coatings:** Developments in materials and coating techniques.
- Future of the Industry:** Commercial changes, mid 1990's market. **Appendices**

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*The list of Council members, committees of Council and section and branch committees for the 1988-89 session was given in full in the September 1988 issue of the Journal following the appointment of Council at the AGM held on 15 June 1988 and of the committees of Council at the Council meeting on 4 August 1988. For ease of reference the names and addresses of the current Honorary Secretaries are shown below for both members and non-members wishing to contact any of the sections or branches.*

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## Contents

Vol. 72 No. 1

JANUARY 1989

Chester Conference Column.....	1
by A. C. Jolly	
Chester Conference 1989: Summaries/Biographies .....	1
News.....	4
<i>Feature: Analytical techniques for surface coatings</i>	
Editorial: The analysis of surface coatings by dynamic mechanical thermal analysis and dielectric thermal analysis .....	9
by G. J. Bratton, E. A. Wasson, J. W. Nicholson and A. D. Wilson	
New applications of gas chromatography in the field of paints and varnishes .....	14
by P. Alessi, M. Orlando-Visalberghi and G. Torriano	
Infrared study of the adsorption of acetone on silica immersed in hexane .....	19
by C. H. Rochester and D. G. Smith	
The identification of blue pigments in paints by derivative spectroscopy .....	21
by C. M. Wakeford and R. H. Wardman	
Identification of black deposits on road markings using infrared spectroscopy .....	28
by M. A. Riad, A. J. Floyd, D. E. Packham, S. M. Massoudi, G.A. Kelany, K. Y. Al-Khalaf	
From the General Secretary .....	34
OCCA Meetings.....	35

Cover: Electron Probe Micro Analyser (EPMA) scan of the interface between a steel substrate and its surface coating showing the diffusion of the Zinc (Red) into the Iron (Green) substrate. The scan is superimposed upon an x-ray micrograph of the interface. Scan length 25 microns. An example of the use of a modern analytical technique for surface coatings.

Forthcoming Features: Feb - Paint Production, Mar - Pigments, April - Automotive/Industrial Coatings. Contributions are welcomed at least five weeks prior to publication date.

**Oil and Colour Chemists' Association**

**Priority House, 967 Harrow Road, Wembley, Middlesex HA0 2SF England**

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## Chester Conference Column

Our plans for the Conference seem to be coming together nicely and there is little more to add to that which the advert and official brochure already detail. Unfortunately the Duke of Westminster's official acceptance of our invitation has been slightly delayed but we should know whether we are to be graced with his presence or not in Christmas week. Naturally we are keeping our collective fingers crossed in the hope that his response will be in the affirmative. The decision will be too late to be published in this column but we hope to have it for the official brochure.

Collecting papers is always a difficult and laborious task but we appear to have attracted more than we can cope with this time. Simon Lawrence has received papers from Japan, Sweden and recently Spain, so the lecturers will be truly international.

For my part I wish you all a very happy and prosperous New Year and hope that you will give your full support to the Chester Conference.

A. C. Jolly ■

Below is included some of the summaries of the papers to be presented and the biographies of their authors. Further details will be published in forthcoming issues of the Journal.

### Summaries of papers and biographies of authors

#### Perstorp creative base for profitable R & D

##### S. Nordberg

###### Summary

Since a large part of Perstorp's activities is based on our own high technological product and process know-how, our future competitiveness will be largely dependent on our ability to renew ourselves and generate new business.

Consequently, successful research and development in its broadest sense is an important condition for making the Perstorp of the future a secure employer and an attractive capital investment.

Our activities are strongly decentralized and we do not have a central research unit. Nevertheless, Perstorp conducts extensive, advanced, intensive and successful research and product development activities. This phenomenon is not just a result of the general business climate that management has strived to create - it has also emerged from the organization of Perstorp's business renewal policy.

Like all aspects of Perstorp's activities, research and development is controlled and guided by the strategy called the five "commandments". This approach will be highlighted in the paper to be presented at Chester.

###### Biography

Sten Nordberg is currently Senior Vice President of Perstorp AB, Sweden. Mr Nordberg has an MSc in Chemical Engineering from the Royal Institute of Technology, Stockholm and is a Licentiate in Technology at Royal



S. Nordberg

Institute of Technology, Stockholm. Mr Nordberg has held a variety of positions within industry: Development Mgr and Production Mgr at STORA, Skutskär (1961-65), General Mgr Decorative and Industrial Laminate, Perstorp AB (1965-70), Member of the Corporate Management Group, Perstorp Corporation (1970-), Head of Corporate Development, Perstorp Corporation (1970-76), Head of Decorative Laminate and Plastics Group, Perstorp Corporation (1976-81), Head of Corporate Development, Perstorp Corporation (1981-). Mr Nordberg is a member of the board of the University of Lund, IDEON Center AB and the Swedish Plastics Federation.

#### Satisfying the safety regulations

##### A. J. Hinton

###### Summary

Profitable research and development

entails investing effort (money) in developing an idea or a product that will be financially successful in a future market. A lot of money is spent on applications research to ensure that new products meet the intended market requirements for technical effect and cost/efficiency.

The increasing complexity of national and international health and safety regulations demands that developers must now consider factors which, in earlier years, featured as relatively minor, for example.

(1) What are the added initial costs of and delays entailed in obtaining the necessary health and safety clearances in the intended markets before the "new substance" can be marketed (e.g. Directive 79/831/EEC, Annex VII)?; and.

(2) What are the longer term prospects of further expensive studies being required if sales develop above 10-100 tonnes/annum in the EEC (e.g. Directive 79/831/EEC, Annex VIII)?

Today it often makes sense to screen new chemical substances for potential toxicity problems at an early stage in the development, to sort out the most likely candidates for further study, before too much effort has been spent on expensive technical evaluation work - this is an added development cost.

Even if no "new substances" are involved, new formulations of existing substances must be assessed for known hazards and future potential problems in a logical and justifiable way (e.g. UK-CPL Regulations and the now-approved "Preparations Directive" 88/379/EEC). Also, records of the assessment need to be kept so that your classification and labelling can be

justified to any EC Member State Competent Authority who requests it!

In addition to the content of the label, which is controlled by specific regulations, how and what safety data should be provided to the user is also becoming more regulated and may well be in a mandatory format for the EEC before too long.

It is obviously important that the cost and delaying aspects of these factors must be taken into account at an early stage to ensure the success of development effort.



A. J. Hinton

### Biography

Anthony Hinton has a first class Honours degree in Chemistry and wide experience of technical management in ICI including new product development, applications and technical service to a large variety of industries on a comprehensive range of chemicals. Mr Hinton, widely travelled, has personal involvement in several patents of major financial significance and has published numerous technical articles.

Immediately prior to forming Hinton Safety Consultants, the Principal was the Product Safety Manager of ICI's Organics Division responsible for ensuring, by appropriate testing when required, that over 3,000 chemical products met the legal safety requirements of the many countries in which they were sold. These activities involved all areas of safety testing, progressing clearance with regulatory authorities and liaison with government regulators, leading to recognition as an expert in product hazard classification, registration and the relevant regulations.

### Profitable product development

#### R. Tulley-Turner

#### Summary

A major objective of Research and Development is the contribution to profitable products, both existing and

new. This paper will aim to focus on the options open to companies to further this objective under the following headings: The Nature of R & D - Fundamental Research, Applied Research, Development, Product Development, Product Market Matrix Organisation.

Some key considerations are:

- What business are we in?
- Corporate objectives
- Product market objectives
- Concentration on profitable areas

This paper will be illustrated by several case histories.

### Biography

Mr Tulley-Turner BSc, CChem, FRSC, FBIM, FIMC, FRSA, FlntSD, is a management consultant with wide executive industrial experience: Unilever - Industrial Chemist and Manager, Reckitts - Works Manager, Client Companies - acted as a General/Functional Manager, Urwick, Orr - Management of a Consultancy Practice. Mr Tulley-Turner specialist activities include: Corporate Business Appraisal, Strategic Planning, Improving Business Competitiveness, Manufacturing Performance, Product Development and Marketing, Organisation and Management Development, and Management Controls.



R. Tulley-Turner

### The development of a new pigment, from initial research to full commercial production

#### E. V. Carter and R. D. Laundon

#### Summary

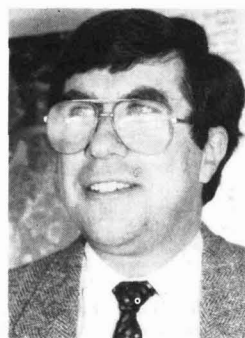
In any industry, the principal objective of innovative technology must be the conversion of new ideas into profit-making end-products. This paper relates the experience of a small research and development company, that hit upon a novel concept; production of micaceous iron oxide (MIO) pigment by chemical synthesis from readily available raw materials.

Hitherto MIO could only be obtained by beneficiation of natural minerals from deposits located in various parts of the world, the quality varying from reasonably good to rather poor. The effectiveness of MIO in protective coatings depends very much on the shape and size range of the pigment particles. The new process could virtually tailor-make the product to achieve optimum performance.

Progress is traced through various stages from initial experiments at the laboratory bench to the construction of a production plant capable of an output of 2,000 tonnes/year. Ultimately it is planned to manufacture 10,000 tonnes/year.



E. V. Carter



R. D. Laundon

### Biographies

Eric Carter entered the paint industry in 1946 and has held technical and marketing posts with Griffiths Bros, Inmont (UK) Ltd and Goodlass Wall & Co. In 1978 he was appointed Technical Director of MIOX Ltd, a new company formed to market micaceous iron oxide pigment obtained from mineral deposits in Austria.

In 1987 he joined MPLC Laboratories Ltd (now called Cookson Laminox) to support their development programme concerned with the synthetic production of micaceous iron

oxide and other lamellar iron oxides. In the new joint venture company formed to manufacture the synthetic pigments in bulk, he will be responsible for marketing and technical service to the paint industry.

Eric Carter has been a member of OCCA since 1956 and is a Fellow of the Professional Grade. He has written and presented several papers over the years dealing with anti-corrosion coatings' technology.

Roy Laundon graduated in Applied Chemistry at Lanchester Polytechnic and received a PhD from the University of Aston in Birmingham for his work on Catalysis.

He has been involved for nearly 20 years in the development of processes for the manufacture of specialised inorganic materials. Dr Laundon is the Research Director of MPLC Laboratories Ltd and has worked on the synthetic micaceous iron oxide project since its inception: taking it through the laboratory and pilot plant stages leading to the design of the production plant.

## Profitable application of R & D for novel anticorrosive pigments

### O. Leblanc

#### Summary

Having acknowledged the need for non-toxic replacements for chromate based anticorrosive pigments, a programme was launched in order to identify the most suitable candidate materials and develop processes for manufacturing them.

Preliminary studies showed that a product combining the performance of zinc chromate in accelerated tests and that of zinc phosphate in actual field conditions would be desirable, while strictly chemical tests had demonstrated the need for the latter material to be rendered more active.

Extensive use of accelerated and outdoor testing, of paints formulated with both commercially known and candidate materials showed the lack of universality of available replacements for chromate based pigments. Careful data handling was required in order that useful conclusions could be drawn.

A simple control method was evolved into a tool which helped some understanding of the relationship between factors such as particle size/shape of pigments or PVC/CPVC ratio with characteristics such as wet adhesion and corrosion protection of paint systems.

Final composition of the novel Actirox and Hispafos chromate replacement pigments was determined with the help of further chemical tests,

supplemented by improved accelerated testing and more comprehensive field performance examination of paints made with the same products.

The capabilities of the new non-toxic pigments were then further explored beyond mere replacement of chromates, with computer-aided formulation being used to generate suggested starting paint formulas intended to ensure profitable use of the new pigments.



O. Leblanc

#### Biography

Oscar Leblanc, born in Toulouse in 1948, is a Chemical Engineer graduate of the Polytechnic University of Catalonia.

His first contact with the world of colour – and Britain – was in 1966 when

being a student, he spent a few months as a trainee at the laboratories of L. B. Holliday & Co in Huddersfield.

He joined Colores Hispania, S.A. in 1971, soon to become Manager of the Applications Laboratory and, since 1981, Deputy Director for New Developments. In these positions he has been sharing his time between extensive travelling for customer service and laboratory based development of new products, with colour measurement on the one hand and anticorrosive pigments on the other as his main focuses of interest.

He has been the author of several presentations to technical meetings, in Spain and other countries, sharing authorship with colleagues from Colores Hispania to 8 published papers so far. He stands also as one of the inventors in 5 patent applications, mostly concerned with anticorrosive pigments.

He has been serving for 12 years now on the Technical Committee of The European Manufacturers of Lead Chromate and Lead Molybdate Pigments, and also on the Steering Committees of some of the research projects on anticorrosive pigments and paints of the Paint Research Association, of which Colores Hispania have been members for 23 years.

Oscar Leblanc is an ordinary member of the Oil and Colour Chemists' Association.

## OCCA CONFERENCE 1989

### “Profitable Research and Development”

### Chester Grosvenor Hotel 21-24 June 1989

### For further details refer to the regular Conference Column in JOCCA on p. 2



## Russel to acquire Granyte

McLeod Russel has secured a recommendation from the board of Granyte Surface Coatings on its offer of £18.2m for Granyte, the UK market leader in industrial wood finishes. This follows on from interim results showing operating profit at £0.84m, up 12%. Granyte has recently successfully launched the intumescent flame retardant paint 'Flamebloc' onto the market. In July, Granyte signed an exclusive licensing agreement with the Italian company OECE Industrie Chimiche Spa to manufacture and market a range of advanced UV curable clear and pigmented coatings.

## PPG acquires European auto refinish business

PPG Coatings and Resins Group has agreed to purchase the automotive refinish business of Sweden's Casco Nobel AB, carried out under the trade names Sadolin and Nordsjo. Acquisition of the business, which has annual sales approaching US\$10m, is to be completed on 1 January. No production operations are involved with the purchase.

Sadolin auto and fleet refinish materials are sold in Denmark, Finland, Great Britain, Ireland, Norway and Sweden, and exported outside Europe. Nordsjo products are sold throughout Scandinavia. PPG supplies European new-car and auto refinish coatings customers from plants in England, France and Italy.

## Croxton + Garry in Blue Circle merge

Croxton + Garry Ltd ('C+G') UK manufacturer and distributor of fillers and additives, are to merge with the Industrial Minerals Division of Blue Circle Industries Plc, a large manufacturer of calcium carbonate with factories at Melton, near Hull, and Swanscombe, near Dartford, Kent. The merger will be achieved by the acquisition by C+G of the relevant part of the Blue Circle business, which will then be managed by C+G.

## Cookson and Magnesium in joint MIO venture

Cookson Group plc and Magnesium International Corporation Ltd have established a joint venture to manufacture synthetic micaceous iron oxide (MIO) pigment. The manufacturing process utilises patented technology developed by MPLC Laboratories Ltd, owned by Magnesium International Corporation Ltd.

The joint venture has formed an operating company, Cookson Laminox Ltd, and production facilities will be set up on MPLC's existing site at Peterlee, near Durham. Construction of the manufacturing plant will be in three phases with a planned capacity of 10,000 tpa. Production is scheduled to commence towards the end of 1989 with initially 30 jobs created.

MIO pigment is used widely in coatings to protect steelwork against corrosion and is traditionally obtained by beneficiation of natural iron ore. The new synthetic MIO has high chemical purity and improved physical characteristics resulting in outstanding durability and corrosion resistance when incorporated in protective coatings.

The pigment will be marketed under the trade name Laminox® on a worldwide basis.

## Via Gellia in group restructure

Derbyshire based pigment producer Via Gellia Colour Co Ltd is now part of the newly formed Cromford Group. Michael Key, managing director of Hopton Minerals of which Via Gellia is a subsidiary, has become managing director of the new group.

The aim of the group is to manage the long term future development of its six member companies, including Via Gellia, by operating as a management services centre. The subsequent strengthening of the management team at Via Gellia (see People) will allow it to continue to expand at the pace demanded by the growing pigment market.

Via Gellia is involved in the production of pigments, directly for use in the concrete industry but also in plastics, paint, rubber and bitumastic products.



Michael Key

## NL UK Bentone capacity up

NL Chemicals Europe Inc, Brussels and Steeley Minerals Ltd, Worksop, UK, is to increase the production capacity of their jointly-owned subsidiary, Abbey Chemicals Ltd, Livingston, Scotland, by 50%. Work on the expansion project is already in hand and the extended capacity will be in operation by mid-1989.

Abbey Chemicals produces the well-known NL Chemicals range of Bentone organoclay rheological additives, widely used in the paint and surface coatings industries, as well as in plastisols, ink, grease and cosmetics, for thickening, anti-settling, anti-sagging and flow-control.

Abbey Chemicals has for some time been engaged in a programme to obtain registration under British Standard 5750 Part 2 - Quality Systems. This is also expected to be complemented in 1989.

## Courtaulds £19m offer for Taubmans

Courtaulds today announced a £19m offer for the minority interests in Taubmans Industries Ltd. Taubmans is an Australian-listed company 56% owned by Courtaulds. The offer values Taubmans at £43.5m. Its principal activities are the development, manufacture and marketing of high

quality paint and coatings for the protection and decoration of surfaces against wear, weather and corrosion. Taubmans is a leading manufacturer of paint and coatings for the Australasian and South Pacific markets with subsidiaries in Australia and New Zealand and associated companies in Papua New Guinea and Fiji.

## Products

### Exxon introduce PU sealant plasticiser

**E**xxon Chemical has just introduced a non-reactive plasticiser offering several advantages to producers of polyurethane sealants used in construction, glazing, protective coatings and road surface materials. Called Actrel 400, the plasticiser offers increased life, lower addition ratios, better moisture resistance, lower drying times, and good tensile strength and hardness properties. In addition, the product has low viscosity and is water-white.

*For further information Enter A101*

### New flattening agent

**P**PG Industries (USA) has introduced a new silica flattening agent, with broad application in coatings, which allows manufacturers to meet tough environmental standards of low volatile organic content (VOC) coatings and still get exceptional flattening performance without viscosity buildup.

*For further information Enter A102*

### Improved repair aids

**S**onneborn & Rieck's repair aids for finishes damaged during or after manufacture have been enhanced by the introduction of an improved 'Jaxa Repair Paint Box'. Using the new formulation repairs dry to a matt finish which reduces the level of hand work needed to complete the repair. The matt finish also makes it easier for the colours to be applied and blended to the required effect. *For further information Enter A103*

## Radiation curing in Japan

**D**uring 8-27 October 1988, John Bernie of the PRA headed a five-man team on a DTI-sponsored Overseas Technical Mission to investigate radiation curing in Japan. Other members of the group – all specialists in the field – including Prof R. B. Cundall of Salford University and, representing industry, Mr Peter Elliott from Coates Brothers, Dr Robert Head from ICI and Dr Sharif Salim from Harcros Chemicals.

The team's punishing schedule, which took them to Osaka, Kyoto, Fuji City, Nagoya, Yokohama, Hiratsuka and, of course, all over Greater Tokyo, involved a dozen individual visits to key companies as well as to Tokyo University. Kansai Paint, Dainippon Ink & Chemicals, Toagosei, Mitsubishi Rayon and both Nisshin and Nippon Steel were among the well-known names on their list. In addition, they took the opportunity to attend the Rad Cure '88 Conference in Tokyo with a view to deepening the contacts with leading personalities in the field.

The Mission's objectives were two-fold: first, to explore the potential for scientific co-operation between the UK and Japanese organisations and, second, to promote among senior representatives of British industry a greater awareness of the latest technical advances made in Japan in this area. In the event, the visit has proved successful on both counts.

The team, which gained considerable insight into Japan's commitment to radiation curing and to R & D in general, will present its findings at a special seminar in London, to be organised by PRA on 21 February 1989.

For further information, contact John Bernie on 01 977 4427.

## Equipment

### Cost-cutting UV drying

**T**he French company G2M has developed a range of ultra-violet drying equipment to replace traditional thermal techniques. Large companies like Peugeot and Thomson are already using UV drying.

For standard industrial application, G2M uses electrode lamps which generate UV radiation by passing an electric arc through a tube filled with a rare gas and mercury. The tubes can be as large as 2.1 m with a power output of between 80 and 120W/cm.

*For further information Enter A104*

### New Reedtainer range

**A** new range of lightweight all-plastic cans, ideal for packaging a wide variety of products, has been launched by Reed Plastic Containers. Initial sizes in the range, called "Reedtainer", are 2.5-litre and 5-litre cans.

*For further information Enter A105*

## Literature

### Literature miscellaneous

"The 1989 ASTM Directory of Testing Laboratories". Featuring 1,100 laboratories, contacts and telephone numbers. 1989. Price \$50.00. ASTM European Office.

*For further information Enter A106*

"The Adhesives Directory 1989" (ISSN 0305-3199) 264pp. Price £14.50 (incl p+p). Publ: Turret Group.

*For further information Enter A107*

Data Sheets on UV and IR drying. Wallace Knight Ltd.

*For further information Enter A108*

"ELP-3. The new epoxy modifier from Morton Thiokol" and "LP™ – polysulphide modified epoxy resins for superior adhesion, corrosion protection and flexibility".

*For further information Enter A109*

AICHE Equipment Testing Procedures. "Mixing Equipment – Impeller Type". 2nd Edition. 1987 40pp. ISBN 0816904391. £13.

*For further information Enter A110*

# News

## PA Careers literature

The Paintmakers have published a 4 page 4 colour card entitled "The Colourful World of Paint" together with a 10 page Careers leaflet dealing with all aspects of the Paint Industry. For further information contact the PA on 01-582 1185.

## Meetings

### Powtech exhibition

The 14th international powder, granule and bulk solids technology exhibition will be held at the G-Mex Centre, Manchester, on 28 February-2 March 1989. The Institution of Chemical Engineers will hold five one day short courses from 27 February-3 March on Mixing Powders, Bulk Powder, Testing, Classification of Powders, Particle Degradation in Industrial Processing. For further information contact M. K. Little (on the exhibition) and C. H. R. Hopkins (on the courses) on 0883 716244.

### Quality conference

The Metal Finishing Association will be holding a one day conference on "Quality Assurance in Metal Finishing" at the Crest Hotel, Bristol, on Wednesday, 22 February 1989. For further information call 021-236 2657.

## People

### Via Gellia

Several new appointments have resulted from the restructuring as mentioned in the News this month.

**John Middleton** has been appointed the Company Secretary/Accountant for both Hopton Minerals and Via Gellia. Mr Middleton joined Hopton in 1987 as group financial controller from the Sheffield based alloy and metal traders Tennant Metallurgical.

1989(1)

**Nigel Venn** has been appointed Sales Manager. He joins Via Gellia from pigment blender Procter Johnson and Co Ltd of Flint in North Wales, with experience in the colour, chemical and concrete industries.



Nigel Venn

**Michael Ramsden** has joined the company as General Manager, from pigment distributor H. Haeffner and Co, with wide experience in the pigment industry

### Floridienne appointment

Floridienne (UK) Ltd have appointed **Bob Platts** as Sales Development Manager. He will be responsible for developing sales of Pigments, Resins and Specialised Additives in Northern UK, Scotland, France and Italy. Mr Platts has 25 years' experience in the surface coatings industry - latterly with Bonar Cole Polymers Ltd. Previously he was with Blagden Campbell Chemicals Ltd.

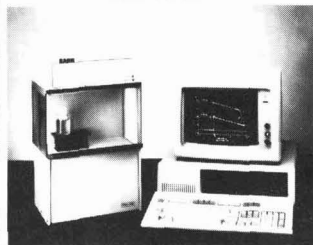


Bob Platts

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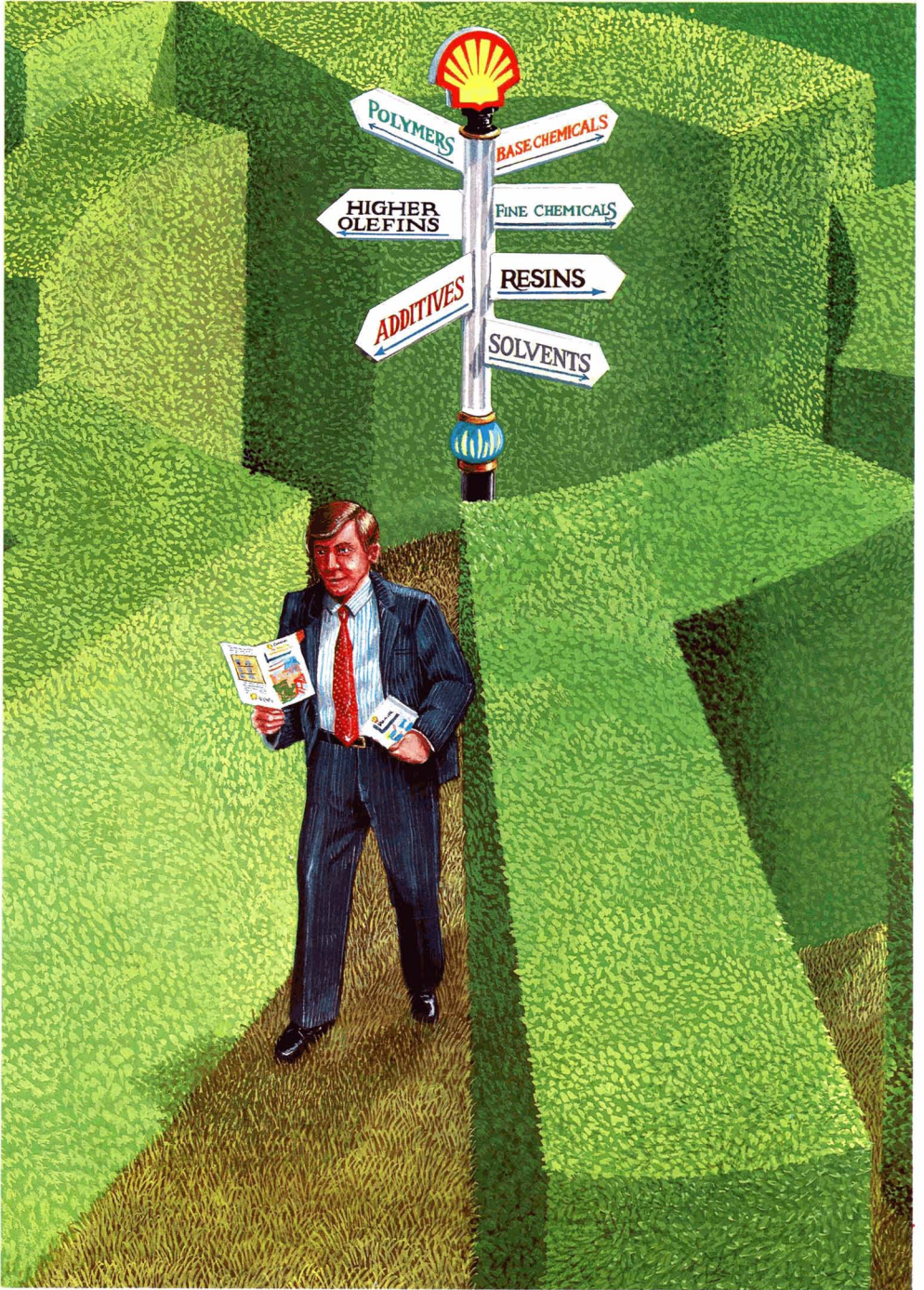
**HIGH PERFORMANCE FIBRES:** Characterise fibre wettability and fibre/plastic interface bonding by surface energy and work of adhesion analysis.

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For further information contact: Scientific & Medical Products Ltd 856 Wilmslow Road, Didsbury Manchester M20 8RX Tel: 061-434-3466 Fax: 061-445-2943 Telex: 668417 Shirly G



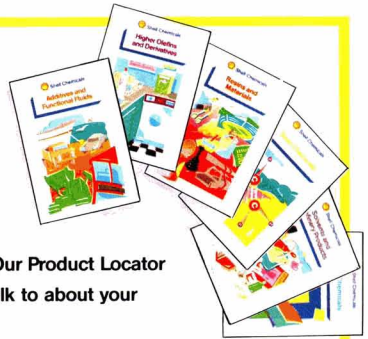
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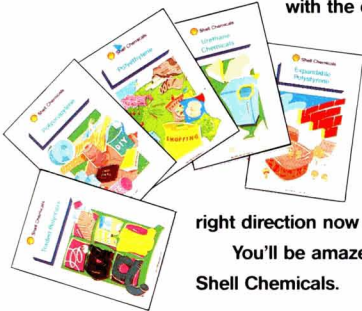
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# The analysis of surface coatings by dynamic mechanical thermal analysis and dielectric thermal analysis

by G. J. Bratton\*, E. A. Wasson, J. W. Nicholson\*\* and A. D. Wilson,  
Materials Technology Sub-division, Laboratory of the Government  
Chemist, Department of Trade and Industry, Cornwall House, Waterloo  
Road, London, SE1 8XY, UK

## Summary

A preliminary study has been made using Dynamic Mechanical Thermal Analysis (DMTA) to examine the curing characteristics, mechanical properties and structure property relationships of commercially available surface coatings, ranging from alkyd paints to butadiene-styrene latices.

The results from DMTA have been compared with those obtained by Dielectric Thermal Analysis (DETA), and the glass transition temperatures ( $T_g$ 's) obtained by both techniques have been shown to be in reasonable agreement. This is despite a difference in the analysis frequency of the two techniques of 100-1000 fold, DMTA being applied at 1 and 10 Hz and DETA at 1592 Hz.

The factors which affect the analysis of surface coatings by DMTA have been investigated. Substrate thickness and type and condition of the coating are the main factors affecting the analysis. There also appears to be a correlation between the measured  $T_g$  and adhesion of the coating to the substrate.

The technique of DMTA has also been used to demonstrate that glass transition temperature may differ appreciably from Minimum Film Formation Temperature (MFFT) in latices.

## Introduction

Dynamic Mechanical Thermal Analysis (DMTA) is a technique which measures storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of materials<sup>1-3</sup>. The ratio of these moduli,  $\tan \delta$ , varies with temperature and reaches a maximum at the glass transition temperature of the

sample.  $T_g$ , so that DMTA is a convenient way of evaluating this property. Since DMTA measures the variation in mechanical properties with increasing temperature, it is also able to give an insight into such features as crystallinity, crosslinking and molecular aggregation in polymeric samples.

The analysis of surface coatings by DMTA has received very little attention in the past. The aim of the work described in this paper was to investigate a range of commercially available surface coatings, studied both attached to substrates and as free films, in order to ascertain the usefulness of the technique. In addition the DMTA results have been compared with those obtained using dielectric thermal analysis, DETA, in order to assess the relative merits of the two techniques.

DETA may be regarded as complementary to DMTA. DETA measures changes in conductance and capacitance of polymeric materials with increasing temperature<sup>4-6</sup>, the ratio of which is also known as  $\tan \delta$ . Again, peaks in  $\tan \delta$  have been used as a measure of glass transition temperature. DETA has previously been used to study a number of features of interest in surface coatings, including the effect of various grades of titanium dioxide pigment on the cure of epoxy powder coatings<sup>5</sup>.

## Experimental

### Materials

The coatings studied are listed in Table 1.

### Sample preparation

(a) Free Films: Free films were examined by DMTA only. They were

prepared by coating onto poly(tetrafluorethylene) or poly(ethylene) sheets using a 100  $\mu$ m drawing bar "K Hand Coater" (ex. RK Print-Coat Instruments Ltd) and cured at room temperature for 24 h. The dried films were readily removed from the sheets for analysis.

(b) Coatings: Prepared for DMTA, the formulations were coated onto one side of a metal substrate, typically aluminium 0.13 mm thick, using a 100  $\mu$ m drawing bar and cured at room temperature for 24 h.

For DETA, the formulations were coated onto one side of tinplated steel 0.20 mm thick using a 100  $\mu$ m drawing bar and cured at room temperature for 24 h.

## Instrumentation

1. DMTA: A Polymer Laboratories DMTA was used coupled to a Hewlett Packard 9121 micro computer, with single and dual cantilever clamping arrangements.

The samples were analysed under the conditions shown in Box 1.

2. DETA: The apparatus for DETA was built at the Laboratory of the Government Chemist, to a specification previously published<sup>5,7</sup>, a schematic diagram of which is shown in Figure 1 (a) and the sample rig arrangement is shown in Figure 1 (b).

The samples were analysed under the conditions shown in Box 2.

The samples were analysed in triplicate for both DMTA and DETA.

## Results and discussions

### Substrate and sample parameters

In both DMTA and DETA the coating needs to be uniform upon the substrate; any discontinuity, such as pinholes, air bubbles or unevenness, causes problems especially in DETA where air gaps between the two electrodes affect the capacitance of the system and produce a temperature gradient across the sample. In DMTA, if the sample is discontinuous, accurate modulus readings are difficult to obtain.

The relationship between the measured glass transition temperature ( $T_g$ ) and different substrate parameters, ie. thickness and type, have been studied:

1. Thickness of Substrate: The results in Table 2 demonstrate that the thickness of the substrate had a

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\*\* To whom any correspondence should be sent.

**Table 1**  
Coatings samples studied

Sample	Supplier	Binder type
1 White Gloss Paint	ICI	Soya bean oil alkyd
2 White Gloss Paint	Macphersons	Vegetable oil alkyd
3 White Enamel	Humbrol	Drying oil alkyd
4 White Model Paint	Humbrol	Drying oil alkyd
5 "Polished Steel" Colour Metal Paint	Humbrol	Acrylic copolymer
6 White Artists Paint	Windsor & Newton	Drying oil
7 "Glascol 616E"	Allied Colloids	Acrylic latex
8 "Emultex VV530"	Harco Emulsions	Acrylic latex
9 "Intex 164"	Enichem	Butadiene:styrene latex (ratio=3:1)
10 "Intex 166"	Enichem	Butadiene:styrene latex (ratio=2:1)
11 "Intex 178"	Enichem	Butadiene:styrene latex (ratio=3:1)
12 "Intex 1493"	Enichem	Butadiene:styrene latex (ratio=3:1)
13 Clear lacquer	International Paint	Epoxy-phenolic
14 Nail polish "Constance-Carroll"	Bawnmore	Nitrocellulose copolymer

**Box 1**

**DMTA: Sample analysis conditions**

temperature range:  $-100^{\circ}\text{C}$  to  $+200^{\circ}\text{C}$   
 heating rate:  $1\text{-}5^{\circ}\text{C}/\text{min}$   
 frequency: —free films/single frequency scan= $1\text{ Hz}$   
 —coatings/single frequency scan= $10\text{ Hz}$   
 displacement: —free films= $16\text{ }\mu\text{m}$   
 —coatings= $32\text{ }\mu\text{m}$   
 sample dimensions: —free film: free length= $1\text{ mm}$   
 width= $10\text{ mm}$   
 thickness= $0.04\text{-}0.10\text{ mm}$   
 (depends on sample)  
 —coating: free length= $2\text{ mm}$   
 width= $10\text{ mm}$   
 thickness= $0.17\text{-}0.44\text{ mm}$   
 (depends on sample and substrate)

**Box 2**

**DETA: Sample analysis conditions**

temperature range:  $-50^{\circ}\text{C}$  to  $+200^{\circ}\text{C}$   
 heating rate:  $7^{\circ}\text{C}/\text{min}$   
 frequency:  $1592\text{ Hz}$   
 sample dimensions: length= $80\text{ mm}$   
 width= $10\text{ mm}$   
 thickness=depends on sample and substrate

profound effect upon the temperature at which the measured  $T_g$  occurred. As the thickness of the aluminium substrate was increased the  $T_g$  appeared to increase, from  $11.8^{\circ}\text{C}$  with  $0.13\text{ mm}$  thick substrate to  $38.9^{\circ}\text{C}$  when the substrate was  $0.34\text{ mm}$  thick. This was accompanied by a higher degree of peak broadening in the  $\tan \delta$  peak. The increase in the measured  $T_g$  with increasing substrate thickness is not due to thermal lag effects, since analysis at

different heating rates ( $1\text{-}5^{\circ}\text{C}/\text{min}$ ), for the largest substrate thickness ( $0.34\text{ mm}$  aluminium), gave similar results ( $+ \text{ or } -0.4^{\circ}\text{C}$ ). Thus, the sample and substrate parameters were shown to influence the value of the measured  $T_g$  obtained. The absolute  $T_g$  value can be obtained from the results by extrapolating to zero substrate thickness; for the above example, the value is  $6.1^{\circ}\text{C}$ . This figure does not agree with the  $T_g$  value obtained for the free film

( $15.4^{\circ}\text{C}$ ), and requires further investigation.

The change in effective elastic modulus was also found to vary with substrate thickness over the  $T_g$  region, decreasing from  $0.281\text{ Pa}$  with  $0.13\text{ mm}$  aluminium to  $0.048\text{ Pa}$  with  $0.34\text{ mm}$  aluminium. This effect would be expected since the overall modulus of the sample is some function of the modulus of the coating plus the modulus of the substrate. Therefore the thicker the substrate, the greater the contribution from the substrate. For DETA, by contrast, the sample and substrate thickness were not found to affect the position of the observed  $T_g$ . However, the sensitivity of the technique did increase when a thinner sample was used. This is due to a larger capacitance output being available for measurement with thinner samples, which in turn gives better quality relaxation data.

2. Type of Substrate: Substrate thickness was not the only factor found to affect the measured  $T_g$  and effective modulus results obtained by DMTA. The type of substrate used also affected these parameters. As can be seen in Table 3, substrates of similar thicknesses, ie aluminium ( $0.26\text{ mm}$ ) and tinplate ( $0.20\text{ mm}$ ) gave different measured  $T_g$ 's and different changes in effective modulus over the  $T_g$  region. Therefore, when quoting  $T_g$  figures for coatings the type of substrate must also be stated. With DETA, however, the type of substrate used was found to have no effect on the position of the measured  $T_g$  peak.

**Analysis of commercially available coatings**

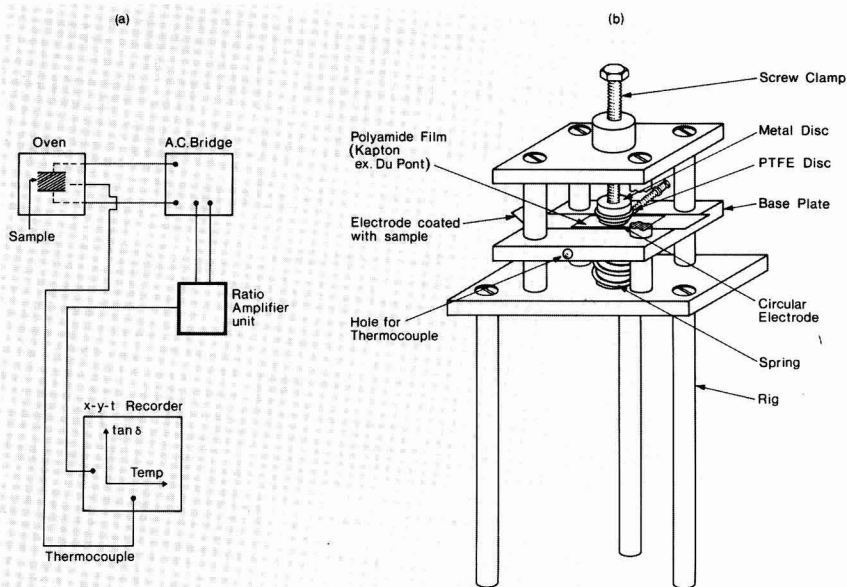
A variety of formulations, latices, epoxy and nitrocellulose coatings were analysed by both DMTA and DETA:

1. Paint Systems: The DMTA spectrum of a typical alkyd paint system is shown in Figure 2. Due to the small quantity of coating present, the only clearly discernible transition is the one due to the  $T_g$  of the sample.

The analysis of paint systems by DMTA shows that different values of  $T_g$  are obtained if the sample is analysed as a free film or as a coating on aluminium substrate. Both of the alkyd gloss paints showed higher measured  $T_g$ 's when coated onto a substrate, whilst the oil paint had a higher  $T_g$  when analysed as a free film, as the results in Table 4 show. This difference is too large to be attributable to either "end effects", produced by poor clamping, or to the difference in analysis frequencies of the free film ( $1\text{ Hz}$ ) and the coating ( $10\text{ Hz}$ ); the difference in frequency would only

**Figure 1**

(a) Schematic Diagram of DETA. (b) The Sample Rig for DETA



**Table 2**

The effect of aluminium substrate thickness on the analysis of Enichem - Intex 1493 Latex by DMTA (Wet-film thickness=100  $\mu\text{m}$  in each case)

Aluminium Substrate (mm)	T <sub>g</sub> (°C)	DMTA Change in * log E'
0.13	11.8	0.281
0.26	24.4	0.074
0.34	38.9	0.048

\* Log E' = The Log of the Storage Modulus (E').

**Table 3**

The effect of different substrates on the analysis of Enichem Intex 1493 Latex by DMTA (Wet-film thickness=100  $\mu\text{m}$  in each case)

Substrate Type	Thickness (mm)	T <sub>g</sub> (°C)	DMTA Change in log E'
Aluminium	0.26	24.4	0.074
Tin-plate	0.20	36.7	0.047

increase a measured T<sub>g</sub> of approximately 50°C by 2-7°C<sup>8</sup>. There appears to be a correlation between the direction of shift in measured T<sub>g</sub> and adhesion of the coating to the substrate. The alkyd paint adhered well (could not be removed by finger rubbing), and its measured T<sub>g</sub> was approximately 20°C

higher as a supported film: the oil paint did not adhere well (could be removed by finger rubbing), and its measured T<sub>g</sub> was about 15°C lower on the substrate. However, the origin of this phenomenon is obscure, and it requires further investigation. The DETA results were similar to the larger

measured T<sub>g</sub> value obtained for samples analysed as either free films or coatings by DMTA; although there is an anomaly with number 6 (the white artists oil paint), which may be due to the poor condition of the coatings obtained with this material.

The measured T<sub>g</sub> value from DETA analysis should be higher than that obtained by DMTA analysis due to the much higher frequency used in DETA and analysis (DMTA 1-10 Hz, DETA 1592 Hz)<sup>9</sup>.

2. Latices: The results obtained by DMTA and DETA for various latices are shown in Table 5. No relationship was apparent between T<sub>g</sub> of the film and the butadiene:styrene ratio (see Table 1) of the binder. The different mechanical properties for seemingly similar latices may be due to various differences in the latex formulations, including particle size and coalescing agents. This would benefit from further study. Film formation by latices is known to be temperature dependent<sup>10</sup>, and there is a minimum temperature below which film formation will not occur. Until recently, workers have assumed that Minimum Film Formation Temperature, MFFT, is closely related to the T<sub>g</sub> of the polymer<sup>11</sup>. From the T<sub>g</sub>'s of the commercially available latices shown in Table 5 and the MFFT values (supplied by the manufacturers) shown in Table 6 this is obviously not the case. The important difference



between MFFT and  $T_g$  is that MFFT is a property of the entire two-phase latex formulation, whilst  $T_g$  is a property of the polymer phase only<sup>12</sup>. However, factors which affect  $T_g$  also have the same effect on MFFT<sup>13</sup>, although the relationship can be a complex one<sup>14</sup>.

3. Epoxy and nitrocellulose coatings: An epoxy can lacquer and a nitrocellulose nail varnish were analysed by both DMTA and DETA, and the results shown in Table 7. Again the DETA results are in closer agreement with the higher of the two measured  $T_g$  values by DMTA, as mentioned previously.

#### Isothermal curing

DMTA can also be used to study the curing characteristics of polymers at a fixed temperature. With the DMTA in the isothermal mode, the effective elastic modulus of the coating under investigation was found to increase with time up to a limiting value. The time taken to reach this point may be taken as the cure time for the coating at that particular temperature. An example is shown in Figure 3, using isothermal conditions at 50°C to cure one of the alkyd gloss paints (ex. ICI; coated on aluminium); under these conditions, this paint took 97 minutes to cure. Obviously at higher temperatures this time would be expected to decrease.

#### The effect of cure temperature on $T_g$ by DETA

Increasing the cure temperature was found to increase the resulting measured  $T_g$  of the coating, as illustrated by the results in Table 8. At 20°C one of the gloss finish alkyd paints took 1440 minutes (24 h) to cure and had a relatively low  $T_g$  (42.8°C). Curing at 50°C for 90 minutes increased the resulting  $T_g$  to 77.7°C while increasing the temperature still further resulted in even higher  $T_g$ 's, until at 200°C for 10 minutes the  $T_g$  reaches 88.5°C. Above 200°C the coating started to undergo thermal degradation.

#### Conclusion

The results show that DMTA is a technique that can give useful information about the cure characteristics and mechanical properties of surface coatings. Such samples have not been studied to any extent previously by this technique. Film quality is important when studying these samples since bubbles and other inhomogeneities in the films affect reproducibility of readings. The present study has shown that the position of the measured glass transition temperature is affected by

**Table 4**  
DMTA and DETA analysis of paint systems

Sample	DMTA		Al Substrate (0.13 mm)		DETA
	Free Film $T_g$ (°C)	Change in $\log E'$	$T_g$ (°C)	Change in $\log E'$	$T_g$ (°C)
1 White Gloss Paint (ICI)	23.3	0.631	43.5	0.112	42.8
2 White Gloss Paint (Macphersons)	36.8	1.653	47.7	0.135	50.9
3 White Enamel*	—	—	(a) 9.6 (b) 53.4	0.049 0.051	10.1 59.1
4 White Model Paint*	—	—	(a) 30.6 (b) 71.3	0.058 0.049	37.2 80.6
6 White Artists Oil Paint	-5.3	1.288	-19.2	0.266	-20.9

\* Films too fragile to analyse; supported films gave two transitions.

**Table 5**  
DMTA and DETA analysis of commercially available latices

Sample	DMTA		Al Substrate (0.13 mm)		DETA
	Free Film $T_g$ (°C)	Change in $\log E'$	$T_g$ (°C)	Change in $\log E'$	$T_g$ (°C)
7 "Glascol 616E"	(i) 40.4 (ii) 59.2	1.019 0.520	21.5 54.6	0.030 0.043	25.7 46.5
8 "Emultex VV530"	32.6	1.903	36.6	0.113	31.8
9 "Intex 164"	-0.8	1.531	3.1	0.095	2.8
10 "Intex 166"	24.2	0.899	33.6	0.063	20.2
11 "Intex 178"	14.1	1.398	31.6	0.131	19.5
12 "Intex 1493"	15.4	1.267	11.8	0.281	12.4

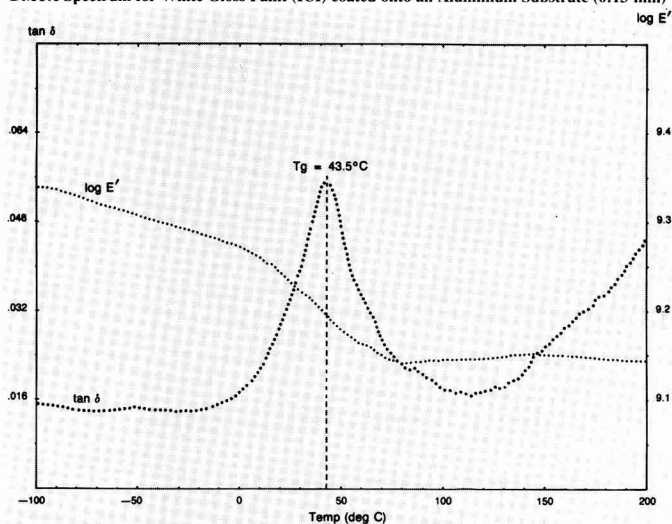
**Table 6**  
Minimum film formation temperature (MFFT) of commercially available latices

Sample	Free Film $T_g$ (°C)		Al Substrate (0.13 mm) $T_g$ (°C)		MFFT (°C)
	7 "Glascol 616E"	(i) 40.4 (ii) 59.2	32.6	(i) 21.5 (ii) 54.6	36.6
8 "Emultex VV530"	32.6	36.6	3.1	3.1	8
9 "Intex 164"	-0.8	3.1	3.1	3.1	20-25
10 "Intex 166"	24.2	33.6	33.6	33.6	20-25
11 "Intex 178"	14.1	31.6	31.6	31.6	20-25
12 "Intex 1493"	15.4	11.8	11.8	11.8	20-25

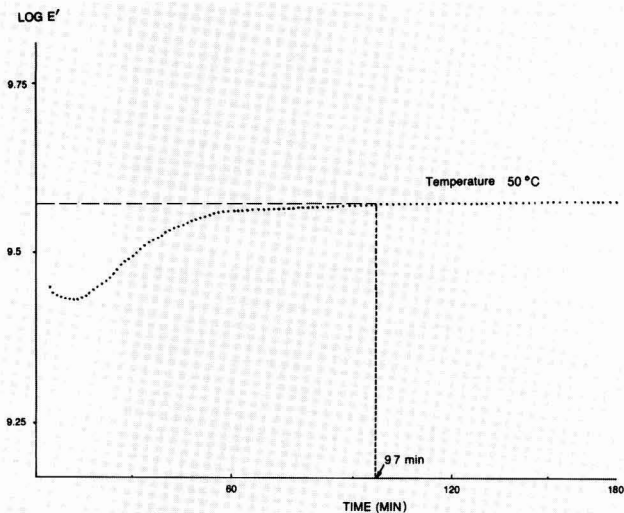
**Table 7**  
DMTA and DETA analysis of epoxy phenolic and nitrocellulose coatings

Sample	DMTA		Al Substrate (0.13 mm)		DETA
	Free Film $T_g$ (°C)	Change in $\log E'$	$T_g$ (°C)	Change in $\log E'$	$T_g$ (°C)
13 Clear lacquer	27.9	1.224	21.3	0.077	26.1
14 Nail polish "Constance-Caroll"	66.3	1.311	52.77	0.148	67.2

**Figure 2**  
DMTA Spectrum for White Gloss Paint (ICI) coated onto an Aluminium Substrate (0.13 mm)



**Figure 3**  
Isothermal Curing of White Gloss Paint (ICI)



**Table 8**  
The effect of cure temperature on the glass transition temperature (Tg) of white gloss alkyd paint (ICI) by DETA

Cure Temperature (°C)	Cure Time (a) (min)	Tg (a) (°C)	Cure Time (b) (min)	Tg (b) (°C)
20	1440	42.8	—	—
50	90	77.7	120	82.9
100	10	78.2	30	87.8
150	10	80.2	30	84.7
200	10	88.5	30	105.1

both the nature and thickness of the substrate. In addition, the difference in values between free and supported films could possibly be utilised to predict coating adherence to the substrate. Coatings which adhered well to substrates gave higher glass transition temperatures when on the substrate than when studied as unsupported films, whereas coatings which adhered poorly gave a higher value of Tg when analysed as free films. However, the origin of this phenomenon is obscure, and it requires further investigation.

The technique of DMTA has also been used to demonstrate that Tg and MFFT of latices are quite different, despite being influenced by the same molecular features.

Finally, the values for measured Tg found by DETA were in reasonable agreement with those obtained using DMTA. As a technique, DETA offers some advantages over DMTA, for example, in not giving Tg peaks which are influenced by the particular substrate used. Conversely, it is more susceptible to problems of non-uniformity of coatings than DMTA.

#### Acknowledgements

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# New applications of gas chromatography in the field of paints and varnishes

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## Summary

Some new applications of gas chromatography in the field of paints and varnishes are reviewed and examples of their application reported. These applications include the determination of the polymer binder transition temperature, cross-linking kinetics and solubility even at the infinite dilution of solvents in the polymer.

## Introduction

Gas chromatography is well-known as a powerful analytical technique for the detection of residual solvents and monomers in polymers and can be successfully used as a means of characterization of physico-chemical and transport properties of polymers. To this end, it was applied using a special procedure known as "inverse chromatography"<sup>1</sup>. In this framework, it has proved to be a profitable tool for the determination of polymer compatibility, of transition temperatures and the influence of plasticizers on these temperatures, for the investigation of the curing kinetics of thermo-setting binders, the thermal stability of films and the evaluation of diffusion coefficients etc. Moreover, inverse chromatography makes it possible to obtain an insight into the situation developed within the films by the last traces of solvent still entrapped at the end of the drying stage of the solvent release process. Therefore, information about solvent solubility in polymers, in conditions of infinite dilution of the solvent, can be evaluated.

This paper gives a brief review of the theoretical principles on which inverse chromatography is based.

Examples of its application to binders for HS coatings and for general industrial use, available in literature, are cited. New data concerning an acrylic/melamine system to be employed as binder for HS industrial enamels are presented.

## Theoretical background

Gas chromatography is based on the partition of a solute between a stationary phase, which can be either a solid (GSC) or a liquid (GLC), and a mobile phase (an inert gas, i.e. the carrier gas). The retention time of a solvent (GC solute) in the column and the retention volume, deduced from it, are governed by the distribution of the GC solute between the two phases. According to<sup>2,3</sup> the specific retention volume  $V_{g,i}^0$  of the "i" GC solute is related to the operative conditions as given in Equation 1, where  $F_a$  is the flow rate of the carrier gas, measured with a flowmeter at the temperature  $T_a$ ;  $J_{2,3}$  is the compressibility factor of the mobile phase, assumed to be an ideal gas;  $P^0$  is the atmospheric pressure in the flowmeter, corrected for the vapour pressure of the aqueous solution at the temperature  $T_a$ ; ( $P_{H_2O}$ ),  $t_r$  and  $t_a$  are the retention times of the solute and the air in the column, respectively,

$$V_{g,i}^0 = \frac{F_a}{W} J_{2,3} \frac{P^0 - P_{H_2O}}{760} \frac{273}{T_a} (t_r - t_a) \quad [1]$$

$$\ln \gamma_i^\infty = \ln \frac{273R}{p_i^0 V_{g,i}^0 M} - \frac{p_i^0}{RT} (B_{i,i} - V_i) \quad [2]$$

$$\ln \Omega_i^\infty = \ln \frac{273R}{p_i^0 V_{g,i}^0 M_i} - \frac{p_i^0}{RT} (B_{i,i} - V_i) \quad [3]$$

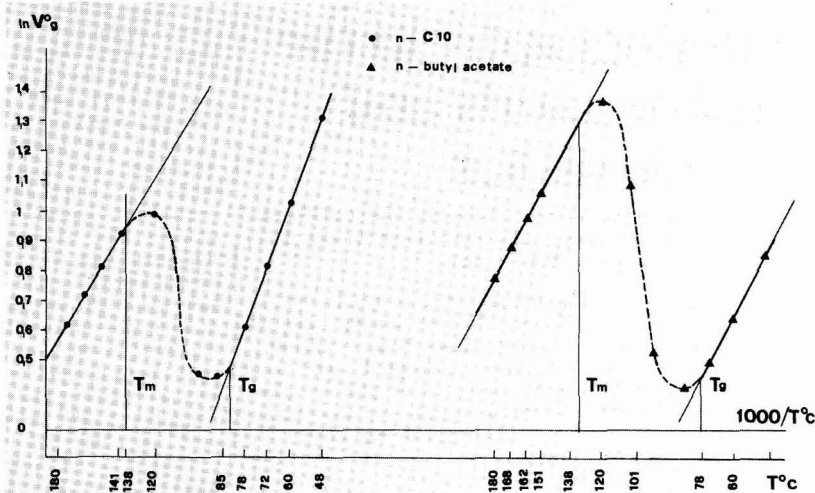
and  $W$  is the weight of the stationary phase in the column. If the mutual solubility between the mobile phase and the stationary phase is considered negligible and the interactions between the solute and the mobile phase are those of the binary mixture solute/carrier gas at the same temperature, then the specific retention volume of the solute will depend mainly on the interactions between the injected solvent (GC solute) and the stationary phase (GC solvent). GC solvent and GC solute can also be polymer/solvent mixtures. In this case, useful information can be obtained on the physico-chemical state and properties of a polymer under various conditions of temperature. The polymer is laid down as a thin film on an inert support in a GC column and a number of solvents of carefully selected properties are injected. The specific retention volumes are evaluated as described above. From this, the activity coefficients "at infinite dilution" of the "i" solvent in the polymer can be deduced, according to Equation 2, where  $M$  is the molecular weight of the stationary phase  $p_i^0$  is the vapour pressure of the "i" solute,  $V_{g,i}^0$  its specific retention volume,  $V_i$  its molar volume and  $B_{i,i}$  its second virial coefficient.

When the stationary phase is a polymer of unknown molecular weight, a "ponderal activity coefficient at infinite dilution" is calculated. The relationship between  $V_{g,i}^0$  and the ponderal activity coefficient at infinite dilution  $\Omega_i^\infty$  is shown by Equation 3, where  $M_i$  is the molecular weight of the solute<sup>2,4</sup>.

## Transition temperatures

The polymers used in industrial practice are of the amorphous type,

**Figure 1**  
 $\ln V_g^0 / 1000/T$  for a thermoplastic high-molecular-weight epoxy resin.



with secondary transition temperatures. Most important among them is the glass transition temperature ( $T_g$ ) at which all the physical and mechanical properties (including retention properties), undergo an abrupt change. Braun and Guillet<sup>2</sup> have demonstrated that transition phenomena are shown by plotting the logarithms of the specific retention volumes versus the reciprocal of the temperature. For polymers with a  $T_g$  and a  $T_m$  these plots often show typical Z-shaped curves. A linear behaviour is found below  $T_g$  (the solute is absorbed by the polymer) and above  $T_m$  (the solute is distributed between the liquid phase and the gas phase). Between the two straight sections of the curve a mixed solid-liquid non-equilibrium zone is found. Transition temperatures are identified where the curves deviate from straight at the end of the zones of linear behaviour representing equilibria with the stationary phase in the liquid state or glassy state.

An example is shown in Figure 1. Here the polymer under investigation is a high molecular weight epoxy, the solvents injected (GC solutes) are alkanes (n-C 10) and esters (n-butyl acetate). The same technique has been applied to a number of derivatives of the

mentioned epoxy system, obtained by cross-linking the high-molecular-weight epoxy with aliphatic isocyanates. Therefore considerations on the effects of network formation and density on  $T_g$  and  $T_m$  could be developed. This technique has been extended to the evaluation of the effects of copolymerization. Braun reports on the case of styrene-butadiene copolymers<sup>3</sup>. More recently, the authors have investigated an oven-curing acrylic-melamine system, consisting of a combination of an experimental acrylic oligomer VR 4618, an experimental melamine resin VR 4494 and a commercial melamine resin, labelled as 1313544 resin. (These materials are described in the Appendix.) Here, the straight line obtained by plotting  $\ln V_g^0$  versus  $1/T$  between 20 and 180°C suggests that no transition phenomena take place within this temperature range.

From the operative point of view, attention is drawn to some phenomena connected with the thermal cycle, which can be carried out either by heating or by cooling (starting from either low or high temperatures, respectively). In the  $\ln V_g^0$  versus  $1/T$  plots, the Z-shaped curves obtained in the first heating sequence generally lie above the corresponding curves

obtained in the subsequent cooling sequence. The curve of a second heating sequence, on the other hand, reproduces the one of the first cooling sequence. Further sequences show that steady conditions are obtained and it follows that reproducibility is good. These variations are accounted for by the fact that the first heating induces smoothing of the irregularities and evens out the surface of the polymer film laid down on the inert support. In fact, just above  $T_m$ , molecular mobility is sufficient to allow a substantial surface rearrangement to a steady condition to take place, in which adsorption phenomena by the inert support are no longer possible, provided the stationary phase/inert support ratio is correct. This suggests that a complete up and down cycle should be performed and the data obtained in the cooling sequence be considered meaningful<sup>4</sup>. For the last few years, a new gas chromatograph has been available which permits operation at temperatures as low as  $-10^\circ\text{C}$ .

#### Mixture properties – solubility at infinite dilution

The determination of the activity coefficients at infinite dilution for a wider number of solvents of different chemical properties in a

polymer leads to the characterization of its solubility in conditions of infinite dilution, such as are encountered within the films towards the end of the process of solvent release, after application. Here the quality of the solvents plays an important role; good solvents favour the extending, poor solvents the coiling of the macromolecules of the polymer binder.

Coupled with the determination of diffusion coefficients (which can be performed with a GC procedure as well<sup>7</sup>), the application of the above-mentioned technique allows the best-suited solvent mixture composition for a polymer binder to be formulated. An example of characterization of solvent-polymer compatibility at infinite dilution has been reported<sup>8</sup> for a high-molecular-weight epoxy polymer. In this instance, from the infinite-

dilution activity coefficients, determined for 13 solvents, it was possible to characterize the polymer compatibility with the last traces of solvent at the end of the solvent release process by evaluating a "solubility parameter at infinite dilution". Table 1 presents the results of the application of the same technique to the acrylic-melamine ternary system, mentioned above with regard to the determination of the transition temperature. Table 1 shows that the most general solubility domain of the system, referred to the total value  $\delta$  of the solubility parameter at 45°C ranges between 16.5 and 21.5 (the cases of nitromethane,  $\delta=24.5$  and acetonitrile,  $\delta=23.8$  will be discussed separately). The solvents with the lowest  $\ln\Omega_i^\infty$  values, and, hence, the best solvency, methylene chloride and trichloromethane, have a  $\delta$  of 19.3 and 18.3 respectively, just in the

midst of the solubility domain, and very close  $f_{hb}$  values<sup>9,10</sup> 20 and 21. According to the information given by the GC technique, it is found that, in the  $\delta$  range between 16.6 and 19.5, solvency requires  $f_{hb}$  values between 13 and 26, the higher figures being generally associated with slightly lower solvency. Within this framework, the value of  $\ln\Omega_i^\infty$  for ethyl acetate suggests that the old value of 17 for the  $f_{hb}$  is more reliable than the newly-proposed value<sup>10</sup> of 31.  $f_d$  ranges between 60 and 47, with a slight tendency to decrease with decreasing solvency. The behaviour of the aromatics is peculiar. They exhibit higher values of  $f_d$ , between 80 and 90, coupled with "regular" values of  $f_{hb}$ ,  $f_p$  accordingly, being very low. Analogous considerations can be made for carbon tetrachloride, suggesting that, together with  $\delta$ ,  $f_{hb}$  is the main partial parameter describing solvency. In

**Table 1**

System=VR 4618 + VR 4494 + 1313544. 45°C logarithms of the ponderal activity coefficients at infinite dilution  $\Omega_i^\infty$ , total solubility parameter  $\delta$  at 45 and 25°C and per cent components  $f_d$ ,  $f_p$ ,  $f_{hb}$ .

Solvent (GC Solute)	$\delta$	$\delta$	$f_d$	$f_p$	$f_{hb}$	$\ln\Omega_i^\infty$
	45°C	25°C				
Methylene chloride	19.3	19.8	9	21	20	1.33
Trichloromethane	18.3	18.8	67	12	21	1.44
Nitromethane	24.5	25.2	40	47	13	2.08
n-butyl Acetate	16.9	17.4	60	23	17	2.60
Toluene	17.7	18.2	80	7	13	2.63
Methylisobutylketone	17.1	17.6	58	22	20	2.63
Ethyl Acetate	17.9	18.4	51	18(37)*	31(17)*	2.68
Tetrahydrofuran	18.9	19.4	55	19(22)*	26(23)*	2.70
Butyronitrile	20.0	20.5	44	41	15	2.70
Methyl Acetate	18.9	19.4	45	36	19	2.73
Benzene	18.3	18.8	78	8	14	2.78
Propionitrile	21.3	21.9	43	34	23	2.80
Acetonitrile	24.0	24.6	41	43	16	2.87
Methylethylketone	18.5	19.0	53	30	17	2.96
Propanone	19.6	20.1	47	32	21	2.99
Methanol	28.5	29.3	36	18	46	3.20
Ethanol	25.5	26.2	36	18	46	3.24
Carbon Tetrachloride	17.3	17.8	85	2	13	3.24
n-propanol	24.0	24.6	40	16	44	3.30
n-butanol	22.7	23.3	43	15	42	3.30
n-C10	15.4	15.8	100	0	0	4.89
n-C9	15.2	15.6	100	0	0	4.98
Ethylcyclohexane	15.9	16.5	—	—	0	5.21
n-C8	14.7	15.1	100	0	0	5.36
Methylcyclohexane	15.6	16.0	—	—	0	5.69
n-C7	14.9	15.3	100	0	0	5.73
n-C6	14.5	14.9	100	0	0	5.73
Cyclohexane	16.4	16.8	94	2	4	5.83

\* Older values, see References 9 and 10.

this context, both the cases of nitromethane and acetonitrile can be explained. They prove to be good solvents, even with a  $\delta$  slightly higher than 21.4. n-butanol, on the other hand, with a  $\delta$  of 22.5 but a  $f_{hb}$  of 43 is a poor solvent. Thus, the chlorinated paraffins C3 and C4 are poor solvents too. Their  $\delta$  values lie at the lower border of the solubility domain and their  $f_{hb}$  values are as low as 8. Finally, it can be suggested by assigning a 45°C-infinite-dilution solubility parameter to the system having a  $\delta$  between 16.5 and 21.5 with a  $f_{hb}$  between 13 and 26. The best solvency is found for  $\delta$  between 18 and 19.5 with  $f_{hb}$  between 17 and 21. Hence, at 25°C,  $\delta$  ranges between 17 and 22 and, for the best solvency, between 18.5 and 20.

When comparing GC data obtained at 45°C with total- $\delta$  data corrected for the temperature of 45°C, according to references 11-13, it is thought to be acceptable, if working on a semi-quantitative basis is permissible, to employ Teas 25°C data for the "f" components of the solubility parameter. Indeed, by applying the temperature correction for the temperature of 45°C to the 25°C data<sup>14</sup> of the  $\delta$  components, as suggested by Hansen and Beerbower<sup>15</sup>, the variations were very small, the temperature interval being of 20°C only. So, the corrections in the corresponding "f" values would have been practically insignificant for the above-discussed correlations. In other words, we have assumed that the fractional values of the total solubility parameter remain substantially constant over the 20°C range between 25 and 45°C. As examples of this, the partial solubility parameters of n-propanol, butanone, methylene dichloride and trichloromethane at

25 and 45°C are given in Table 2.

### Cross-linking kinetics

The cross-linking process of a thermosetting binder can be profitably investigated by following the variations in its retention properties. To this end, the system is laid down in a GC column as a stationary phase and kept at the curing temperature until constant retention values are obtained. From the operative point of view, the column, charged with the stationary phase is introduced into the gas chromatograph preheated to the curing temperature. After stabilizing the column, a restricted number of solvents (GC solutes) are regularly injected until constant retention times are attained. The logarithms of the specific retention volumes, evaluated from the retention times as reported above, are analysed by a 3-parameter model<sup>16</sup> using Equation 4.

$$\ln V_g^0 = B_1 + B_2 \exp(-B_3 t) \quad [4]$$

Here  $B_1 + B_2$  gives the logarithm of the hypothetical specific retention volume at  $t=0$  and at the curing temperature.  $B_2$  gives the  $\ln V_g^0$  variation brought about by the cross-linking process.  $B_1$  is the final  $\ln V_g^0$  value.  $B_3$  is the kinetic parameter.

This technique has the advantage of making available curing rate data obtained under conditions closely reproducing those of the industrial practice. On the other hand, its application has some limitations when the system under investigation cures at very high rates and temperatures, on account of the length of time necessary for the column to stabilize after introduction into the heated chromato-

graph. In these instances, the initial part of the curing process can hardly be followed.

With this technique, the Authors have been able to describe the curing kinetics of a thermosetting system, made up of an experimental, oil-free alkyd resin + hexamethoxymethylmelamine, suitable as a binder for High Solids, oven-curing enamels. The effects of the variation of the curing conditions, over a wide range of temperatures, and of the addition of accelerators have thus been highlighted<sup>17</sup>. Some results, recently obtained with the above-mentioned complex acrylic-melamine system with regard to transition temperatures and solubility at infinite dilution, are summarized in Table 2. The effects of the temperature in the range between 100 and 130°C and of the presence of either of the melamines and of their mixture were investigated, using C9 as GC solute. Table 3 indicates the strong effect of the curing temperature. The experimental resin VR 4494 cures slightly faster than the commercial product 1313544. As far as the retention properties of the cured system are concerned, the  $B_1$  values give a clear indication that curing at low temperatures leads to the build-up of a less impervious network, while appreciable differences are not detected between the networks developed by the different melamines at the same temperature. To attain a deep insight into the properties of the final network and, in particular, of its solvent resistance, further investigations have been planned, in which the non-polar, "non-solvent" C9 will be replaced by the medium-polarity acetates and polar, highly hydrogen-bonded alcohols.

**Table 2**

Teas' per cent components "f" of the solubility parameter at 25°C (Ref. 9, 10) calculated from Hansens' data (Ref. 15) and at 45°C, calculated from Reference 15 according to References 12 to 14.

Solvent	$f_d$	25°C			45°C		
		$f_p$	$f_{hb}$	$f_d$	$f_p$	$f_{hb}$	
n-propanol	39.80	16.92	43.28	39.87	17.17	42.96	
butanone	53.16	29.90	16.94	53.09	30.20	16.71	
methylene chloride	59.48	20.59	19.93	59.26	20.88	19.86	
trichloromethane	66.92	11.65	21.43	66.85	11.86	21.29	

**Table 3**Coefficients of the equation:  $\ln V^0 = B_1 + B_2 \exp(-B_3t)$ , (n-C9 as GC Solute).

	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	(B <sub>1</sub> + B <sub>2</sub> )	Sum of Squares
System=VR4618 + VR 4494 + 1313544					
130°C	1.54	0.51	7.54	2.05	4.46.10 <sup>-3</sup>
115°C	2.75	0.50	1.04	3.25	1.15.10 <sup>-2</sup>
100°C	3.25	0.36	0.61	3.61	2.54.10 <sup>-2</sup>
System=VR4618 + VR 4494					
115°C	3.01	0.65	1.18	3.66	7.34.10 <sup>-2</sup>
System=VR 4618 + 1313544					
115°C	2.78	0.58	0.63	3.36	3.74.10 <sup>-2</sup>
100°C	3.19	0.38	0.42	3.57	1.44.10 <sup>-2</sup>

This technique has been also used to investigate the thermal stability of both thermoplastic and thermo-setting binders. To this end the binder, laid down as a GC phase in a GC column, is kept in the gas chromatograph at the temperature at which the resistance must be checked and the retention times for a number of GC solutes determined at regular time intervals. Increases in the retention times, after a reasonable period in which this parameter is constant, give an indication that modifications (degradation) of the network are taking place.

From the above, it follows that a new versatile, simple and easily operated method, based on GC techniques, has been made available for the determination of binder properties such as transition temperatures, solubility at infinite dilution, crosslinking kinetics and high-temperature resistance.

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#### Appendix

##### Materials

VR 4494 - Butylated melamine resin 55% solution in a n-butanol/i-sobutanol 1.2/1 mixture. Gardner colour 1, Gardner viscosity N-R.

VR 4618 - Low MW hydroxy-

lated acrylic copolymer 60% solution in a xylene/n-butanol mixture. Gardner colour 1, Gardner viscosity U-W, acid number 36, OH-number 85.

3131544 - Cymel 325, the American Cyanamide Company.

#### Apparatus

The GLC apparatus used was a thermal conductivity chromatograph Fractovap Model B (Carlo Erba). 1 m long, 4 mm internal diameter copper columns were employed. The solid support was Chromosorb W silanized. The stationary phase/support ratio was 1/3 by weight. The carrier gas used was hydrogen. The flow rate was checked with a soap flowmeter. Quantities of solute injected were about .2 microlitres. Temperature was measured with an electronic thermometer Avo Comark and controlled to within .1°C. ■

*Continued from p.38*

upon style, cut, colour and appropriate cost, after which Jackie Parker introduced ideas for accessories, ie, belts, bracelets, hats and handbags.

Examples of wear were not restricted to ladies' outfits, but included socks, shirts, ties and boxer shorts, with the additional information for the gentlemen present, 'Beware, these things are noted!'

The lively, entertaining and sometimes hilarious evening was brought to a close at 10.00 pm with a vote of thanks proposed by Mrs R. Lewis.

M. J. Round ■

# Infrared study of the adsorption of acetone on silica immersed in hexane

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## Summary

Infrared spectra of powdered silica immersed in solutions of acetone in hexane exhibit infrared bands due to surface silanol groups which are perturbed by hexane molecules and acetone molecules. Absorbance data taken from the spectra allow quantitative values of the relative proportions of silanol groups perturbed by the adsorption of each component of the liquid phase to be calculated. Hence an equilibrium constant for the adsorption of acetone on silica immersed in hexane has been deduced.

## Introduction

Some important aspects of the application of infrared spectroscopy to the study and characterisation of surface-adsorbate interactions *in situ* at the solid/liquid interface have recently been emphasised<sup>1</sup>. The infrared technique has great potential as a method for gaining direct information about chemical bonding at interfaces between solids and liquids and hence for providing a better understanding of a wide variety of surface phenomena related, for example, to colloid stabilization, adhesion, corrosion inhibition and surface modification. An infrared study of silica immersed in heptane + benzene and heptane + toluene mixtures showed that the spectra enabled adsorption isotherms to be deduced for the separate components of the liquid phase<sup>2</sup>. This approach is here extended to silica in acetone + hexane mixtures in which there is a much greater difference between the relative strengths of adsorption of the two components than in the case of the hydrocarbon mixtures. Surface coverage of silica by adsorbed acetone would be expected to be high at relatively low solution concentrations. The aim was to test whether the data derived from infrared spectra could be used to deduce a reliable value of an equilibrium constant for the adsorption reaction between silica and acetone in hexane.

## Experimental

Aerosil silica (Degussa) had a surface area of 176 m<sup>2</sup>g<sup>-1</sup>. Hexane and acetone

(both 99.5%) were purified by triple distillation and a series of freeze-pump-thaw cycles under vacuum and were stored in the vacuum apparatus under nitrogen.

The infrared cell had silica optical windows and a liquid circulating system which promoted the rapid attainment of equilibrium in adsorption experiments and enabled the circulating liquid to be thermostatted<sup>3</sup>. The cell was glassblown to a vacuum apparatus which included a system of vessels and burettes for the storage and manipulation of liquids and solutions<sup>4</sup>.

Procedures for the recording of spectra of a compressed disc of silica immersed in a series of solutions of increasing concentration of one component have been described elsewhere<sup>3</sup>. Before immersion in hexane the silica was heated at 873 K in oxygen (13 kN m<sup>-2</sup>) for 2 h and in vacuum (16 h) and subsequently allowed to cool to room temperature. Spectra were recorded with a Perkin Elmer 683 spectrophotometer linked to an Infrared Data Station. Circulating acetone + hexane mixtures were thermostatted at 298 K during the adsorption experiments.

## Results

The spectrum of silica which had been heated at 873 K displayed a single sharp infrared band at 3750 cm<sup>-1</sup> due to the OH-stretching vibrations of isolated surface silanol groups. Chemisorbed water giving adjacent interacting silanol groups was completely desorbed during the thermal treatment. Isolated silanol groups were perturbed by interactions with hexane molecules when silica was immersed in hexane and the infrared band at 3750 cm<sup>-1</sup> shifted by  $\Delta\nu_{OH}=39$  cm<sup>-1</sup> to 3711 cm<sup>-1</sup> (Figure 1a). Subsequent addition of acetone resulted in decreases in the intensity of the band at 3711 cm<sup>-1</sup> and the growth of a broader maximum the position of which shifted slightly with increasing intensity from ca. 3430 cm<sup>-1</sup> to 3380 cm<sup>-1</sup> (Figure 1b-g). This maximum is ascribed to silanol groups which are perturbed by hydrogen bonding interactions with adsorbed acetone molecules<sup>5</sup>. A shoulder at 3420 cm<sup>-1</sup> arises because of a

weak band at this position in the spectrum of acetone. All the spectra contain a fixed contribution from a band at 3660 cm<sup>-1</sup> due to bulk hydroxyl groups in the windows of the infrared cell.

Absorbance values taken from the spectra at 3711 and 3400 cm<sup>-1</sup> were a linear function of each other confirming a proportionality between the loss of one band and the gain of the other as the liquid composition was changed. The absorbance data at either spectral position may therefore be used to calculate the fractions  $f_H$  and  $f_A$  of the total number of surface silanol groups which were perturbed by interactions with heptane and acetone, respectively. The fractions are given by

$$f_H = (A_A - A)/(A_A - A_H)$$

and

$$f_A = (A - A_H)/(A_A - A_H)$$

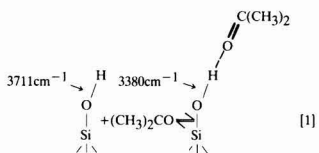
where  $A_H$ ,  $A_A$  and  $A$  are the absorbance values at a particular wavenumber for a silica disc immersed in hexane, a strong solution of acetone in hexane (corresponding to complete coverage of the silanol group sites by acetone) and a hexane + acetone mixture, respectively. The fractions  $f_H$  and  $f_A$ , taken as the means of the values deduced from the absorbance data at 3711 and 3400 cm<sup>-1</sup> are given in Table 1. The mole fractions of acetone are equilibrium values. The added concentrations of acetone were corrected by subtracting the amounts of acetone in the adsorbed state. The latter were calculated from the total surface area of silica in the disc and the fractions  $f_A$ , and by assuming that one adsorbed acetone molecule interacts with one surface silanol group<sup>6</sup> and that the surface concentration of silanol groups was 2.0 nm<sup>-2</sup><sup>7</sup>.

## Discussion

The shift  $\Delta\nu_{OH}$  of 39 cm<sup>-1</sup> which occurred when silica was immersed in hexane compares with shifts of 44 and 45 cm<sup>-1</sup> for silica in heptane<sup>2,8</sup> and 2,2,4-trimethylpentane<sup>9</sup>, respectively. Corresponding shifts of 30 and 45 cm<sup>-1</sup> have been reported for the adsorption of hexane and heptane vapour on silica<sup>10</sup>. The infrared band due to silanol groups perturbed by hydrogen bonding interactions with acetone molecules has previously been recorded at 3380 cm<sup>-1</sup> for silica immersed in carbon tetrachloride<sup>5</sup> and 3360 cm<sup>-1</sup> for silica in heptane or toluene<sup>8</sup>.

The adsorption equilibrium for the interaction of silanol groups on silica in hexane with acetone may be represented by Equation 1 which involves the exchange of hexane and acetone molecules in the adsorbed layer interacting with





isolated silanol group surface sites. If the solution and adsorbed phases are assumed ideal then Equation 2, in which  $x_{II}$  is the mole fraction of hexane

$$K = (f_A x_{II} / f_{II} x_A) \quad [2]$$

in the solution phase represents an equilibrium constant expression for the reaction in Equation 1. Previous tests of this equation<sup>3,9</sup> have involved taking the mole fraction of the predominant component of the liquid phase as *ca.* 1 for all solutions. Hence, with  $f_{II} = (f_A - 1)$ , a plot of  $(x_A/f_A)$  against  $x_A$  should be linear with unit slope and intercept  $(1/K)$  on the  $(x_A/f_A)$  axis. The plot is shown in Figure 2 in which the line has unit slope. Hence  $K$  is 345 for acetone adsorbed from hexane on silica at 298 K. In the present case it is more realistic to evaluate  $x_{II} = (1 - x_A)$  which falls to 0.97 for the highest acetone concentration studied and then either calculate a value of  $K$  for each experimental point or plot  $(x_{II}/f_{II})$  against  $(x_A/f_A)$  to gain a linear graph with slope  $K$ . The latter (Figure 3) is more sensitive to experimental error than the plot in Figure 2 and the derived value of  $K$  becomes 340.

The present data illustrate the usefulness of infrared spectroscopy for quantitative analysis of adsorption behaviour at the solid/liquid interface. We have recently embarked on an extension of this method to the detailed characterization of chemical interactions at the interfaces between oxitic surfaces and adhesive films in the presence and absence of silane and titanate coupling agents.

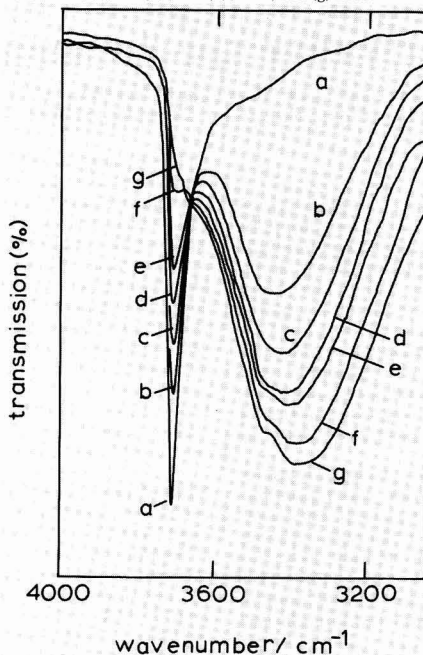
**Table 1**

Fractions of the total surface silanol group population perturbed by hexane and acetone molecules for silica immersed in hexane + acetone mixtures at 298 K

$10^3 x_A$	$x_{II}$	$f_A$	$f_{II}$
1.89	0.998	0.438	0.562
3.72	0.996	0.604	0.396
7.20	0.993	0.700	0.300
8.81	0.991	0.746	0.254
10.4	0.990	0.772	0.228
11.9	0.988	0.816	0.184
14.7	0.985	0.846	0.154
19.9	0.980	0.860	0.140
29.3	0.971	0.992	0.008

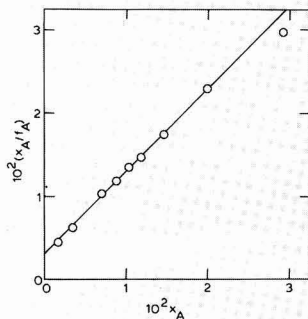
**Figure 1**

Spectra of silica immersed in (a) hexane, (b)-(g) acetone + hexane mixtures with mole fractions  $x_A$  of acetone given by  $10^3 x_A$  equal to (b) 1.93, (c) 3.78, (d) 7.26, (e) 8.90, (f) 20.0, and (g) 50.0.



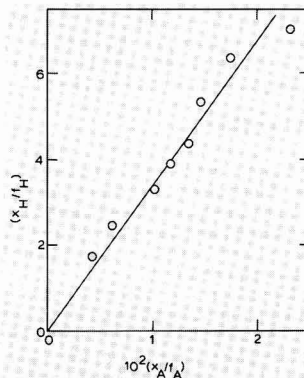
**Figure 2**

Plot of  $(x_A/f_A)$  against  $x_A$ .



**Figure 3**

Plot of  $(x_{II}/f_{II})$  against  $(x_A/f_A)$ .



#### Acknowledgements

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# The identification of blue pigments in paints by derivative spectroscopy

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## Summary

The identification of pigments by examination of reflectance curves is hindered by the dependence of spectral reflectance on packing density of the pigment powder and by the broad nature of the spectral profiles. A method has been developed in which the reflectance spectra of pigments in paint films are measured. By conversion of reflectance to  $\log(K/S)$ , using the Kubelka-Munk equation, concentration effects of the pigment in the paint are reduced.

Differentiation of the  $\log(K/S)$  profiles leads to one profile which is characteristic for a given pigment. The second-order derivative profile, which enhances spectral detail without excessive interference due to noise, has been found to be most suitable and permits distinction between the blue pigments studied.

The amplitudes of first-order derivative  $K/S$  profiles have been found to give linear relation to the proportion of  $\alpha$  and  $\beta$  forms of phthalocyanine in mixtures. It is suggested that this measure could be used to monitor the  $\alpha$  to  $\beta$  conversion of phthalocyanines in paints, plastics and printing inks.

## Introduction

A variety of methods is available for the identification of pigments, ranging from simple spot tests to instrumental techniques such as x-ray diffraction<sup>1</sup>, microscopy<sup>2</sup>, visible<sup>3,4</sup> and infra-red spectrophotometry<sup>5,6,7</sup>.

Identification in the visible region is based on the transmission spectrum of the pigment in solution or on the reflectance spectrum of the solid. Solution spectrophotometry was established by Abbott and Stearns<sup>8</sup> and developed further<sup>9,10</sup> to include a wider range of pigment types, by the use of a variety of solvents. Billmeyer et al<sup>3</sup> have further refined the technique and described a procedure for the extraction of the pigments by successive treatment of the sample in up to four solvents. The pigment is identified by inspection of the log-absorbance spectrum of the resulting solution and comparison against a library of reference spectra.

The technique of reflectance spectrophotometry for the identification of pigments is less well developed. Simple inspection of spectral reflectance curves can provide useful clues<sup>11</sup> but their interpretation can be very difficult, even for an experienced colourist. More usually, the Kubelka-Munk analysis<sup>12</sup> of the absorption and scattering of light through the colourant layer is employed,

$$\frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \quad [1]$$

where  $K$  and  $S$  are the absorption and scattering constants of the pigment respectively, and the  $R_\infty$  is the reflectance of the layer at complete opacity. However the measurement of the reflectance spectra of pigments in powder form presents a procedural difficulty. It is necessary to measure the pigment in a powder sample holder and the density of packing can significantly influence the reflectance. For example, Figure 1 shows the second derivative  $\log(K/S)$  spectra of two samples of Irgalite Blue BCA, measured separately in a powder holder. For this reason the use of paint films for the identification of pigments was studied. It is assumed, as first shown by Duncan<sup>13,14</sup>, that the absorption coefficient for a mixture of pigments is the sum of the  $K$  values of the individual pigments, and similarly for the scattering coefficient,  $S$ . Then for a mixture of a white and chromatic pigment

$$\frac{K}{S} = \frac{c_w K_w + c_p K_p}{c_w S_w + c_p S_p} \quad [2]$$

The scattering coefficient of a white pigment (such as titanium dioxide) is very much higher than that of the chromatic pigment, so that in mixtures of the two  $S$  is due to just the white<sup>3</sup> and remains fairly independent of concentration. Hence

$$\frac{K}{S} = \frac{K_w + c_p K_p}{S_w + c_w S_p} \quad [3]$$

A further assumption can be made that in the visible region, the white

pigment absorbs radiation very weakly, so that the  $K_w/S_w$  term is negligible and

$$\frac{K}{S} = \frac{c_p K_p}{c_w S_w} \quad [4]$$

Thus the  $K/S$  spectral profiles will relate to the absorbing properties of the chromatic pigment.

The form of these profiles will be approximately the same for various concentration ratios of chromatic pigment to white. Consequently, as with the log-absorbance spectra of solutions, the  $\log(K/S)$  profiles will have approximately the same shape. Differentiation of the  $\log(K/S)$  curves with respect to wavelength, will result in a single curve, characteristic of the chromatic pigment.

The derivatives of spectral profiles possess some useful properties, which aid the identification of absorbing materials<sup>15</sup>. The resolution of overlapping absorption bands is enhanced in derivative mode<sup>16,17,18</sup> to an extent dependent on the band-width of the component bands. Thus in the  $n^{\text{th}}$ -order derivative, the amplitude  $D_n$  of the band is related to its band-width  $W$  by

$$D_n \propto (1/W)^n \quad [5]$$

For two overlapping bands  $X$  and  $Y$ , of band-widths  $W_x$  and  $W_y$  respectively, the relative amplitude in the  $n^{\text{th}}$ -order derivative is given by

$$\frac{D_n(X)}{D_n(Y)} = \left( \frac{W_y}{W_x} \right)^n \quad [6]$$

and if band  $Y$  is a broad interfering band then it can be seen readily how the  $n^{\text{th}}$ -order derivative amplitude of band  $X$  is increased, relative to that of band  $Y$ . If the background absorption is a linear function of wavelength, then it should be eliminated in the second derivative spectrum. Thus, interferences due to weak, broad band absorption by the white pigment component or the resin of a paint film, for example, are reduced or eliminated, especially in the higher order derivative spectral profiles.

The advantages of resolution enhancement and removal of matrix interferences have to be balanced against the disadvantages of satellite interference and noise, which progressively reduce the quality of the profiles obtained, as the derivative order increases.

In this work, the second derivative  $\log(K/S)$  spectral profiles have been used, a mode of analysis which has been successfully applied to dyes on textile fibres<sup>19</sup>. Nine pigments, considered to be the most widely used blue pigments, have been examined, in admixture with rutile titanium dioxide white pigment.

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formulated into paints. The second derivative log(K/S) spectral profiles of the paints should be independent of the blue:white pigment ratio and of the absorbing properties of the resin matrix of the paint film.

## Experimental

### Materials

The pigments chosen for this work are shown in Table 1. The Irgalite Irgazin and Chromophtal pigments were kindly supplied by Ciba-Geigy Pigments Ltd, Paisley, Renfrewshire, Scotland. We are also grateful to Craig and Rose plc, Edinburgh, who supplied Duroval white gloss paint and obtained samples of Vilkyd 220W alkyd resin and the other pigments for use in this work.

### Paint preparation

Stainers were prepared by ball-milling pigment powder (1 part) in the Vilkyd resin (2 parts) and white spirit (2 parts), for twelve hours. An addition of resin (4 parts) and white spirit (0.75 parts) was made and milling continued for one hour. The resulting fineness of grind size, as tested with a Hegman gauge<sup>20</sup> was <20  $\mu$ m.

Reductions of the stainers with Duroval white gloss paint were produced at 1, 2.5, 5, 10 and 20% stainer:white (by weight) for all pigments. The reductions were applied to a Mostert chart<sup>21</sup> using a 150  $\mu$ m K-bar applicator, to produce a smooth, even paint film. The 150  $\mu$ m film thickness was found to give 100% opacity in every case. The paint films were air dried in a dust free environment.

The Duroval white gloss paint contained dispersion stabilising additives, including an anti-floitation agent. The final paint films showed no evidence of flocculation or flooding effects.

### Apparatus

Measurements of reflectance spectra were made on a Pye-Unicam SP8-200 uv-vis spectrophotometer, with the diffuse reflectance spheroid accessory. The spheroid gives 8° illumination and diffuse viewing and all measurements were made with the specular component excluded. The spectrophotometer was interfaced with an Apple IIe microcomputer, equipped with twin disk drives (5.25 in), Anadex printer and Sweet-P Model 100 plotter (Enter Computer Inc San Diego, Ca, USA).

### Data processing

The reflectance spectrum of each paint film was recorded nine times at 1 nm

intervals between 325 and 755 nm. The nine reflectances at each wavelength were averaged and the complete averaged spectrum stored on floppy disk. The averaging of nine spectral reflectance values improves the signal to noise ratio by a factor of two<sup>22</sup>. The reflectance at each wavelength was corrected for the first-surface reflection using Saunderson's relation<sup>23</sup>

$$R_{\text{corr}} = \frac{R_m - k_1}{1 - k_1 - k_2(1 - R_m)} \quad [7]$$

where  $R_m$  is the measured reflectance,  $R_{\text{corr}}$  the corrected reflectance,  $k_1$  the Fresnel reflection coefficient and  $k_2$  the diffuse internal reflection coefficient. Values of 0.04 for  $k_1$  and 0.4 for  $k_2$  were used in this work. Since the specular component was excluded from reflectance measurements,  $k_1$  was omitted from the numerator in the above equation<sup>24</sup>. The K/S values were calculated by Equation 1, from the corrected reflectances.

A number of methods is available for the differentiation of spectral data sets and some of these have been reviewed<sup>15</sup>. The method employed in this work was that of Savitzky and Golay<sup>25,26</sup>, favoured because of its simplicity and speed. The log(K/S) spectra were smoothed using an 11-point quadratic-cubic algorithm and then differentiated using a 15-point cubic-quartic algorithm. Second derivative spectral profiles were generated by repeated application of the first order algorithm, rather than by direct use of the second order algorithm, to achieve a better signal to noise ratio<sup>22</sup>.

## Results and discussion

The second derivative profiles of the spectral log(K/S) curves were generated for each of the five concentration levels

of each pigment studied. These profiles were overlaid and Figure 2 shows, as an example, the characteristic features of Irgalite Blue BL. Over the wavelength range 325-525 nm, the derivative spectral features of the titanium dioxide white interfere with those of the chromatic pigment, so that the profiles do not overlap completely in this region. Rutile titanium dioxide absorbs radiation strongly at around 380 nm (Figure 3(a)), consequently its second derivative log(K/S) profile shows satellite peaks in the visible region which influence the profiles of white/chromatic pigment mixtures to about 525 nm (Figure 3(b)). In the region above 525 nm the titanium dioxide does not interfere and the derivative log(K/S) profiles are characteristic of the chromatic pigment only. In this region the absorption of light by blue pigments is greatest, hence it is here that the most significant spectral detail can be expected to be found.

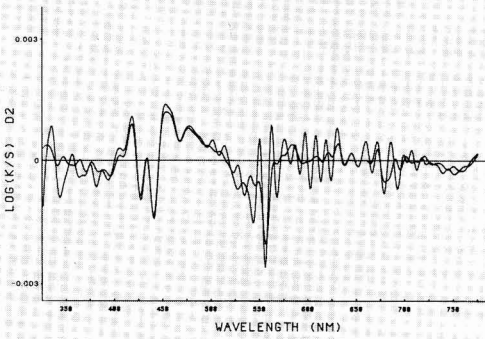
The average of the second derivative log(K/S) spectra of the five concentrations was calculated and the resulting spectral profiles for the pigments studied are shown in Figure 4. The wavelengths at which peak maxima and minima occur, together with wavelengths of zero crossover, should provide sufficient information to permit distinction between the profiles of the various pigments. Tables 2-9 detail the characteristic features of the pigments, with the exception of the ferric ferrocyanide, for which no characteristic features could be identified.

Inspection of the profiles in Figure 4 shows that the various chemical types can be distinguished from each other fairly easily. Thus the two very sharp troughs at 423 and 436 nm are very characteristic of the  $\beta$ -phthalocyanines and even distinguish them from the  $\alpha$ -phthalocyanines (Figure 4c and 4d). The  $\alpha$ - and  $\beta$ -phthalocyanines are

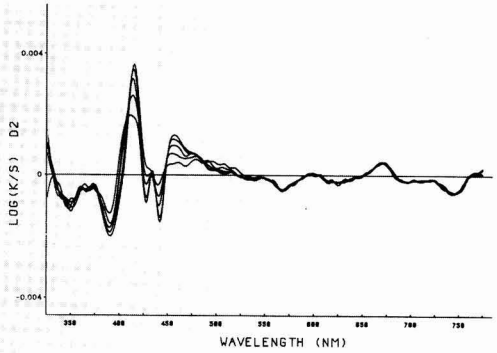
Table 1

Trade Name	C.I. Number	Composition
Irgalite Blue BL	Pigment Blue 15	Unstabilised $\alpha$ -CuPc
Irgalite Blue BCA	Pigment Blue 15:1	Untreated stabilised $\alpha$ -CuPc
Irgalite Blue BCFR	Pigment Blue 15:2	Stabilised non-flocculating $\alpha$ -CuPc
Irgalite Blue GLA	Pigment Blue 15:3	Multi-purpose $\beta$ -CuPc
Irgalite Blue GFR	Pigment Blue 15:4	Non-flocculating $\beta$ -CuPc
Irgazin Blue 3-GT	Pigment Blue 16	Metal free phthalocyanine
Manox Iron (Prussian) Blue. Pigment Grade 10	Pigment Blue 27	Ferric ferrocyanine
Reckitts Ultramarine Blue	Pigment Blue 29	Polysulphine of sodium aluminosilicate
Cromophtal Blue A3R	Pigment Blue 60	Indanthrone

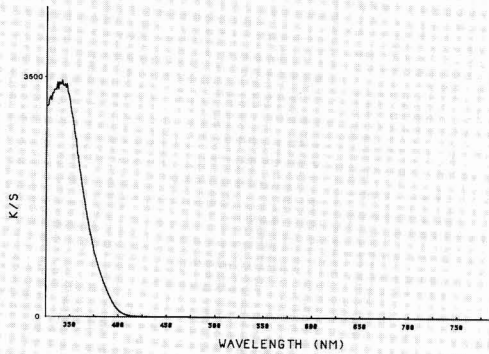
**Figure 1**  
**Reproducibility of second derivative log(K/S) curves of Irgalite Blue BCA, measured in a powder holder.**



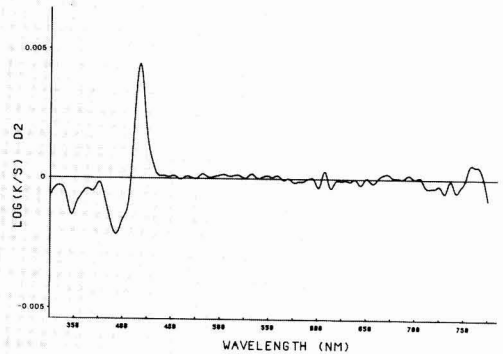
**Figure 2**  
**Second derivative log(K/S) curves of Irgalite Blue BL at five concentration levels.**



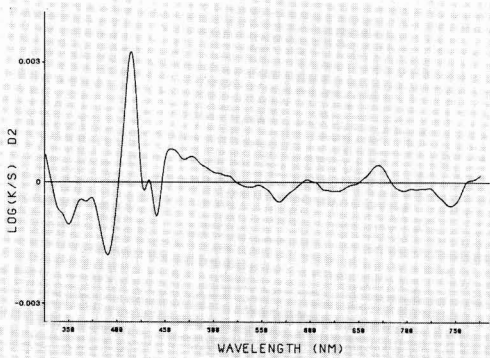
**Figure 3**  
**Spectral curves of rutile titanium dioxide**  
**(a) K/S curve**



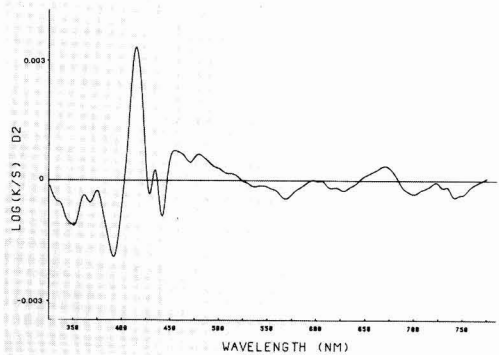
**(b) second derivative log(K/S) curve**



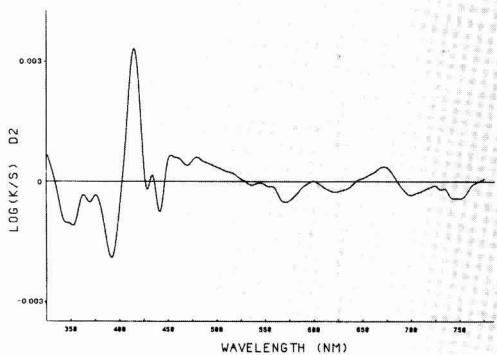
**Figure 4**  
**Second derivative log(K/S) curves (average of five concentration levels)**  
**(a) Irgalite Blue BL**



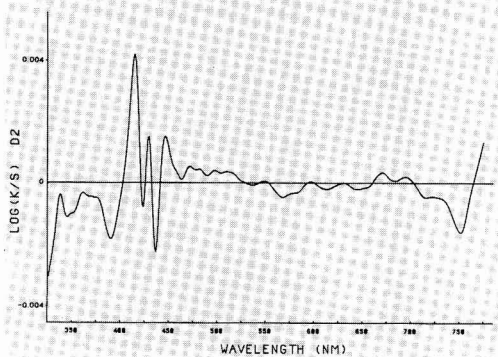
**(b) Irgalite Blue BCA**



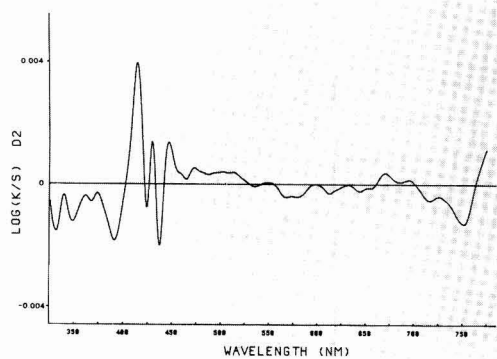
(c) Irgalite Blue BCFR



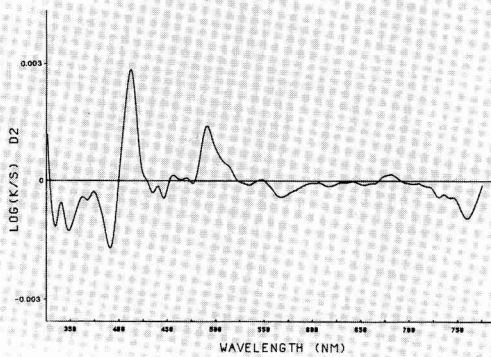
(d) Irgalite Blue GLA



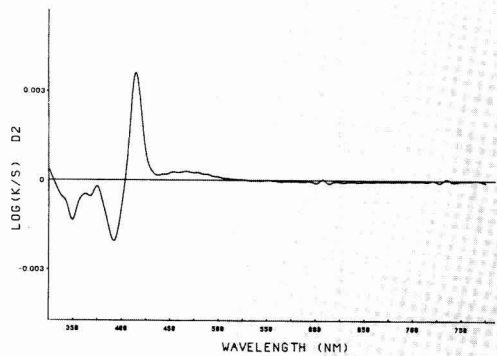
(e) Irgalite Blue GFR



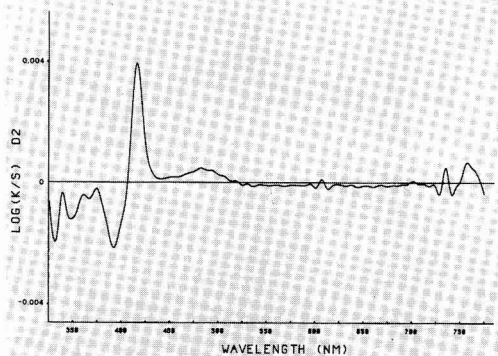
(f) Irgazin Blue 3-GT



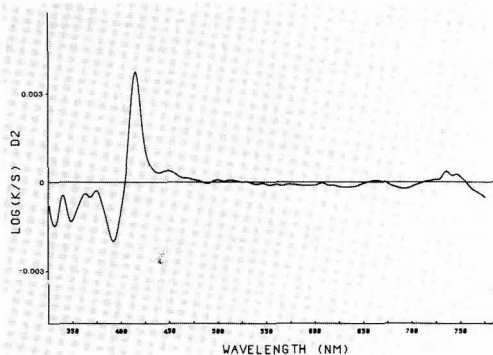
(g) Manox Iron (Prussian) Blue



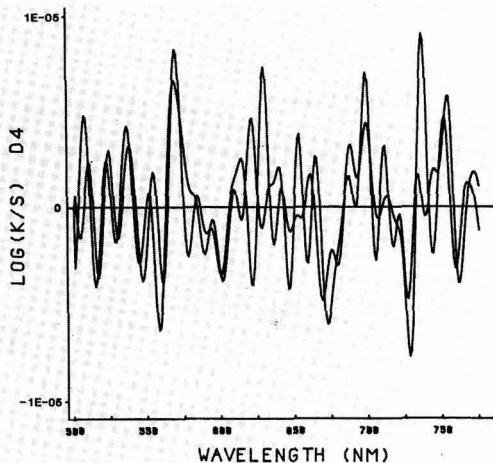
(h) Reckitt's Ultramarine Blue



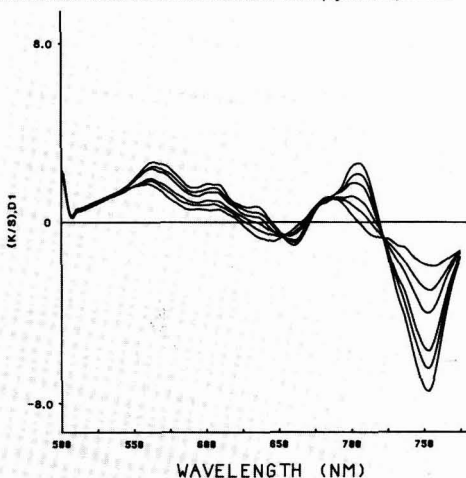
(i) Cromophtal Blue A3R



**Figure 5**  
Fourth derivative log(K/S) curves of Irgalite Blue BCA and Irgalite Blue BCFR



**Figure 6**  
First derivative K/S curves of mixtures of  $\alpha$  and  $\beta$  phthalocyanines.



further distinguished, firstly by the presence of a peak in the  $\beta$ -forms (a trough in the  $\alpha$ -forms) at 695 nm, and secondly by the deep trough of the  $\beta$ -forms at 750 nm. The  $\alpha$ -phthalocyanines exhibit a characteristic waveform between 525-725 nm, with the peak at 668 nm a prominent feature. It is important to remember however that the  $\alpha$ -unstabilised form is not intended for paint systems and that some conversion to the  $\beta$ -form could occur in the paint film. In this work the reflectance spectra were measured within 24 hours of the paint film drying, but it is still possible that some conversion to the form may have occurred.

The metal free phthalocyanine (Figure 4f) gives troughs at 570 and 760 nm, characteristic of all phthalocyanines, but is further characterised by a prominent peak at 490 nm. This peak is absent in the copper phthalocyanines.

The three other blue pigments studied exhibit less spectral detail, though they can be distinguished satisfactorily. Thus whilst the ferric ferrocyanide (Figure 4g) shows virtually no characteristic spectral features, due to its very broad absorption over the visible region, the Ultramarine (Figure 4h) and indanthrone (Figure 4i) pigments show differences between 450-500 nm and between 725-750 nm.

It is less easy to distinguish between the variants within a chemical class. Thus whilst the  $\alpha$ -,  $\beta$ - and metal-free forms of phthalocyanines can be readily distinguished, the differences between the unstabilised, untreated stabilised and stabilised non-flocculating  $\alpha$ -forms are more subtle. A similar situation exists with the multipurpose and non-flocculating  $\beta$ -forms.

Of the three  $\alpha$ -forms studied, the profile of the unstabilised form (Figure 4a) shows an almost flat plateau between 680-720 nm, a feature which distinguishes it from the other two  $\alpha$ -forms. Distinction between these latter two forms is difficult, the only difference of any note is the double trough of the untreated stabilised form at about 600 nm, which is only a single trough in the case of the stabilised non-flocculating form (Figures 4b and 4c). Further differentiation to fourth order should resolve this minor detail, but a deterioration in signal to noise ratio occurs. Consequently slight differences in the profiles of the various concentrations, which are barely discernable in the second derivative profiles, become so pronounced in the fourth derivative profiles that the usefulness of the fourth order is significantly reduced. Examples of their fourth derivative log(K/S) spectral profiles are overlaid in Figure 5.

The two  $\beta$ -forms of the phthalocyanine studied show no discernible differences in their second derivative  $\log(K/S)$  spectra, so that their distinction by this method is not possible.

### Analysis of $\alpha/\beta$ Phthalocyanine Mixtures

The different reflection behaviour in the red region of the spectrum may be used to quantify the proportions of the  $\alpha$ - and  $\beta$ -forms in mixtures of the two.

For this purpose the K/S spectra, not the  $\log(K/S)$  spectra are used, since the influence of concentration on derivative amplitude is now of interest. The first derivative of the spectral K/S profiles have been found to provide a suitable measure and Figure 6 shows the family of such profiles obtained for mixtures of untreated stabilised  $\alpha$ - and multi-purpose  $\beta$ -phthalocyanines (see Table 1) of known composition. These mixtures were formulated separately into paints at concentration 10% with 90% white and paint films prepared for measurement as described above.

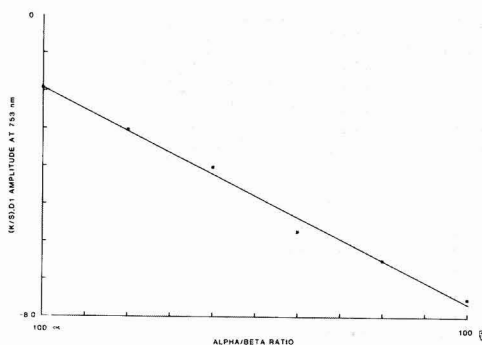
The derivative amplitude  $D_{753}$  (baseline to trough at 753 nm) exhibits linear correspondence with concentration (Figure 7) over the full range, from 100%  $\alpha$  to 100%  $\beta$ . The calibration graph indicates that the composition of such mixtures could be determined to an accuracy of approximately 5%.

It is important to stress that the magnitude of derivative amplitude is dependent on both the method by which reflection measurements are made and by which the derivative amplitudes are calculated. Instrumental factors such as illuminating/viewing geometry, and bandwidth will influence the measured reflectance values. The algorithm used for smoothing digitised spectra and for generating the differentiated spectrum directly influence the amplitudes of peaks and troughs in derivative spectra. Hence the calibration graph (Figure 7) will be specific to a particular set of measurement conditions and method of numerical analysis. Nevertheless, the technique is general and may be applied to monitoring the  $\alpha$  to  $\beta$  conversion in inks and plastics as well as paints.

### Conclusions

The identification of various chemical classes of blue pigments in paint films is possible by the use of the second derivative of the  $\log(K/S)$  spectral profiles. Beyond the spectral range in which the titanium dioxide white pigment interferes, the profiles of various reductions up to 20% of stainer overlay well to give features

**Figure 7**  
Calibration line of first derivative amplitude at 753 nm for mixtures of  $\alpha$  and  $\beta$  phthalocyanines.



**Table 2**  
Characteristic features for Irgalite Blue BL

	Peak	Trough	Zero Crossover
Wavelength (nm)	433	427-428	590-592
	451-454	439-441	603-606
	594-597	565-568	649-651
	668-671	740-744	681-684
			759-762

**Table 3**  
Characteristic features for Irgalite Blue BCA

	Peak	Trough	Zero Crossover
Wavelength (nm)	433-434	427-429	592-594
	452-457	441	643-644
	476-479	468-470	684
	668-670	566-568	768-772
		699-702	
		741-746	

**Table 4**  
Characteristic features for Irgalite Blue BCFR

	Peak	Trough	Zero Crossover
Wavelength (nm)	431-433	427-428	641-643
	451-452	440-441	685
	477-478	468-469	
	667-671	568-571	
		697-701	
		741-745	
		749-750	

**Table 5**  
Characteristic features for the Irgalite Blue GFR

	Peak	Trough	Zero Crossover
Wavelength (nm)	429	423-424	432-433
	446-447	436-437	441-442
	472-473	463-464	527-533
	667-669	566->582	539-543
	686-695	715	660
		748-751	700-701
			762-764

**Table 6**  
Characteristic features for Irgalite Blue GLA

	Peak	Trough	Zero Crossover
Wavelength (nm)	428-429	422-424	432-433
	446-448	436-437	441-442
	471-472	462-464	543-544
	669-670	565-569	552-553
	692-695	712-717	592-593
		750-751	600-602
			659-660
			702-704 763-765

**Table 7**  
Characteristic features for Irgazin Blue 3-GT

	Peak	Trough	Zero Crossover
Wavelength (nm)	438-439	433-435	450-451
	454-455	444-445	536-548
	467-468	461-465	666-667
	489-490	473-475	690-692
	676-680	564-570	
		729-730	
		757-760	

**Table 8**  
Characteristic features for Cromophthal Blue A3R

	Peak	Trough	Zero Crossover
Wavelength (nm)	658-663	688-691	651-654
	732-735		670-675
			708-712
			755-756

**Table 9**  
Characteristic features for Reckitts Ultramarine Blue

	Peak	Trough	Zero Crossover
Wavelength (nm)	734	727-728 740-742	730-732 737-740

characteristic of the pigment. However it is necessary to average many scans of the spectrum to achieve this level of correspondance and despite this, the reduction in signal to noise ratio deteriorates to such an extent as to severely limit the use of the corresponding fourth order profiles.

The method is based on enhancing differences in spectral detail and whilst the second order profiles are satisfactory for distinguishing between chemical types, the various modifications of the  $\alpha$ - and of the  $\beta$ -forms of phthalocyanine cannot easily be distinguished. Since such modifications are not intended to confer

colour differences to the pigments, it is not surprising that this difficulty occurs.

Paint films have been found to provide a satisfactory medium in which to analyse blue pigments. It follows that the technique can be applied in the context of determining the nature of a blue pigment in an unknown paint sample, for example in forensic analysis. However the technique in this application may be less straightforward if mixtures of pigments are present in the paint film.

The method is likely to be less suitable for chromatic pigments which absorb at wavelengths lower than the blues, because the titanium dioxide

white causes spectral interference in derivative modes. Such interference could be removed by subtracting the K and S components of the white from the K/S of the paint film, according to Equation 3, to leave a profile characteristic of the chromatic pigment. An alternative approach may be to formulate a paint using an alternative white pigment to titanium dioxide. However there is no such suitable substance, which possesses a low absorption coefficient to minimise interference with spectral detail of the chromatic pigment, and a high scattering power so that an opaque paint layer is obtained.

### Acknowledgements

We are grateful to Dr R. M. Christie for his useful comments during the preparation of this paper.

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Continued on p.34



# Identification of black deposits on road markings using infra-red spectroscopy

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## Abstract

Road markings in Riyadh, in common with many other places in the Middle East, are subject to rapid blackening. To identify black deposits on traffic paint surfaces, I.R. spectra were obtained from possible candidate materials and from the paints and these were compared with spectra of the black material itself. Each of the materials involved, asphalt, aggregate, dust, paint and rubber from vehicle tyres gave spectra indicating the presence of hydrocarbons. Asphalt can be easily recognized only by the absorption peak at  $1575\text{--}1600\text{ cm}^{-1}$  which fully represented the absorption of the asphaltene components and at the same time its position on spectrum does not interfere with the broad and intense absorption bands arising from heavily filled compositions of rubber, dust and paint. No evidence concerning the existence of asphalt or its oxidation products in black deposits was found. Further analysis by pyrolysis-I.R., was carried out. The spectra of the pyrolysate of the black deposits and tyre treads confirmed the presence of rubber in the black material.

## Introduction

Road markings, lane dividers, stop bars and so forth play an indispensable role in contributing to the safety of road transport. Two types of marking material are widely used solvent-based thermosetting paints involving chlorinated rubber<sup>1</sup> and hot applied thermoplastic materials<sup>2</sup>. The stability and durability of these materials then are topics of technological importance. Generally road marking materials remain effective for periods measured in years depending, as would be expected, on service conditions especially traffic density<sup>3,4</sup>. There are circumstances, however, where the useful life of the markings may be reduced by their becoming obscured by some form of soiling<sup>4,5</sup>. As long ago as 1952 Keese and Benson noted a problem of discolouration by "road dust

and tyre film"<sup>6</sup>. Two decades later somewhat similar observations were made by Rumar and Ost in Sweden<sup>7</sup>.

A problem of discolouration during a dry summer in Britain was investigated by Green in the 1970s. A black deposit built up on motorway markings especially in the inner lanes. The problem was associated with "total loss" automatic lubrication systems for lorries which deposited mineral oil on the carriage way. This, mixed with tyre wear debris and dust, comprised the black deposit<sup>8,9</sup>. The action of rain at the end of the dry period lead to its dissipation.

A much more serious and persistent problem of blackening of road markings occurs in certain hot, dry dusty environments with heavy traffic load. In extreme circumstances, for example the approach to traffic lights on a busy road, the markings can be obscured in a matter of weeks.

Certain parts of the Middle East are among areas where this problem is serious. The Saudi Arabian Standards Organization (SASO) has undertaken

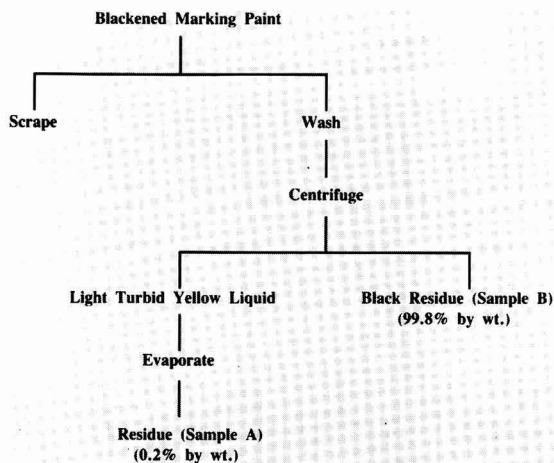
an investigation of the blackening occurring in the streets of Riyadh, and this paper is one of a series reporting the findings.

The literature on the problem<sup>6-9</sup> is not extensive, and none of it refers specifically to the problem in the peculiar conditions of the Middle East. The opinions of traffic engineers, paint technologists and others who have expressed a view have been sharply divided. Some blame asphalt oxidation or some other pavement surface failure, some deterioration of tyre rubber, others unsuitable marking paints. The present work of SASO was designed to decide between these various possibilities by examination of the quality of the asphalt road surface, by analysis of the black deposit and by road trials of different types of marking paint.

The first paper in the series<sup>10</sup> directly addressed the question of deterioration of the bitumen road surface. Analysis of core samples taken from various roads in Riyadh showed them to be of "satisfactory/superior" grades with good ability to withstand the effect of time and weather. This then is indirect evidence against deterioration of the asphalts being a significant cause of the blackening of the markings.

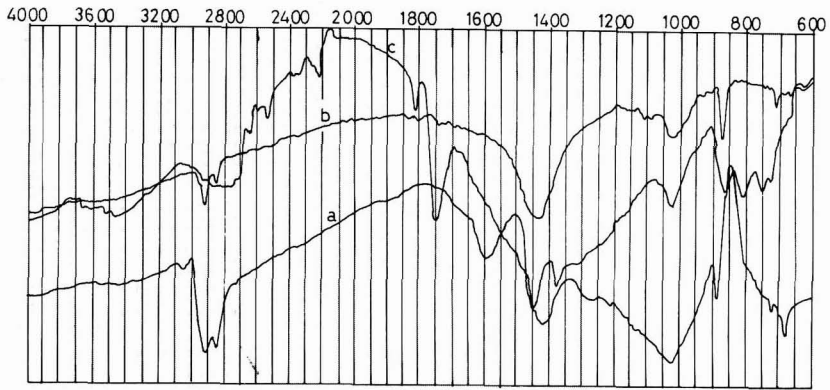
In a subsequent paper in preparation<sup>11</sup> further analysis of the black deposits by pyrolysis-gas chromatography shows that they contained natural, butadiene and styrene-butadiene rubber. In addition, solvent extraction and thermogravimetric analysis were used to split the deposits into four fractions (i) extractable organic compounds (ii) organic polymer

Figure 1  
Sampling of black material from discoloured road markings



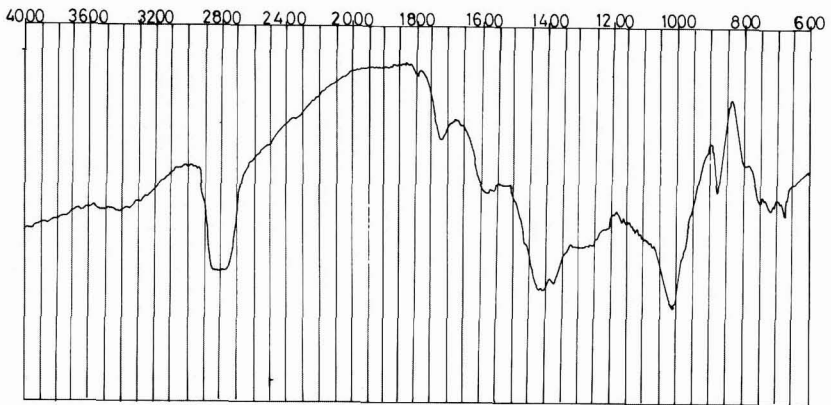
**Figure 2**

(a) Spectrum of asphaltene obtained by N-pentane extraction of bitumen. (b) Spectrum of rubber obtained by abrasion of tyre tread. (c) Spectrum of a thermoset road marking paints.



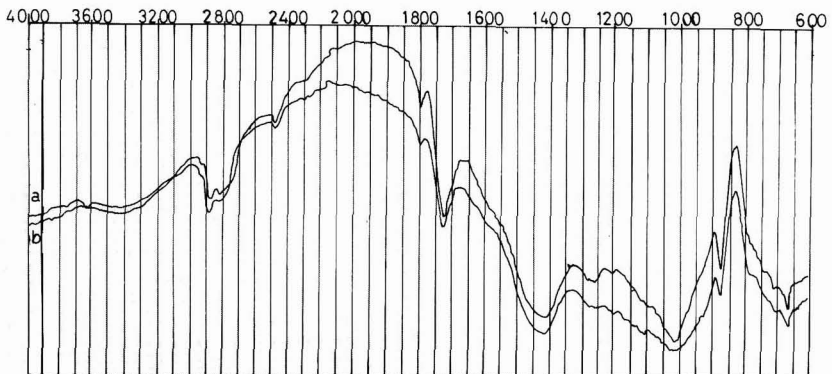
**Figure 3**

Spectrum of thermoset paint mixed with 5% asphaltene.



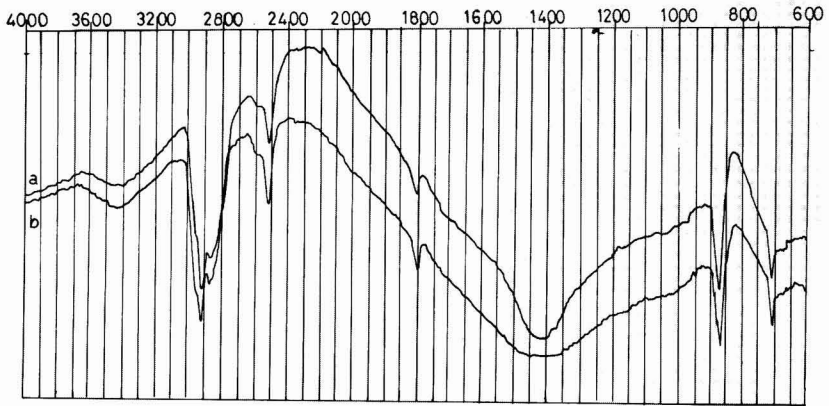
**Figure 4**

Spectrum of: (a) Thermoset paint. (b) The same paint mixed with tyre tread rubber.



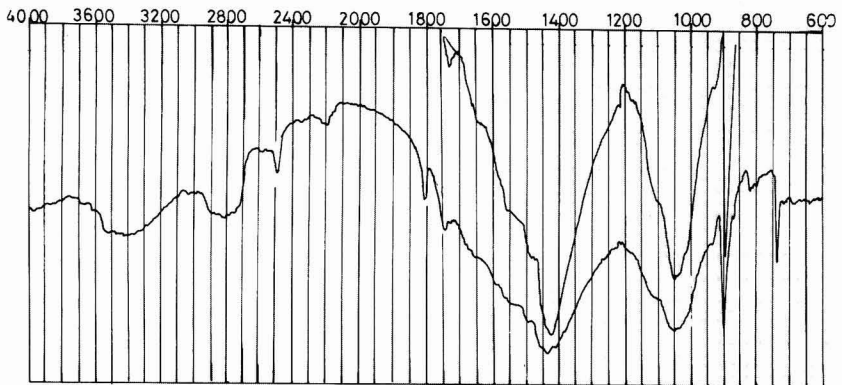
**Figure 5**

Spectra of thermoplastic paint: (a) Original thermoset paint. (b) Black materials scraped from the same paint.



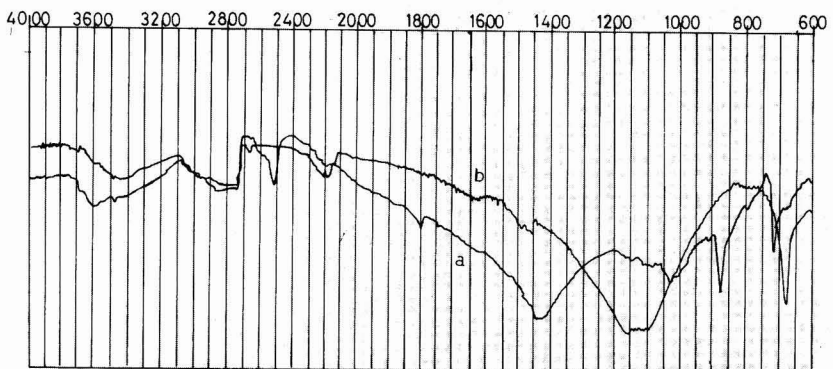
**Figure 6**

Spectra of black Residue B obtained by washing blackened thermoset paint.



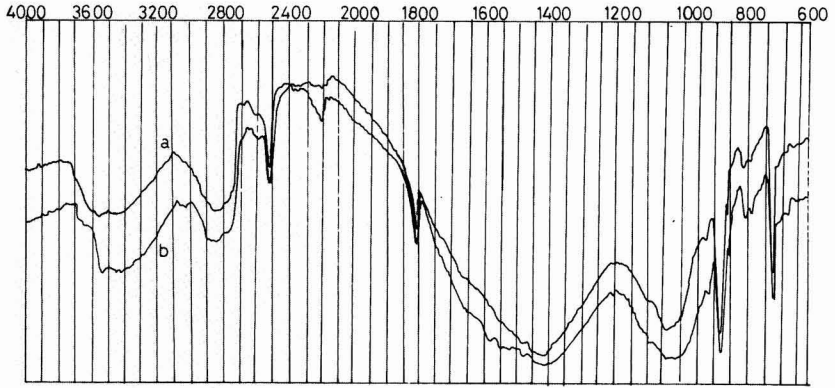
**Figure 7**

Spectrum of: (a) Original road aggregate. (b) After treatment to remove carbonaceous material.



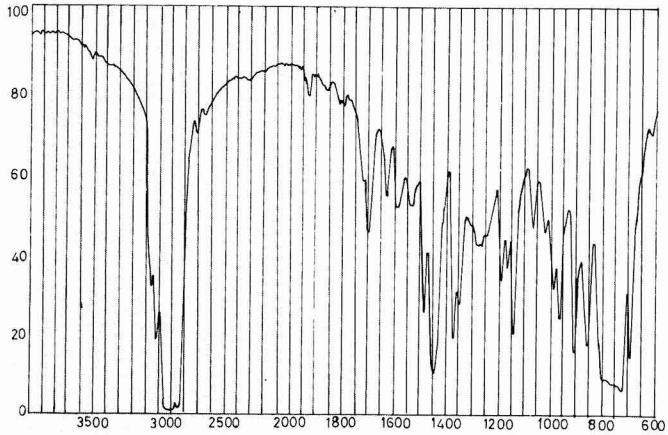
**Figure 8**

Spectrum of black Residue B obtained by washing: (a) An old asphalt road surface. (b) A newly laid (one month) asphalt road surface.



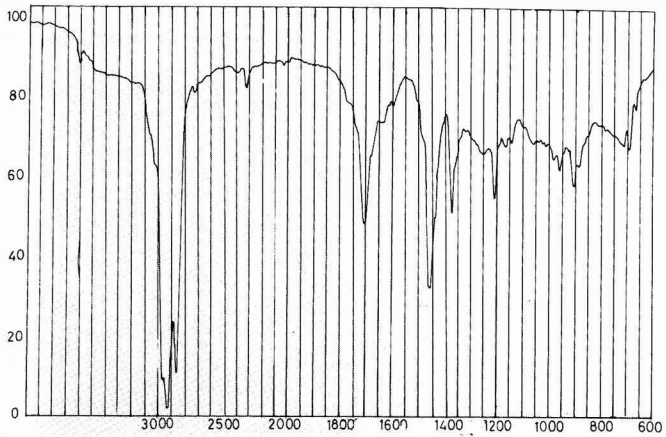
**Figure 9**

Spectrum of pyrolysate of car tyre tread.



**Figure 10**

Spectrum of pyrolysate of black residues (Sample-B) from washing road markings.



(iii) carbon black (iv) an inorganic residue. The ratio of (i), (ii) and (iii) were found to be very similar to the corresponding ratios for typical tyre tread rubbers.

The present paper gives attention directly to analysis of the black deposit itself using infra-red spectroscopy.

### Outline of the investigation

The black deposit can be removed from the markings either by scraping or by washing the markings with clean water using a sponge and expelling the washings for the sponge into a suitable container. On centrifuging at 45,000 r.p.m. the washings yield a black residue (B) and a yellow supernatant liquid which gives, on evaporation, a yellow-solid (A), see Figure 1. In both cases the samples of black material will be contaminated, not only with general dirt, but also with the marking paint (for the scrapings) and any soluble material from the adjacent asphalt (for the washings).

Three materials, paint, rubber from tyres and bitumen may be responsible for that blackening. Traffic paint is a complex mixture consisting of resins, plasticising material, pigment, filler, extender and solvent<sup>1,2</sup>. The composition of rubber is an organic rubber polymer, plasticising material and extending oil and carbon black filler. Bitumen consists of solid brown asphaltene hydrocarbons dispersed in a mixture of oil and resins. Bitumen oxidation results in complex changes which includes an increase in the asphaltene content<sup>10,12</sup>. The presence of asphaltene in I.R. spectra was selected as an indication of the contribution of bitumen in blackening traffic paints. Confusion may arise in the study of heavily filled compositions by I.R., since silica, diatomaceous earth and other common fillers in paint and rubber have broad and intense absorption bands<sup>13</sup>. Further the hydrocarbon absorbance expected will not indicate whether it is because of the presence of bitumen or of rubber in the black material. A clear absorption peak for asphaltene can be expected at 1575-1600  $\text{cm}^{-1}$  without any interferences from fillers, rubber and paint components. The Pyrolysis-I.R. technique cannot be used to obtain clearer spectra to identify bitumen, because of the change in the nature of bitumen during pyrolysis. The pyrolysis method is however a valuable means for infra-red examination of many insoluble resins and rubber<sup>14-17</sup>. This technique is useful in identifying rubber in the black deposits.

The analytical problem then is not a

trivial one. The samples are likely to be mixtures and contaminated with extraneous matter. It is desired to distinguish between rubber debris, paint residues and asphalt degradation products, all of which are essentially hydrocarbon in nature. The method adopted therefore was to compare the spectra of the black deposit with those of "pure" samples of the materials of interest and of mixtures of these materials.

### Experimental

Black deposits were collected from both thermoplastic and thermoset road marking paint surfaces by two means: scraping and washing with water. The washings were centrifuged at 45,000 r.p.m. resulting in a black residue (Sample-B) and yellow washing which gave on evaporation a yellow residue (Sample-A), Figure 1.

#### Identification of asphaltene

Infra-red analyses were undertaken of various materials paint, rubber, asphaltene, aggregates and black deposits in the form of discs pressed with potassium bromide. Reference samples for asphaltene detection were made using 5% asphaltene mixed with paint materials. The asphaltene was identified by an absorption peak at 1575-1600  $\text{cm}^{-1}$ .

#### Identification of rubbers

The pyrolysis infra-red method was broadly based on that described in BS 4181(17). Rubber samples T1, T2 and T3 from locally used tyres were cut up and were then extracted for about 16 hrs. with methanol in soxhlet, followed by drying at 100°C. Pyrolysis in a test tube with bunsen flame (BS 4181 alternative method) was employed. The pyrolysate was dissolved in carbon tetrachloride and dried. Infra-red spectra were recorded immediately after pyrolysis using cells of 0.5 mm path length. Solvent absorptions were cancelled out using similar reference cells containing carbon tetrachloride. The spectra are shown in Figures 9 and 10.

### Results and discussion

Figures 2a, 2b and 2c represent the spectra of asphaltene, rubber and thermoset paint. The materials involved are mixtures, usually with many components, and often the organic material is diluted with inorganic substances. As expected in such circumstances, the spectra are somewhat lacking in sharpness

nevertheless by comparison with the other spectra useful conclusions can be arrived at.

Rubber (Figure 2b) from an abraded new tyre gave a spectrum indicating the presence of hydrocarbon, but it was not sufficiently well-defined for the particular elastomer to be identified.

A sample of asphaltenes (Figure 2a) from a batch of 60-70 penetration bitumen showed some absorption peaks which clearly distinguished it from rubber and paint. The absorption peak at 1575-1600  $\text{cm}^{-1}$  is due to the contributions of polar chromophoric groups of aromatic and olefin derivatives.

Thermoset paint spectrum was characterized (Figure 2c) by a series of four small absorptions at 2650, 2525, 2350, 2200  $\text{cm}^{-1}$  which can be identified by comparison with the spectra of individual components of the paint. They correspond to talc (2650 and 2525  $\text{cm}^{-1}$ ), chlorinated rubber (2350  $\text{cm}^{-1}$ ) and alkyd resin (2200  $\text{cm}^{-1}$ ). Absorption at 1800  $\text{cm}^{-1}$  is due to calcium carbonate and absorption at 1725  $\text{cm}^{-1}$  is for the carbonyl group of ester resins. Common absorption in the three spectra, like absorption at 1030  $\text{cm}^{-1}$ , can be attributed in the case of asphaltene to the stretching vibration of C-O-C system. In the rubber spectrum, it will be due to the contributions of carbon-sulphur bonds and inorganic fillers. In the paint spectra it is due to silicates and other inorganic compounds.

Thus those absorptions present in the rubber sample are also present in the paint making it impossible to observe the rubber in the presence of paint (Figure 4). By contrast the asphaltene has a characteristic absorption frequency (Figure 2a) which can still be observed when a small amount of asphaltene is added to paint (Figure 3).

The spectra of the scraped black materials collected from thermoplastic paint surfaces (Figure 5) are identical with the original paint. There was no indication of the existence of asphaltene. In addition, the similarities of these spectra may indicate that the structure of the black materials could be considered as a composite of hydrocarbon and inorganic filler such as tyre rubber. This idea is strongly supported by the similarities of this figure with Figure 4 of the paint mixed with rubber. The black material residues from washing the markings (Residue B see Figure 1) were similarly analysed and represented in Figure 6. The insoluble part of the washing consists of inorganic and organic materials. Again there is no support for the idea of oxidation products of bitumen being a cause of

blackening, since there is no absorption due to asphaltene.

The spectrum of the black deposits (Figure 6) is in fact very similar to the spectrum of the road aggregate used in pavement construction (Figure 7a). The aggregate itself contains traces of hydrocarbon material which is destroyed after treatment with concentrated sulphuric acid and heating to 550°C (Figure 7b). As a further check on the stability of the asphalt road surface, the washing technique (Figure 1) was applied to the road surface itself and spectra of the black residue B were recorded. Figures 8a and 8b show that the residue is substantially the same as the aggregate (Figure 7a) except that a trace of asphaltene can be seen in the residue obtained from the newly laid (one month old) road surface (Figure 8b). Presumably at this stage it is not completely cured. In summary then the results presented in Figures 2 and 8 show that the black material responsible for discolouring the road markings is not derived from the asphalt surface. The results are consistent with the black materials coming from tyre rubber and dust, but does not prove this directly.

#### Identification of rubbers

Direct indication that the black material from the markings contained rubber was obtained from the infra-red spectra of the pyrolysate of the Residues A and B obtained from washing the markings.

Spectrum 9 as a typical representation of tyre treads tyres is very similar to the standard spectrum of Styrene-butadiene rubber<sup>17</sup>. The diagnostic absorptions 699, 775, 962 and 1490  $\text{cm}^{-1}$  are for styrene, while absorption at 909 and 990  $\text{cm}^{-1}$  are for  $-\text{CH}=\text{CH}_2$  group in butadiene. Other characteristic absorptions at 3030, 1640, 1370  $\text{cm}^{-1}$  are for aromatic-hydrogen, olifins, aliphatic-hydrogen respectively<sup>16</sup>. Additional absorptions in the 1200-1000  $\text{cm}^{-1}$  region are due to the presence of sulphur bonds in the vulcanised rubber. The spectrum of the pyrolysate of black residues (Figure 10) shows the same diagnostic absorptions, 699, 775, 909, 990 and 1490  $\text{cm}^{-1}$  founded in the spectrum of the pyrolysate of tyre tread (Figure 9). These findings indicate the presence of styrene-butadiene rubber in residues of the black materials from the road markings.

#### Conclusions

The results presented show clearly that the present of asphaltene can be detected by infra-red spectroscopy even when they are present as a minor component with road paint. The spectra

of the black material obtained by both scraping and washing the marking paint show no indications of the presence of asphaltenes. The spectra are consistent with the presence of rubber in the black material. A more positive indication of the presence of rubber is given by the similarity between the spectra of pyrolysates of residues from washing the markings and of pyrolysates of the tyre treads. Further confirmation of this conclusion is being sought<sup>11</sup>.

#### Acknowledgement

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## JOCCA – One Year On

The year 1988 saw great change for the Journal, some would say dramatic change, and it is perhaps worthwhile to consider how the Journal has evolved during the last twelve months and where it is going during 1989.

At the start of the year the Journal was completely re-designed, with a new front cover, introducing colour for the first time, a new typeface throughout and a different three column format, for both the news and technical articles. Editorially, the feature programme was introduced, together with an editorial comment page and extended news of companies and their products. The new Journal also saw the introduction again for the first time of a prepaid reader reply card, to enable readers to seek further information about the products advertised, or featured in the Journal and also to enable OCCA members or prospective members to notify address changes or to seek information on membership.

These major changes to the Journal were introduced by the Publications Committee who were most concerned that the Journal was no longer attracting sufficient good quality and interesting articles and had appeared to have lost the support of companies and their advertisements. It was the late Don Newton as Chairman of the Publications Committee who recognised the need for change, although it has been John Taylor who has had the more difficult task of carrying the changes through.

The re-launch took place at the same time as the build up to SURFEX 88 with an additional burden on editorial staff to produce a comprehensive and well supported Official Guide and Review of the Exhibition. Given the resources of the Association it was inevitable that there would be some changes in design, layout and contents of the Journal in successive months since the April 1988 launch. Hopefully, many of these changes have now settled down and for 1989 the format of the

Journal will not change dramatically throughout the year, although it is likely that a number of small improvements will take place in response to reader feedback and improvements in print management.

The most controversial change to the Journal was the decision to adopt a three column format for technical articles and this decision has generated a degree of controversy and critical comment. It has now been decided to revert to the more traditional two column layout for technical articles during 1989 and to review the situation in twelve months' time. The original decision to move to a three column format for the technical articles was reached because it was felt that this gave more flexibility in layout and design and produced a more attractive appearance to the printed pages.

However, the decision did not allow for the complex print format of technical articles with the result that word count on the 55 mm columns was not sufficient. It is hoped that the revision to the two column format for technical articles will improve their reception amongst the readers of the Journal.

The feature article policy has been well received by readers and, after initial problems in attracting sufficient articles to justify the editorial feature, a good flow of articles is now being received, particularly from Sections Symposia. The increased profitability of the Journal has enabled more articles to be printed and the Journal has also been able to attract outside editorials in support of the feature articles.

The editorial programme for the remainder of 1989 is shown below and already a good number of articles have been promised for these features.

February	Paint Production
March	Pigments
April	Automotive and Industrial Coatings
May	Fire Retardant Coatings/Chester Conference Preview
June	Paint and the Environment
July	Printing Inks
August	Additives for the Surface Coating Industries
September	Painting of Plastics/Pigments & Resin Show Preview
October	Marine and Offshore Coatings
November	Wood Finishes

December

Waterborne Coatings.

John Taylor welcomes the submission of good quality articles in support of editorial features and any reader who wishes to contribute should make contact with John as soon as possible. In addition to the editorial articles, the Journal still carries the Transactions and Communications that are a traditional feature of *JOCCA*.

The Publications Committee is making strenuous efforts to increase the number of good quality papers considered for publication as these are considered vital to the maintenance of the Journal as a leading English language Journal for the surface coating industries.

The News sections have been welcomed by companies and readers and it is hoped that these sections will be expanded to include more up to date information on products and materials, linked to a re-designed reader reply service to enable readers to obtain up to date information on products. These product notes will be complemented by more detailed reports on new developments in the industry and hopefully a more critical review of major economic and financial matters of impact to readers.

We hope you like the new style *JOCCA*, but remember, and this is addressed to Association members, it is your Journal, the Journal of the Oil & Colour Chemists' Association. If you have any comments, criticisms or praise, please let us know by telephone, letter or fax. Feedback from members is vital to the well being of the Journal and you can rest assured that all comments will be carefully considered by our Publications Committee and staff.

May I wish all our readers a happy and prosperous New Year and hope you enjoy reading your Journal during 1989.

## OCCA/PRA SYMPOSIUM

### The Role of Surface Coatings in Fire Protection

14-15 March 1989  
Heathrow  
LONDON

## Bristol Section

### Meetings various

The first lecture in the 1988/9 session was held at the Bowl Inn, Lower Almondsbury, Bristol, under the chairmanship of Chris Shaw and was the annual conjoint meeting of the Birmingham Paint, Varnish and Lacquer Club and Bristol OCCA. The lecturer was Mr D. Chant from OEH Scientific Ltd, who discussed the proposals and the effect of COSHH (the Control of Substances Hazardous to Health Regulations) to be introduced to the paint industry in 1989.

The consultative document was issued in 1984 by the Health and Safety Commission and contained a new concept in legal requirements that govern substances which are hazardous to the health of persons. Major changes were then made to these regulations and the final proposals were published in July 1987. The proposals were produced to govern the working practices of both the employer and employee to ensure safety when dealing with hazardous substances.

The lecturer then discussed the following new and important proposals:

1. Attention to all substances or types of substances to which employers are liable to be exposed. Account should be taken of the consequences of possible failure of any control measure provided to meet the requirements of the Regulation.
2. The effects the substances so identified can have upon the body.
3. Whether the substances are likely to be present in the working environment and, if so, in what form.
4. The ways in which any groups of employees or other persons could be potentially exposed. The extent of the potential exposure should also be assessed. Care should be taken to note the nature of the process and to observe any deterioration or failure in any control measure.
5. Estimate of the actual exposure should be obtained. This estimate

may take into account existing engineering control measures and systems of work.

6. Estimates of exposure should be compared with accepted standards which are deemed to represent adequate control i.e. Occupational Exposure Limits or maximum Exposure Limits.

The main part of COSHH is the assessment of health risks which governs such items as Control of Exposure, maintenance testing and recording of exhaust ventilation plant such as paint spray booths. This has been monitored previously and represents the traditional Occupational Hygiene part of the work. In the new COSHH there will be strict obligations on medical overseeing of certain specific substances for example isocyanates.

The regulations to the Assessment of Health Risks requires that the employer will assess the risks of his employees to substances used in their work and that the necessary control measures to carry out the assessment is made by properly trained staff.

The assessment of the effect of these substances is to be clearly monitored for both effects of possible failure of any control measures, the effect on the health of the employee, the substances likely to be present in the working environment and in what manner the employee may be exposed to these substances. Measurement of possible exposure must be obtained and must be compared with the Occupational Limits or M E Limits.

The lecturer then discussed how his company could assist in Surface Coating Industry in the requirements of the Act by the use of consultancy, appropriate equipment, analytical services and by seminars to the staff as On Job Training. A useful amount of printed data on the services provided and on COSHH was then provided to all those present.

A vote of thanks to the speakers was proposed by Mr M. Prigmore. This was followed by a buffet provided by the Bristol Section to their guests from BPVLC which

included their President Mr J. Mitchell.

The second meeting of the Section was the ladies' evening when arrangements were made to visit one of the first gas cooled nuclear power stations which is soon to be shut-down after supplying the National Grid since 12 June 1962.

The station was the Berkeley Power Station situated on the Severn Estuary. Visits to this location are always excellently planned by the Authority allowing a tour of all of the plant. One member of the party is asked to carry a digital monitor to measure the amount of radiation to which they might be exposed during the visit to the nuclear pile. The amount of radiation measured by the monitor is zero! Before the party is split up into smaller groups a video of details of the visit including some data on the fundamentals of nuclear fission is shown.

The guides have an excellent knowledge of the general working of the plant, any more technical questions are usually answered by the professional members of the staff of the power station.

The evening was concluded by a meal at a local inn. The occasion was well attended and it was unfortunate that due to the need to attend a company meeting in Wales the writer was unable to attend.

*J. R. Taylor* ■

## Hull Section

### Competitive emulsion paint thickeners

The first meeting of the 1988-89 session consisted of a lecture entitled "Competitive Thickeners for Emulsion Paints" delivered by Dr L. Dahlgren of Berol Kemi AB.

Dr Dahlgren pointed to positive contributions other than thickening made by the subject products at low concentrations, namely water retention, steric stabilisation, adhesion and film formation.



Considering cellulose ether types, exemplified by ethyl hydroxy ethyl cellulose, many variations are possible depending on degree of polymerisation, degree of substitution and type of substitution. Dissolving character is highly dependent on particle fineness but with very fine grades, lumping was more likely. In order to delay solution and obtain good dispersion, hence avoiding lumping, additives such as glyoxal were used.

The lecturer explained and demonstrated the advantages of high, medium and low viscosity grades with respect to such paint properties as open-time, spatter, levelling, enzyme degradation, brush resistance, hiding power and water resistance.

Chemical resistance and biostability increased as the substituted anhydroglyucose units in the cellulose molecule increased. Even substitution was all-important in ensuring such resistance which was said to be particularly high with certain Bermocoll grades. The hydrophilic and lipophilic nature of hydroxyl and ethyl hydroxyl groups in EHEC gave rise to surfactant behaviour which could be used to improve pigment dispersion.

Dr Dahlgren then summarised the contributions made by the cellulose derivatives during manufacture, application and storage.

He went on to consider associative thickeners, their mode of action involving bonding between their lipophilic groups and latex and pigment particles and the three types on the market; polyurethanes, anionic acrylics and non-ionic cellulose polymers. Polyurethanes gave increased high shear viscosity, good levelling and low spatter. Acrylics also exhibited good levelling and low spatter but high shear viscosity was low. Polyurethanes suffered poor sag resistance and recoating.

Combinations of polyurethane or acrylic types with cellulose derivatives had great potential particularly with respect to colorant 1989(1)

compatibility, levelling and hiding power.

Dr Dahlgren dealt competently with a variety of questions concerning cellulose ether combinations, link between spatter and elasticity, prediction of spatter from rheology, assessment of spatter, determination of uniformity of substitution and the consequent improvement in paint stability.

A vote of thanks was proposed by Mr J. A. Hasnip and endorsed by the audience who went on to enjoy a buffet and bar sponsored by Berol.

*D. Robinson* ■

## London Section

### Safer solvents

The second Technical meeting for the 1988/89 session was held on Thursday, 20 November 1988, at the Naval Club, Hill Street, Mayfair. Mr Stuart Lloyd, Product Manager, Speciality Chemicals, Samuel Banner & Co Ltd, gave a presentation on "The Trend to Safer Solvents".

Over the last decade, demands placed upon solvent suppliers have led to the replacement of more traditional solvents by cleaner, lower odour, environmentally acceptable solvents. This change has not been driven by the performance characteristics of the traditional solvents, but more by toxicological and environmental consideration.

The different types of solvents used commercially were outlined along with their performance, solvency and toxicological advantages and disadvantages. The product groups illustrated included aliphatic and aromatic hydrocarbons, glycol ethers, nitroparaffins and chlorinated solvents. Each group possessed its own particular problems which had led to the use of other solvents and/or generation of new products.

The changes that had occurred through use of potentially

carcinogenic aromatic hydrocarbons were dealt with in some detail. Here the trend has been back to natural aromatic hydrocarbons or over to aliphatic hydrocarbons. Glycol ethers also represented an area of great interest where second and even third generation solvents such as EEP are finding increasing uses because of their versatility.

Mr Lloyd concluded his presentation by saying that the trend towards cleaner products had resulted in a reduced number of suppliers. However, this did not necessarily mean an increase in prices. The increasing public concern over the environment and toxicology nevertheless meant that further new, clean products were required to meet constantly changing legislation.

Mr Ken Arbuckle proposed the vote of thanks for an interesting lecture which was endorsed by the audience after a lengthy question and answer period.

*G. J. Steven* ■

## Manchester Section

### Fire certification testing

The November technical meeting was held at the Mechanics' Institute, Manchester, on Monday, 7 November. Fifty members and guests attended the meeting, at which a paper entitled "Fire Certification Testing to BS 476, 1992 and Beyond" was presented by John Barnfield of Warrington Research Centre.

John Barnfield introduced the lecture by outlining the requirements of fire production in buildings, what fire is, how it develops, and briefly describing the surface spread of flame tests and their significance.

The lecturer went on to develop the main theme of the talk which was based on the effects of fire in a structure once it has got well established, the main goals being to protect life and prevent conflagration. The aims of fire design and how buildings are

divided into fire compartments to prevent fire spreading and structures collapsing was illustrated, the structure must remain intact and fire must be prevented from spreading.

The three main criterion for fire resistance in the construction of a building are:

- Stability
- Integrity
- Insulation

Specifically, steelwork is the area where fire resistant coatings are used, the effect of temperature on various types of steel was outlined and the reason why a building is normally loaded to half its design strength illustrated. Most steels have lost half their normal design strength at about 550°C therefore provided the steel is not allowed to get hotter than this, the building will remain stable.

Traditional methods of protecting steel such as concrete, insulating board, and spray plaster materials were described, but these have the disadvantage of not being decorative. Intumescent coatings have been around for 20 to 30 years, and their main property is to expand when subject to heat to produce an insulating char layer. The decorative effect of these products now available to architects was illustrated. Up to 1½ hours fire protection is now possible with thin film intumescent coatings. The time relates to BS 476 Part 8 or more recent Part 21, the curve being derived from the rate of heating possible in the furnaces available about the turn of the century.

The fire test itself is fairly severe, a comparison of the test with real fire situations was illustrated, the test furnace itself and the way fire testing is carried out also being outlined. Steel sections of different types heat up differently and the significance of the Hp/A factor in relation to this was described.

The lecturer concluded by outlining the characteristics of an intumescent coating, the type of faults which can arise, and the effect of the shape of the steel

section on coating performance. The various characteristics affecting the performance of intumescent coatings, and how performance graphs for them are derived was illustrated, and as the film thickness is critical the requirements for on-site control described.

The lecture was followed by a lively question and answer session, and the vote of thanks proposed by Roger Nicholls was enthusiastically supported by those present, who were then able to partake of a buffet subsidised by the Section.

## Ink adhesion with zirconium

The second printing ink lecture of the 1988/9 session, entitled "Improving Ink Adhesion with Zirconium Compounds", was presented by Dr P. S. Moles of Magnesium Electron Ltd, at the Silver Birch, Birchwood Centre, Warrington, on Monday, 21 November 1988, and was attended by 36 members and guests.

Zirconium a Group IV(b) element is characterised by its desire to polymerise, the chemistry involved was described in detail, and the basic cationic, anionic, and neutral polymers in general use were outlined. Zirconium polymers tend to react with both hydroxyl and carboxyl groups, and the mechanisms involved in this were illustrated.

Zirconium polymers have a number of industrial uses, but the main area is as adhesion promoters in printing inks. Their effectiveness compared with other polymers was outlined and the theory behind their effectiveness described. In order to be effective on difficult substrates such as plastics, there must be functionality on the polymer surface, free carboxyl groups being the most effective.

Zirconium polymers can be used to improve scrub and water resistance of water based inks and paints, the theory behind this was briefly described, however care in formulation is required, as excess zirconium compound can give

inferior results.

Thixotropy in emulsion paints can be induced with the use of zirconium compounds, and how this occurs was outlined, based on acrylic polymer emulsions, although the compounds can be effective with other types of polymer.

The lecture was followed by a question and answer session, the vote of thanks was proposed by Tony Wright, and those attending were then able to partake of a buffet sponsored by Magnesium Electron.

M. G. Langdon ■

## Midland Section

### J Newton-Friend Lecture: Styling workshop

The final meeting of the Midland Section for the 87/88 session was held at the Clarendon Suite, Stirling Road, Edgbaston, Birmingham. Members, guests and partners at this social meeting were entertained with a fashion workshop presented by Victoria White and Jackie Parker of Lewis's department store.

Victoria White described the fashion industry as one selling image, glamour and interest.

Co-ordination was the key to a successful range of products. However, the department store introduced a completely new range every six months to cover the Spring/Summer and Autumn/Winter seasons. In addition, the fashion industry had to appeal to men since it is acknowledged that they provide most of the money for purchases.

The products marketed had to appear 'new' and this was reflected in the styles picked for any one season, 'cut' and names given to colours. For example, red was now referred to as 'scarlet'.

Three distinct themes of dress were modelled during the evening. Each example was accompanied by a commentary from Victoria White

*Continued on p.19*

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## INDEX TO ADVERTISERS

Page

### G

Joshua Greaves & Sons Ltd ..... Inside Front Cover

### S

Scientific & Medical Products Ltd ..... 7

Shell Chemicals UK Ltd ..... 8, 9

### T

Thiokol Chemicals..... Back Cover

### W

Wymark Technical Products Ltd., Inside Front Cover

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