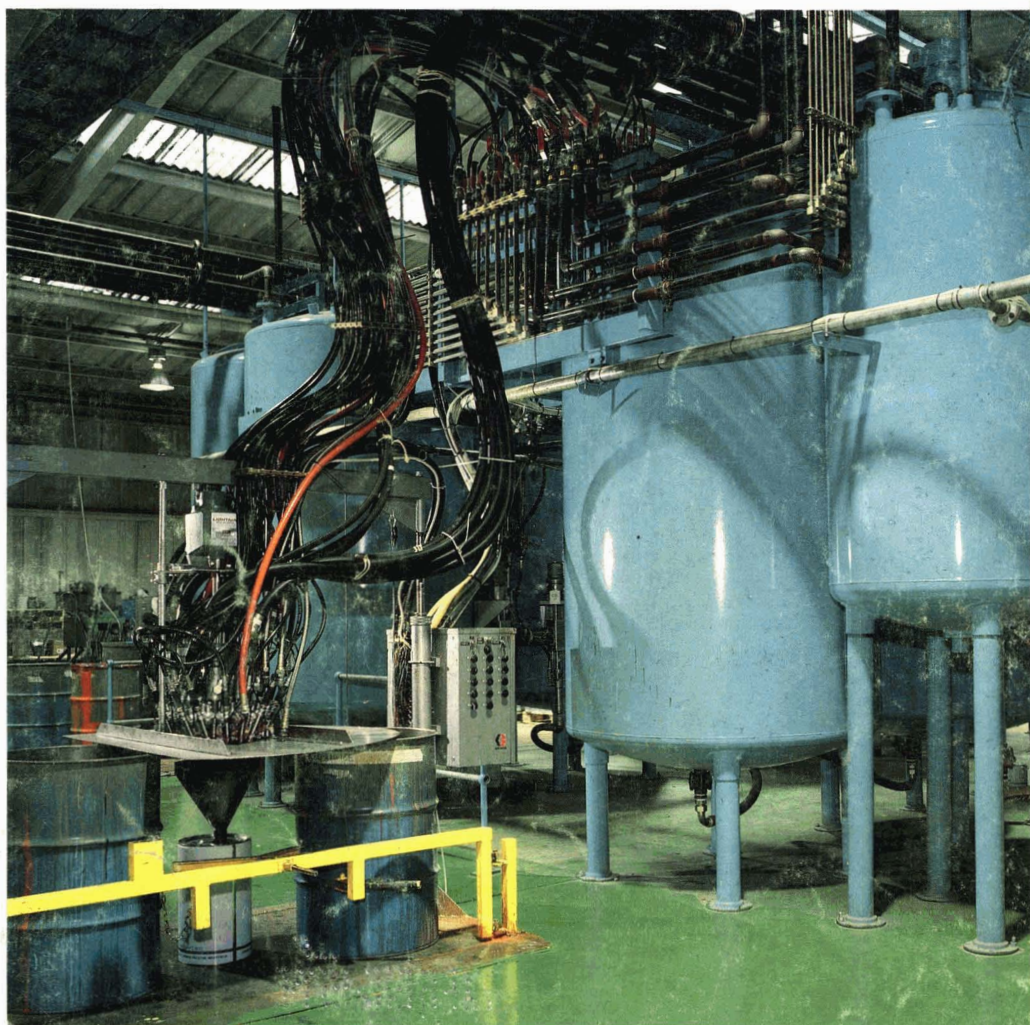




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## Contents

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An Official Journal of the Society of British Printing Ink Manufacturers and the Paintmakers Association of Great Britain Ltd.

News	354
<b>Feature: Additives</b>	
The dynamic surface properties of surfactants by C. Hsu and P. D. Berger	360
Coating compositions of insecticidal activity by M. Moustafa, A. Z. Gomaa and M. M. Metwally	366
<b>Transaction and Communication</b>	
Silicone resin emulsions: Binders for high performing façade coatings by J. M. Pouchol	370
<b>Short Communication</b>	
Iron tannate anticorrosion pigment by A. J. Seavell	377
<b>Horizons</b>	
PRA: A research association for the 1990s by H. Jotischky	378
The development of alkali soluble acrylic resins for use in aqueous printing inks by J. B. Clarke	380
<b>Process operation</b>	
Pumping	385
From the General Secretary	386
OCCA Council 1990-91	387
OCCA Committees of Council 1990-91	388
OCCA Section Officers and Committees 1990-91	389
<b>Exhibition Preview</b>	
Finishing 90	391

**Cover:** A computer/microprocessor controlled unit which automatically dispenses concentrated dispersions used in the manufacture of air drying alkyd-based enamels at Joseph Mason Paints. Pumps used in this installation include air-powered positive displacement reciprocating pumps. (Photo by courtesy of Graco UK)

**Forthcoming Features:** October—Physical Testing; Process Operation (PO): Energy Conservation; European Paint Show; November—Application & Film Formation; PO, Valves December—Weathering; PO, Feeding and Packaging. Contributions are welcomed at least five weeks prior to publication date.

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## BASF Corporation assigns new automotive "use patent" to Tioxide

A non-exclusive licence covering BASF-developed technology for the use of micro  $\text{TiO}_2$  pigments in automotive paints has been granted by the BASF Corporation to the Tioxide Group PLC. The agreement was recently signed at BASF Coatings & Colorants Division Headquarters, Clifton, NJ.

The Tioxide agreement is similar to the licence granted by BASF in November, 1989 to two Japanese pigment makers—Tayca Corporation and Ishihara Sangyo Kaisha Ltd.

The British company has developed various grades of micro-fine pigmentary  $\text{TiO}_2$ , some smaller than 0.1 micron in particle size. Now under construction by Tioxide in Scarlino, Italy is an \$8-million manufacturing facility for micro-fine pigments, expected to go on stream in 1991.

At BASF, the technology licensed to Tioxide was developed by Sol Panush, Manager of Color, BASF Automotive OEM Coatings Research Centre, Southfield, MI. The claims and applications in the licensed patents, transferred by Mr Panush to BASF, are all directed to the use of micro  $\text{TiO}_2$  pigments in auto paint compositions.

The inventor has combined micro  $\text{TiO}_2$  with resins, solvents and other pigments to create a totally new paint product. It is available for 1991-model-year automobiles.

The "use patent" licences provide for the licensees to make, use and sell the pigments for application in automotive paints worldwide.

### Hickson acquire Macostan

Hickson, the chemicals, coatings, timber protection and merchant distributor group has acquired Macostan for £0.75m. Macostan is a leading Dutch manufacturer of factory-applied wood finishes and of coatings for metal furniture. In both these sectors it has been at the forefront of the development of 'environmentally-friendly' waterborne and two-component high solids content coatings.



BASF-Tioxide micro  $\text{TiO}_2$  agreement. Seated from left: Wulf E. Crasselt, Senior Vice President, BASF Corporation and John R. Gush, Managing Director of Tioxide Chemicals Ltd. Standing, left to right, are Graham Brown, Product Manager, Tioxide; BASF Inventor Sol Panush; Michael R. Chipalowski, Patent Attorney, BASF northeast region; and Rob H Kuhn, New Products Manager, Tioxide America Inc.

### Becker 125 and going strong

Leading Paint Manufacturer, AB Wilhelm Becker is this year celebrating its 125th Anniversary, with worldwide parties commemorating the event. The UK is no exception in celebrating — Becker Industrial Coatings recently held a huge anniversary party for its employees in the grounds of Speke Hall in Liverpool.



### Hird Hastie gain BS5750

Hird Hastie Paints have recently Registered under the British Standard Institute's BS 5750 Scheme for their Quality Management Systems. This is a major achievement in their centenary year for this Scottish independent paint company and is the first to be successfully awarded this Registration in the West of Scotland.

### H Haeffner & Co Ltd to distribute new anti-corrosion vehicle latices

H Haeffner & Co Ltd are to market styrene butadiene latices produced by Doverstrand for anti-corrosion vehicle coatings. The new latices Revinex 3018 and Revinex 3020 are water-based SBR dispersions that when compounded offer improved elasticity, solvent resistance and abrasion resistance over existing systems.

### Johnstone's adds to depot network

Johnstone's Paints has added to its depot network with the opening of a new Sales and Distribution Branch in Southampton. The 5,000 square foot depot, at Unit 9B on the Central Trading Estate, is the company's 23rd branch in a network that began in Liverpool in 1950.

### Capricorn Chemicals relocates

From 1 September, Capricorn Chemicals Ltd. is relocating from its London base to Ely in Cambridgeshire. On the new site, Capricorn will join Ely Chemicals, another Dane Group company, which already manufactures under

licence some of the speciality additives offered by Capricorn to the surface coatings, inks and plastics industries.

Peter Gaskell, Director of Capricorn Chemicals, says "You must remember that Capricorn has grown to occupy its current prominent market position from quite small beginnings. It was inevitable that, at some point, we would expand into larger premises. This well-planned move represents a new stage in our development and gives us the opportunity to offer an even better service to our customers. We will be taking on more people locally to join our established central core of staff."

## US Focus

By Abel Banov  
Co-publisher  
American Paint and  
Coatings Journal

Hostile environments are held at bay by new technology based on compounds described as neoalkoxies, and anticorrosive paints are expected to be improved by them.

Protons from the substrate binds with some of the neoalkoxy groups, forming a merger that keeps out moisture and chemicals. What's more, Kenrich Petrochemicals, the company that developed the new materials, reported at the recent annual Seminar of the Pacific Northwest Society for Coatings technology that the materials are adhesion promoters and deglomerators, and they are excellent wetters, and dispersers when used to coat inorganic pigments.

Blends of these with pyrophosphates are reported to make them water soluble.

### Surface-treated pigments

At the same Seminar, Hoechst had a speaker discussing new surface treatments for pigments, which hold promise for eliminating a few coatings problems.

Dr Romesh Kumar said that the additives from the new group are selected to match at least some of the characteristics of the pigment to which it is to be attached. The new

agents add functional groups to the pigment surface, allowing stronger tints through heavier pigment loading.

These surface treatments provide steric repulsion, according to Dr Kumar, which, in effect, causes each pigment to repel all others.

He reminded us that one of the ways to improve tinting strength is to reduce particle size, but, then, he said, opacity is reduced.

Conversely, the larger the particle size, the greater the opacity. He also reminded us that pigments should be dispersed and not dissolved, because if dissolved they become dyes and have unexpected crystal structure and hue.

The new technology, using the new surface treatments, also takes into account particle size, and polarity of pigment surfaces and the pigment concentration in the mill base and in the finished paint.

### New round of research likely

Word is out that the Boeing Aerospace Co., a sister company of the makers of giant Boeing transatlantic aircraft, wants paint makers to provide coatings able to withstand 350-400F in space for many years.

Several polymer firms are believed to be working on the problem, and, beyond question a number of high performance coatings firms are going after the space contract. Since volume will not be great, nor monetary reward, the big payoff should be in advanced technology and the jump it gives a company.

### New water-reducible urethane developments

Triols are now being put into the backbone of certain waterborne urethanes by crosslinking, which adds improved properties of a crosslink on drying.

A urethane-acrylic copolymer is now available from the ICI America division, which differs from the usual urethane-acrylic blend, which usually works by formation of discrete pockets of urethane and acrylics. The copolymer, however, forms a shell with the urethane on the outside, giving coatings based on it the usual urethane characteristics—but at

reduced cost. With addition of M-pyrrol as a co-solvent, coatings using this copolymer have proved suitable for finishing plastics, reports Gail Pollano, Technical Marketing Manager for ICI America, who also said that a new universal urethane polymer has been developed that permits addition of urethane properties to other polymers.

### Replacement for acrylate technology

A new family of oligomers and monomers is being offered by Allied-Signal Co. for formulators who want to get away from acrylate technology. The products are named VEctometer (TM) and are described as low-odor prepolymers and diluents. They are functionalized by vinyl ethers and cure rapidly under cationic conditions.

What's supposed to be advantageous is their high-speed cure, toughness, and barrier properties. According to researchers working for the company, these products have been found to be completely non-mutagenic when tested with the Ames Assay.

### Non-crystalline diatomaceous earth

Here, and probably elsewhere, regulatory authorities are concerned about crystalline silica in various silicas. One of the products that have proven useful and are now affected by this concern is diatomaceous earth, one of the best flattening agents available to the industry.

This extender is of two types: one with a considerable amount of crystalline silica; the other with a negligible amount. All diatomaceous earth, sometimes called diatomites, start off amorphous. The trouble is that most of them, those that originated in salt water seas, are dark in color and have to be calcined to whiten them and to make them suitable for use. The calcining process converts them into crystalline forms; hence the concern about possible mutagenicity.

The form that has virtually no crystallinity originates in fresh water. They are sufficiently close to white that the naked eye can't tell the difference. They don't have to

be calcined for use and, thus, have no negligible crystallinity; some grades have as little as 0.1 per cent.

For latex flat paints they are available with a Hegeman grind of 1-1½, and for semi gloss 4-4½. The latter is used for semi gloss because it imparts a smooth finish. Big trouble is that use in formulations must be limited to about one-half lb. ga., because the high oil absorption — 112-116 — has too much binder demand for more.

The material, mined inland at Fernley, Nev., is getting a fairly big play here, where paint makers have become very conscious of silica crystallinity.

## Products

### New Baxenden moisture scavenger

**A** new moisture scavenger for use in the production of storage stable, moisture curing polyurethane surface coatings, has been launched by the Speciality Chemicals Division of Baxenden Chemicals.

Para Toluene sulphonyl isocyanate or Trixene ASF, as it will be called, is a monofunctional isocyanate which reacts readily with water and other compounds that contain reactive hydrogen groups. This is in addition to Trixene AS monofunctional isocyanate, which has been manufactured by Baxenden for many years.

*For further information Enter 1101*

### Antimony trioxide new product

**A** range of Antimony Trioxide products has been released by Crestchem Limited which provide a cleaner environment for manufacturing staff. Antimony Trioxide has become established as a flame retardant additive for both PVC and rubber and interest is now being shown in surface coatings. Historically, the standard powder form of this product can cause dust problems in the workplace and Crestchem offers a number of alternative forms which combat this aspect. For example an Antimony Trioxide paste dispersion can be used in surface coating.

*For further information Enter 1102*

### Courtaulds extends powder colour range

**T**he Interpon D range of architectural powder coatings, from International Paint Ltd, part of Courtaulds Coatings, has been extended to provide even more colour choice and a wider range of product selection. More than 330 products in gloss, satin or matt are now available in the Interpon D range, including over 150 new RAL colours.

*For further information Enter 1103*

## Equipment

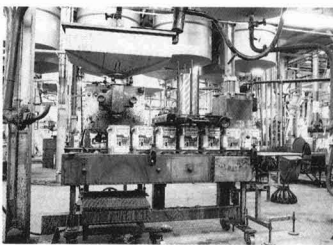
### Batch recipe management software

**R**otork Instruments has launched a versatile new batch recipe management software package that will simultaneously run numerous batches in several multi-stage plants while also holding additional recipes in reserve, ready for manufacture as plant becomes available.

*For further information Enter 1104*

### Mobile can filling machines

**O**n Solignum's manufacturing line the complex problem of efficiently filling and packaging a range of over 35 speciality products into four can sizes of two different can shapes and lid types has been solved by the use of two mobile De Vree V31 filling machines supplied by OBS Machines. Specifically designed for the economic handling of small batch runs, the versatile V31 units also feature a solvent auto rinse cycle which enables rapid changeover between handling products of different shade. Currently Solignum use De Vree



units to fill 1, 2, 5 and 25 litre round and rectangular cans.

*For further information Enter 1105*

### New lift truck

**H**yster has upgraded its H2.00-3.00XL series of engine powered, counterbalanced lift trucks. The Isuzu diesel engine, already known for its reliability, economy and low emission levels, has been improved. The engine as fitted in the new H2.00-3.00XL units reduces the truck noise level by 5 dB(A) giving an average of 81.5dB(A) according to BITA RP20.



*For further information Enter 1106*

### New mixing technique for alkyds

**L**eading independent manufacturer Varnish Industries Ltd of Bolton has achieved significant improvements in the production of alkyd resins by introducing new mixing techniques at its new custom-built resin facility. Resins used for oil-based paints are produced at high temperature in a reactor, then mixed with solvents in blending tanks kept at ambient temperature and atmospheric pressure, before being filtered and shipped to paint manufacturers for further processing.

Varnish Industries decided to investigate alternatives to its existing agitation methods when ordering a new £350,000 plant. This comprises one 20 tonne reaction vessel, a 50 tonne blending vessel, thermal fluid heating system, recirculatory cooling water system, and an automatic liquids and powders feed system—all operated from a central control room.

Morstan supplied the new reactor with an overhung dual axial flow

turbine system fitted with foam breakers of the comb type, and a stuffing box as the vessel seal, plus a flame-proof motor. The blenders were fitted with overhung single axial flow turbine systems, the agitators being fitted with low pressure stuffing boxes and flame-proof motors. The result has been a 30 per cent increase in production due to the new mixing equipment allowing bigger batches.



For further information Enter 1107

### Quality and safety from Sheen

Sheen Instruments believe that with increasing attention being paid to the clauses on safety control in the Health and Safety at Work regulations, the use of electrically driven instruments for testing solvent-based coatings could in some circumstances contravene regulations. Sheen offer a number of their instruments fitted with air driven motors.

For further information Enter 1108

### New particle size analyser

Malvern Instruments are to introduce a new, budget priced laser particle size analyser, the MasterSizer E based on their successful MasterSizer model. The analyser will be designed for research or quality control applications involving powders, suspensions or emulsions in the 0.1-600µm range.

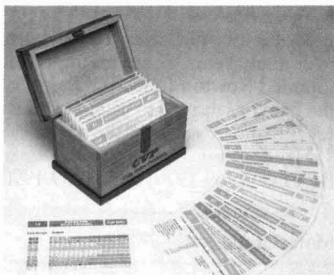


For further information Enter 1109

## Literature

### CVP wood finish information pack

Cray Valley Products Limited has produced a new information pack on wood finishing systems. The information package is intended as a progressive reference system which will be updated from time to time, and added to when further sections are completed. The package is seen as a valuable aid in the laboratory or office, and gives formulating guidance notes together with a comprehensive selection of starting point recipes.



For further information Enter 1110

### ICIS weekly chemical reports

Independent Chemical Information Services publish by fax over 50 individual current chemical pricing reports on a weekly basis. Global monitoring of chemical markets: transactions, trends and chemical pricing. For further information contact ICIS, 18 Upper Grosvenor Street, London W1X 9PD. Tel: +44 71493 3040.

### HSE consultation on safety of computer controlled systems

An extensive government consultation exercise has begun (until 30 September) into the safety of computer controlled systems. As such systems become more widely used, there is growing concern that a system failure could have serious or even fatal consequences.

'SafeIT 1: the Safety of Programmable Electronic systems: a government consultation document on activities to promote the safety of computer-controlled systems' and 'SafeIT 2: A Framework for Safety Standards'

are available free of charge from the ICSE Secretariat at the Department of Trade and Industry, Room 840, Kingsgate House, 66-74 Victoria Street, London, SW1E 6SW.

### Literature in brief

Electrochemical Impedance Monograph. Schlumberger.

For further information Enter 1111

Total Quality Management Training Package. Ad-Qual Ltd.

For further information Enter 1112

IAL Guide to European Adhesives Industry. £175, 160pp.

For further information Enter 1113

Complete Abstract of all new US Patents on CD-ROM 16yrs. £560, Chadwyck-Healey.

For further information Enter 1114

Stay Polymers & Sealants booklet on water dispersible epoxies.

For further information Enter 1115

## Meetings

### Corrosion course

A two-day course on the principles of corrosion and its control will be held at the National Physical Laboratory on 21 and 22 November 1990. The course will follow the general pattern established on previous occasions (1982 and 1984) when the highly successful event was held. It will be aimed at the engineer or technologist who is not a corrosion specialist, but for whom it is important to have a basic understanding of the corrosion behaviour of materials in his work in design, operation or maintenance of plant and equipment. Although some basic theory will be introduced as an aid to interpretation the emphasis of the course will be on practical aspects of the subject. To assist NPL in this objective the National Council of Corrosion Societies (NCCS) will provide guest lecturers with wide industrial experience, representing several of the societies in the UK

concerned with the many aspects of corrosion and its prevention.

A fee of £320 + VAT covers documentation, luncheons and light refreshments on both days.

For further details contact: Dr P E Francis, Division of Materials Metrology, National Physical Laboratory, Teddington, Middlesex TW11 0LW. Tel: 081-943 6481.

#### UK Corrosion 90

The 10th annual UK Corrosion Conference and Exhibition, will be held at the Sandown Park Exhibition Centre, Esher, Surrey 29-31 October 1990. UK Corrosion 90 is the premier corrosion event in Europe and will encompass a wide ranging technical programme: Symposia — 120 papers in 4 parallel streams for 3 days and a large exhibition of nearly 100 stands.

The symposium topics include: Corrosion of metals in concrete, Cathodic Protection, Pipeline Problems, Protective Coatings and Corrosion monitoring techniques.

For further details contact: the Conference Organiser, PO Box 253, Leighton Buzzard, Beds. LU7 7WB. Tel: (0525) 851967, Fax: (0525) 376690.

#### Laboratory design

Good Design Parameters for Laboratories, 5-7 November 1990, Amsterdam. Contact: The Center for Professional Advancement, Palestrinastraat 1, 1071 LC Amsterdam, The Netherlands. Tel: 020/662 30 50.

#### Emballage 90

The "1990 International Packaging Congress" will be organized jointly by the Institut Français de l'Emballage et du Conditionnement - IFEC Promotion (The French Packaging Institute) and Atochem. It will be held during the Emballage 90 Exhibition on 4 and 5 December 1990. This world exhibition will bring together several hundred specialists. Further information contact: IFEC Promotion, 3 rue de la Terrasse, 75017 Paris, France. Tel: (33-1) 43 80 92 77.▷

## Appointments

### Paintmakers Association appoints new President

The Paintmakers Association of Great Britain has appointed Mr David Penrice as its new President. Mr Penrice, aged 54, has been a member of the Association since 1971.

Over this period, Mr Penrice has been Chairman of the Midlands Section (1978-1980); member of council since 1982 and Chairman of the Open Tech and Training Committees since 1984. He was presented with the Silver Medal Award for meritorious service to the paint industry earlier this year.

Commenting upon his appointment, Mr Penrice said, "British paintmakers face a great challenge in the years ahead — an increasingly competitive market; the prospect of further national and EC legislation and an increased awareness of environmental, health and safety issues. We will also address the challenge of training for national standards of competence."

Mr Penrice has extensive background experience in the industry, gained over many years. From his apprenticeship at Arthur Holden & Sons, he co-founded Newton Industrial Paints of Birmingham in 1962. More recently the firm has moved to Tamworth, where it now employs 30 people and has recently been accredited with the BS 5750 Part 2.

Mr Penrice is also a member of the OCCA and former President of BPVLC (1969-1970) and (1989-1990) — itself a member of FSCT.



#### Material analysis

Bohlin Reologi and Stormage Scientific Systems are to join forces in October with the presentation of two 1-day seminars, 18 October Manchester, 19 October London, which will examine in depth the practical uses of materials characterisation techniques. Both seminars free. To register please contact Joan Caswell at Bohlin Reologi, Blackstone Road, Huntingdon, Cambridgeshire PE18 6EF. Tel: (0480) 411559.

#### CEP 90

1990 Continuing Education Programme: Industrial Electrostatic Hazards, 8 October 1990, Newcastle. Preventing Dust Explosions, 9 October 1990, Newcastle. Reactor Design in Practice, 8-11 October 1990, Dorset. For further information contact: Conference Section, Davis Building, 165-171 Railway Terrace, Rugby CV21 3HQ, England. Tel: 0788 78214.

**OCTOBER JOCCA  
PHYSICAL TESTING**

#### RHEOX appoints UK and Eire agents

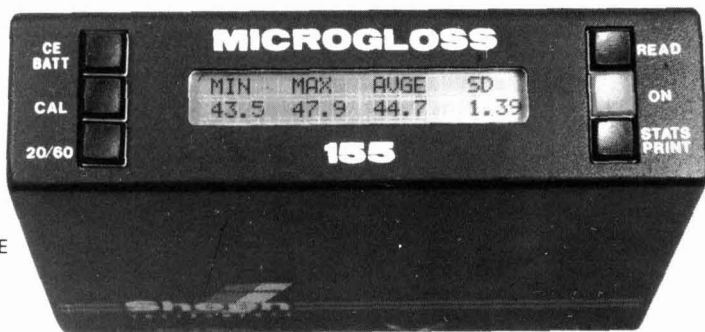
Steetley Minerals Ltd have been appointed agents in the UK and Eire for the products of RHEOX Inc. and sold under the THIXCIN, THIXATROL, M-P-A, RHEOLATE and NALZIN trademarks. Steetley Minerals have been responsible for selling the BENTONE rheological additives range for many years.

#### Mearl restructures

In a restructuring move to enhance its global image, The Mearl Corporation, manufacturers of Pearlescent Lustre Pigments, has announced the following assignments: Mr Frank J. Piser, formerly Marketing Manager, has been appointed to the position of General Manager, Global Sales and Marketing. At the same time it was also announced that Mr Ponce de Leon has been named Sales Manager for all Mearl operations in the Eastern Hemisphere, including all of Europe, Africa, Asia, Australia and New Zealand.



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**SCHWEGMANN**

# The dynamic surface properties of surfactants

by C. Hsu and P. D. Berger, Witco Corporation, Organics Division, 3230 Brookfield Street, Houston, Texas 77045, USA

## Introduction

Surfactants play a major role in coatings technology. Among their many applications one finds them used as emulsifiers, wetting agents, penetrants, dispersants, defoamers, antistatic agents, corrosion inhibitors, flow modifiers, and leveling agents, corrosion inhibitors, flow modifiers, and leveling agents. The performance and value of surfactants is largely due to their ability to significantly alter surface and interfacial properties at low concentrations. Many studies have been performed on the surface tension lowering properties of surfactants and on their structural/performance relationships. Only recently, however, has it been possible to include the dimension of time to these studies. We have used the maximum bubble pressure technique, MBP<sup>1</sup>, to study the dynamic surface tension and surface dilatational viscosity of various surfactants and have correlated these properties to several time related applications such as penetration and wetting<sup>2</sup>. We believe the study and understanding of the dynamic surface properties of surfactants will play a significant part in the development of new and improved coating systems and provide a better understanding of the benefits and problems surfactants create. Some of the applications for which surfactants are used and the surface problems they may create are shown in Table 1.

Table 1

Some applications for surfactants in coatings

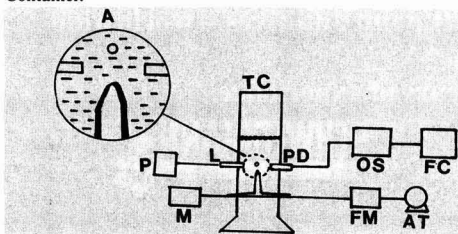
Applications	Possible Problems
Defoaming, Dispersing, Grinding Aids, Wetting, Leveling Agents.	Pinholes, Craters, Orange Peel, Fisheyes, Floating, Poor Adhesion, Silking, Poor Recoating, Crawling, Beading, Foaming.

## Apparatus for the Maximum Bubble Pressure Technique

Figure 1 shows the apparatus we used to determine the dynamic surface properties of various surfactants using the maximum bubble pressure technique. This procedure was recently reviewed by Mysels<sup>1</sup>. We have used a design based on

Figure 1

Schematic Diagram of Maximum Bubble Pressure Apparatus: A) Capillary Tube, FM Flow Meter, AT Air Tank, L) Light Diode, PD) Photo Detector, OX) Oscilloscope, FC) Frequency Counter, M) Manometer, P) Power Supply, TC) Tensiometer Container.



that of professor Wasan's group at IIT. The solution of material containing the surfactant under study is contained in the specially designed tensiometer vessel (Reliance Glass Works Inc, Bensenville II). This is fitted with a cooling jacket to keep temperature constant and a precision bore capillary tube through which air or a second liquid is pumped. When measuring dynamic surface properties, air or another gas is accurately metered by a dual stage regulator and a precision flow meter (Gilmont Instruments Inc, Great Neck, N.Y.). The gas passes through the capillary creating a bubble at the tip. The pressure within the bubble is measured using a precision digital monometer (Meriam Instrument Co, Cleveland OH). The bubble formed at the tip of the capillary passes between a photodiode and a light source after detachment from the tip of the capillary. The bubble disrupts the light source and the frequency of bubble detachment is measured using a frequency counter (John Flude Mfg Co, Everett WA) which is channelled through an oscilloscope (Leader Instrument Corp, Hauppauge, N.Y.).

## Theory of Maximum Bubble Pressure Technique

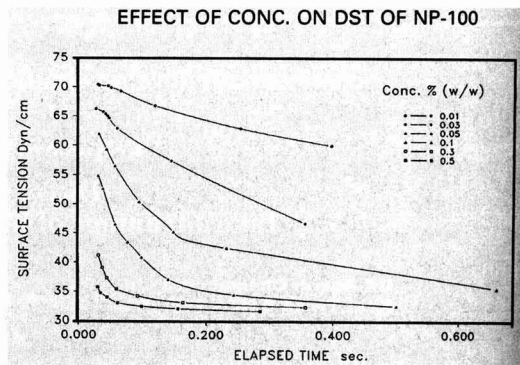
The pressure within a bubble is maximum when the bubble is spherical. A bubble emerging from the tip of a clean, precision bore capillary reaches its maximum pressure when the diameter of the bubble is equal to the internal diameter of the capillary. In the MBP technique the diameter of the capillary is determined by optical measurement and by calibration with a known liquid such as pure water. We found the radius of our capillary to be 87.30 $\mu$ m using distilled deaired water as a standard. The pressure within the bubble is measured using the monometer and corrected for the hydrostatic head of solution above the capillary. Knowing the radius of the capillary and the maximum pressure within the bubble, the surface tension can be calculated using the following relationship:

$$\sigma = (P_m - dh)gr_c/2, \quad (1)$$

where  $\sigma$  is the dynamic surface tension in dyne/cm,  $P_m$  is the maximum pressure within the bubble in gm/cm<sup>2</sup> corrected for the atmospheric pressure,  $d$  is the density of the liquid in g/cm<sup>3</sup>,  $h$  is the height of the liquid above the capillary in cm and  $g$  is the gravitational constant in cm/sec<sup>2</sup>.

By measuring the maximum bubble pressure at various flow rates, a series of surface tensions can be obtained each for a

Figure 2



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particular rate of bubble formation. The frequency counter is used to determine the rate of bubble detachment in kHz or reciprocal milliseconds. Knowing the frequency one can plot the surface tension on the Y-axis against the inverse frequency on the X-axis to obtain a plot of the surface tension as a function of elapsed time in milliseconds. This is shown in Figure 2 for a series of solution of 10 mole ethoxylated nonylphenol of differing concentrations.

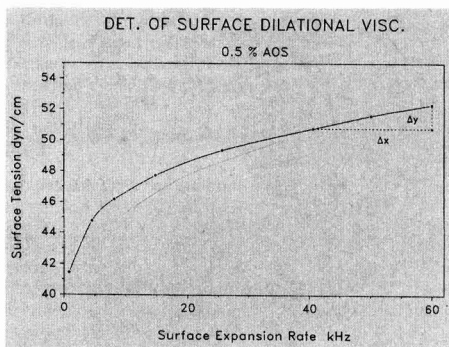
Knowing the flow rate one can calculate the expansion rate of each bubble using the relationship:

$$\epsilon = Q/\pi r_c^3 \quad (2)$$

where  $\epsilon$  is the surface expansion rate in Hz, Q is the flow rate in cc/sec, and  $r_c$  is the capillary radius in cm as before.

The surface dilatational viscosity can be obtained by examining the dynamic surface tension values at various rates of surface expansion. The gradient of the dynamic surface tension with respect to expansion rate can be obtained in the linear region of large expansion rates as shown in Figure 3. In this region the rates of surface expansion are much larger than the rate of surfactant adsorption<sup>4</sup>. The gradient of the curve calculated in this area is the surface dilatational viscosity in poise  $\times 10^3$ .

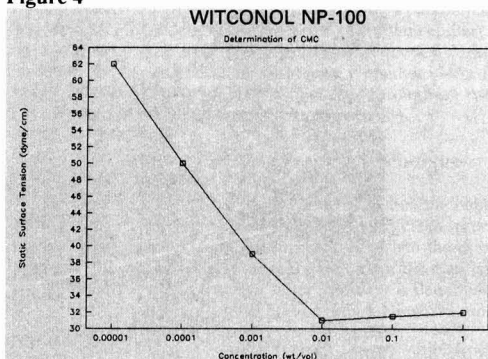
Figure 3



## Effect of concentration on dynamic surface tension

Referring back to Figure 2 one can see the result of measuring the surface tension at various frequencies for different concentrations of a 10 mole ethoxylated nonylphenol solution (WITCONOL NP-100). The results show that the surface tension values decrease as the concentration increases and that the surface tension reaches its minimum value faster as the concentration is increased. From the curves it can be seen that the minimum concentration necessary to give maximum surface tension lowering and probably maximum performance changes with bubble formation frequency. As the speed of bubble formation is increased, more surfactant is necessary in order to reach a minimum surface tension. If all the curves containing concentrations at or above the static CMC are extended to infinite time they will all reach a surface tension value equal to the minimum surface tension value found in Figure 4 where the CMC was determined from static measurements using a Du Nuoy ring<sup>6</sup>.

Figure 4



Notice that in Figure 2 the dynamic surface tension curves continue to change far above the CMC. This is because the CMC is determined for a static system and we are looking at a dynamic system during our measurements. The curves for concentrations above the CMC will never reach the minimum surface tension. The CMC can be looked at as the concentration whose dynamic surface tension curve, when approaching time  $\infty$ , gives the minimum surface tension found for the product.

Much of the literature describes the CMC as the concentration range where many surface related phenomenon are maximized or minimized<sup>5</sup>. It is claimed that interfacial tension and surface tension is minimum at the CMC and that foaming, detergency and wetting are maximized at or above the CMC.

If one wishes to choose a concentration for a surfactant which gives optimum surface tension lowering in a dynamic process such as high speed jet printing, spray coating or wetting, they can

## Experimental results and discussion

Dynamic surface tensions and surface dilatational viscosities were obtained for several surfactants described in Table 2.

These properties were compared in some cases to observed performance characteristics to determine the importance of dynamic surface properties to surfactant performance.

Table 2

Surfactants used in the study

Name	Description	Applications
WITCONOL NP-60	6 Mole Ethoxylated Nonylphenol	Oil Wet., Grind
WITCONOL NP-80	8 Mole Ethoxylated Nonylphenol	Wetting, Grind
WITCONOL NP-100	10 Mole Ethoxylated Nonylphenol	Wetting, Grind
WITCONATE AOS	C14-16 $\alpha$ -Olefin Sulfonate, Na	Foam, Detergent
BUBBLE BREAKER 260	Fatty Acid Soap	Foamer
BUBBLER BREAKER 3056A	Reacted Silica	Defoamer, Antifoam
EMCOL 4161L	Monooleamido Sulfosuccinate	Pigment Disp.
EMCOL 4300	Monolaurate Sulfosuccinate	Oil Wet, Grind
EMCOL 4500	Di 2-ethylhexyl Sulfosuccinate	Wet, Grinding
EMCOL 4910	Polypropoxy, C12-15 Alkyl Sulfosuccinate	Pigment Disp.
EMCOL K-8300	Mono alkanolamide Sulfosuccinate	Pigment Susp.
EMCOL CC-9	Polypropoxy Quaternary	Pigment Susp.

examine a series of curves such as Figure 2 and determine the concentration necessary to give maximum lowering in the period of time required by the process.

Figure 5

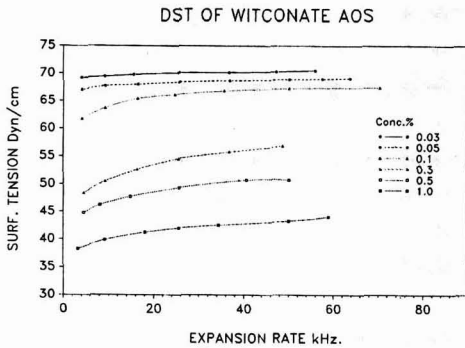
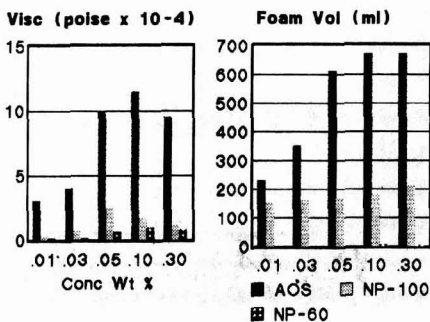


Figure 5 presents similar data as in Figure 2 but using expansion rates as the X-axis instead of time and WITCONATE AOS, a C14-16  $\alpha$ -olefin sulfonate, as the surfactant. From the linear region of the slope of these curves at high expansion rates (>40 kHz) the surface dilatational viscosities can be calculated. If the curves are extended to expansion rates=0, they will intersect the Y-axis at the lowest surface tension found by static measurements for concentrations at or above the CMC. The CMC for AOS was found to be around 0.2% as on an "as is" basis and its minimum surface tension was found to be 35.1 dyne/cm. Those curves representing concentrations below the CMC will intersect the Y-axis at values above this minimum for expansion rates=0.

Figure 6



### Surface dilatational viscosity and foaming

Figure 6a shows the surface dilatational viscosities for WITCONOL NP-100 (10 MOLE EO) and WITCONATE AOS (C12-14  $\alpha$ -olefin sulfonate). The AOS gives higher surface dilatational viscosities across the entire concentration range. Both products have been adjusted to a per cent active basis since the original activity of WITCONATE AOS is 40% compared to 100% for the WITCONOL NP-100.

Figure 6b compares the results of foaming tests on various concentrations of WITCONATE AOS at 25°C with those for WITCONOL NP-100. The tests were run by mixing 100ml of each solution in a Waring™ blender jar at high speed for 30 seconds and pouring the resulting foam into a 1,000ml graduated

cylinder. The initial foam volume and the time elapsed when 50ml of liquid appear (half-life) are recorded. There is a good correlation between the concentration giving the maximum surface dilatational viscosity and the concentration giving the best foam performances. This indicates that an optimum surfactant concentration exist for a dynamic process like foam generation and that performance falls off when concentrations are below that concentration. WITCONOL NP-100 is a low foaming nonionic giving a maximum foam height of 150ml compared to the 670ml maximum produced by AOS.

Figure 7

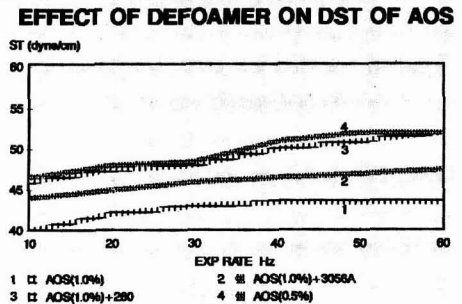


Figure 7 shows the dynamic surface tension curves for WITCONATE AOS and AOS containing two defoamers, BUBBLE BREAKER 260 and BUBBLE BREAKER 3056A. WITCONATE AOS is used as a component for many detergent formulations because of its foaming and dispersive properties. The curve for the 1.0% solution of AOS shows it to be effective in lowering surface tension rapidly even at frequencies of 60 kHz. BUBBLE BREAKER 3056A is only partially effective in reducing the foaming tendencies of AOS while BUBBLE BREAKER 260 is extremely effective. The curves show that addition of 0.1% 260 to 1.0% AOS slows down the speed at which surface tension is lowered and in fact changes the surface tension profile to that of a 0.5% AOS solution.

### Effect of dynamic surface tensions on wetting properties

Table 3 shows the results of various tests to determine several properties of a series of sulfosuccinates. The structures of these anionic surfactants were previously described in Table 2. Properties measured for each sulfosuccinate were foaming by the Ross-Miles test procedure, wetting by the Draves Method, surface tension after 33 milliseconds by the Maximum Bubble Pressure Procedure, static surface tension by the De Noy ring method and surface dilatational viscosity also by the Maximum Bubble Pressure Procedure.

The data from Table 3 is plotted in Figure 8. From the figure it can be seen that a relationship exists between the dynamic surface tension at 33 millisecond and the surface dilatational viscosities with wetting times in seconds and the foam heights after five minutes. The latter two properties are dynamic properties involving short time intervals. The two surface properties found to show a correlation with them are also dynamic surface properties. The static surface tensions of all products are very low and the initial foam heights are also very similar. From these results it can be shown that surfactants giving low surface dilatational viscosities will not produce as stable foam as those with high surface dilatational viscosities. Also surfactants which lower surface tension rapidly will wet faster than those which lower surface tension more slowly. All surfactants which lower surface tension significantly will produce high foaming levels

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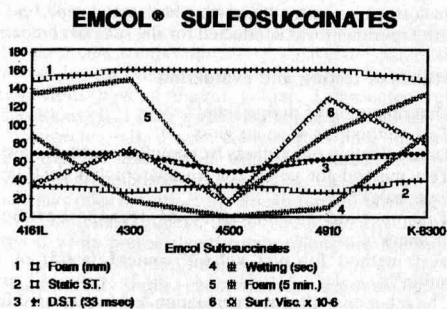


**Table 3**  
Properties of Emcol sulfosuccinates, 0.10% at 25°C

Product	Foam, mm init/5min	Wetting sec	Sur. Tens., 33msec	dyne/cm static	Sur. Dil. Visc poise x 10 <sup>-6</sup>
4161L	150/135	90	70.3	34.0	35
4300	162/151	18	69.8	28.1	75
4500	160/15	>1	49.5	34.5	15
4910	163/92	10	63.6	26.8	130
K-8300	150/135	90	70.3	42.1	80

however the volume and stability of this foam is not related to the degree of surface tension lowering.

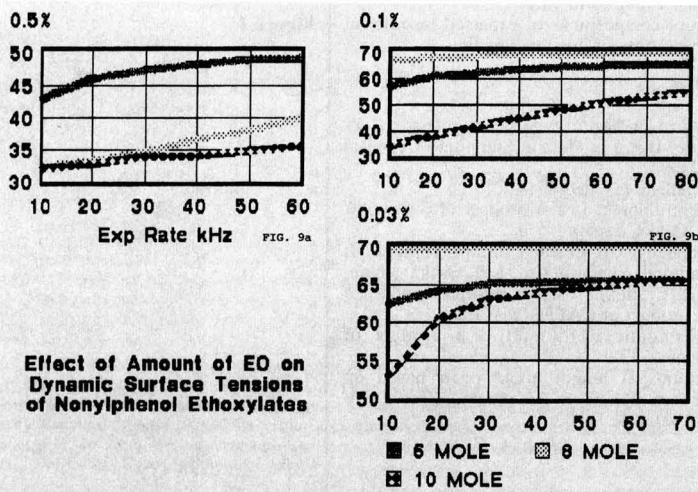
**Figure 8**



**Effect of solubility on dynamic surface tension**

Figures 9a,b,c show the dynamic surface tension profiles for various concentrations of WITCONOL NP-60, WITCONOL NP-80 and WITCONOL NP-100. Figure 9a shows that the 10 mole adducts is fastest at lowering surface tension followed by the 8 mole and finally the 6 mole. As the concentration is decreased from 0.5% to 0.1%, Figure 9b shows the 6 mole to be faster than the 8 mole. As the concentration is further decreased as shown in Figure 9c, the difference between the NP-100 and NP-60 becomes less. This effect is due to the difference in solubilities between these nonylphenol ethoxylates. The 10 mole is most

**Figure 9**



soluble and the 6 mole least soluble in water. As the concentration is reduced the NP-60 becomes as completely soluble as the NP-80 and finally as the NP-100 and when it is present *in solution* at concentrations equal to either of the others it is actually as good or a faster surfactant.

**Conclusions**

The Maximum Bubble Pressure technique is a rapid and accurate means of measuring dynamic surface tension and surface dilatational viscosities of surfactants. Many properties of surfactants, including wetting and foaming are dependent on dynamic surface properties. The technique can be used to determine the optimum concentrations of surfactants and the best surfactants for systems where speed as well as effectiveness is of importance.

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# Coating compositions of insecticidal activity

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## Summary

Various coating compositions were formulated and evaluated for their insecticidal activity. Three different types of binders were used; namely chlorinated rubber, polyurethane and alkyd resins. Three kinds of insecticides with trade names Sumicidine, Sumithion and Cyanox were studied. Cockroaches were the target insect. Compositions based on alkyd or chlorinated rubber and containing 4% Cyanox or Sumithion as insecticide showed promising results as insecticidal and insect repellent coatings.

## Introduction

Insecticides are chemicals which are used to control damage or annoyance from insects. Generally, control is achieved by poisoning the insects by oral ingestion of stomach poisons, by contact poisons that penetrate through the cuticle or by fumigants that penetrate through the respiratory system<sup>1</sup>.

Three major classes of synthetic organic insecticides; organochlorine, organophosphorus and carbamate dominated usage with the rapidly developing synthetic pyrethroids<sup>2</sup>. The literature survey of insecticidal coatings is scant and the subject has not been extensively studied.

Pesticidal coatings can be prepared by using different insecticides with different binders. For example, DDT, aldrin, dieldrin, chlorodane, benzenehexachloride, etc., may be combined with some special resins such as amino resins, urea-formaldehyde, synthetic rubber, oleoresinous or alkyd resins to confer the coating various degrees of insecticidal characteristics<sup>3-10</sup>.

Wall paper resisting insect coatings are prepared via combinations of emulsion, lacquers, vinyl, acrylic or oil types together with the insecticidal solution in polar organic solvents<sup>11</sup>.

An insect repellent coating is made of 2-tert-butyl-4-hydroxyanisole and film forming resin base<sup>12</sup>.

The formulation of compositions of expected insecticidal activity is the main purpose of this investigation.

## Materials and Methods

**Sumicidin:**  $\alpha$ -Cyano-m-phenoxybenzyl- $\alpha$ -isopropyl-P-chlorophenyl acetate. It is a product of Sumitomo Chemical Co., Ltd. Osaka, Japan.

**Sumithion:** 0,0-Dimethyl(0-(3-methyl-4-nitrophenyl)phosphorothioate. It is a product of Sumitomo chemical Co., Ltd, Osaka, Japan.

**Cyanox:** 0-4-Cyanophenyl 0,0-dimethyl phosphorothioate. It is a product of Sumitome Chemical Co., Ltd. Osaka, Japan.

**Chlorinated rubber:** (Clortex). It has a chlorine content of about 67%. It is a product of CAFFRO — Italy.

**Polyurethane:** (Desmodur E1160). It is a product of BAYER — Germany.

**Alkyd resin:** Medium oil length alkyd resin based on sunflower oil. It has colour 7 (Gardner), viscosity V (Gardner) and acid value 6.

## Test containers

A frame of wood of dimensions 40cm  $\times$  10cm  $\times$  15cm

with a sliding partition in the middle, so as to divide the container, when desired, into two separate chambers, was covered by a net of wire gauze. Each test panel was placed individually in a container with a certain number of cockroaches. The containers were kept in a testing cabinet in the laboratory and observed to evaluate the effectiveness of the insecticidal compositions on the cockroaches. It is noteworthy to mention that within each set of experiments, a blank experiment was conducted for the sake of comparison.

## Methods of testing and evaluation

Determination of drying time<sup>13</sup>.

Test method for specular gloss<sup>14</sup>.

Determination of hardness by penudum hardness tester<sup>15</sup>.

Test method for colour of transparent liquids (Gardner colour scale)<sup>16</sup>.

Test method for viscosity of transparent liquids (Gardner)<sup>17</sup>.

Test method for non volatile content (solid) of resin solution<sup>18</sup>.

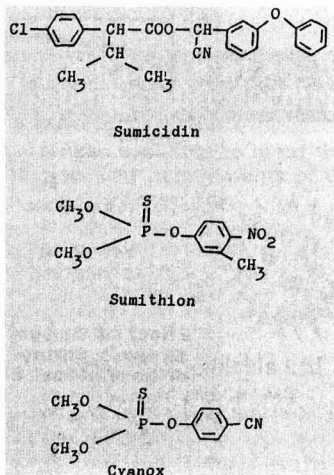
The other analytical and evaluation techniques used in this work were based on standard methods.

## Results, discussion and conclusions

The adoption of insecticidal coatings for general application was slow for many reasons, attention was therefore directed to formulating various insecticidal compositions that could be used for the control of insects affecting public health such as cockroaches.

Three different types of binders were selected for this investigation namely chlorinated rubber, polyurethane and alkyd resins. Also, three insecticides of the Sumitomo Chemical Co., were used. They have the chemical structures shown in Figure 1.

Figure 1





Sumicidin is effective at remarkably low dosages and has a rapid action as well as a long residual effect that could not have been expected when using a single insecticide of a conventional type. Sumithion is a broad spectrum organophosphorus insecticide to control various insect pests. Noteworthy is its low toxicity to warm blooded animals. Cyanox is an organophosphorus insecticide. It is claimed to be an effective destroyer of domestic insects<sup>19</sup>.

Preliminary trials were conducted to determine the most suitable insecticidal coating compositions. The results indicated that varnishes with an active ingredient (sumicidine, sumithion or cyanox) of under 2%, based on solids, showed undesirable results against cockroaches. Table 1 illustrates three series of compositions under investigation. Further films and varnish characteristics were carried out and the results are given in Table 2.

The following generalizations were noticed from the data given in Table 2:

1. Polyurethane compositions (II<sub>a-g</sub>) have the paler colour and the lowest viscosity at 30% solids, while alkyd compositions have a darker colour. Chlorinated rubber compositions (I<sub>a-g</sub>) have a viscosity C and a colour 6.
2. As expected, alkyd resin compositions have the longest drying time in comparison with chlorinated rubber and polyurethane compositions. In general, the presence of the insecticides does not affect the drying time of test panels.
3. Regarding the hardness, the alkyd resin shows the lowest hardness while polyurethane compositions are the highest. Chlorinated rubber films lie in between.

Film durability studies of the various varnish compositions indicated that all compositions showed outstanding film

performance regarding the gloss, flexibility, water, acid, alkali and solvent resistances. The presence of the insecticides

**Table 1**  
Various insecticidal coating compositions

Varnish No.	Type of varnish	Active ingredient* /solids (%)
I	a Chlorinated rubber	0.00
	b Chlorinated rubber/Sumicidine	2.00
	c Chlorinated rubber/Sumicidine	4.00
	d Chlorinated rubber/Sumithion	2.00
	e Chlorinated rubber/Sumithion	4.00
	f Chlorinated rubber/Cyanox	2.00
	g Chlorinated rubber/Cyanox	4.00
II	a Polyurethane	0.00
	b Polyurethane/Sumicidine	2.00
	c Polyurethane/Sumicidine	4.00
	d Polyurethane/Sumithion	2.00
	e Polyurethane/Sumithion	4.00
	f Polyurethane/Cyanox	2.00
	g Polyurethane/Cyanox	4.00
III	a Alkyd resin	0.00
	b Alkyd resin/Sumicidine	2.00
	c Alkyd resin/Sumicidine	4.00
	d Alkyd resin/Sumithion	2.00
	e Alkyd resin/Sumithion	4.00
	f Alkyd resin/Cyanox	2.00
	g Alkyd resin/Cyanox	4.00

\* Sumicidine, Sumithion or Cyanox.

**Table 2**  
Film and varnish characteristics of various compositions

Varnish No.	Solids content (%)	Viscosity (Gardner)	Colour (Gardner)	Air dry time (hr)	Film thickness		Hardness <sup>†</sup> (sec.)		Gloss, 60° <sup>‡</sup> (%)		
					a*	b**	a*	b**	a*	b**	
I	a	30	C	6	0.25	20	30	151	99	96	81
	b	30	C	6	0.25	20	20	119	64	94	76
	c	30	C	6	0.25	20	20	70	46	96	95
	d	30	C	6	0.25	20	20	140	132	96	98
	e	30	C	6	0.25	20	24	79	73	95	100
	f	30	C	6	0.25	20	30	134	74	97	87
	g	30	C	6	0.25	20	20	103	63	96	96
II	a	30	B	1	0.50	20	24	147	111	97	98
	b	30	B	1	0.50	20	24	144	127	95	96
	c	30	B	1	0.50	20	24	139	121	97	97
	d	30	B	1	0.50	20	24	146	126	95	97
	e	30	B	1	0.50	20	24	146	115	97	98
	f	30	B	1	0.50	20	20	139	139	98	98
	g	30	B	1	0.50	20	20	137	127	86	95
III	a	50	W	7	6.00	20	30	13	12	91	93
	b	50	T	7	6.00	20	30	16	10	92	93
	c	50	N	7	6.00	20	30	7	7	93	93
	d	50	W	7	6.00	20	24	8	10	90	94
	e	50	V	7	6.00	20	30	7	6	91	91
	f	50	W	7	6.00	20	30	7	8	93	93
	g	50	W	7	6.00	20	26	10	8	92	91

† Hardness of films is evaluated through damping effect of an oscillation. The damping will increase with increasing the "softness" of the coating to be tested. The reference value is the time (in Seconds) expressed as the damping period, which the pendulum requires to slow down from the initial value to a lower value.

‡ Gloss is often described as the attribute responsible for the shiny or lustrous appearance of an object. Specular gloss or specular reflectance is simply the fraction of the incident light reflected from a surface in the mirror direction within a specified angular tolerance.

\* a means film with two coats.

\*\* b means film with three coats.

have no significant effect upon the varnish and film characteristics.

Following the preparation of the various insecticidal varnish compositions, the work was extended to evaluate their effectiveness against cockroaches. Every group of 20 cockroaches was subjected to test panels coated with two and three coats of varnish separately and was observed for two weeks. Mortality results are given in Tables 3, 4 and 5 and plotted in Figure 2.

From the above data, the following observations were noticed:

1. Within the experimental conditions employed, the order of insecticidal reactivity is Cyanox > Sumithion > Somicidine.

2. The insecticidal activity of the various insecticides tested were found to be affected by:

a) The type of binder used, polyurethane greatly reduces the insecticidal activity, while alkyd-based compositions has no effect especially regarding those corresponding to Cyanox insecticide.

b) The number of films coated, i.e. film thickness, regardless of the type of active ingredient concentration.

c) The concentration of the insecticide present.

It is noteworthy to mention that, composition III<sub>g</sub> (alkyd resin/4% Cyanox) showed an extended effect for four months, as a matter of fact, when a group of 20 cockroaches was exposed to three coated films they died after five days. However, the four months duration of the tests were not long enough to provide conclusive information on the lasting activity of the insecticidal coatings. So, prolonged exposure tests are deemed necessary to determine the residual activity of the varnishes under evaluation.

Supplementary studies were carried out in which varnishes that showed low insecticidal activity were evaluated as insect repellents. Films with 2% of either Cyanox or Sumithion showed promising results against cockroaches.

In conclusion, there are many reasons to believe that when the insecticidal coating compositions are properly and wisely used it would help man to control insects in houses, storage areas and elsewhere. Further research in this area is now in progress.

#### Acknowledgement

The authors are greatly indebted to Professor Dr. A. M.

**Table 3**

**Effect of various insecticidal chlorinated rubber compositions against cockroaches**

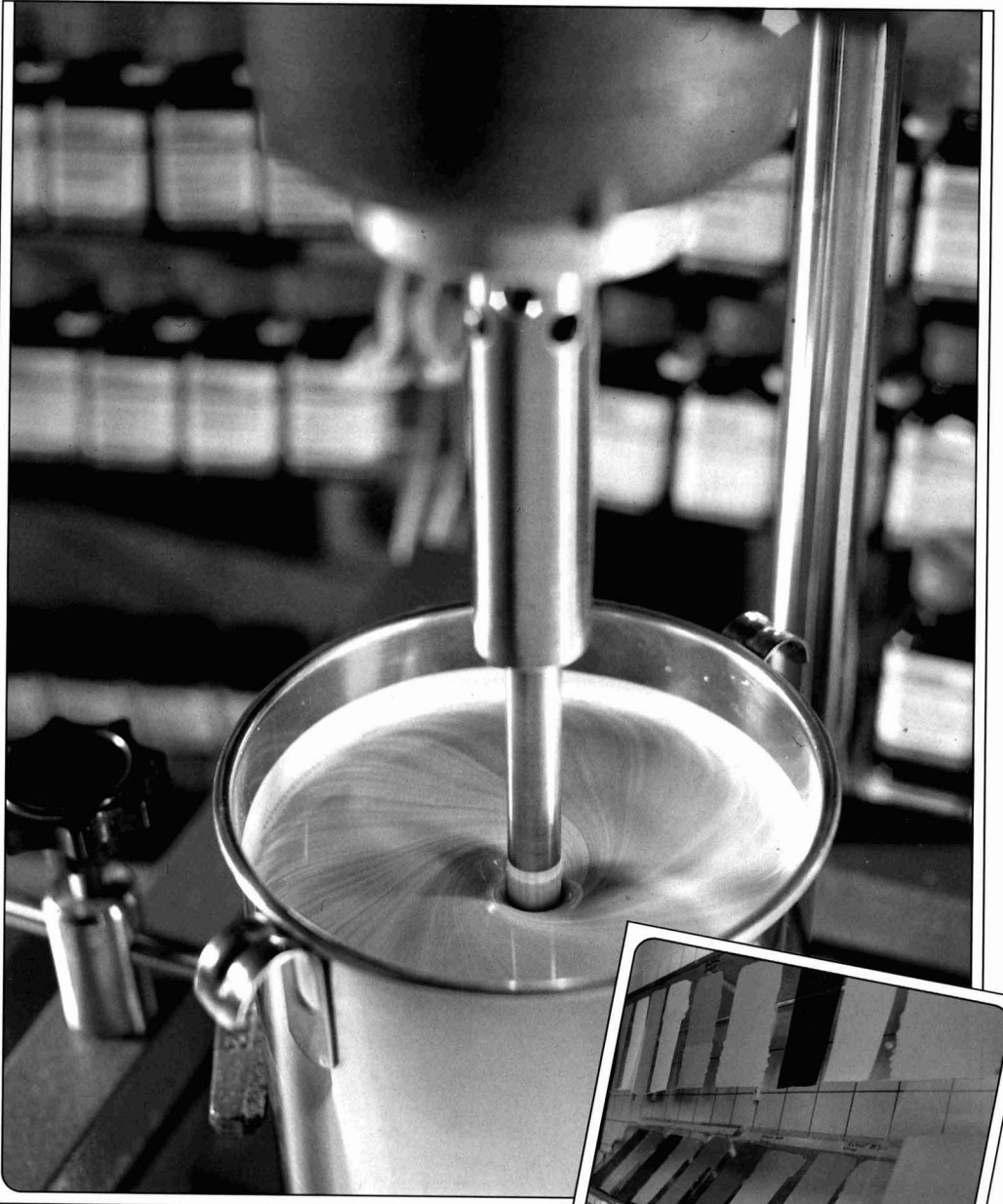
Varnish No.	No. of coated films	Mortality %													
		Time (days)													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
I															
a	2	20	20	20	20	20	40	40	40	40	40	40	40	40	
b		20	20	20	20	20	40	40	40	40	40	40	40	40	
c		20	20	20	20	20	40	40	40	40	40	40	40	40	
d		20	20	20	20	20	40	40	40	40	40	40	40	40	
e		20	20	20	20	20	40	40	40	40	40	40	40	40	
f		20	20	20	20	20	40	40	40	40	40	40	40	40	
g		80	80	80	80	80	80	80	100	—	—	—	—	—	
I															
a	3	20	20	20	20	20	40	40	40	40	40	40	40	40	
b		60	80	80	80	80	80	80	80	80	80	80	80	100	
c		40	80	80	100	—	—	—	—	—	—	—	—	—	
d		20	40	100	—	—	—	—	—	—	—	—	—	—	
e		60	100	—	—	—	—	—	—	—	—	—	—	—	
f		60	100	—	—	—	—	—	—	—	—	—	—	—	
g		60	100	—	—	—	—	—	—	—	—	—	—	—	

**Table 4**

**Effect of various insecticidal polyurethane compositions against cockroaches**

Varnish No.	No. of Coated films	Mortality %													
		Time (days)													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
II															
a	2	20	20	20	20	20	20	20	20	20	20	20	20	20	
b		20	20	20	20	20	20	20	20	20	20	20	20	60	
c		20	20	20	20	20	20	20	20	20	20	20	20	60	
d		20	20	40	60	60	60	60	60	60	60	60	60	60	
e		20	20	40	40	40	40	40	40	40	60	60	60	80	
f		40	40	40	40	40	40	40	40	60	60	60	60	60	
g		40	60	60	60	60	60	60	80	80	80	80	80	100	
II															
a	3	20	20	20	20	20	20	20	20	20	20	20	20	20	
b		20	20	20	20	20	20	20	20	20	20	20	40	40	
c		40	40	40	40	40	60	60	60	60	60	60	60	60	
d		40	40	40	40	40	40	40	40	40	40	40	40	40	
e		20	20	20	20	20	20	20	20	40	40	60	60	60	
f		20	20	20	20	20	20	20	20	20	20	40	60	60	
g		20	20	40	40	60	60	60	60	60	80	80	80	80	

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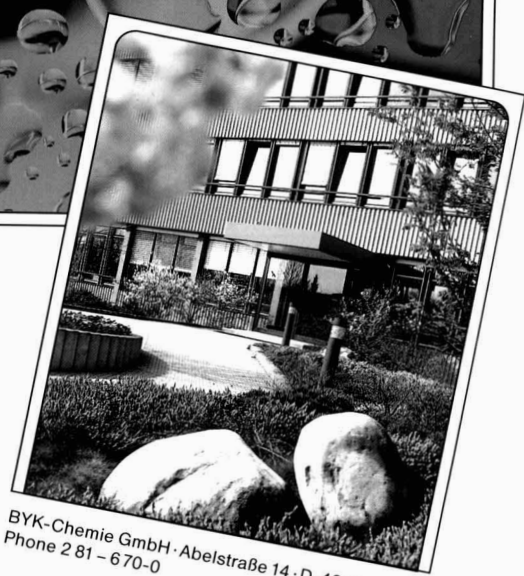
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Naser, Faculty of Science, Al-Azhar University and Professor Dr. Z. A. Zidan, Faculty of Agriculture, Ain-Shams University for their valuable assistance during this work.

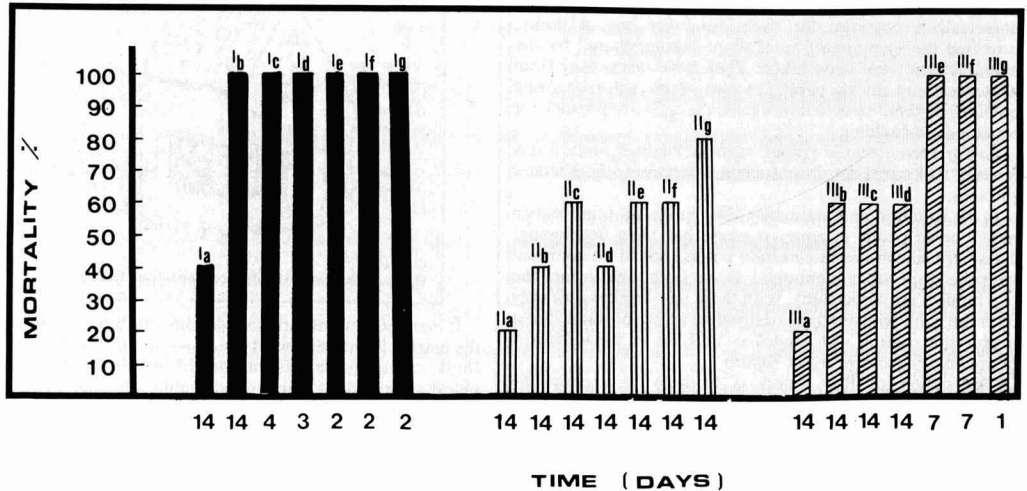
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**Figure 2**

Effect of various insecticidal compositions against cockroaches (compositions defined in Table 1)



**Table 5**

Effect of various insecticidal alkyd compositions against cockroaches

Varnish No.	No. of coated films	Mortality %													
		Time (days)													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
III	a	20	20	20	20	20	20	20	20	20	20	20	20	20	20
	b	20	20	20	40	40	40	40	40	40	40	40	40	40	40
	c	20	20	20	40	40	40	40	40	40	40	40	40	40	60
	d	20	20	40	60	60	60	60	80	80	80	80	100	—	—
	e	40	40	60	60	60	80	80	80	80	80	80	100	—	—
	f	20	20	20	40	60	100	—	—	—	—	—	—	—	—
	g	100	—	—	—	—	—	—	—	—	—	—	—	—	—
III	a	20	20	20	20	20	20	20	20	20	20	20	20	20	20
	b	20	20	20	40	40	40	40	40	40	40	40	40	40	60
	c	20	20	20	20	20	40	40	40	40	40	40	40	40	60
	d	20	20	20	40	40	40	40	40	40	40	40	40	40	60
	e	20	40	80	80	80	80	100	—	—	—	—	—	—	—
	f	80	80	80	80	80	80	100	—	—	—	—	—	—	—
	g	100	—	—	—	—	—	—	—	—	—	—	—	—	—

# Silicone resin emulsions: Binders for high performing façade coatings

by J. M. Pouchol, Department Silicones, Rhône-Poulenc Chimie, Cédex 29 92097, Paris la Défense, France

## 1. Building paints . . . is there anything new?

For the DIY enthusiast who decides to repaint the outside of his weekend cottage, or the builder responsible for restoration or cleaning, what is more attractive than paint in aqueous phase? In addition to the ecological advantages of not giving off toxic solvents, brushes and containers are far easier to clean.

Fortunately the time is long past when vinyl paints in dispersion in water discouraged contractors with little inclination to go into the mysteries of *coalescence* of polymer particles during drying of the paint. For them, a water-based paint meant that it was not waterproof — in fact the distemper of our ancestors.

Today, acrylic, acrylic styrene, versatic and other paints are universally recognised for their durability out of doors, provided the elementary precautions recommended by the manufacturer have been taken. They have taken over from whitewash and silicate paints, in spite of the still-recognised qualities of these so-called inorganic paints, very popular for restoring old buildings.

As for solvent-based paints, such as Pliolites, only a few fanatics still use them, in particular for renovating powdery surfaces.

Is the situation now stationary? No: in the past ten years a new type of paints in aqueous phase has been developing. These are silicone resin *emulsion* paints, not to be confused with the dispersions mentioned above (although in fact the two binders are associated). With these new binders, not only does the paint withstand the destructive action of water, but it makes the coating *water-repellent* in spite of paradoxically being *more porous to water vapour*.

The object of this report is to help to explain the physicochemistry of these performances, through some of the most significant results obtained in our Saint-Fons laboratories.

## 2. Damage caused by damp

This is well-known, and is shown in Figure 1. It is caused by the weather to which the outside walls of any building are exposed, and depends on their position.

The most serious types of damage are undoubtedly the following:

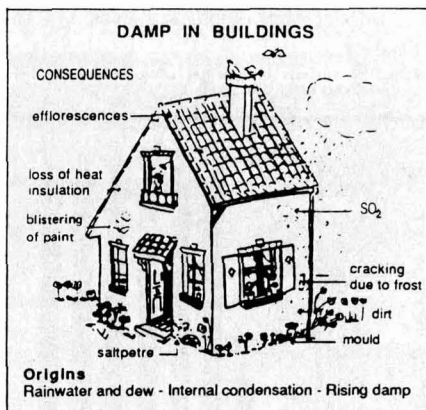
- loss of the insulating power of the walls* (whether they are covered with thermal-insulating materials or not), which increases heating costs.
- faster chemical corrosion of the material* through air pollution in urban areas. The combustion of petroleum products and coal from heating and cars are sources of sulphur dioxide and nitric oxides. The first few minutes of rain, and morning fogs, are critical, because the water has a high sulphuric and nitric acid content and inevitably penetrates the capillaries of the material if it has not been protected. This acid rain is the main cause of sulphation of the material, which destroys the binder.

## 3. Künzle's theory of wall protection

Impermeability to liquid water is naturally one of the

qualities required of paint to be used on walls, but there is also an increasing demand for *permeability to water vapour*, which should be at least equivalent to that of the substrate. The aim is to cause no significant change in hydrothermal exchanges between the interior and the exterior, so as to avoid damage such as blistering and separation of coatings, or insufficient carbonation of hydraulic coatings.

Figure 1



It is true that conventional coatings which have come on to the market in the past twenty years — water-based paints and thick coatings in dispersion in water or in solvent phase — provide a fairly good compromise between good impermeability to liquid water and a certain permeability to water vapour, so that in general, damp evaporates from the wall fairly quickly. But there are big differences from one type of paint to another:

- silicate paints, whether they have one or two components, though very permeable to water vapour, are too permeable to liquid water;
- on the other hand, solvent acrylic paints of the Pliolite type, at the pigment volume concentrations at which they are formulated, are very waterproof but do not "breathe" well;
- acrylic and acrylic styrene dispersion paints seemed in fact to be the best, because the microporosity of the film of paint imparts relative permeability to water vapour, and the binder provides good weatherproofing.

Künzel attempted to link permeability to water vapour with resistance to liquid water by means of equations combining two important factors:

- a) the *Sd* factor: this is the thickness in metres of a layer of air which, at rest, would have the same resistance to the diffusion of water vapour as a given material (concrete substrate, thick coating, paint).

*Sd* is easily calculated by measuring permeability to water vapour (DIN 52615). In the case of a film of paint, it naturally depends on the PVC and on particle size, and of course on the thickness. It ranges from 0.1 for the most permeable paints, such as silicate paints, to 2 for the least microporous paints (Pliolite paints).

A recent article<sup>1</sup> mentions common values of the Sd factor of various materials, and gives an example of calculation for a complex system.

b) The W factor: this is the material's coefficient of liquid water regain by capillary action.

W is calculated by measuring the weight of liquid water absorbed per surface unit of the material as a function of time. The law of weight variation as a function of the square root of the time is generally a straight line (Poiseuille's law), and W is the gradient of the straight line (DIN 52617).

For the coatings with which we are concerned, paints and thick plastic coatings, Sd and W should naturally be as low as possible. In Künzel's opinion, the optimum film will meet the following three conditions:

$$Sd \leq 2 \text{ metres}$$

$$W \leq 0.5 \text{ kg}/(\text{m}^2 \times \text{t}^{1/2})$$

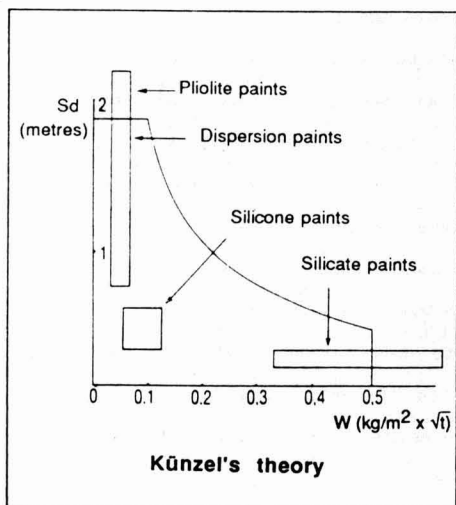
$$(t = \text{time in hours})$$

$$Sd \times W \leq 0.2 \text{ kg}/(\text{m} \times \text{t}^{1/2})$$

(DIN 18550)

This determines a field illustrated in Figure 2 where, according to Jager<sup>2</sup>, "silicone" paints occupy the optimum position.

Figure 2



#### 4. Silicone resin emulsions

##### 4.1 The structure of a hydroxylated silicone resin

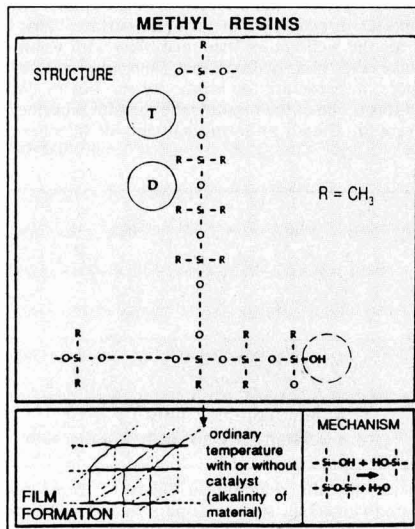
Without attempting to give a lecture on the chemistry of silicones, on which there are excellent books on a specialised<sup>3</sup> or general<sup>4</sup> level, we will recall<sup>5</sup> that hydrolysis of mixtures of dichlorosilanes and trichlorosilanes results in the formation of a network, functionalized to a varying degree, depending on the ratio of D (difunctional) and T (trifunctional) structural units introduced.

a) It will be seen that the resin can already be defined by an R:Si ratio in which R represents the average number of methyl radicals (CH<sub>3</sub>) attached to the silicon atom. Theoretically this ratio varies from 2 (the structure of silicone oil consisting only of D units) to 1 (the structure of the most highly-functionalised resin with the greatest number of T units).

b) Another parameter affects the structure of the resin. This is the average molecular weight which, to simplify, we will link to the hydroxyl group content of the macromolecule. These OH groups are the key to the formation of the film.

These different points are summarised in Figure 3.

Figure 3



##### 4.2 Comparison of film formation by a silicone resin emulsion and an acrylic dispersion

Anyone familiar with dispersion paints immediately thinks, for the binder, of the product obtained by polymerisation in emulsion of mixtures of monomers such as styrene, vinyl acetate or acrylic ester, in the presence of a surfactant (anionic or non-ionic). The molecular weight of the copolymer obtained is very high and permanent. As we have already pointed out, film formation takes place through coalescence of the solid "latex" particles after the water has evaporated. The film obtained remains thermoplastic, and an attenuation of its tendency to soil is closely linked with a higher vitreous transition temperature of the binder. Hence the number of possible combinations of the basic monomers, and the current fashion for certain "photocrosslinking" emulsions which are reported to produce a film that is hard on the surface but flexible underneath.

With methylsilicone resin emulsions, we are a long way from polymerisation in emulsion.

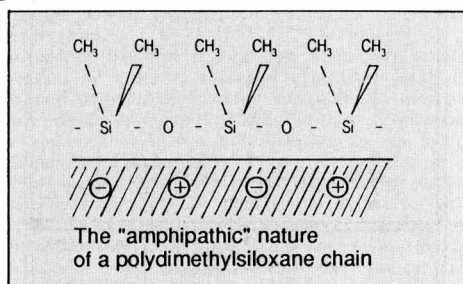
The binder manufacturer emulsifies one (or more) liquid silicone resin(s) of low molecular weight by finely "dispersing" the resin(s) by an appropriate process, specific to each company. An emulsion is obtained, generally with an active ingredient content of about 40% and an average particle size ranging from 0.1 to several micrometres, depending on the technology used.

The film forms after the water has evaporated from the emulsion applied to the substrate. The silanol groups condense at ordinary temperature with elimination of water, as shown in Figure 3. This reaction is promoted by alkalinity.

After a few hours' or a few days' crosslinking, naturally promoted by a higher temperature, the liquid resin is transformed into a film of varying hardness, here again depending on the structure of the resin, the molecular weight of which will gradually increase. The slightly polar nature of

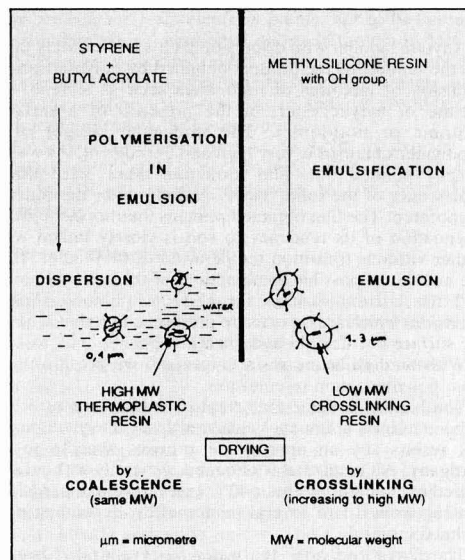
the Si-O bond, combined with the great flexibility of the chain formed by the D units, allows interactions of the dipole-dipole type to develop with a polar material (the substrate, pigments and fillers — see Figure 4). The presence of T structural units and hydroxyl functions increases the polar nature. This explains the satisfactory binding power of a silicone resin, in spite of the fact that its "amphiphatic" nature causes preferential orientation of the methyl groups in the opposite direction to the contact surface. This is the reason for the well-known incompatibility with water which will make the film hydrophobic, and also with organic substances, in particular the acrylic styrene binder. We shall see that this is one of the reasons why the film is permeable to water vapour, already an intrinsic quality of silicones.

Figure 4



To sum up, the diagram in Figure 5 compares film formation in an acrylic styrene dispersion and a silicone resin emulsion.

Figure 5



#### 4.3 Factors affecting the binding power of a hydroxylated silicone resin

The binding power of a polymer for paints is related to the cohesion and hardness of the film obtained after drying.

□ the first factor involved in the case of a silicone resin is, as we have already said, the trifunctional T-group content.

In an earlier publication<sup>6</sup> we compared, in the same paint formulation, four resins with very different R:Si ratios. We used the wet abrasion test, which is a good reflection of the cohesion of the film. The results are shown in Table 1.

Table 1

Resistance to wet abrasion of silico-acrylic paints 42% PVC	
acrylic-styrene	40
silicone	60
R:Si of silicone binder	Resistance to abrasion
1.5	3,000 brush strokes = 50% wear
1.4	5,000 to 10,000 brush strokes = 50% wear
1.3	start of wear at 10,000 brush strokes
1.2	> 100,000 brush strokes without wear

It is clear that a structure with a high trifunctional group content will be favourable to a high binding power. This is logical, because the intermolecular cohesion of the polysiloxane chains is increased.

□ The second factor is the number of hydroxylated reactive groups which cause crosslinking of the polymer after the water has evaporated. In our experience, two things speed up the phenomenon:

- the alkalinity of the system,
- the presence of a crosslinking agent such as potassium methylsiliconate (our commercial product is known as Rhodorsil Siliconate 51 T), the manufacturing principle and crosslinking process of which are shown in Figure 6. Although the structure obtained, even in a thin coat, is far too rigid (R:Si=1!) for this product to be used as a paint binder, it is perfectly suitable for bridging hydroxylated methylsilicone resin chains, after the water has evaporated, as illustrated in Figure 7.

We see that when a small quantity (generally 1%) of the siliconate is added to the emulsion, it serves both as a crosslinking agent, through the trifunctional structural units added, and as an alkaline agent, since the pH of the product is 13, which is favourable to crosslinking kinetics.

We shall now show this where the degree of cohesion obtained can be judged from the very simple test of observing the pendulum hardness of the film, as a function of time, after the water has evaporated.

From Table 2, it is clear that an alkaline pH is not enough to ensure fast crosslinking kinetics. The process is speeded up by increasing the number of reactive groups and by the presence of methylsiliconate. Because of problems of the pot life of the emulsions, and hence of paints treated in this way, manufacturers of both emulsions and paints must carefully choose the hydroxyl content of the resin and the Rhodorsil Siliconate 51 T content respectively.

Table 2

Crosslinking conditions	Remarks or pendulum hardness	
	resin with 2% OH groups	resin with 5% OH groups
emulsion pH < 7	film tacky after 7 days' drying	
neutralised emulsion pH 9 with NH <sub>4</sub> OH	ditto	
neutralised emulsion pH 9 with Siliconate 51T	film dry in 24 hours hardness 100 sec. after 8 days	film dry in 2 hours hardness 100 sec. after 24 hrs



Figure 6

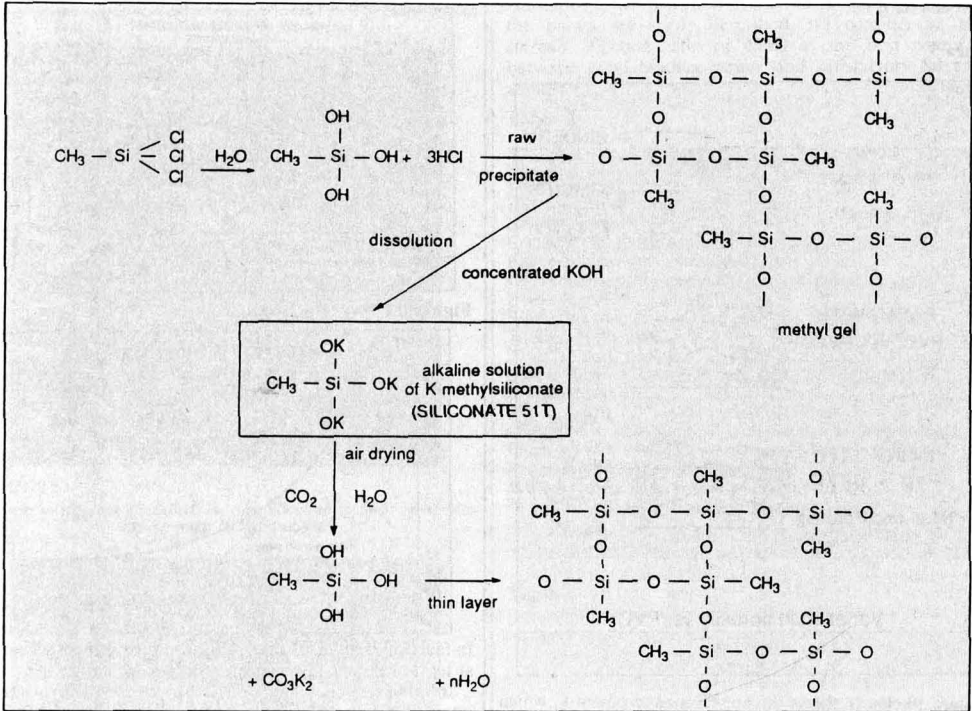


Figure 7

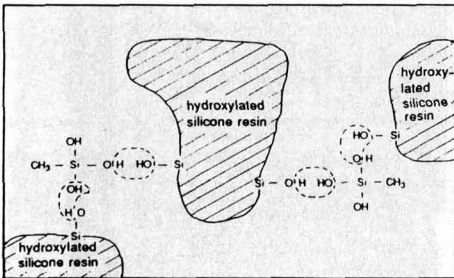


Figure 8 illustrates the case of a paint with a 100% silicone resin binder. The kinetics of the increase in pendulum hardness are typical of a polycondensation reaction, speeded up by heat. The course of the curve would obviously be quite different with a conventional dispersion paint containing a thermoplastic binder.

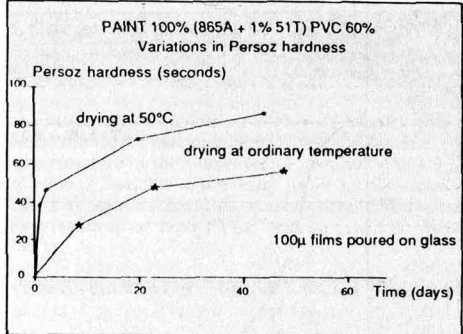
**5. The reasons for associating a silicone resin emulsion with an acrylic (or acrylic styrene) dispersion**

There is a basic reason for this: to comply fully with Künzel's principle of obtaining low Sd and W values, in order to renovate old thick coatings, or to cover heat insulation.

Let us reconsider the variation in the porosity of a film of paint as a function of its pigment volume concentration (PVC), illustrated in Figure 9.

With an acrylic or acrylic styrene dispersion paint, a

Figure 8



suitable value for the Sd factor will be obtained once a critical factor, known as the CPVC, has been exceeded.

The increased porosity will however be obtained at the expense of the W factor, resistance to liquid water. Furthermore, the paints will have a greater tendency to chalk.

At these high PVCs, the use of silicone resin emulsion is sometimes advised, to impart water-repellency. It is however a risky choice from the point of view of binding power and durability. We will return to this subject later.

We prefer to give details of the surprising results obtained at PVCs far lower than the CPVC. For example, we formulated some paints with a PVC of 42%, as shown in Table 3, employing our two emulsions, Rhodorsil 865 A and Rhodopas DS 910, in decreasing ratios from 100:0 to 0:100 (the former being a silicone emulsion and the latter an acrylic styrene).

The Sd and W factors were measured according to DIN 52615 and 52617.

Figure 9

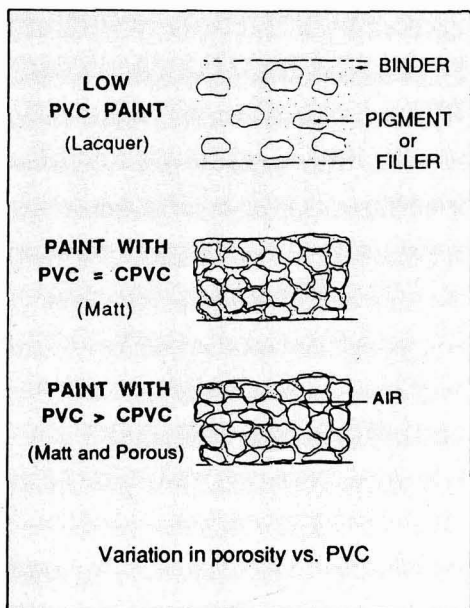


Figure 10 clearly shows the appearance of porosity, which increases with the quantity of silicone emulsion co-binder.

Figure 10

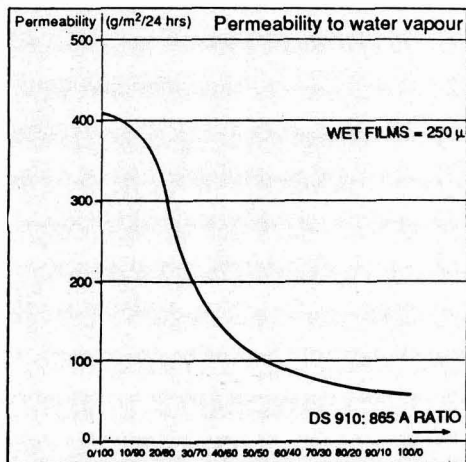


Figure 11 gives the corresponding Sd and W values.

Figure 12 is a graph illustrating the privileged position of these paints in Künzel's diagram, and a few electron microscope pictures, all at the same enlargement, enable us to compare the porosity of an all-silicone and a silicone-acrylic paint with that of an all-acrylic-styrene (Figures 13, 14 and 15).

There could be a temptation to minimise the part played by the silicone resin because, in the formulation chosen, the all-acrylic-styrene paint already has a low Sd value (0.4 metres).

Figure 11

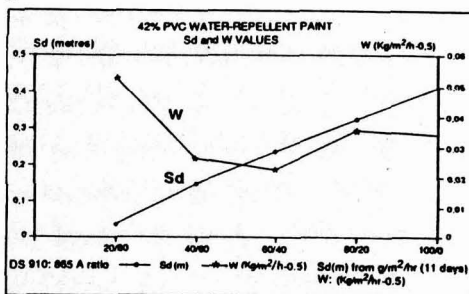
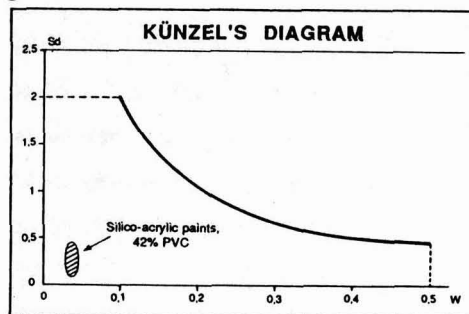


Figure 12



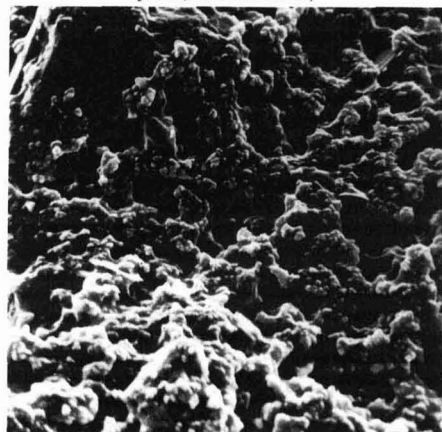
In fact, it is manifestly interesting to observe that this value is at least ten times lower at high silicone contents.

In our previous paper we tried to give a physicochemical interpretation of this increased porosity below the CPVC<sup>6</sup>. In our opinion, it is the result both of the low surface tension of the liquid silicone resin and of its incompatibility with the organic binder.

In fact, this calls into question the whole concept of the definition of the CPVC. We will return to this subject at the 1990 FATIPEC congress.

Figure 13

Electron microscope examination, magnification  $\times 5000$  All-silicone paint (Rhodorsil 865 A)

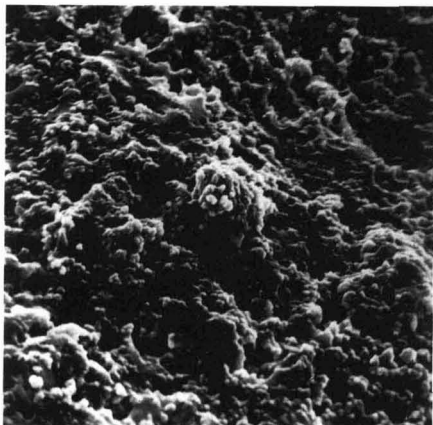


6. The reasons for employing an acrylic (or acrylic styrene) dispersion with a silicone resin emulsion

This is to maintain a satisfactory binding power imparting durable resistance to weathering.

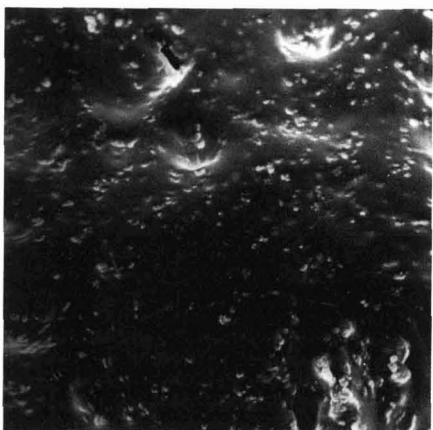
**Figure 14**

Electron-microscope examination, magnification  $\times 5000$  Silico-acrylic paint (60:40 Rhodorsil 865 A: Rhodopas 910)



**Figure 15**

Electron microscope examination, magnification  $\times 5000$  all-acrylic-styrene paint (Rhodopas 910)



**Figure 16**

Renovation of thick coating. With 40% PVC, an illustration of the superiority of a silico-acrylic paint over a paint with no silicone:  
 - better impregnating power  
 - marked beading effect



As would be expected, the silicone resin lowers the resistance to wet abrasion of the film of paint (Table 4). For the paints previously described, we consider an acrylic styrene: Silicone ratio of 40:60 as the best compromise between good binding power and satisfactory Sd and W values.

**Table 3**

Formulation with 42% PVC	
Water .....	1.25
10% solution of sodium hexametaphosphate (dispersing agent) .....	2.00
Cemulsol ON 10-20 (non-ionic wetting agent-Rhône-Poulenc Spécialités Chimiques) .....	0.20
0.4% solution of Rhodopol 23 (xanthan gum thickener-Rhône-Poulenc Spécialités Chimiques) .....	5.00
RL 60 (titanium dioxide-Rhône-Poulenc Minerale Fine-Thann et Mulhouse) .....	11.40
20 MO (Talc de Luzenac) .....	3.60
Durcal 5 (calcite-Omya) .....	27.00
20% ammonia .....	0.20
Rhodopas DS 910 (acrylic styrene emulsion, solids content 50%, Rhône-Poulenc Spécialités Chimiques)....	16.80
Rhodorsil 865 A (silicone emulsion, solids content 40%, Rhône-Poulenc Spécialités Chimiques) .....	31.50
Texanol (coalescing agent-Eastman Chemie Int) .....	1.00
Parmetol DF 18 (fungicide-Phagogene Industrie) .....	0.05
	<b>100.00</b>

**Table 4**

Wet Abrasion	
Doitteau Plynometer (AFNOR T30082)	
Water-Repellent Paints 42% PVC	
100 $\mu$ films poured on 250 $\mu$ black PVC panels	
drying: 3 days at ordinary temperature - 24 hours at 50°C	
DS910/865A = 0/100 :	80 wearing strokes = 50%
DS910/865A = 10/90 :	150 wearing strokes = 50%
DS910/865A = 20/80 :	90 wearing strokes = 50%
DS910/865A = 30/70 :	190 wearing strokes = 50%
DS910/865A = 40/60 :	12,000 wearing strokes < 5%
DS910/865A = 50/50 :	12,000 wearing strokes < 5%

Resistance to wet abrasion is also affected by two other factors, the acrylic binder content being the same:

- the structure of the silicone resin: as we saw in 4.3, a low R:Si ratio is desirable in the resin, for better film-formation;
- the PVC of the paint: this is not surprising, as cohesion is greatly reduced at high PVCs, and particularly above the CPVC.

**7. The formulation of "Silicone" paints—the economic aspect**

This aspect should not be neglected, as users will tend to complain that the silicone resin emulsion costs more than the employed acrylic dispersion.

Although carbon is chemically close to silicon, the price of the raw materials is not the same. There is a simple reason for this: the raw material of silicones is silicon, obtained by reducing sand... at a temperature of around 2000°C. Coal and petrochemicals, on the other hand, are inexpensive sources of conventional organic binders such as acrylic or vinylic dispersions.

The immediate reaction of paint manufacturers is too often to keep down the price of the formulation through two factors:

- the quantity of silicone is often so small that the silicone resin emulsion is no longer a co-binder but merely an additive;

□ the PVC is often too high for exterior paints.

The conclusions from numerous tests in our laboratories are however categorical:

□ increased permeability to water vapour (the Sd factor), the main objective of silicone paints, is obtained only if the silicone binder predominates, and it cannot be considered as an additive;

□ this increase is far more marked at low PVCs than at those close to or above the CPVC of the acrylic styrene binder.

As for resistance to liquid water, too often a simultaneous water-repellent effect is expected, in the form of a "beading effect" of rainwater on the surface of the paint, again with small quantities of silicone emulsion. This ignores the fact that the quantity of silicone, diluted in the coat of paint, is insufficient to saturate the capillaries formed during drying. This is very different from water-repellent treatment of walls, well-known to specialists, by impregnating the surface of the material with significant quantities of water-repellant in solvent phase. It is in fact much better to use the latter product as a water-repellent *adherence primer* under the coat of dispersion paint, which can be silicone or simply acrylic. This point was dealt with in our previous paper<sup>6</sup>.

To conclude, we will describe a recent experiment in our laboratories, comparing paints with a PVC of 40% and 60%, and acrylic-styrene: silicone ratios of 40/60.

Three acrylic dispersions of varying flexibility were associated with our Rhodorsil Emulsion 865 A. As the photographs in Figures 16, 17 and 18 show, we simulated renovation of thick coating. The following observations were made:

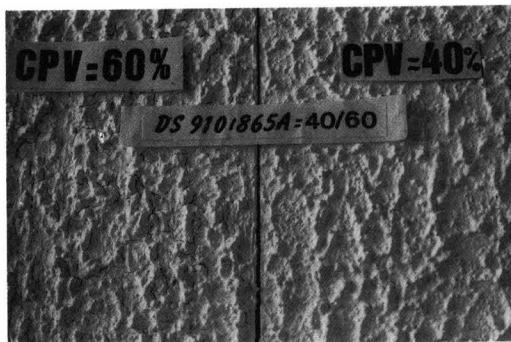
□ all the paints with a 60% PVC cracked, whatever the flexibility of the acrylic styrene co-binder, while there were no defects in the paints with a 40% PVC;

□ the paints with a 40% PVC had a marked beading effect. It is obvious that the low surface tension and the incompatibility of the silicone with the acrylic styrene binders promoted the formulation of a substantial surface coating (much more than with a 60% PVC). This was sufficient to reproduce the classic phenomena in water-repellent treatment of walls;

□ the impregnating power of silico-acrylic paints is far superior to that of acrylic-only paints (surface irregularities are coated better). This results in a saving, as only one coat is necessary.

**Figure 17**

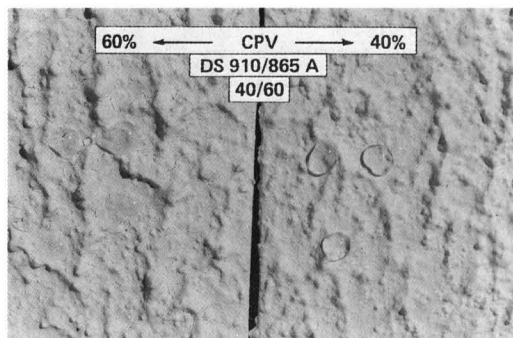
Renovation of thick coating. Silico-acrylic paint-with the 40% PVC formulation, the cracking observed with 60% PVC did not occur.



All these experiments tend to show that silicone resin emulsions are suitable for formulating high-quality water-repellent paints which breathe, provided care is taken with the formulation.

**Figure 18**

Renovation of thick coating. An enlargement of the photograph in Figure 17, and an illustration of the beading effect with a low PVC.



## 8. Conclusion

Silicone resins were already reputed in the field of coatings for metals. Their high heat stability and resistance to ultraviolet rays and to weathering made them the ideal binders for paints exposed to high temperatures, or used to protect cladding panels (coil coating) or for high-quality maintenance.

These silicone resins were already often associated with conventional organic binders, such as alkyd resins. But all these paints were in solvent phase.

Silicone resin emulsions offer a twofold innovation:

□ the use of a silicone binder in aqueous emulsion.

□ protection of buildings, which was hitherto done with dispersions, generally acrylic or acrylic styrene, with which they are in fact associated.

The tests in our Rhône-Poulenc Chimie laboratories at Saint-Fons, in the suburbs of Lyon, confirmed the advantages of our silicone resin emulsions in significantly increasing permeability to water vapour and also imparting an additional water-repellant effect. This makes the paint more durable out of doors, by reducing soiling and promoting gaseous exchanges within the material.

Our laboratory tests are being confirmed by exterior ageing in an industrial atmosphere on the walls of our factory.

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## Iron tannate anticorrosion pigment

by A. J. Seavell, "Edendale", Hooton Road, Willaston, South Wirral L64 1SJ, UK

The first evaluation of metal tannates in anticorrosion paints was carried out by the Paint Research Association on pigments prepared in the mid-1950s by T. J. White. While some results were promising, others showed unacceptable variability in performance and the investigation was discontinued.

The cause of this lack of reproducibility was later sought in work done by the author on behalf of African Territories Wattle Industries Fund. A number of causes were established

and an iron tannate pigment has now been prepared on the laboratory scale which gives reproducible properties and, unlike earlier preparations, gives 100 per cent yield.

Exposure trials on an industrial site in a coastal area and accelerated performance tests done by the Paint Research Association give clear evidence that a suitable prepared iron tannate can rival red lead and other widely used anticorrosive pigments in performance and in tolerance to the practical conditions frequently met, especially in maintenance work.

Iron tannate is some 95 per cent tannin based made from Mimosa (Wattle) from the bark of trees having a life-cycle of 8-10 years. The plantations are constantly replanted; also tannin is non-toxic and preparation of the pigment involves no polluting effluent.

A paper on the anticorrosion property of iron tannate will be submitted in the near future for publication in the JOCCA.

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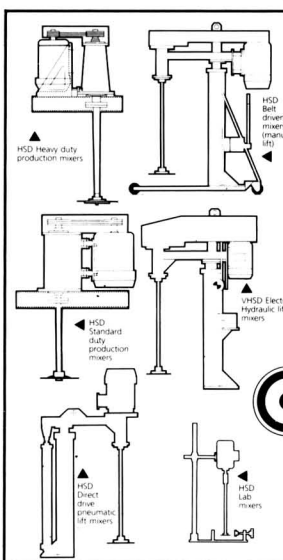
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## PRA: A research association for the 1990s

by H. Jotischky, Paint Research Association, 8, Waldegrave Road, Teddington, Middlesex TW11 8LD, UK

PRA was born in 1926 out of a critical need; a few far-sighted OCCA Members were among the first to recognise it. Paint technology was rapidly changing then yet lacked a scientific basis. The industry consisted of mainly small family-run concerns; a few dabbled in research, more engaged in testing. Today, nearly all paint companies have laboratory facilities, often linked to computers, and some apply R & D on a large scale. Yet the need for an independent research organisation is still there. Paint technology has indeed progressed immensely, but our knowledge of some of the basic mechanisms is still hazy. Many avenues still await exploration. Nor do today's commercial pressures foster this type of investigation on a company basis. An independent organisation, with links to both industry and the wider scientific community, has a real place in the 1990s.

### In the beginning

Sixty-four years ago the path of paint research was still largely uncharted. Everything was new and everything cried out for investigation. Instrumental techniques were primitive and their application to particular tasks at hand was still untried. Hence the newly founded Association could happily skip from one subject to another – from tung oil (PRA's first Technical Paper) to pigments, from gloss measurement to weathering – and still make a serious contribution to the scientific literature. Over two hundred Technical Papers and nearly 400 Research Memoranda as well as some 60 Bulletins appeared during PRA's first forty years. Some – such as Technical Paper 138 in 1944 – *The Electron Microscope and its Application to the Study of Pigments* – were seminal works. Not only had PRA pioneered the application of electron microscopy to paint research; it had also built its own prototype model. By the 1950s and '60s its work on microbiology and colour stood at the forefront of technical knowledge. Other early classic papers covered oil polymerisation, artificial weathering, adhesion, mould growth, pigment flotation, to mention but a few<sup>1</sup>.

This wide-ranging approach could not go on. What was desirable in the 1930s and '40s, and still technically feasible in the '50s and '60s, was becoming amateurish in the '70s as well as financially prohibitive by the '80s. Paint technology had become more sophisticated; instruments more complex. The days of the generalist were numbered. In the 1970s PRA still engaged in up to a dozen research projects at any one time, but by the mid-1980s this approach proved too fragmented.

### The new approach

The appointment in 1986 of John Bernie as PRA's Managing Director proved a turning point. It was he who introduced the new approach: fewer but larger projects; teams rather than single researchers; a return to fundamentals; collaboration with industry and harnessing of outside expertise where appropriate. With Government funding ever more difficult, industrial sponsorship became essential. Indeed, success hinged on the whole-hearted involvement of industry. Members who agreed to sponsor research sat on steering committees and working parties; they contributed not only with money but with advice and sometimes with services in kind. A partnership was being forged. The topics studied were broad and pre-competitive and of general interest. Four years later this new approach has already borne fruit.

Research projects into the mechanisms of corrosion

inhibition and drying were the first candidates for the new approach. The subjects had to be sufficiently broad to reflect Member's mainstream interests as well as being fundamental in nature. Few questions are as basic as how paints dry or how they protect metal from corrosion. Both seemed an ideal choice<sup>2</sup>.

### Investigating corrosion inhibition

Studying the action of anticorrosive paints was the subject of a three-year £400,000 project funded by DT and industrial sponsors.

Fundamental as the subject is, it does hold important practical implications. Traditionally, anticorrosive paints were based on two toxic materials, chromate and lead. A better understanding of the complexities of the protection mechanism is bound to assist in the development of suitable substitutes.

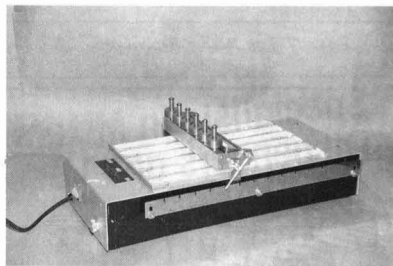
Electrochemical studies have figured prominently in this project. The attack was many-pronged, consisting of initial AC impedance studies on, both free films and intact coatings, followed by a battery of other techniques. The intricacies of impedance studies form a subject in its own right. Many other side issues merited investigation and have yielded interesting results. For instance, in examining the state of dispersion of pigments within paint films, wide variations were found in a series of zinc phosphate pigments both in regard to their particle size and shape. This might be one explanation for the variability in their performance so often observed in practice.

### Studying the mechanisms of drying

This was another substantial three-year programme – totalling £416,000 and partly DTI funded – and another very basic subject yet ultimately of practical significance. By seeking to understand how auxiliary driers (lead and zirconium) modify primary driers (cobalt), the project aimed to explain the essential differences between the action of lead and its replacements (e.g. zirconium), and then use that insight in the selection of more effective substitutes.

Four hypotheses were tested by an array of analytical techniques, namely

- Drier inhibition by volatile autoxidation products
- Selective catalyses of multi-stage autoxidation reactions
- Cobalt activation by auxiliary driers and
- Non-autoxidative cross-linking.



Prototype solvent droplet tester

Testing these hypotheses proved an intriguing piece of analytical detection. Fourier Transform-Infra-red Spectroscopy (FTIR) became the mainstay technique. Often

a combination of methods was employed to advantage. For instance, low molecular weight gel permeation chromatography was used to separate partially cured methyl linoleate samples into fractions which were then examined by infra-red spectroscopy. Some results were unexpected. The development of a solvent droplet tester, as an alternative measure of drying, was one of these. The technique which monitored cross-linking by comparing the solvent resistance and recoatability of various paint systems, became the basis of an automated prototype instrument built by the Mickle Laboratory Engineering Co to a PRA design.

### Collaboration with a European dimension

Collaboration has enriched both these projects. The corrosion project, for instance, utilised the academic expertise at UMIST and Oxford, while that on driers had access to the ultra-modern technique of EXAFS (Extended Absorption X-ray Fine Structure), undertaken by ICI at the SERC Synchrotron as the Company's contribution in kind.

However, the current four-year project on Self-stratifying Coatings represents collaborative research with a European flavour. Funded in part under the EC's BRITE programme, with PRA as the lead contractor, it numbers no fewer seven partners – all European research institutes, namely, CoRI (Belgium), CERIPEC (France), EOLAS (Ireland), FPL (Germany), NIF and DTI (both Denmark) and TNO (Netherlands).

Its aim is equally ambitious: to investigate the formulation of *self-stratifying coatings*, that is single-coat systems based on incompatible resins, which spontaneously separate into two functional primer and topcoat layers in one application. The advantages are immediately obvious: superior technical properties with labour-saving as a bonus.

The ECU 2.2m project, now well into its second year, demands high-calibre theoretical work utilising such tools as solubility parameters. The background to this work – the prediction of phase behaviour and the factors influencing stratification – has been described in greater detail by Chris Carr<sup>3</sup>.

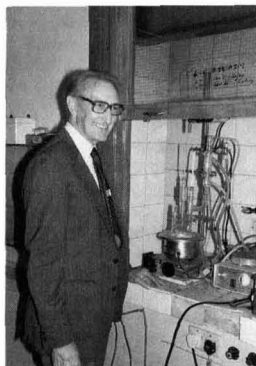
### Protecting wood

PRA's latest four-year project on the protection of wood – at £820,000 its largest ever – follows the pattern established by the two earlier ones on corrosion and drying. A new generation of wood care products – exterior stains, microporous finishes, water-borne systems – makes a fundamental review of the mechanism of protection of wood by surface coatings both timely and opportune. An *integrated* approach is the project's hallmark. The study will take into account the *substrate*; the *coating* as well as the *interface* between the two by characterising the physical, chemical and microbiological degradation processes. This will involve monitoring physical degradation by using PRA Test House facilities, extensively supplemented by the analytical techniques. FTIR appears as an ideal candidate for obtaining information on the chemical changes in applied films; the use of a photoacoustic accessory will produce spectra from surfaces which have been roughened and eroded by exposure. Microtome techniques are expected to reveal the sub-surface and interface regions of coatings. The complexity of degradation reactions might require a combined chromatography/spectroscopy approach. At the same time, PRA's well-established microbiology facility will focus on studying the microbiological degradation of coatings.

In addition, PRA will be able to call on a wide circle of outside expertise. Imperial College, for example, will investigate the way in which micro-organisms utilise wood as a food source. Other academic and government establishments will provide additional technical support<sup>4</sup>.

### The clean technologies

With environmental considerations looming ever larger, today's research focus is clearly fixed on the clean technologies. In the coatings field this means the elimination or reduction of organic solvents. PRA's main effort in this area is currently concentrating on low-solvent systems based on NAD technology. The aim of its new two-year research programme is to develop solvent-free acrylic non-aqueous polymer dispersions as a basis for factory-applied high solid coatings. This was one of the first projects to attract half funding under the DOE's Environmental Protection Technology (EPT) scheme. The object is to produce coatings with a solvent content of less than 5%. With solvent levels of typical industrial coatings at 50-70%, these novel systems would result in a substantial reduction of solvent emissions.



Derek Walbridge, PRA's Principal Research Scientist, in action

The research programme envisages the preparation of acrylic particles, the preparation and investigation of plastisols, the development of a model, followed by the selection of the most promising candidates for scale-up and evaluations.

### New horizons

More on clean technologies is on the horizon. A project on radiation curing is currently being prepared for submission and new R&D initiatives are being considered on powder coatings. Of course, PRA has been involved in powder coatings intermittently in many ways. The latest effort is a technology transfer consultancy, in conjunction with several European partners, under the EC's SPRINT programme.

### A complete service

Research must form the hallwork of a research association. Nonetheless, PRA's activities range wider. In effect, it aims at providing a *complete* service, extending to consultancy, testing, analytical and environmental monitoring, publications, conferences, training and database development.

In recent years, information transfer has become a worthy adjunct to technology transfer and increasingly in demand in the techno-commercial and toxicological-environmental fields. Legislation, both national and European, puts an increasing premium on this type of information. PRA is endeavouring to meet this demand in various ways. Two regular publications – *World Surface Coatings Abstracts* (WSCA) and *Hazards Pollution and Legislation in the Coatings Field* – summarise recent developments touching on occupational hygiene and the environment specifically tailored to the coatings industry. WSCA, in addition, is also

*Continued on p.384*

# The development of alkali soluble acrylic resins for use in aqueous printing inks

by J. B. Clarke, Coatings & Specialities Division, Allied Colloids Ltd, Low Moor, Bradford, West Yorkshire BD12 0JZ, UK

## Introduction

Historically water based inks have been around for many years but in 1970 legislation in the USA enforced reductions in solvent usage in the coatings industries due to increasing pressures from health and safety and environmental pollution lobbies.

Later on in 1974, the oil crisis provided additional impetus away from expensive solvents. Resin and pigment manufacturers invested heavily in research and development to accommodate requests from paint<sup>1</sup> and ink manufacturers for water-based systems, or at least water dilutable systems. In consequence the coatings industries have seen phenomenal growth in products and application technology which do not require organic solvents as diluents.

Significant progress has been made by many flexible packaging converters in moving from solvents to water. The road has not been easy and has required contributions from machinery manufacturers as well as resin and pigment suppliers. The successful companies have been those who have been fully committed to making water based systems work.

Until the mid '80s water-based systems had been confined to areas where the demands of drying, gloss, adhesion, print quality and product resistance had not been too severe. All these areas presented problems to traditional water-based formulations.

Traditionally water-based printing inks were based on resinated maleics and Shellac and were used for the flexographic printing of paper sacks – typically brown kraft.

Shellac, being a naturally occurring resin can be converted to water solubility by neutralising with a suitable base. In the USA ammonia was popular whilst in the UK monoethanolamine was preferred. Unfortunately like most naturally occurring resins, Shellac was susceptible to inconsistencies both in performance and price.

As the synthetic resin industry developed the printing ink industry became a target application area for the speciality resin manufacturer and over the past 20 years a wide range of resin products has become available.

Modern water based resins are usually copolymers of a variety of different monomers which are capable of undergoing additional polymerisation, and alkali solubility introduced through carboxyl containing monomers.

## Acrylic polymers

The term "acrylic polymer" is commonly applied to a variety of homo and copolymers of esters of acrylic and methacrylic acids.

Methyl and ethyl acrylates were first prepared in 1873 but were not observed to polymerise. In 1927 the first commercial production of acrylic monomers was begun in Germany by Rohm and Haas. 60 years later the reported world production of acrylic monomers is in excess of 1 million tonnes p.a.

In coatings technology acrylic polymers have become well established because of their superior properties of water resistance, film clarity and UV resistance.

Almost all acrylic monomers can be polymerised and will

copolymerise well with each other in either emulsion form, solid grade bead form or in a suitable solvent.

The film properties, particularly flexibility, toughness and softening point of acrylic polymers may be varied substantially by varying the monomer composition. These properties may be compared by reference to the Glass Transition Temperature – Tg. Table 1.

**Table 1**  
Tg values of some common homopolymers

Polymer	Tg°C
Methyl Acrylate	6
Ethyl Acrylate	-24
N-Butyl Acrylate	-45
2-Ethyl Hexyl Acrylate	-60
Methyl Methacrylate	105
Butyl Methacrylate	20
Styrene	100
Acrylonitrile	105
Vinyl Acetate	28

The number of acrylic monomers is large and the number of combinations is extensive. Subtle variations in properties can be achieved by relatively minor changes in:

1. Chemical Composition
2. Molecular Weight
3. Polymer Structure
4. Physical Form

## 1. Chemical Composition

Whilst there is an enormous variety of monomers which could be used in theory, in commercial terms the choice is somewhat limited due to the cost and availability.

The commonly used monomer can be conveniently divided into three groups:

- backbone monomers
- modifying monomers
- functional monomers

The principal *backbone monomers* are the methacrylates along with styrene, and vinyl acetate. They provide the principal film forming characteristics of the polymer and the basic adhesion properties.

The most commonly used methacrylate is methyl methacrylate, which has the highest Tg and exhibits excellent toughness, light fastness and chemical resistance properties.

Styrene and its derivatives are also used to create the hard backbone of the polymer.

*Modifying monomers* are principally the acrylates and methacrylates of lower Tgs. They are used to soften and flexibilise the polymer and/or to modify the solution properties.

One of the softest acrylates is methyl acrylate but this is prone to hydrolysis and thus reduces water and alkali resistance. Even more commonly used is ethyl acrylate which improves flexibility and compatibility but unfortunately is the



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most odorous of acrylic monomers. 2-ethyl hexyl acrylate imparts extreme flexibility but has poor fat and oil resistance. Butyl acrylate improves flexibility and adhesion.

**Functional monomers** are used at relatively low levels to introduce specific properties such as alkali solubility, acid solubility, cross-linking or external cross-linkability.

Alkali solubility can be introduced into these resins by copolymerising into the system a carboxyl containing monomer such as acrylic acid.

When homopolymerised to a low molecular weight such polymers exhibit excellent inorganic pigment dispersing properties. Sodium polyacrylate of average molecular weight 2000 is used widely in the paper coating and emulsion paint industries to disperse clays, carbonates and titanium dioxide<sup>2-5</sup>.

As little as 5 mole per cent of acrylic acid will convey alkali solubility into an otherwise hydrophobic polymer composition.

Methacrylic acid and monoesters of maleic anhydride are also commonly used. In addition, sulphonic acid containing monomers such as acrylamido methyl sulphonic acid may be used but has limited commercial application in these fields.

Carboxyl containing polymers may be post cross-linked which is a useful additional property to have available.

Typical cross-linking agents are melamine/formaldehyde and urea/formaldehyde resins which provide covalent cross-linking, or Zn or Zr containing compounds which cross-link ionically and depending upon the base polymer can exhibit a number of useful effects.

An alternative cross-linking functionality may be introduced by hydroxyl containing monomers - typically hydroxyethyl methacrylate.

Cationic character may be introduced into this type of system by incorporating quaternary ammonium monomers. This chemistry introduces acid solubility, and is used in electrophoretic paint systems.

## 2. Molecular weight and molecular weight distribution

In general terms, molecular weight variations can produce variations in film properties such as toughness, flexibility, abrasion resistance and adhesion.

Molecular weight may be varied by adjusting initiator levels, polymerisation temperature, or polymerisation time.

Molecular weight distribution can be a critical factor in designing for optimum performance. One aspect of this parameter is discussed later under pigment dispersion.

## 3. Polymer structure

Polymers may be tailored to an essentially linear structure, a branched chain structure or taken to the extreme of developing a highly cross-linked three dimensional structure where the product may become insoluble depending upon chemical constitution. This latter variation can be used to modify rheological properties and to introduce resistance properties for example, heat resistance.

## 4. Physical form

Low molecular weight polymers are generally available in solid or solution form depending upon composition, or either as aqueous alkaline solutions or solutions in solvents.

As molecular weight increases then emulsion polymers have to be produced so that the viscosity parameter is overcome, because increasing the molecular weight of any polymer in solution is always accompanied by an increase in

viscosity.

Solid grade polymers may be produced by a number of techniques including the spray drying of emulsions, bead polymerisation, flaking of solutions in solvent.

In tracing the development of water-based resins for use in printing-inks, the initial target for the resin manufacturer was to produce a material which was more consistent than the naturally occurring resins.

Early attempts to match these properties lead to two types of carboxyl containing polymers.

(i) solid grade bead/flake products which could be converted to aqueous solution by neutralisation

(ii) emulsion products, which, if carboxylated, could be dissolved up in aqueous alkali or if not could be used as lead down vehicles for pigment dispersions, however produced.

The solid grades were developed to give the ink manufacturer a solid for a solid. It was quickly recognised that emulsion products could be handled more conveniently and more cost effectively.

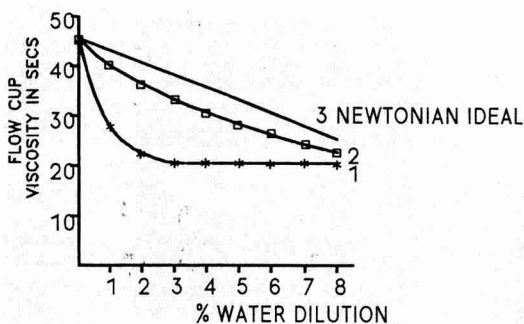
Traditional water-based systems and the earlier acrylic systems comprised a single resin in which was combined all the required properties eg, pigment dispersion, viscosity, transfer, rub resistance. However with trends to use water-based inks for wider and wider applications it became impossible to build into one polymer the optimum dispersion, pigment carrying and colour development properties combined with the often opposed properties of transfer, rub-resistance, gloss, adhesion, etc. Polymers were developed which could be combined with one another to optimise individual application requirements.

As an example of the way in which selected properties can be built into a polymer for a specific end use. Figures 1 and 2 compare viscosity variation with respect to:

- (i) aqueous solution concentration at a fixed pH and
- (ii) pH at a fixed concentration.

### a) Viscosity/dilution characteristics. (Figure 1)

**Figure 1**  
Viscosity/dilution characteristics



The stability of an ink running on a printing press is significantly affected by the rate of loss of solvent, in this case water, by evaporation and absorption. This leads to an increase in viscosity which initially can be tolerated but as the increase gets greater so the print quality deteriorates. This action is inevitable but the viscosity/dilution characteristics of the resin can influence the severity of the problem. Thus if the resin shows a *rapid change* in viscosity (curve 1) with water loss then the print quality will more rapidly deteriorate. If, however, the viscosity/dilution curve is more Newtonian (curve 2) with a gradual increase in viscosity then the ink is

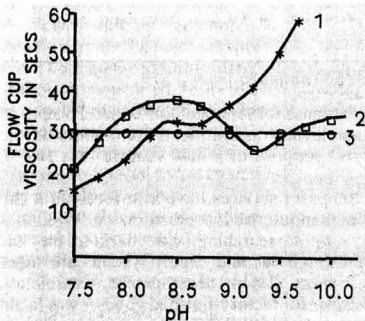
much more controllable and the print quality is easier to maintain.

Most resins show a rapid drop in viscosity, and this viscosity profile gives the greatest problems, since at operating viscosity small changes in water content produce massive changes in viscosity. However, by careful choice of monomers and by control of the molecular weight distribution, it is possible to design a polymer which will show only a gradual increase in viscosity with loss of water and which approaches the Newtonian ideal.

#### b) Viscosity/pH characteristics. (Figure 2)

Figure 2

Viscosity/pH characteristics



Water-based systems of this type rely on a volatile alkali as the neutralising agent, and in printing, this alkali tends to evaporate causing a fall in pH. If the resin shows major viscosity changes with minor changes in pH, compare curves 1-3, then once again the ink becomes unstable and the print quality suffers. However, by careful polymer design, represented by curve 3, it is possible to produce a polymer which will not change in viscosity until the pH gets close to 7.0 so that by operating at pH 8.0-9.0 the system will be unaffected by alkali losses.

For alkali soluble ink systems it is also relevant to consider carefully the choice of neutralising agent.

The alkali used to neutralise the polymer can make significant differences to the final properties of the ink. Most common alkalis can be used but their effects are quite different.

The most commonly used alkalis are ammonia and the lower molecular weight alkanolamines, particularly monoethanolamine.

In selecting the base a number of factors may be taken into consideration.

- (i) As the basicity decreases then the amount required to neutralise a particular resin will increase.
- (ii) All volatile alkalis should produce the same degree of water resistance in the dried ink film, but the rate at which this water resistance is achieved will depend upon relative evaporation rates.
- (iii) The speed of resolubility increases with increasing molecular weight of the base.

#### Improvements in pigment dispersion and colour development

The largest cost item in any printing ink is the pigment. Improvements in colour utilisation are constantly sought. Whilst differences in mechanical methods exist an important factor is the pigment wetting efficiency of the resin system.

Extensive research has been carried out over the years by

polymer suppliers to the coatings industries to optimise the performance of dispersing agents for pigments in aqueous media. The biggest success has been in the dispersion of inorganic pigments for emulsion paints and paper coating systems where dispersant composition and the control of molecular weight distribution have been shown to be essential for optimum cost effective performance.

For example, it has been shown that the dispersing efficiency of polyacrylate dispersants improves as the molecular weight distribution is controlled. This work proved that the maximum fluidity and stability of a calcium carbonate slurry was achieved by eliminating very low molecular weight species and very high molecular weight species from the polymer.

By and large the dispersion of organic pigments has been maximised by combinations of non-ionic surfactants plus resins containing low levels of carboxylation.

The experience gained through optimising compositions for inorganics has been used to develop polymeric species for dispersing organics.

A major development in water based ink formulation was the use of low molecular weight solution polymers as pigment grinding vehicles. Such polymers exhibit high pigment carrying and colour development characteristics as their principle criteria.

The colour development of certain pigments for instance has been improved by as much as 30% over formulations based solely on surfactant technology.

This development automatically led to the use of two component resin systems consisting of:

- (i) a pigment grinding vehicle to generate colour development and
- (ii) a let down vehicle to produce the desired ink performance i.e. printability, adhesion etc. In consequence it has been possible to focus attention on optimising gloss and substrate adhesion characteristics of the let down vehicle without having to consider what the effect of resin modification may have had on the pigment wetting and dispersing characteristics.

Additional advantages of reduced foam and improved water resistance have been achieved through the reduction and, in some cases, elimination of surfactants which were relied upon to maximise pigment wetting properties.

Low molecular weight carboxylated acrylates and styrene acrylates are now well established in this area.

As the environmental issues become more apparent, resin requirements have become much more demanding. In recent years very significant advances have been made in water based technology to reduce VOC emissions.

Resin systems have been developed for a wide variety of once 'difficult' areas.

To look briefly at a few.

#### 1. Inks for non absorbent surfaces

One of the problem areas for water based inks has been non absorbent surfaces. The increasing use of plastic films and foils in the packaging industry has created this new demand.

Problems, mainly associated with wetting and adhesion have been gradually overcome by the design of speciality polymers which now give good adhesion to these more discerning substrates. Inks prepared on these resins exhibit good gloss, adhesion, flexibility and water resistance on a wide variety of substrates including polyester, polythene coated board, vinyl wallpaper and aluminium foil. Resistance to water, soap, alkali, milk, orange juice is excellent. These properties can be further improved by cross-linking the resin during the drying process.

## 2. Inks for absorbent surfaces

The use of water-based flexographic inks for the printing of newspapers is becoming increasingly common in the United States but it is not so far advanced in the UK. Only the Daily Mail and the London Evening Standard are produced using water based inks. However, resin systems are now available which offer the ink technologist the opportunity to formulate successful water based flexographic inks for newspapers or other highly absorbent substrates. These newly developed resins combine rapid drying on newsprint to eliminate second impression set-off with excellent resolubility on the press and good machine stability to ensure very long runs without wash-up and rapid recovery of print quality after prolonged stoppage. Because these resins have very little tack during the drying phase, they avoid problems of paper tear and linting due to collection of fibres on the ink surface.

## 3. Heat resistance

The increasing use of pre-printed liners for corrugated cartons has offered the ink producer an attractive high volume market provided that the main criteria of gloss and heat resistance can be met. New heat resistant resins are now available for both grinding medium and let down which allow the manufacture of inks with hot scuff resistance of the order of 200°C and possessing the gloss which allows them to be used in both inks and overprint varnishes. The use of external cross-linking agents in this type of systems can improve heat resistance still further.

## 4. Gloss inks

Gloss, of course, is relative. It can depend upon:

- (i) the absorption characteristics of the substrate
- (ii) the press speed
- (iii) drying conditions, as well as
- (iv) the ink formulation

The demand for cheaper substrates, faster press speeds has laid the problem back with the ink and resin manufacturer. This demand has been answered in two ways.

Firstly, by formulating inks using higher binder levels which promotes 'hold out' which is required to promote the gloss and secondly, by resorting to 'glossy' overprint varnishes.

## Polymeric additives

Improvements in print quality can be achieved by the use of polymeric additives. One such product is a low-medium molecular weight water soluble polymer, usually non-ionic in character, which when used at low concentration, typically 2-5% on the ink, promotes greater control over ink film weight and improves printability by allowing reduction in impression and producing sharper prints.

A secondary advantage in the use of transfer additives is the improvement in open time on the press without affecting the drying rate on the paper. Faster resolubility and cleaner printing results.

## What for the future

Current developments seek to improve further in gloss, heat resistance, adhesion to the newer packaging substrates as they appear, and chemical resistance properties. The changeover from solvent to water is rapidly expanding and

aqueous alkali soluble polymers are an important component of existing and future resins systems.

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## Paper presented to OCCA Newcastle Section, 1 March 1990

*Jotischky, H., continued from p.379*

the prime database for *technical* literature. To keep Members informed specifically on European Community developments is the express purpose of a new venture, the *1992 Coatings Club*.

PRA's computer services have also received a substantial boost. The computerised production of WSCA, complemented by on-line searching, date back to the mid-1970s. Commercial databases and expert systems are more recent additions. Expert System development - culminating in a *Coating Selector* for factory-finished goods - was facilitated by an EC grant under its SPRINT programme; another instance of a collaborative venture with a European dimension. It is also a good example of the merging of technical expertise and information transfer by harnessing computer capabilities.

Industry's requirements in the '90s will be increasingly varied and complex, with targeted information becoming more highly valued. To this PRA is already making a contribution, showing that a research association can and must move to meet the needs of the time.

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## CALL FOR PAPERS

JOCCA is seeking technical papers for publication in the March 1991 issue on **Corrosion**.

Papers are invited from research organizations, raw material suppliers and paint manufacturers covering the latest technological and scientific developments in this field.

Papers should be a maximum of 10,000 words (10A4) and may include up to 25 tables, figures and graphs (combined total). Magnetic media is also acceptable (3½ or 5¼ floppy discs with ASCII and generic word processor files).

Deadline for the March issue is 15 January 1991. For further information contact Dr Peter Fyne Tel: 081-908 1086; Fax: 081-908 1219.

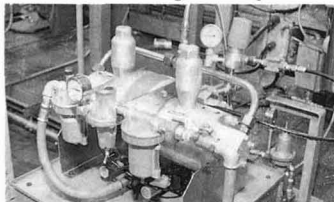
**BERWYN's** Chemical Gear Pump is capable of dispensing, with a high degree of accuracy, a wide range of aggressive chemicals for many purposes. Manufactured in talc-filled Polypropylene, it incorporates a standard spur gear arrangement manufactured from Solef PDVF, which is chemically inert and avoids contamination of chemicals being pumped. It is totally sealed and maintenance-free. Flow rates are variable up to 600 litres per hour.

*For further information Enter I301*

**BLAGDON PUMPS** offer a wide range of specialist air operated double diaphragm pumps for the paint and ink industries. These include pumps fitted with PTFE elastomers or cost effective polyester capable of withstanding many of the solvents used in inks and paint and providing extended life and low cost replacement. Special nylon coated pumps are available to reduce contamination and for ease of cleaning as are pumps fitted with multiple porting options.

*For further information Enter I302*

**GRACO** have specialised in the manufacture and installation of Pumps and Fluid Handling Systems in the Paint and Ink Industry for many years but recent trends particularly towards Waterbased Coatings have enabled us to develop new products specifically for these new applications. For example, the **GLUTTON** Range of Pumps are



now all available in Stainless Steel construction. The main benefit of a Graco Glutton Pump is that its patented seal will operate efficiently even when exposed to abrasive fluids. The Glutton Pump being air powered is ideal for hazardous areas and its leakproof design and excellent resistance to waterbased and corrosive fluids makes it ideal for applications in the Coatings Industry.

*For further information Enter I303*

**HILGE** manufacture quality pumps in rolled stainless steel. The smooth surface finish offers superior resistance to corrosion and improves the pumps' ability to be "Cleaned-in-Place". Pumps are available with quick release clamp arrangement for fast and simple stripdown ensuring ease of maintenance. For handling liquids

containing solids and fibres, several impeller options are available including open, freeflow, channel and flexible. The pump range includes single and multi-stage centrifugal, liquid ring — self priming and flexible impeller pumps for more viscous liquids.

*For further information Enter I304*

For the first time in the world a dosing pump is available from **Prominent Fluid Controls Ltd** to make fluid dosing programmable. A specially developed micro-processor increases safety in an automatic process system. The standard version of this high-tech pump, called 'ProMinent gamma/4' embraces a programmable dosing system that is extremely easy to operate and capable of communicating with an external computer. The actual operation status is displayed on an LCD readout. An intelligent combination of the desirable and the practicable in dosing technology is thereby achieved. ProMinent also supply other highly reliable metering pumps (solenoid-or-motor-driven), controllers, sensors and water purification systems for all requirement levels world-wide.

*For further information Enter I305*

As well as the design and construction of complete bulk liquid storage and distribution systems, **ROBAN ENGINEERING** have also concentrated on the development of a range of air operated double diaphragm pumps, flameproof solvent pumps, the Tokheim range of industrial flowmeters and liquid dispensers for handling hazardous and flammable liquids, balancing advanced technology with experience to obtain practical working designs with quality and reliability as the main features. Roban will undertake to extend existing plant to clients' requirements or provide a complete service of planning, design, procurement, site management and commissioning from the greenfield site to the completed installation.

*For further information Enter I306*

A single stage chemical pump, specifically designed to avoid any risk of liquid loss in applications where there may be explosion hazards, has been introduced by **SIHI PUMPS**. Called the Novametic ZNC, its construction features the use of a canned motor which avoids the need for shaft sealing and thereby prevents any possibility of product leakage from packed glands or mechanical seals. Construction can be in either SG cast iron or all stainless steel, and there is a choice of seventeen pump sizes for delivery heads up to 100m and capacities up to 280m<sup>3</sup>/h. A range of vacuum pumps with many

improved features, designed specifically to achieve low initial and maintenance costs, has been also introduced by **SIHI Pumps**. Suitable for pumping nearly all gases and vapours at suction pressures down to 33mbar, the new single stage liquid ring pumps are available in three different constructions, designated LEM, LEL and LEH respectively.

*For further information Enter I307*

**SSP Positive**, rotary lobe stainless steel pump ranges include SR Range fully modular pumps, SK Range pumps for ultra hygienic duties and AP Range high capacity models up to 300 mm dia. port size. Complementary SK Range pumps embody the circumferential piston principle. DRI Range rotary lobe pumps have ductile iron construction. DRM Range rotary lobe pumps are designed for sludge transfer and the SANSEAL ranges of air operated diaphragm pumps offer a choice of many models with metal or plastic, construction.

*For further information Enter I308*

**TUTHILL UK** manufacture a range of cast iron internal gear series 4000 process pumps for use with viscous fluids with capacities from 2.25 lpm to 225 lpm. The pumps are fitted with carbon bearings and therefore are not dependent on the fluid being pumped for lubrication. In addition different types of mechanical seal can be fitted featuring different face materials and elastomers to suit specific applications. Also available from Tuthill are our range of stainless steel magnetically driven gear pumps with flows up to 11.00 lph. These can be supplied coupled to a variety of different motors/controllers for dosing/injection applications.

*For further information Enter I309*

**WILO SALMSON**, the Derby-based pump specialists, have given details of a range of air cooled units designed for high temperature applications which is now available via its UK distributor network. The pumps are suitable for heat transfer applications in the hydrocarbon and other process industries. There is a total of 13 models in the GET range — manufactured in Laval — which is designed to operate at a maximum head of 32m (105 ft) and provides flow rates of up to 75m<sup>3</sup>/h (275 igpm). They each have a special air cooled mechanical seal — eliminating the need for supplementary water cooling coils and packing glands — and can handle water temperatures of 210°C at pressures of 23 bar.

*For further information Enter I310*

**PROCESSING OCTOBER:  
ENERGY CONSERVATION**

## Paintmakers Annual Open Tech Certificates Awards Ceremony



Eleven PA Open Tech students were honoured at the Annual Awards Ceremony held at Alembic House, London on 3 July, when they received certificates and prize money for their studies over the past twelve months. The certificates were presented by the retiring Chairman of the Training Committee and new President, David Penrice.

The annual prize giving ceremonies were started in 1988 and awards are made to those students who have completed all the paint modules. This year four students were present to collect their certificates; Richard Loadmore of Sonneborn & Rieck, John Needham of Joseph Mason, John Tynam of Macphersons and Steve Bowen of Sadolin.

Additionally, five more students were awarded the newly introduced President's Award Certificate on the nomination of each of the tutoring areas of South, Midlands, North and Eire. The nominated students had all obtained at least merit levels in two or more modules, although the judging criteria was not entirely on the marks obtained.

The five recipients of the certificates were Marion Baldwin of Granite Surface Coatings, John

Davies of Crown Berger, Martin Long of Engelhard Engineering, Michael Tompkins of Sonneborn & Rieck and Andrew Symonds of BIP.

Finally, the Venables Awards were given to the best two students who had studied the first of the new Powder Coating module. First prize to Philip Morris of Holden Surface Coatings and Ian Greenwood of ICI Powder took the second prize.

The ceremony was concluded with the award of two special certificates to Don Clement, the PA's training supremo and ex Director of the Association, Michael Leveté, for his spoken commentary on the taped material used in support of the courses.

The photograph shows the recipients of awards and PA staff and officers after the Awards Ceremony. ■

**MANCHESTER SECTION  
TOWARDS A GREENER  
COATINGS INDUSTRY  
20-21 September 1990**

**To Register  
contact  
Terry Wright  
061-434 3511**

### Letter from Marian Morris to the General Secretary

5 August 1990

Dear Chris,

Thank you for sending the two copies of JOCCA containing appreciations of Don by his brother Colin, David Penrice and Bob Rouse. I felt that they struck the right note in remembering Don as he always was, cheerful, witty and sincere. Thank you gentlemen.

I have written to many OCCA members who were kind enough to send condolences but, unfortunately, not all of them contained addresses and so I would appreciate it if you would express my thanks to them in the next copy of JOCCA. My thanks also for the cheque sent on behalf of the Association to the National Asthma Campaign.

I hope that OCCA will continue to flourish and I, personally, will remember with affection many of the members whom I met when accompanying Don to many functions around the world.

Yours sincerely,

MARIAN

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# FINISHING 90

183 exhibitors, 193 stands and three open days. These are the basic statistical facts that almost certainly make Finishing '90 the most important event ever for the UK's metal finishing industry. The exhibition will be held at the Telford Exhibition Centre, Telford, Shropshire and will be open for three days — 25-27 September 1990.

Finishing '90 covers every facet of the technologies used in applying and testing finishes on metal substrates. Both sections of the industry — electroplating and paint/powder coating technologies — are well represented and most of the best-known company names in both areas are in attendance.

A selection (at the time of going to press) of surface coating equipment manufacturers include:

**C & W SPECIALIST EQUIPMENT LTD.**, the leading UK design and manufacturing company in the specialist Salt Spray, Humidity and Composite Multi Test Chamber industry, is displaying and demonstrating its range of corrosion cabinets which are widely used throughout the Finishing Industry for quality control and research. On display will be the NEW 1990 design of Salt Spray Cabinets which incorporate all the latest instrumentation available, and the popular composite Multi-Test Corrosion Cabinet, supplied over the last three years to an increasing number of major automotive manufacturers and suppliers.

*For further information Enter 1401*

**COATEST** is a new company set up to supply the Coatings Inspector with the high quality, reliable and reasonably priced instruments he needs. Whilst the Company will be specialising in coating thickness gauges it will also offer all those instruments that you cannot normally purchase from one source and these include Wet and Dry coating thickness gauges, Adhesion Testers, Pin Hole Detectors, Whirling Hygrometers, Surface Thermometers, Shot and Gritblast Standards. The main feature on display at Finishing is what is perhaps the World's smallest Coating Thickness Gauge yet, complete with separate probe to access those awkward corners. The Instrument has a range of

1000 microns (40 thou) with an accuracy of better than  $\pm 5\%$ . It comes complete in a vacuum-formed package which can then be used as a bench stand.

*For further information Enter 1402*

**ELCOMETER INSTRUMENTS LTD** will be exhibiting their range of tool and measurement instruments for surface coatings.

In addition to a full range of instruments for the measurement of coating thickness, Elcometer have units for checking surface profile after blast cleaning, for measuring humidity and temperature, for detecting pinholes in coatings and for testing adhesion and gloss. Featured on the stand will be the microprocessor-based coating thickness gauges, Models 246, 256 and 300, together with the PC-based software to collect data from the memory of the Model 300.

*For further information Enter 1403*

A range of portable thickness gauges for the measurement of surface coatings on a metal base will be exhibited by **ELEKTRO-PHYSIK GB LTD.** The MINITEST range consists of four models having such features as application memories divided into batches, high and low limit settings, print-out facility and down loading to a computer. All gauges are battery operated and fully portable and therefore suitable for site work as well as in the factory or laboratory.

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**FISCHER INSTRUMENTATION (GB)** will be exhibiting their latest developments in the following: Coating

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*For further information Enter 1406*

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*For further information Enter 1408*

**MINOLTA (UK) LIMITED** will be exhibiting their world-famous range of Colorimeters, the Minolta Chroma Meters. New for this year is a software package that will satisfy the needs of quality control together with advanced file handling capabilities. Also on display will be the new Chroma Meter CR-241, the only Colorimeter that will target down as low as 0.3mm diameter, for checking the colour of very small samples in a wet or dry state.

The Company will be demonstrating their portable Spectrophotometer, the CM-1000 which also has new software

for a variety of colour difference equations as well as Yellowness and Whiteness Indices.

Details will be available on the range of lighting cabinets that Minolta market together with their Gloss Meter and Statistical Process Control Analyser, the Dataputer.

*For further information Enter I409*

**PEARSON PANKE EQUIPMENT** will be showing a selection from the wide range of Erichsen test equipment. This will include the portable statistical glossmeter.

Also on show will be the latest film thickness gauges with software plus instruments for measurements on non-metallic substrates.

A new cost effective programmable viscometer with software will be on display which should be of particular interest to those who wish to measure the viscosity of structured products.

*For further information Enter I410*

Tickets for Finishing '90 are available from the Exhibitions Division, Turret Group plc, Turret House, 171 High Street, Rickmansworth, Herts, WD3 1SN. Tel: 0923 777000. Fax: 0923 771297, or telephone the 24 hour ticket line on: 0923 770337. ■

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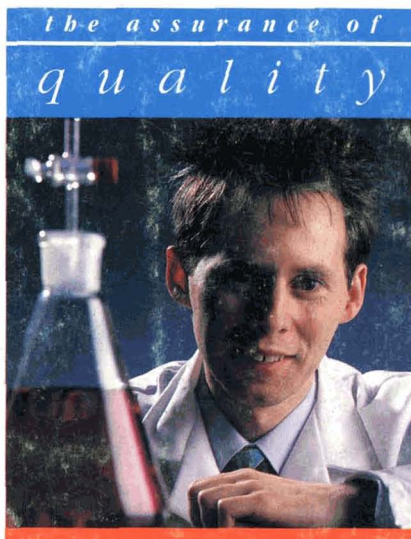
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