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## OCCA Monograph No. 1

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# JOURNAL OF THE SOCIETY OF COLOUR CHEMISTS' ASSOCIATION

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A radio tracer study of the competitive adsorption on titanium dioxide of stearic acid paired with linoleic acid and with palmitic acid

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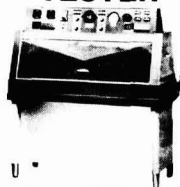
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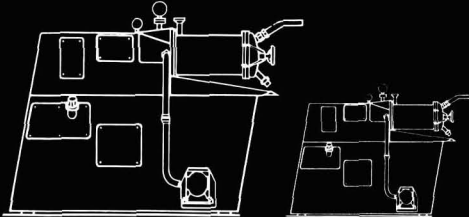
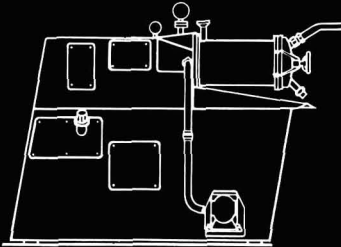
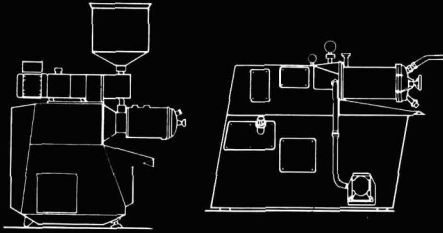
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# A low shear viscometer: An instrument for measuring flow and sag resistance in coatings\*

By M. L. Colclough, N. D. P. Smith† and T. A. Wright†

ICI Ltd, Paints Division, Wexham Road, Slough, Berkshire SL2 5DS

## Summary

A new low shear viscometer (LSV) of robust design is described. The instrument provides a method of assessing the flow-out characteristics of coating materials by simulating the rheological conditions under which surface perturbations caused by application processes, such as brushing or roll coating, are removed.

The brushmark flow theory of Smith, Orchard and Rhind-Tutt is used to define the engineering constants which permit simulation of the flow process. Experimental results are described which demonstrate the effectiveness of the approach.

## Keywords

*Equipment primarily associated with analysis, measurement or testing viscometer*

*Types and classes of coatings and allied products emulsion paint alkyd coating*

*Properties, characteristics and conditions primarily associated with coatings during application flow sagging*

*Processes and methods primarily associated with application of coatings and allied products flow control sagging brush coating*

*materials in general thixotropy*

## Un viscosimètre à faible vitesse de cisaillement: un appareil pour mesurer la résistance à étalement et à la formation de draperies de revêtements

### Résumé

On décrit un nouveau viscosimètre à faible vitesse de cisaillement (LSV) et de construction solide. L'appareil, fournit une méthode pour déterminer les caractéristiques d'étalement des revêtements par la simulation des conditions rhéologiques sous lesquelles les perturbations de la surface, provoquées par les procédés d'application, tels que ceux qui utilisent le pinceau ou le rouleau, sont absentes.

On emploie la théorie de l'étalement des traces de pinceau formulée par Smith, Orchard et Rhind-Tutt pour définir les constants opératoires qui permettent la simulation du processus d'étalement. On décrit les résultats expérimentaux qui démontrent l'efficacité de cette ligne d'attaque.

## Ein Viskosimeter für niedrige Schubspannungen zur Messung des Verlaufens und des Widerstands von Anstrichstoffen gegen Gardinenbildung

### Zusammenfassung

Ein neues, robust konstruiertes, Viskosimeter wird beschrieben. Es gestattet die Messung der Verlaufseigenschaften von Anstrichstoffen, unter rheologischen Bedingungen welche die Beseitigung der durch die Auftragsmethode, sei es Pinsel oder Rolle, verursachten Oberflächenstörungen, nachahmen.

Die Verlaufstheorie von Smith, Orchard und Rhind-Tutt wird angewendet um die Konstanten auszuarbeiten die das Simulieren des Verlaufsvorganges gestatten. Die experimentellen Ergebnisse bestätigten die Fruchtbarkeit dieser Methode.

### Introduction

*Ref. 1*

Over the last decade or so, paint manufacturers have taken advantage of new materials and techniques to obtain a better control of the rheology of their products. This has allowed thicker coatings to be applied in one operation, reduced the tendency of paints to form hard settlements during storage, and made paints easier and cleaner to apply. However, the improvement has sometimes been made at the expense of the ability of the paint to flow out to a completely smooth surface. A particular difficulty is

the somewhat delicate balance between the freedom of flow to achieve good levelling and the restraint necessary to avoid excessive flow on vertical surfaces.

This balance has been achieved in the past, for the most part, by observation of practical brush-outs which is a highly subjective and time consuming process, if an adequate number of replicates is analysed to ensure statistical significance. The need for a more objective and discriminating method that could be used to assist in the investigation of the complex interactions involved has stimulated many authors to examine the subject. However, the use of the various types of rheometer that are available

\*Paper based upon a lecture given to the Thames Valley Section in March 1978

†Now retired

does not seem to have helped very much. This can be attributed, partly, to the complex behaviour of the fluids themselves which make conventional rheology difficult and, partly, to the inability of the equipment used to reproduce the rheological conditions under which a freshly applied paint coating flows out.

The objective of this paper is to describe a new low shear viscometer (LSV) of robust design which provides a method of objectively assessing the flow out characteristics of coating materials by simulating the rheological conditions under which brushmarks flow-out. As such, the instrument makes no comment on the influence of drying on brushmark flow and sag resistance. Thixotropic recovery is a process which normally affects flow-out and sag resistance at an earlier time than, say, solvent loss<sup>1</sup> so that the ability to separate the two mechanisms can be seen as an advantage from a formulating point of view.

The paper takes the form of a general discussion on the most widely accepted theory of levelling, which is used to define the variables and range of variables over which any instrument must operate if it is to match the flow-out process. Some of the engineering design features which make such a match possible in the LSV are described, followed by a discussion, and presentation of experimental results.

**2. Levelling and sagging**

**2.1 Introduction**

*Refs. 2-5*

The theory of brushmark flow-out<sup>2</sup>, ignoring gravitational effects, describes the levelling process as a competition between surface tension derived stresses which cause surface perturbations to flow-out and viscous stresses which resist fluid movement. In a practical experiment brushmark radius of curvature can be seen to increase with time as the brushmark height decreases and since the stresses attributable to surface tension are inversely proportional<sup>3</sup> to the radius, then the driving stresses for flow-out decrease, i.e. they relax, and the flow-out process slows down. Hence, any instrument which parallels or matches the flow process must be of the stress relaxation type.

The instrument described in this paper is of the stress relaxation type in which a relaxing spiral spring matches the relaxing flow stresses which are resisted by the viscous forces of the sample itself.

The instrument differs from similar devices<sup>4,5</sup> in that its operation is matched to the flow process via the theoretical approach of Smith, Orchard and Rhind-Tutt<sup>2</sup> which permits a quantitative definition of the correct instrument design limits.

**2.2 Brushmark theory**

The analysis of brushmark flow<sup>2</sup> emphasises the fact that the stresses which cause levelling change continually during flow-out and that the shear rate associated with this process is a rapidly changing function of shear stress and the rheological character of the coating. In order to achieve the aim of instrumental matching of flow, the first step was to determine realistic quantitative values of the shear stress, shear strain and shear rate. This was done by substituting the practical values of the variables which

characterise the brushing and levelling process into the equations of Smith<sup>2</sup> *et al* which follow.

In the simple case for which the viscosity and surface tension ( $\sigma$ ) are constant, and the mean coating thickness ( $h$ ) is small compared to the width of brushmarks ( $\lambda$ ), the amplitude of a brushmark ( $a$ ) at a time ( $t$ ) is given by the expression:

$$a = a_0 \exp - 16 \pi^4 h^3 \sigma t / 3 \lambda^4 \eta \dots \dots \dots (1)$$

where  $a_0$  is the initial depth of the brushmarks. The maximum shear stress ( $\tau_{max}$ ) is given by the expression

$$\tau_{max} = 8 \pi^3 \sigma h a / \lambda^3 \dots \dots \dots (2)$$

The maximum shear strain ( $\gamma_{max}$ ) at the point of maximum shear stress is given by:

$$\gamma_{max} = 3 \lambda (a_0 - a) / 2 \pi h^2 \dots \dots \dots (3)$$

and the associated maximum rate of shear given by the expression

$$(d\gamma/dt)_{max} = 8 \pi^3 \sigma a h / \lambda^3 \eta \dots \dots \dots (4)$$

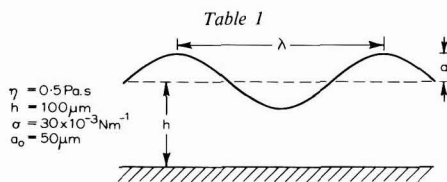
The selection of meaningful values of  $\lambda$  and  $a_0$  for substitution into these equations presents some real problems, since in a brush-out there is a distribution of widths and amplitude of brushmarks which give rise to a spectrum of shear stresses, shear strains and shear rates. The problem of a spectrum of parameters of this type cannot be solved instrumentally, so that there is little option but to select one value of  $\lambda$  and  $a_0$ . The values selected were  $\lambda = 2.5$  mm and  $a_0 = 50 \mu\text{m}$  and were determined by a set of subsidiary experiments. The value of  $\lambda$  was determined by formulating a number of solvent-borne paints with different flow characteristics, performing brush-outs and allowing the film to dry. Customer opinion trials were used to determine which panels characterised the transition from good to bad brushmarking. Profilometer measurements indicated that if widths of less than 2.5 mm were present the product was classified as unacceptable. Longer brushmark widths characterised acceptable products.

Consequently,  $\lambda = 2.5$  mm was selected as a wavelength of practical importance.

The value of  $a_0$  was estimated from a study of the time of decay of brushmarks and from high speed photography. During brushing, high amplitude brushmarks do occur; however, they decrease in amplitude so rapidly in their early stages that they do not present a problem until in the region of  $50 \mu\text{m}$  whence they may take a considerable time to decay.

By these means the authors have selected from the spectrum of practically occurring values two quantitative estimates of  $\lambda$  and  $a_0$  which characterise the transition between brushmarks which are visible and distressing and those which are acceptable.

The practical situation is apparently further complicated by the fact that the viscosities of many paints are time dependent and will increase in effective viscosity during flow-out in a way which is not very amenable to mathematical analysis. However, it should be noted that equations (2) and (3) are independent of the viscosity of the coating so that if they are used to provide a basic specification for a measuring system, the system will be independent of viscosity of whatever type.



		$\lambda$ (cm)					
		$a$ ( $\mu\text{m}$ )	0.1	0.2	0.25	0.3	0.4
Maximum Shear Stress (Pa)	50	37.2	4.65	2.38	1.38	0.58	
	5	3.72	0.46	0.24	0.14	0.06	
Maximum Shear Strain	5	2.15	4.3	5.37	6.4	8.6	
	0	2.4	4.8	6.0	7.2	9.6	
Maximum Shear Rate $\text{sec}^{-1}$	50	74.0	9.3	4.76	2.8	1.2	
	5	7.4	0.9	0.5	0.3	0.1	

An alternative way of viewing this statement is to describe the flow-out of brushmarks as a process of balancing forces. The levelling force supplied by surface tension is resisted by the viscous forces which characterise the fluid; these viscous forces can be time dependent, have elastic components or whatever, but they only serve to increase (or decrease) the effective resistance to the surface tension. Hence the type of "viscosity" is immaterial: either flow-out occurs and can be measured or it does not.

By substituting the values of  $\lambda$  and  $a_0$  into equations (1), (2), (3) and (4) and by assuming practical values of Newtonian viscosity and surface tension it is possible to obtain, for a given film thickness, numerical values of the maximum shear stress, maximum shear strain and maximum shear rate involved in the decay of a brushmark over the  $50 \mu\text{m}$  to  $5 \mu\text{m}$  amplitude range. Typical figures are given in Table 1 which illustrate the overall dependence of flow on  $\lambda$  and the fact that for  $\lambda = 2.5 \text{ mm}$ , the shear stress, shear strain and shear rate values are all very small.

### 2.3 Sagging

For a paint of density,  $\rho$ , and a coating of thickness,  $h$ , the maximum shear stress,  $\tau_{max}$ , is  $\rho gh$ ; for a paint of unit density, and a coating of  $100 \mu\text{m}$  thickness,  $\tau_{max}$  is  $0.98 \text{ Pa}$ . This is effectively the shear stress that is required before instability sets in, and for good sag resistance the paint should always be able to resist the gravitational stress.

Further analysis than this presents real problems, since the volume flow rate of paint is highly dependent on thickness, which means that if a coating is not completely uniform, i.e., it has brushmarks, the thicker parts of the coating can overtake the thinner parts immediately below. This gives rise to the unstable situation in which the characteristic runs are formed. It is thus difficult to apply any useful numerical analysis to these unstable phenomena, but it is clear that the shear stresses are in the region of  $1 \text{ Pa}$  at the start of the process and may be greater than this in the runs. Sag resistance and flow represent the extreme opposites of the practical property requirement and as shown by Table 1, an instrument which parallels the flow-out of brushmarks is able to make measurements in the shear stress range required to describe sag resistance. Practical examples to illustrate this point are described in section 4.

### 2.4 Summary

The preceding discussion has highlighted a number of requirements for an application and flow simulation instrument. With a number of other practical points, the instrumental needs can now be summarised as:

- (1) As a prelude to both flow and sag resistance measurement, the device must be able to shear the test fluid in such a way as to parallel application conditions.

For brushmark flow-out, the instrument should have the ability to:

- (2) Apply a shear stress which relaxes with time.
- (3) Measure the shear strain as a function of time.
- (4) Be of such design that the shear stress and shear strain ranges are representative of actual brushmark flow-out.

In addition, for the assessment of sag resistance the instrument must have the ability to:

- (5) Apply a shear stress in the practical range.
- (6) Perform continuous or repeat measurements over a period of time.

From an experimental point of view further requirements are robustness, ease of cleaning, rapid temperature control and quick operation to overcome the difficulties of current rheological techniques.

### 3. Instrumental design

Ref. 6

The theoretical and practical design requirements have been met by a rotational viscometer of the relaxation type with thin film geometry. Figure 1 shows a schematic diagram of the instrument in which a compressed air bearing (1) is used to support the rotational member (2). An automatic gear train (5) is used to provide high shear rate conditioning to the sample which sits between the parallel plates (3) and (4). The general requirements for accommodating the sample and accurately controlling its temperature are the same as for the commercially avail-

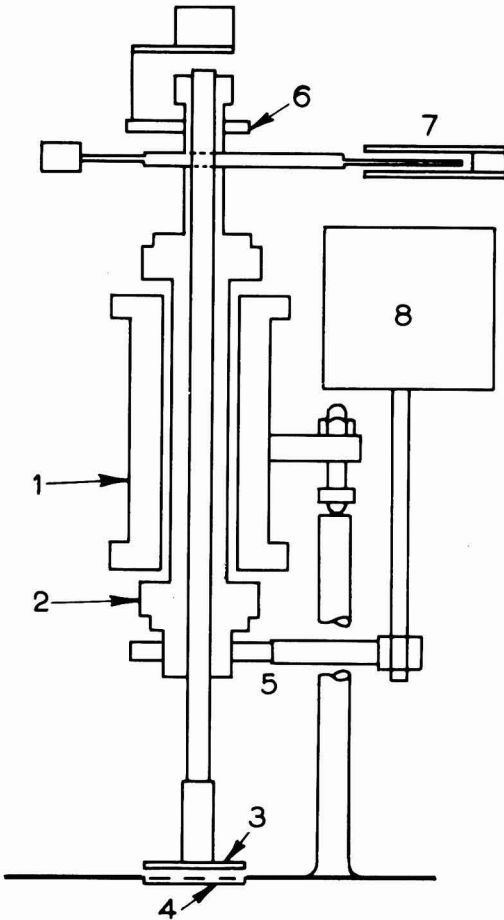


Figure 1. Schematic diagram of the Low Shear Viscometer

able ICI/REL high shear cone and plate viscometer<sup>6</sup> upon which the structural design of the new instrument is based.

The shear stress which decays with time in a practical brush-out is simulated in the instrument by a horizontally mounted spiral spring (6) attached to the friction free rotor (2). The spring is wound up to such a point that at the start of the experiment it applies a shear stress to the rotor equivalent to that experienced by the liquid when a brushmark of width 2.5 mm and height 50 μm is about to decay. Furthermore, the movement of the rotor is controlled through the spring modulus to be equivalent to the shear strain in the brushmark flow process. A capacitance transducer (7) which places no measurable constraint on the rotor is used to monitor the shear strain change with time as the spring relaxes against the viscous restraint of the liquid.

Facilities are available on the finished instrument so that the output from the transducer can be recorded on a chart recorder to give a continuous plot of shear stress or shear strain against time. Alternatively, for rapid opera-

tion the curve can be sampled at a number of points, and numerical values of shear strain at preset times used to characterise the curve. In the latter case, simple memory circuits are used to hold the data for the convenience of the operator. The curve is sampled at three points; after 3, 10 and 25 seconds, which, when combined with the maximum shear strain value at zero time, gives four points to characterise the curve.

The sample loading procedure is identical to that used in the ICI/REL high shear viscometer<sup>6</sup>, and is a simple manual operation. Data recording is automatically started when the run button is pressed, and the memory accessed by a switch operation after the end of the run.

By incorporating a motor (8) to drive the gear train (5) which can be coupled or decoupled from the central rotor it is possible, if desired, to shear the sample before performing the experiment. In this way all of the principal features described as necessary for the instrument are incorporated. However, before proceeding to illustrate how the LSV responds in practice, there remains the important task of determining the engineering constants, i.e. spring strength, plate radius, gap setting, which are needed for the instrument to parallel the flow process.

### 3.1 Matching of the instrument to flow

Ref. 4

As has been discussed above, the flow theory for selected values of brushmarks width and initial height allows a quantitative estimate of the maximum shear stress and shear strain that characterises the process. For values of  $\lambda = 2.5$  mm and  $a_0 = 50 \mu\text{m}$ , as shown in Table 1, the shear stress should decay from a maximum of about 2.4 Pa as the shear strain decreases from ca 5.4 strain units. Given that, in the instrument, the shear stress is applied by a relaxing spring and the shear strain by the differential plate movement under the action of the spring, the problem is now to determine the instrument constants which make the attainment of the flow matching conditions possible.

This matching of instrument constants has been achieved by comparing the basic equations of flow with the equivalent equations for the viscometer. It can easily be shown that under the effect of a relaxing spring, the angular displacement,  $\theta$ , of the upper plate of the viscometer is given, after time  $t$  by,

$$\theta = \theta_0 \exp \left( -2 d K_s t / \pi R^4 \eta \right) \dots \dots \dots (5)$$

where  $\theta_0$  is the initial angular displacement,  $K_s$  is the spring constant,  $R$  is the plate radius and  $d$ , the plate separation.

If equation (5) is compared with equation (1) and it is assumed that for matching of flow, the change in brushmark amplitude "a" should match the change in the angular displacement  $\theta$  of the viscometer plate then:

$$\theta_0 = 3 \lambda d a_0 / 2 \pi h^2 R \dots \dots \dots (6)$$

If the viscometer is constructed with the correct ratio of  $d:R$  for given values of  $\lambda$  and  $h$ , then the movement of the upper plate will be directly proportional to the decay of brushmark height. A further consequence of this relationship is that the exponential terms in equations (1) and (5) must also be equal, which with rearrangement gives an expression for the spring constant i.e.:

$$K_s = \frac{8 \pi^5 h^3 R^4 \sigma}{3 \lambda^4 d} \dots \dots \dots (7)$$

If now into equations (6) and (7) the values  $h = 100 \mu\text{m}$ ,  $\lambda = 2.5 \text{ mm}$ ,  $a_0 = 50 \mu\text{m}$  are substituted, the information is obtained that the maximum angular rotation ( $\theta_0$ ) of the top plate should be 5.5 angular degrees ( $\angle^\circ$ ) and the spring constant ( $K_s$ )  $27.5 \times 10^{-5} \text{ N cm}/\angle^\circ$  for a plate radius of 1.59 cm and a plate gap of  $250 \mu\text{m}$ .

In this way it is ensured that the instrument matches exactly the flow-out process of a 2.5 mm wide brushmark from an initial height of  $50 \mu\text{m}$ . Moreover, as a consequence of this matching procedure the ordinate of the relaxing stress versus time plot can not only have the dimensions of stress and shear strain, but as already seen, brushmark height as well, which means that the apparent viscosity can readily be calculated – see Patton<sup>4</sup> for a full description of the procedure.

In addition, the instrument has been designed automatically to output the average apparent viscosity calculated over two preset shear stress ranges and to store the information for access. This operation fulfils two important needs:

- (1) It allows the instrument readily to be calibrated with Newtonian oils.
- (2) It provides a sensitive and numerical indicator of the rate at which sag resistance develops.

The calculation of average apparent viscosity is, in essence, an alternative and numerical way of describing the stress relaxation curves. However, for the purpose of this report it is preferred to describe the results in terms of brushmark amplitude decay curves, which as shown by equation (6), can be directly related to the angular displacement of the upper plate. Sagging is described in terms of shear stress.

**4. Results and discussion**

In order to maintain continuity of the text, a number of points worthy of discussion have not been included in this section. Topics such as instrument gap geometry, shear rates in application and inertia effects are consequently included in the Appendices.

The authors have found that, in general, four separate relaxation runs are required to assess instrumentally the levelling and sagging of brushmarks. The first run is performed without high shear rate conditioning, and gives an approximate indication of condition in the can. The second run is much more important, in that high shear rate conditioning is applied to simulate brushing prior to the relaxation run. This relaxation indicates whether or not the fluid breaks down, and hence whether or not brushmarks are likely to flow out. The third and fourth runs, carried out after say 2 and 4 minutes, without high shear conditioning, indicate the rate of recovery of the structure, and are particularly important in estimating the flow-out of longer wavelengths to give a perfect finish, and in determining whether or not sagging is likely to occur.

The nomenclature, *A/B/C*, has been adopted in the discussion, where *A* is used to denote the value of the volume mean shear rate conditioning (normally  $2500\text{s}^{-1}$ ), *B* the time that the shear rate is applied, and *C* the time

from the start of the experiment.

**4.1 Solvent-borne systems**

Experiments were carried out on a standard paint, formulated using titanium dioxide and a long oil soya bean alkyd. In the three systems described, part of the binder alkyd was replaced by amounts of a thixotropy inducing resin. The replacement quantities were for paint (1), 10 per cent by weight with a final pigment/binder ratio of 1:1, for paint (2), 16 per cent by weight, also with a pig-

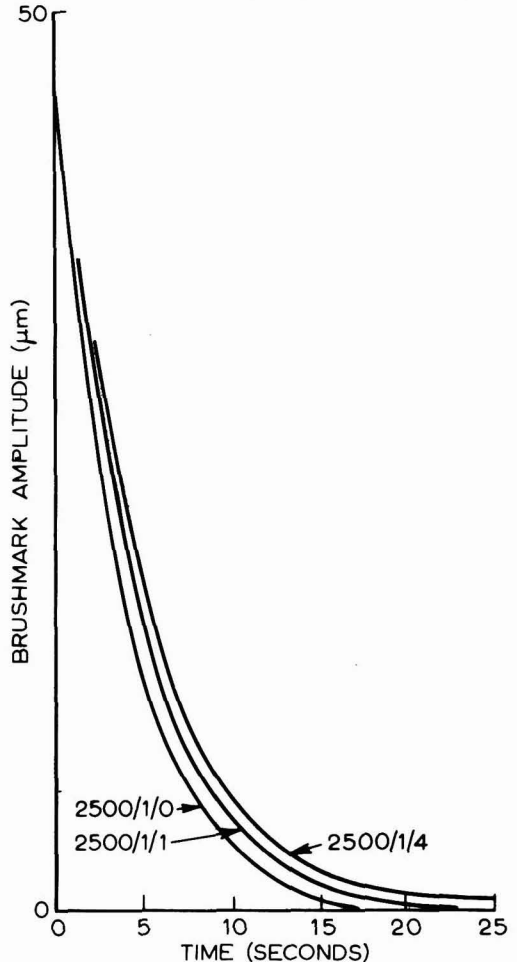


Figure 2. Amplitude decay curves for alkyd paint (1) containing 10 per cent by weight thixotropic resin

ment/binder ratio of 1:1, and for paint (3) 25 per cent by weight and a pigment/binder ratio of 0.75:1.

Figure 2 shows the performance of paint 1, which contains the lowest amount of thixotropic resin. These specimens were measured after one week's storage at ambient temperature in closed cans in the laboratory.

Curve 2500/1/0, that is the profile of the decrease in brushmark amplitude with time immediately after con-

ditioning for 1 second, shows that brushmarks of amplitude  $50\mu\text{m}$  flow out after about 20 seconds. The conclusion is clearly that this product has very good flow properties, but to determine whether it continues to flow, it is necessary to repeat the experiment at later times.

Curves 2500/1/1 and 2500/1/4 show that even after one, and then four minutes, the viscous resistance to the surface tension forces remains so low that the product continues to flow. From the point of view of sag resistance, it is clear that unless there is an appreciable increase in viscosity with time, say 3-5 minutes after application, so that the film can resist gravitational stresses of *ca* 1 Pa, then sagging will occur. In this case, as shown in Fig. 2, the contribution of viscous resistance hardly exceeds 0.2 Pa, with the inference that despite having excellent flow properties the formulation with 10 per cent of a thixotropic-inducing resin has very poor sag resistance. In practical brush-out trials, this formulation levelled exceedingly well, and on a vertical surface sagged badly.

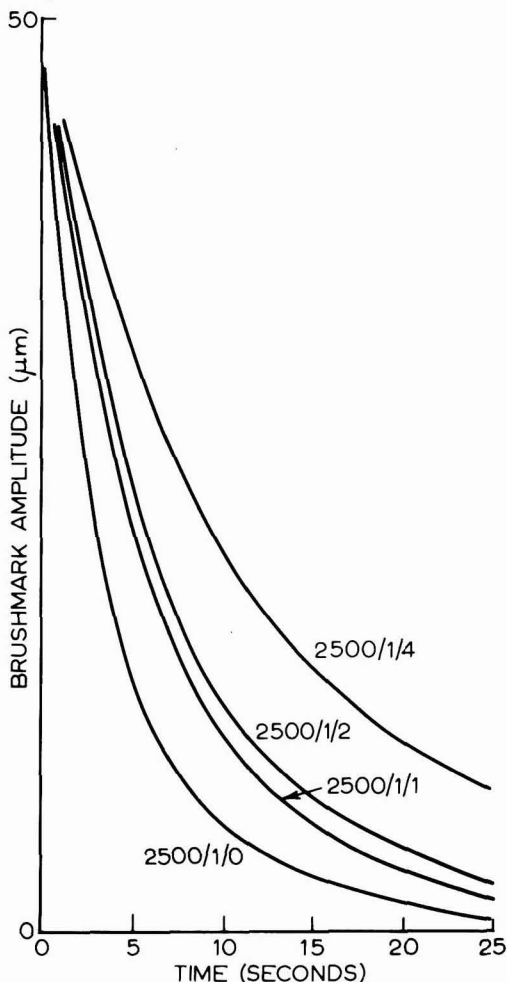


Figure 3. Amplitude decay curves for an alkyd paint (2) containing 16 per cent by weight thixotropic resin

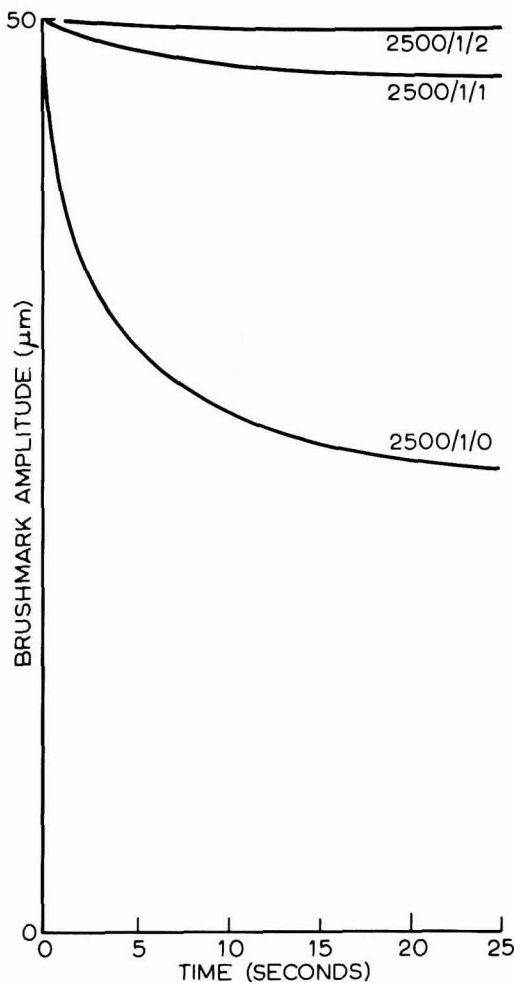


Figure 4. Amplitude decay curves of an alkyd paint (3) containing 25 per cent by weight thixotropic resin

Paint (2) with a higher level of thixotropic resin may now be considered. The data is shown in Figure 3. Curve 2500/1/0 indicates that the paint readily breaks down under the brush, but quite clearly not to the extent of paint (1).

Curve 2500/1/1 shows that after one minute a noticeable, although not large, recovery has occurred which is indicative that flow of longer wavelength brushmarks is continuing despite the linking together of molecular species to increase the apparent viscosity. Curve 2500/1/4 shows how the resistance to surface movement gradually increases with time.

However, by applying the criteria for sag resistance it can be deduced that despite the increased percentage of thixotropic resin, adequate performance has not been achieved. In a practical evaluation the paint levelled well and sagged badly, but there was a subjective statement that paint (2) appeared to sag less readily than paint (1),

which supports to a limited extent the instrumental findings.

By formulating with 25 per cent thixotropic resin, a dramatic change in properties was obtained. Figure 4 shows that this large amount of resin still allows the paint to break down under the applied shear stress, i.e. curve 2500/1/0. However, the viscous resistance that it generates is so great that under the action of surface tension forces the brushmarks only decay to about half their original height, i.e. about  $25\mu\text{m}$ . For a gloss, semi-gloss or undercoat the presence of such large amplitude surface features would be unacceptable.

Under all conditions the formulation appears able to resist a gravitational stress of 1 Pa, so that the LSV predicts excellent sag resistance. Practical brush-outs confirmed these findings.

An interesting point to note is that not only is the breakdown under high shear rate affected by these resin additions, but so is the rate of thixotropic recovery, as shown by the spacing of the curves after the same time interval.

Using the digital output mode of data recording (from which all figures in this paper are plotted), the three experiments took 30 minutes which included time for temperature equilibration and cleaning.

#### 4.1.2 Bentone additives

An alternative method of creating structure in solvent-borne paints is to add bentone and an activator. Consequently, to the above mentioned formulation 15 per cent by weight bentone gel and 1.0 per cent activator were added.

Figure 5 shows a comparison of the formulation with bentone (broken line), and without bentone (solid line). The change in performance over a 4 minute period with bentone is quite marked. As is expected, there is very little difference between the curves after high shear rate conditioning, since the bentone in such small unlinked packets will not contribute very much to the base formulation viscosity.

Both formulations flow out very well with the brushmark height falling from  $50\mu\text{m}$  to  $0\mu\text{m}$  in 10 to 20 seconds. Without bentone, the paint does not increase its resistance to surface tension or gravitational stresses as indicated by curve 2500/1/3, so that the prediction is that the paint flows well, but sags badly. With bentone, however, the instrument shows an appreciable viscous resistance increase after 4 minutes which is probably quite sufficient to resist settling stresses, but not enough to resist those associated with sagging. These findings were again confirmed by practical brushing tests.

#### 4.2 Water-borne systems

As an example of the use of the LSV for optimising water-borne systems, a typical PVAc copolymer latex system at approximately 65 per cent solids was examined after water additions. Dilution of trade products is common in practice and it is necessary for the manufacturer to recommend a level of dilution. Four formulations were examined.

Figure 6 shows the curves for the undiluted paint. The

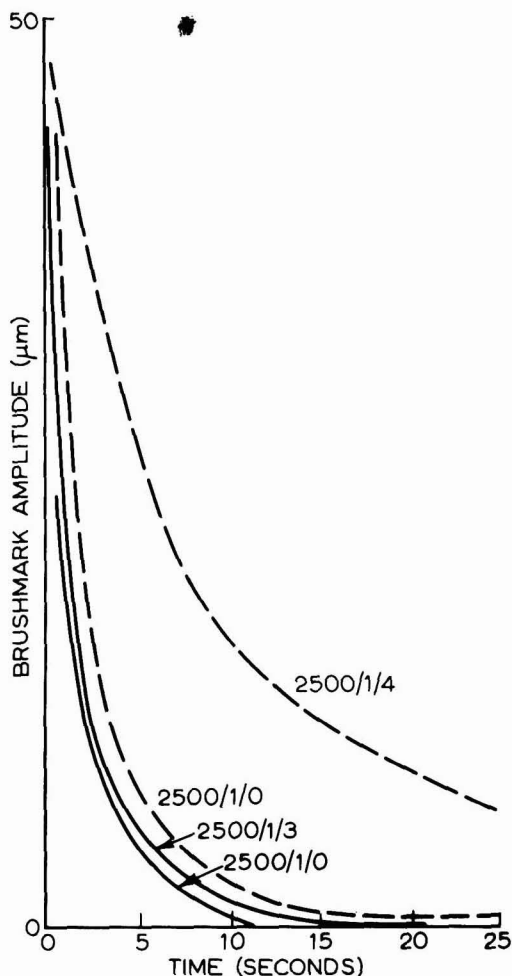


Figure 5. Amplitude decay curves for soya bean alkyd based paint with bentone (broken line) and without bentone

paint in this case was several months old, so that 0/0/0 curve may be considered to be fairly typical of the in-can condition. Some products are very shear rate sensitive, so that the act of sampling and the viscometer loading causes a breakdown. In such cases the 2500/1/3 curve may have higher values than the 0/0/0. The 0/0/0 curve is thus only considered to give an approximate figure for in-can conditions.

In Figure 6, the 0/0/0 curve indicates that the specimen has gelled between the parallel plates, and that the yield point is in excess of 2.38 Pa. The fact that the curve is not horizontal could be due to the normal Hookian response of the gel to the applied stress, or caused by slow creep. After high shear rate conditioning, the gel structure is seen to break down. Curve 2500/1/0 shows that viscous resistance to surface movement is high, stress relaxation has occurred only partially and the residual brushmarks are of high amplitude, *ca*  $30\mu\text{m}$ . Rapid structure recovery is shown to occur by curves 2500/1/1 and 2500/1/3, so

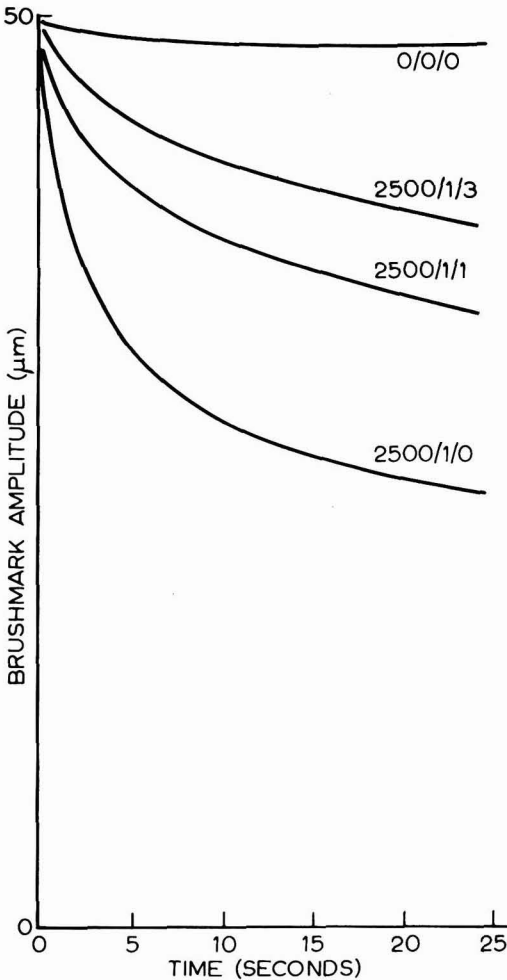


Figure 6. Amplitude decay curves for a typical high solids water-borne paint

that the prediction for flow properties is poor, but for sag resistance, very good.

The addition of 10 per cent by weight of water was followed by vigorous stirring and a 30 minute rest period before testing. The LSV results are shown in Figure 7, which indicates that from the 0/0/0 curve the nature of the gel has changed from one which resists almost completely the load applied by the spring to one which creeps quite quickly.

The effect of the water addition on the response after conditioning, i.e. curve 2500/1/0, is quite considerable, the curve stabilising when the surface tension forces become equivalent to the viscous forces with a residual brushmark height of *ca* 13  $\mu\text{m}$ . The other curves in Figure 7 indicate that the structural recovery rate has also been reduced and that sag resistance is attainable after 3-4 minutes.

Figures 8 and 9, for 15 and 25 per cent water addition

by weight, indicate quite clearly that as more water is added, the resistance to the surface tension forces, as duplicated by the viscometer spring, becomes less and the levelling becomes better, giving residual brushmarks of approximately 8  $\mu\text{m}$  and 4  $\mu\text{m}$  height respectively.

In both cases there is some thixotropic recovery, since the 0/0/0 curve in this experiment may be considered equivalent to the 30 minute recovery situation; however, the rate of recovery is reduced so much that any sag resistance must be a function of drying or wicking, etc. and not of thixotropic recovery. It is worth noting that the sag problem at high dilution can be overcome by a skillful tradesman, by the expedient of applying thin uniform coatings, which not only assist external factors, such as drying, but reduce the gravitational shear stress responsible for sagging.

This experiment was selected to show how the flow properties of a water-borne paint change with water additions and demonstrates how easily the LSV can be used to

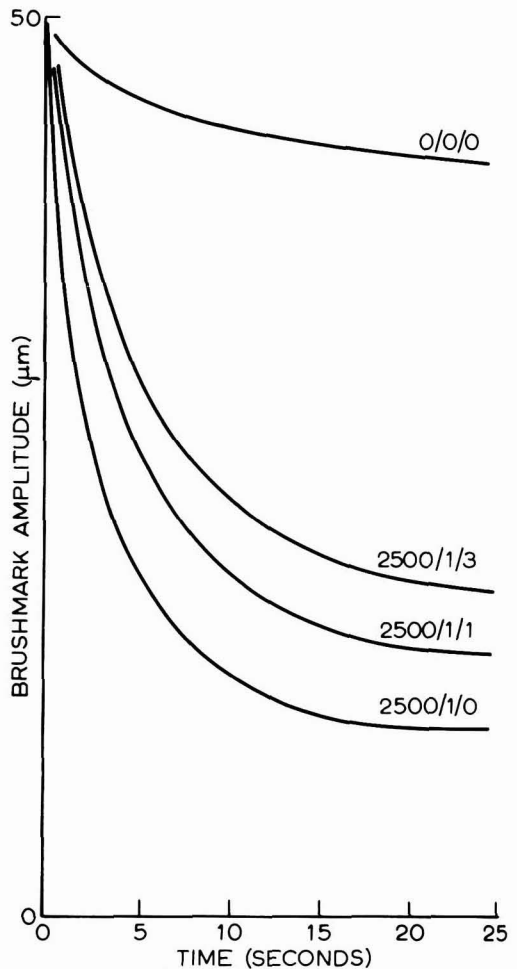


Figure 7. Amplitude decay curves for a water-borne paint diluted with 10 per cent by weight water



assess rheological parameters which have a direct bearing on product performance.

Many other experiments have been performed on both water-borne and solvent-borne paint systems, where the effects of driers, pigments, extenders, polar resins, etc. on the levelling properties have been examined, as well as using the instrument to characterise much simpler systems, such as creams and thinned resins.

## 5. Conclusions

The use of the theory of sinusoidal brushmark decay to determine the design parameters for a new instrument which parallels the flow process has proved successful. Comparison between subjective visual assessments from practical brushing trials, and results from the viscometer, show very high degrees of correlation. Furthermore, the ladder addition type experiments described in this paper provide a means of indicating that the LSV produces

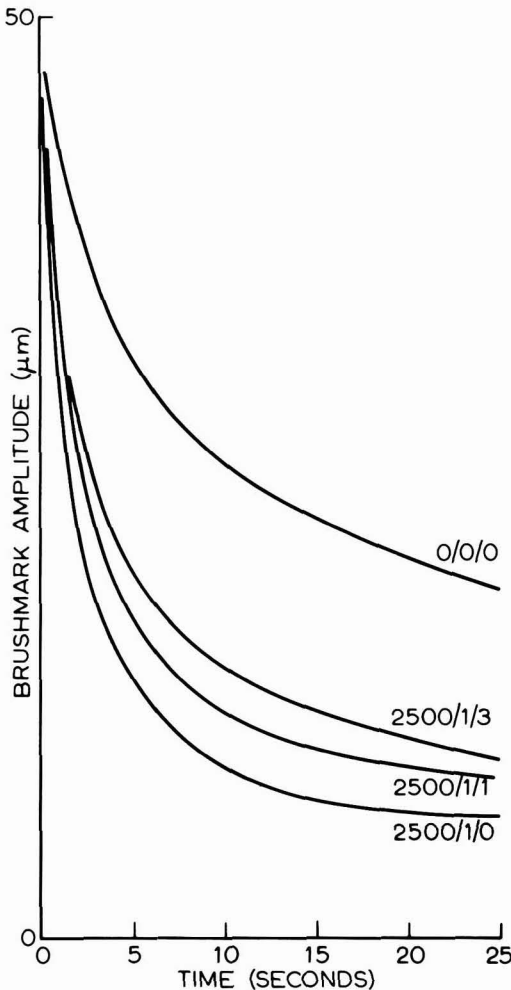


Figure 8. Amplitude decay curves for a 15 per cent by weight dilution with water of an aqueous paint

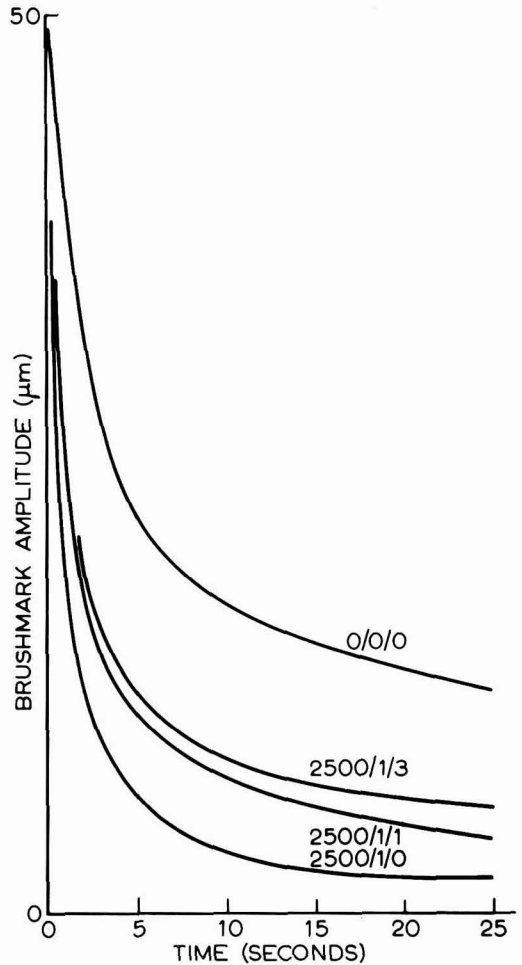


Figure 9. Amplitude decay curves for an aqueous paint diluted with 25 per cent by weight of water

meaningful results when uncertain evidence is available from visual assessment. The results are particularly useful in that they describe rheological features, which are not confused with drying effects that can cause massive scatter in day to day results as substrate absorption and weather conditions change. Moreover, since the formulating factors which control, say, thixotropic recovery are different from those which control drying, the paint formulator can rapidly detect the cause of the problem and know the direction to take for a solution.

## Acknowledgements

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6. References

1. Cooke, P. J. *et. al*, *JOCCA*, 1972, **55**, 275.
2. Smith, N. D. P., Orchard, S. E. and Rhind-Tutt, A. J., *JOCCA*, 1961, **44**, 618.
3. Waring, R. K., *J. Rheology*, 1931, **II**, 307.
4. Patton, T. C., *J. Paint Technol.*, 1966, **38**, No. 502, 656.
5. Beeferman, H. L. and Bergren, D. A., *J. Paint Technol.*, 1966, **38**, No. 492, 9.
6. Monk, C. J. H., *JOCCA*, 1966, **49**, 543.
7. Glass, J. E., *JOCCA*, 1975, **58**, 169.
8. Strivens, T. A., *J. Colloid & Interface Sci.*, 1976, **57**, No. 3, 475.
9. Dodge, J. S., *J. Paint Technol.*, 1972, **44**, No. 564, 72.

Appendix I

Refs. 2, 8

Gap geometry

A recent publication by Strivens<sup>8</sup> on shear thickening effects in concentrated dispersions indicates that considerable care must be exercised in using cone and plate geometry. For a high solids dispersion of monodisperse spheres of polymethyl methacrylate stabilised in a hydrocarbon medium, an interesting finding was reported concerning the relationship of particle size to rheometer geometry. For both the parallel plate and the cone and plate geometry, the viscosity depends on the gap width, unless the clearance exceeds 250 times the average dispersion particle diameter. For cone and plate geometry, with all but the smallest particle sizes, this condition is almost always exceeded in practice, particularly for paints containing extender particles. It should be stated, however, that the particulate solids levels are rarely as high as in the systems used by Strivens. Unfortunately, the effects of particles and geometry at lower concentrations was not investigated in this work.

As a consequence of the work of Strivens, it would appear that for the paint rheologist, extreme caution must be exercised in the interpretation of cone and plate data, particularly at high solids, and in the presence of large particles. For the LSV, which applies very low stresses, the effect of particles, even at low concentration, with cone and plate geometry, would be significant because of the small gap at the centre of the cone. To avoid such particle "grinding" effects, the parallel plate geometry was selected.

A further consequence of adopting parallel plate geometry is that during the initial high shear conditioning step, the sample is subjected to a distribution of conditioning shear rates and consequently the figure of 2500 sec<sup>-1</sup> as quoted in this paper is a volume mean figure. This in itself is not disadvantageous, in that it further parallels the events that occur in practice. In a practical brushing operation, bristle clumping<sup>2</sup> occurs which gives rise to a varying film thickness so that the paint is subjected to a distribution of shear rates. The level of agreement between the two distributions is not known, although from brushing and LSV tests it is felt that a figure of 2500 sec<sup>-1</sup> is not widely inaccurate.

Appendix II

Shear rates in application

The rates of shear occurring during this operation have been discussed by many authors. A rough approximation can be obtained by assuming that the brush can be regarded as a flat spreading surface parallel to the surface being painted, and calculating the rate of shear from an estimate of the speed of the brush and the thickness of the coating. There is some uncertainty about whether the separation between brush and surface is equal to the coating thickness or up to twice this value, but for a fairly thick coating of 100 μm, such as might be applied with a structured paint, and a brushing speed of 50 cm/sec, the calculated rate of shear is 5000s<sup>-1</sup> or 2500s<sup>-1</sup>

according to what assumption is made about the separation.

Estimates such as this have been taken as the criterion for the rate of shear that should be used for making measurements of "brushability". However, a more important issue in the present context is the extent to which the structure of the paint is broken down by brushing, since this will affect subsequent processes, such as levelling and sagging. Although the rate of shear under the brush has attracted much attention, very few authors have commented on the very short time for which this shear persists. If the speed of brushing is 50 cm/sec and the dimension of the brush in contact with the coating in the direction of brushing is 2.5 cm, then the paint will be sheared about 1/20 sec at each stroke of the brush, allowing about 10 strokes of the brush for completing the operation gives a total time of about 1/2 sec. Such estimates can be only very approximate, but practical experiments have shown that shearing for 1 second at 2500s<sup>-1</sup> gave samples in very similar condition to those conditioned by actual brushing-out.

Appendix III

Inertia effects

Refs. 4, 9

A general criticism levelled against stress relaxation rheological techniques is that for low viscosity systems, the inertial effect of the swinging rotor becomes significant, with respect to the viscous damping of the rotor movement. The motion can be described by the following general torque balance equation.

$$I \frac{d^2\theta}{dt^2} + K_g \eta \frac{d\theta}{dt} + K_s = 0$$

Where *I* is the inertia of the moving assembly, *K<sub>s</sub>* is a geometry constant, which for cone and plate is given by 2πR<sup>3</sup>/3α, where α is the cone angle, and for a parallel plate given by πR<sup>4</sup>/2d, where *d* is the plate separation. *K<sub>s</sub>* is the spring constant and θ the angle through which the rotating member moves.

For systems where the viscosity is high, the effect of inertia is small enough to be neglected, and the solutions proposed by Patton<sup>4</sup> are valid. However, as pointed out by Dodge<sup>9</sup>, at low viscosities the inertial contribution becomes significant, so that viscosity determinations from the relaxation curves can be made only by a full solution of the complete inertia balance equation. For the movement of the rotor between the angles θ and θ<sub>1</sub>, over times *t* to *t*<sub>1</sub>, the solution of the equation is:

$$\ln \theta / \theta_1 = -b \left[ -b + \sqrt{b^2 - c^2} \right] (t - t_1) \dots \dots \dots (1)$$

which on rearranging gives

$$b = -\frac{(t - t_1)}{\ln \theta / \theta_1} \left[ c^2 + \left( \frac{\ln \theta / \theta_1}{t - t_1} \right)^2 \right] \dots \dots \dots (2)$$

where *b* = *K<sub>g</sub>*η/2*I*

and *c*<sup>2</sup> = *K<sub>s</sub>*/*I*

Relaxation experiments were performed on a low shear viscometer with graphical output, using six standard oils. From the output, the times for the spring to relax from θ = 5° to θ = 1° were measured and substituted into equation 2 above, which was then solved for viscosity. The results are plotted in Figure 10, which shows how the error in the observed viscosity due to inertia increases very rapidly at values lower than about 0.4 Pa.s, but becomes vanishingly small at higher viscosities. The transition occurs when the motion of the rotor changes from being underdamped to overdamped. In the overdamped case, the rotor approaches zero deflection without oscillation, and the error diminishes rapidly with increase in viscosity, which is obviously the favoured situation. Figure 10 can be used to

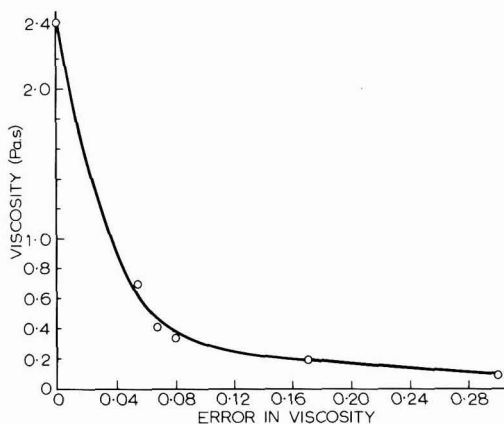


Figure 10. Calibration curve to illustrate the effect of inertia at low viscosities

correct the inertia component. In the undamped case, where decaying oscillatory motion occurs, the viscosity corrections are

very large. For viscosities less than about 0.2 Pa.s, there is great difficulty in measuring accurately ( $t-t_0$ ) because the values are so small, and the nature of the curve in such an area means that large errors can occur.

The critical viscosity for the changeover can be derived from equating the constants  $b$  and  $c$ , or from:

$$\eta_c = \frac{2}{K_g} \sqrt{K_s I}$$

which gives a critical viscosity of 0.37 Pa.s. Quite clearly this critical viscosity can be lowered either by increasing the geometry constant by decreasing the plate separation, or by decreasing the spring constant and the inertia.

When examining brushmark flow-out, however, products in the low viscosity region always give characteristic curves, which indicate degrees of excellence. As described, for a thixotropic system, it is the movement out of this low viscosity response zone with time that is important, so that in this case, and with poor flow-out systems the error becomes diminishingly small. Consequently, inertial corrections should be made if the instrument is to be used as a rheological tool at low viscosities, but as a brushmark flow viscometer to be used in a paint laboratory they are hardly worth applying.

# The chromatographic analysis of fatty polyamide resins after alkali fusion

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## Summary

A re-examination of the analysis of a series of resinous polyamides used in a IUPAC co-operative study is reported. The prolonged acid hydrolysis has been replaced by alkali fusion followed by separation of the individual components using chromatographic procedures. The scheme reported is applicable to all of the samples and is conducted in a fraction of the time

mentioned in the earlier report.

Quantitative estimations of the components are nearly achieved, the principal limitations being due to variation of the fatty components because of thermal effects experienced during both polyamide preparation and analysis.

## Keywords

*Raw materials for coatings binders (resins, etc) polyamide resin*

*Raw materials used in manufacture or synthesis of ingredients for coatings amine dibasic acid tall oil fatty acid*

*Processes and methods primarily associated with analysis, measurement or testing hydrolysis gas chromatography gel permeation chromatography*

## L'analyse chromatographique, après fusion avec alcali, des résines polyamides aux acides gras

### Résumé

On rend compte du nouvel examen de l'analyse d'une série de polyamides résineuses qui étaient utilisées dans une étude coopérative de l'IUPAC. L'hydrolyse prolongée par voie acide a été remplacée par fusion avec alcali et par la séparation subsé-

quente des constituants individuels, au moyens de la chromatographie. Le procédé ci-décrit s'applique à tous les échantillons et il peut être effectué en beaucoup moins du temps que l'on a mentionné dans le rapport antérieur.

## Chromatographische Analyse von Fettsäure-polyamiden nach Schmelzen mit Alkalien

### Zusammenfassung

Die in einer kooperativen IUPAC Studie berichteten Analysen von harzartigen Polyamiden wurden wieder geprüft. Die andauernde saure Hydrolyse wurde durch eine alkalische Schmelze ersetzt und die einzelnen Komponenten wurden dann chromatographisch getrennt. Die Methode erwies sich auf alle Muster anwendbar und liess sich viel schneller ausführen.

Nahezu quantitative Bestimmungen der Komponenten wurden erzielt. Die hauptsächlich Beschränkung der Methode ergab sich aus der Variation der Fettsäurekomponente infolge des Einflusses der Hitze während der Herstellung und Analyse der Polyamide.

## Introduction

Refs. 1-14

A recent IUPAC co-operative study<sup>1</sup> reported in this *Journal* by O'Neill and Christensen<sup>2</sup> has highlighted the lack of a reliable systematic method of analysis for fatty polyamides, and a further study of the literature failed to disclose any analytical procedures for the materials. The procedures indicated in the report are in part repetitive, extremely time consuming, of limited accuracy and generally unsuitable for any type of routine characterisation. Whilst some information was obtained by preliminary chemical and spectroscopic examination, prolonged acid hydrolysis was necessary to obtain the reactant acid for chromatographic analysis and the amine compounds for spectrophotometry.

The acid hydrolysis of polyamides, mainly higher molecular weight linear materials of the nylon type, has been studied by various workers<sup>3-9</sup> and some of the procedures have employed chromatography to facilitate the analyses<sup>6-9</sup>.

Anton<sup>6</sup> effected the hydrolysis of nylon samples resulting from diamine-dicarboxylic acid condensation by refluxing for twenty-four hours with 6N hydrochloric acid at atmospheric pressure, or for four hours at 40 psi, the former conditions being representative of those used in the IUPAC study. The hydrolysate was divided and the diamines were extracted with n-butanol from the alkaline solution for examination. The methyl esters of the dicarboxylic acids were prepared with methanol-boron trifluoride and examined chromatographically. Mori and co-workers<sup>7</sup> employed the same acid hydrolysis but at

130°C with an additional derivative step to allow separation of the products. Nylon 6 required 2 hours, nylon 66, 4 hours and nylon 11 and 12, 8 hours of digestion to effect cleavage. The hydrolysis products were esterified with hydrochloric acid and methanol and then reacted with trifluoroacetyl anhydride (TFA).

The same co-workers<sup>8</sup> reported a modified procedure involving a single derivative step. It involved trimethylsilylation of the diamine hydrochlorides, the dibasic acids and the  $\omega$ -aminoalkanoic acid hydrochlorides from the hydrolysate. The dried products were directly silylated with bis-(trimethylsilyl) acetamide (BSA) and examined chromatographically. The effect of hydrochloric acid on the trimethylsilyl derivative formation was avoided by the addition of triethylamine to the reaction products. An essentially identical procedure using hydrochloric acid and trimethylsilyl derivative formation was reported at about the same time by Tengler<sup>9</sup>.

The degradation of polyamides and polyimides using hydrazine has been reported by Mlejnek and Cveckova<sup>10</sup>, but the procedure, which involves a prolonged (8 hour) pre-treatment with hydrochloric acid, is of little utility as it is less attractive than the method of Anton<sup>6</sup>.

The rapid hydrolysis of amides and imides has been effected by Siggia and various co-workers<sup>11-13</sup> using alkali fusion. The reactions in solution have been limited by the concentration of base present and the reaction temperature possible. The procedure involved heating the polymer with a 50 mole per cent excess of solid alkali and flux (1-10 per cent) within a device attached to the injection port of a gas chromatograph, into which the liberated amine was passed for identification. The reduced hydrolysis period was subsequently used by Glading and Haken<sup>14</sup> in an analytical procedure for both diamine-

dicarboxylic acid and  $\omega$ -aminoalkanoic acid type polyamides requiring one to two hours and providing quantitative results.

The IUPAC study considered five fatty polyamides of known composition as shown in Table I, these being the usual type of condensation products of low molecular weight polyfunctional amines with difunctional dimer acid materials.

The present paper demonstrates the application of the alkali fusion procedure to the standard polyamides and demonstrates that considerable improvement of the analytical procedure is possible.

## Experimental

### Samples

The polyamides *A*, *C*, *D* were samples remaining from the IUPAC study whilst the materials *B* and *E* were produced in the laboratory by simple condensation according to the formulation shown in Table I and using a procedure suggested by an international producer. The dimer acid used was Empol 1022 (Unilever-Emery). The products *A* and *E* with significantly high amine content are of the reactive type.

### Gas chromatography

An F and M model 810/29 gas chromatograph with flame ionisation detector was used for all gas chromatographic separations. Diamine-TFA derivatives were separated on 2 metre  $\times$  3 mm inside diameter (id) aluminium columns packed with 5 per cent (w/w) neopentyl glycol succinate on Gas Chrom Q 100-120 mesh. The column and injection port were maintained at 220°C. Helium was used as carrier gas at 100 ml/min. The hydrogen and air pressure were maintained at 100 psi and 40 psi respectively. The amplifier sensitivity used was  $4 \times 10^2$  fsd. Tall oil fatty acids were separated on a 4 ft length aluminium column  $\frac{1}{4}$  inch outside diameter (od), packed with 6 per cent OV-1 silicon gum rubber on Gas Chrom Q 100-120 mesh. The column was operated at 200°C. Low molecular weight monobasic esters were separated on the same column operated isothermally at 130°C.

The dicarboxylic esters were readily separated into monomeric, dimeric and trimeric compounds using gel permeation chromatography. This separation was considerably better than that achieved by gas chromatography and was used throughout the work.

### Gel permeation chromatography

The gel permeation chromatograph unit was constructed from individual Waters modules, namely, the 6000A pump, U6K injector and R-400 differential refractive index detector. The columns used contained  $\mu$ -Styragel packing of nominated exclusion limits  $10^5$ ,  $10^4$ ,  $10^3$ , 500 and 100 Å.

The tetrahydrofuran solvent, THF, was distilled from potassium metal and filtered through a 0.05  $\mu$ m filter before use. BHT antioxidant was added at a rate of 25 ppm and the solvent was kept under a nitrogen blanket in the instrument reservoir. However, even with all these precautions it was still found necessary to use freshly distilled solvent every second day. 0.1 per cent w/v solu-

Table I  
Composition of IUPAC polyamides

Polyamide	Component	Weight per cent
<i>A</i>	Methyl epoxy stearate	16.0
	Tall oil fatty acids	37.3
	Tetraethylene pentamine	46.0
<i>B</i>	Common dimer acid <i>A</i> *	73.8
	Tall oil fatty acid	9.1
	Diethylene triamine	15.1
	p-tert butyl phenol novolac	2.0
<i>C</i>	Common dimer acid <i>B</i> *	80.0
	Propionic acid	6.0
	Hexamethylene diamine	9.0
	Ethylene diamine	5.0
<i>D</i>	Distilled dimer acid <i>A</i> *	63.4
	Azelaic acid	17.3
	Ethylene diamine	6.1
	Piperazine	13.2
<i>E</i>	Common dimer acid <i>A</i> *	63.0
	Tall oil fatty acid	2.6
	Triethylene tetramine	24.0
	Tetraethylene pentamine	10.4

\*The common dimer acid *A* contained (determined by GC by the supplier) monomeric monocarboxylic acid 11.9 per cent, dimeric monocarboxylic 3.9 per cent, dimeric dicarboxylic 66.2 per cent, trimeric 18.0 per cent. Common dimer acid *B* gave 7.0, 4.7, 70.7 and 17.6 per cent respectively for the same components. For the distilled dimer acid, the corresponding figures were 7.1, 0.7, 92.2 and 0.0 per cent.

tions were used for all standards. A constant temperature of 21°C was maintained.

### Alkali fusion

*Ref. 15*

Alkali fusion was carried out using 0.01 g of polymer with 0.1 g of a pre-fused mixture of potassium hydroxide and 0.5 per cent sodium acetate prepared according to the work of Siggia and his co-workers<sup>15</sup>. The reaction was carried out in 10 mm od. borosilicate glass tubes that were sealed under vacuum. Three identical tubes were prepared and heated in a cylindrical block of stainless steel containing four holes of suitable diameter. The block was heated by resistance heaters, and the input current regulated to give a temperature of 260°C. The temperature was monitored by placing a thermometer in one of the four holes. The reaction mixture was allowed to reflux for half an hour and the reaction mixture allowed to cool to room temperature.

### Separation

For the diamine analysis, each tube was conveniently cut open and trifluoroacetic anhydride (2 ml) added to the reaction mixture. The liberated free amine in the tube reacts with TFA forming an amine-TFA derivative. The reaction is usually complete after fifteen minutes of stirring and standing. The excess TFA is destroyed by adding sufficient water which is also sufficient to dissolve the potassium salt in the tube. The amine-TFA derivative is dissolved by adding tetrahydrofuran (6 ml) to the mixture and then extracting with two 20 ml portions of chloroform.

The extracted solution was dried over anhydrous sodium sulphate and filtered. The solvents were partially removed under vacuum to give approximately 2 ml of solution. 2  $\mu$ l of this final solution was examined chromatographically. The diamines were identified by comparing their retention times and separation temperatures in the gas chromatograph with the TFA derivatives of known diamines.

For the dicarboxylic acid analysis, the aqueous solution remaining from the above extraction was acidified with dilute hydrochloric acid and the liberated dicarboxylic acid extracted with two 20 ml portions of toluene. The toluene solution was dried using anhydrous magnesium sulphate and the volume reduced under vacuum to about 20 ml. Boron trifluoride-methanol reagent (20 ml) was added to this solution and the mixture was refluxed for half an hour. The resulting solution of the diester was transferred to a separating funnel containing 20 ml of water and then extracted with toluene. The toluene solution was once more dried over anhydrous magnesium sulphate and the volume reduced under vacuum until all the toluene was removed. 0.5  $\mu$ l of the final solution was examined chromatographically.

For low molecular weight monobasic acids which are soluble in water the aqueous solution remaining after the toluene extraction above was esterified as above and examined chromatographically.

### Results and discussion

*Refs. 2, 14, 16-23*

The IUPAC materials, or those prepared to the

appropriate formulations, were each examined and the results of the individual samples are shown. The analyses have been conducted generally on a qualitative basis, although it has been shown with conventional linear polyamides<sup>14</sup> that essentially quantitative results were achieved with diamines and simple dicarboxylic acids.

It will be indicated elsewhere<sup>16</sup> in a general analytical scheme for resinous polyamides that the diamines and modifying monocarboxylic acids are essentially quantitatively cleaved. Recovery of the fatty materials is less clear cut, as whilst both tall oil fatty acids and dimer acids have been separated by gas chromatographic procedures, the recovery after cleavage of a resin is less satisfactory as oxidative and isomerisation reactions will occur in some circumstances during the thermal fusion reaction used in the analysis. Despite the possibility of these reactions, the procedures reported clearly show the presence of tall oil and dimer acids in the samples considered with near quantitative results.

Tall oil fatty acids have been examined as methyl esters by several groups of workers<sup>17,21</sup> and the procedures applicable to fatty acid esters generally with separation on polyester columns are readily applied. The separation of dimer acids by gas chromatography has been the subject of several reports<sup>22,23</sup> all using polysiloxane gum columns at high temperatures. These procedures gave quite poor separation of the dimer esters and gel permeation

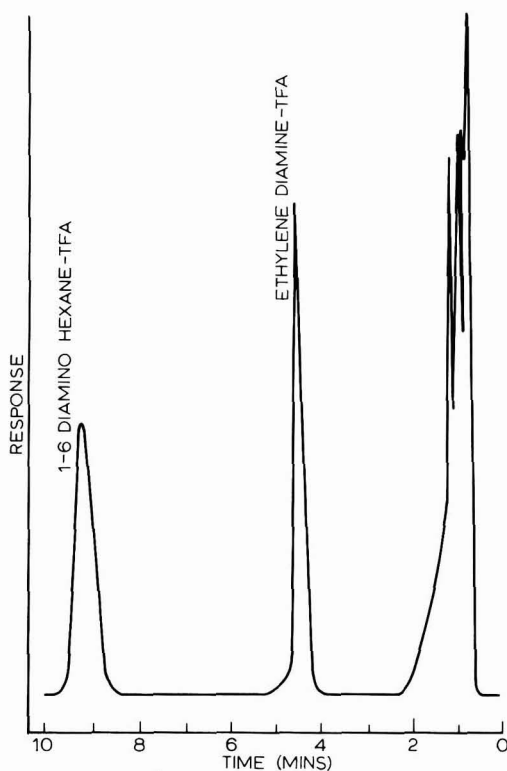


Figure 1. Gas chromatogram showing separation of TFA derivatives of 1,6-diaminohexane and ethylene diamine

chromatography which provides a much superior separation has been used in such a way that the monomer (C18), dimer (C36) and trimer (C54) components may each be estimated.

Separations of tall oil fatty acids and tetraethylene pentamine from Sample *A* were carried out without difficulty. The methyl epoxy stearate was not separated by gas chromatography; this result is in agreement with the earlier report of O'Neill and Christensen<sup>2</sup> who indicated that the common ring opening reaction of amine-epoxy would occur, so that the ester would not be recovered after the hydrolysis. The use of gel permeation chromatography produced a peak which did not coincide with the dimer ester and is a further indication of the formation of an additional compound.

Sample *B* was separated with the derivatives of diethylene triamine and of tall oil esters being determined by gas chromatography, whilst the monomer, dimer and trimer components of the dimer acids were examined using gel permeation chromatography. The anti-oxidant, *p*-tert butyl phenol novalak was not detected by the analysis.

The diamines present in sample *C* were readily resolved and the chromatogram is shown in Figure 1, whilst Figure 2 shows the separation of the dimer esters by gel permeation chromatography. The methyl propionate was identified by chromatography of the extract containing water-soluble esters.

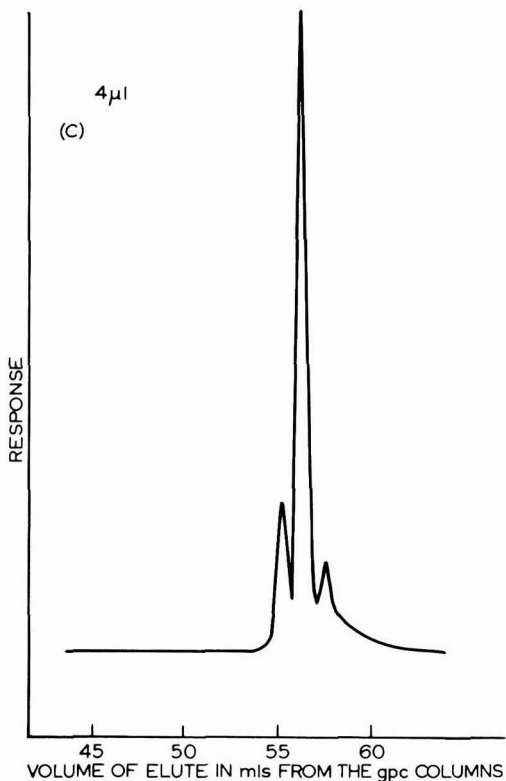


Figure 2. Gel permeation chromatogram of dimer acid methyl esters

The analysis of sample *D* was parallel to that of sample *C*; the separation of ethylene diamine and piperazine is shown in Figure 3. The azelaic acid was readily detected by gas chromatography, it having been estimated quantitatively previously<sup>14</sup> as a component of nylon 610, and is shown in Figure 4.

Figure 5 shows a chromatogram of the derivatives of triethylene tetramine and tetraethylene pentamine from sample *E*. The dimer acids were separated by gel permeation chromatography, whilst Figure 6 shows the gas chromatographic separation of the tall oil acid methyl esters.

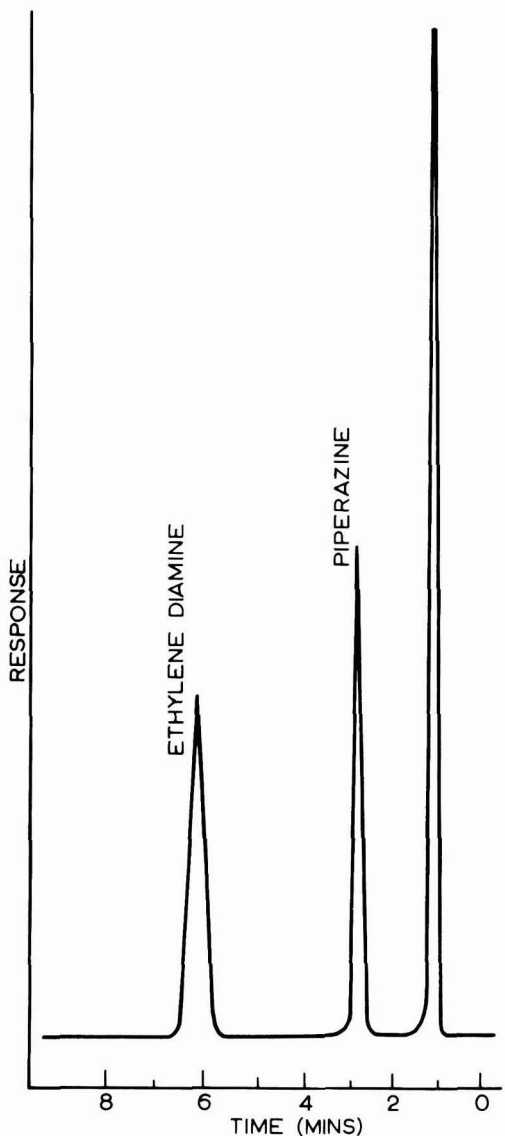


Figure 3. Gas chromatogram showing separation of TFA derivatives of ethylene diamine and piperazine

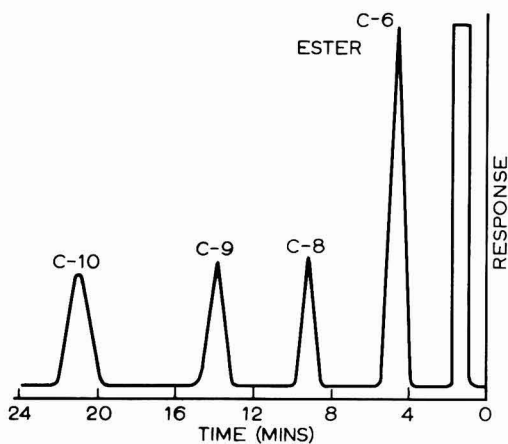


Figure 4. Chromatogram showing separation of the methyl esters of aliphatic dicarboxylic acids

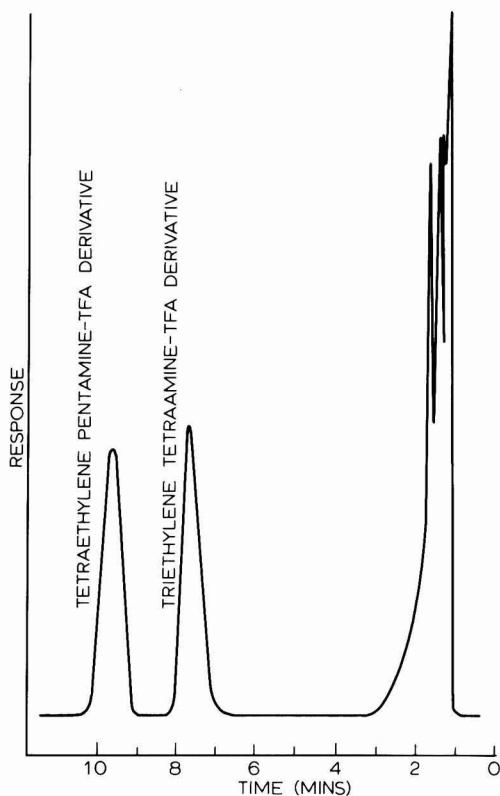


Figure 5. Gas chromatogram showing separation of TFA derivatives of triethylene tetramine and tetraethylene pentamine

### Conclusions

Ref. 16

The alkali fusion procedure employed for the hydrolysis of

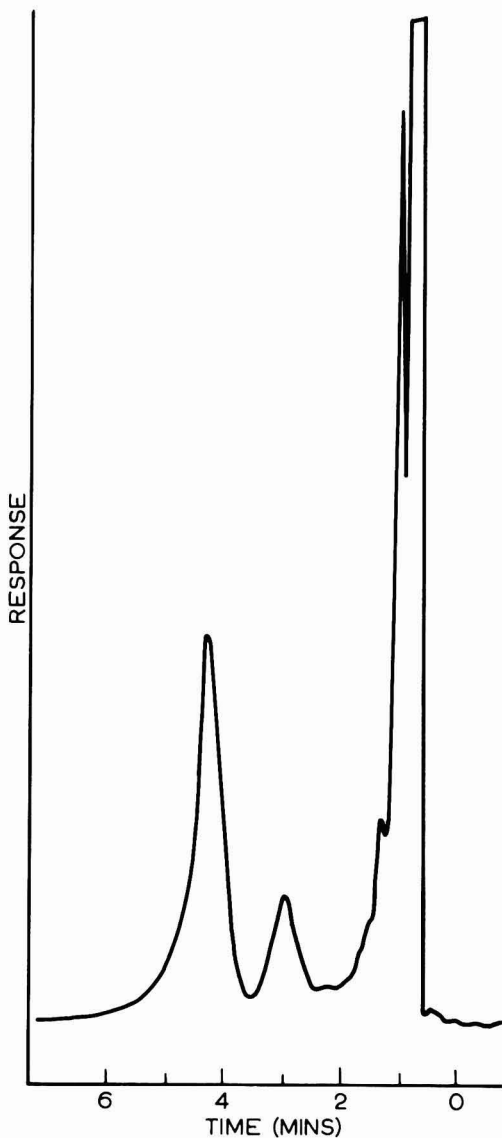


Figure 6. Gas chromatogram of tall oil fatty esters

the polyamide is effected much more rapidly, i.e. 30 mins, than the prolonged acid hydrolysis used previously with nylon samples and adopted by the IUPAC collaborators. Separation of the hydrolysis products by chromatographic means is considered to be more satisfactory for the diamines than the spectroscopic methods previously used, whilst gel permeation chromatography has been found to be more valuable for the resolution of the components of dimer acids than high temperature gas chromatography on a non-polar stationary phase.

In addition to the analytical scheme reported, concurrent examination by infrared spectrometry is suggested. This is a valuable procedure which provides a



certain, although restricted, amount of information, but at almost negligible cost; other extensive chemical examination is not considered to be justified.

The procedure reported is believed to be generally applicable and provides within a few hours an analysis which is in part quantitative and in part semi-quantitative within the well-known constraints indicated.

A number of other components have been found in commercially available resinous polyamides that have been examined and polyamide analysis generally has been considered elsewhere<sup>16</sup>.

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### References

1. Working party on supported polymer films of the Macromolecular Division of the International Union of Pure and Applied Chemistry 1976.
2. O'Neill, L. A. and Christensen, G., *JOCCA*, 1976, **59**, 285.
3. Mori, S. and Takeuchi, T., *J. Chromatography*, 1970, **47**, 224.
4. Raven, D. J. and Earland, C. J., *J. Soc. Dyers Colour*, 1970, **86**, 313.
5. Thielemann, H. Z., *Anal. Chem.*, 1975, **276**, 304.
6. Anton, A., *Anal. Chem.*, 1968, **40**, 1116.
7. Mori, S., Furusawa, M. and Takeuchi, T., *Anal. Chem.*, 1970, **42**, 138.
8. Mori, S., Furusawa, M. and Takeuchi, T., *Anal. Chem.*, 1970, **42**, 959.
9. Tengler, H. *Plastverarbeiter*, 1971, **22**, 329.
10. Mlejnak, O. and Cveckova, L., *J. Chromatography*, 1974, **94**, 135.
11. Frankoski, S. P. and Siggia, S., *Anal. Chem.*, 1972, **44**, 2078.
12. Whitlock, L. R. and Siggia, S., *Sep. Purif. Methods*, 1974, **3**, 299.
13. Schlueter, D. D. and Siggia, S., *Anal. Chem.*, 1977, **49**, 2349.
14. Glading, G. J. and Haken, J. K., *J. Chromatography*, 1978, **157**, 404.
15. Frankoski, S. P. and Siggia, S., *Anal. Chem.*, 1972, **44**, 507.
16. Haken, J. K. and Obita, J. A., *J. Chromatography* (In Press).
17. Zielinski, W. L., *J. Am. Oil Chem. Soc.*, 1954, **31**, 5.
18. Payler, R. G., Feinland, R. and Conroy, N. H., *Anal. Chem.*, 1968, **40**, 1354.
19. Arlt, H. G., *US Patent*, 3,367 953 (1968).
20. Firestone, D., *J. Am. Oil Chem. Soc.*, 1963, **40**, 247.
21. Nelson, J. P. and Meilun, A. J., *J. Am. Oil Chem. Soc.*, 1975, **52**, 81.
22. Nestler, F. H. M. and Zinkel, D. F., *Anal. Chem.*, 1967, **39**, 118.
23. Zinkel, D. F., *Tappi* 1975, **58**, 109.

# Correlation of the adhesion of a polystyrene lacquer to inorganic substrates and their wetting characteristics

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## Summary

No evidence was found for weak boundary layer formation when the adhesion of polystyrene lacquer to various high surface tension substrates was measured, using a spontaneous peeling method. The results showed a considerable variation from one substrate to another, and the interfacial work of adhesion seems to be related to the dispersion component of the substrate surface tension.

Correlation was found between polystyrene adhesion to and the wetting of the substrates by organic liquids. It was confined to those governed solely by dispersion forces, as is polystyrene. Results for the critical surface tension of the substrates indicate that their wetting behaviour is dominated by an adsorbed surface layer of water. This layer does not, however, seem to influence the adhesion of the polystyrene coating.

## Keywords

*Properties, characteristics and conditions primarily associated with materials in general*

adhesion  
contact angle  
surface tension

*dried or cured films*

peeling

*Types and classes of coatings and allied products*

clear coating

*Raw materials for coatings binders (resins, etc.)*

polystyrene resin

## La corrélation de l'adhérence d'un vernis polystyrène aux subjectiles inorganiques avec leurs caractéristiques de mouillabilité

### Résumé

On n'a trouvé aucune indication de la formation d'une couche interfaciale faible lorsqu'on a déterminé l'adhérence d'un vernis polystyrène aux divers subjectiles à tension superficielle élevée, au moyen d'une méthode de pelage spontané. Les résultats indiquaient une variation importante entre les subjectiles, et l'effort interfacial d'adhérence paraît être en rapport au composant de dispersion de la tension superficielle du subjectile.

On a trouvé une corrélation entre l'adhérence de polystyrène

aux subjectiles et leur susceptibilité à être mouillés par les liquides organiques. Elle se bornait à ceux, tels que polystyrène qui sont influencés exclusivement par les forces de dispersion. Les résultats pour la tension superficielle critique des subjectiles indiquent que leur mouillabilité est régie par la couche superficielle de l'eau adsorbée. Il paraît que cette couche n'exerce aucune influence sur l'adhérence du revêtement polystyrène.

## Die Beziehungen zwischen Haftung von Polystyrollacken an anorganischen Substraten und deren Benetzbarkeit

### Zusammenfassung

Die Haftung von Polystyrollacken an Oberflächen mit hoher Oberflächenspannung wurde mit Hilfe einer Ablösmethode gemessen. Es wurde kein Beweis für eine schwache Grenzflächenschicht gefunden; beträchtliche Unterschiede für verschiedenen Substrate wurden festgestellt und es erscheint, dass die Haftungskraft mit der Dispersionskomponente der Oberflächenspannung des Untergrundes in Beziehung steht.

Die Haftung des Polystyrols stand in Beziehung zu der

Benetzung des Substrats durch organische Flüssigkeiten was aber auf jene beschränkt war die, wie Polystyrol, von Dispersionskräften beherrscht werden. Die kritische Oberflächenspannung des Substrats wies darauf hin, dass die Benetzbarkeit von einer adsorbierten Oberflächenschicht von Wasser abhängig ist, die jedoch nicht die Haftung des Polystyrols beeinflusst.

## Introduction

Refs. 1-10

Adhesion is a crucial and complex aspect of technology

that has been the subject of a considerable body of literature. Various aspects have been reviewed recently by Wake<sup>1</sup>. Prominent amongst the theories on adhesion is one proposing that "adhesive" strength depends on a weak boundary layer (WBL) within one or both components of

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the joint and that failure in adhesion really represents cohesive failure of a component<sup>2</sup>. It would not be expected that there would be any correlation between adhesion and surface properties. Data have been presented<sup>3</sup> to demonstrate the presence of WBLs; and critiques of the WBL hypothesis have appeared elsewhere<sup>1,4</sup>.

Other studies have, however, shown a correlation between adhesive strength and surface chemical properties of the joint constituents<sup>5-7</sup>. In these, both the adhesive and substrate were polymeric materials. In contrast, the data now presented have been obtained using inorganic substrates. This study was designed to measure the adhesion of a polystyrene lacquer by spontaneous peeling and to explore its correlation with the contact angle of various liquids on the same substrates; the effect of initial concentration of the coating solution and ambient humidity were also investigated.

Spontaneous peeling was used to measure adhesion of the coating; it is simple experimentally and the results provide a further test of the method<sup>8</sup>. It relies on the internal strain energy generated in the coating as it dries to overcome the interfacial work of adhesion of the coating to the substrate. It appears to agree well with other methods of measuring adhesion<sup>8</sup>.

**Spontaneous peeling and adhesion**

A coating can spontaneously peel or flake from its substrate under the action of internal strain or stress. Internal strain energy accumulates as the coating thickness increases until at a critical thickness,  $t_p$ , it becomes sufficient to overcome the interfacial work of adhesion. This condition can be stated as:

$$\gamma_A \leq U_R \cdot t_p \dots \dots \dots (1)$$

- where  $\gamma_A$  = interfacial work of adhesion
- $t_p$  = coating thickness at which peeling occurs
- $U_R$  = recoverable internal strain energy stored in unit volume of the coating<sup>8</sup>.

It is possible<sup>8</sup> to measure  $U_R$ , which remains constant for a given coating, and if  $t_p$  can be measured as the minimum thickness that will provoke peeling for a coating-substrate interface,  $\gamma_A$  can be determined. Internal strain arises in a coating (or adhesive) because of volume shrinkage due to solvent evaporation or chemical change. The area of the coating is constrained to remain at its "wet" size by adhesion to the substrate, so that any further changes after the coating solidifies (prior to its final dry state) result not in shrinkage but in strain (stress) in the plane of the coating. Resultant internal strain can be very large, depending on the coating formulation<sup>9</sup>, and may adversely affect its performance.

An energy balance analysis<sup>10</sup> can be applied to various adhesion tests to account for the effect of internal strain. For the 90 degree peel test<sup>8</sup>:

$$\frac{F}{b} = \gamma_A - U_R \cdot t_c \dots \dots \dots (2)$$

- where  $F$  = force required to peel the coating
- $b$  = width of the peeled coating
- $t_c$  = coating thickness.

In the pull-off test<sup>8</sup>:

$$\sigma = \left[ \frac{2K}{t_c} (\gamma_A - U_R \cdot t_c) \right]^{\frac{1}{2}} \dots \dots \dots (3)$$

where  $\sigma$  = stress necessary to pull the coating from the substrate

$K$  = bulk modulus of coating.

In both these cases the internal strain energy can overcome the interfacial work of adhesion,  $\gamma_A$ . If coating thickness,  $t_c$ , in either the peel test or the pull-off test is greater than or equal to  $t_p$  (equation 1), then the adhesive strength,  $F$  or  $\sigma$  respectively, is zero and the coating must peel from the substrate spontaneously.

Measuring  $t_p$  for a coating does not require attachment to the coating or application of any external force. The stress responsible for the loss of adhesion is an intrinsic property of the coating formulation and acts in the plane of the coating, eliminating some of the difficulties associated with conventional adhesion tests, such as peeling or pull-off.

**Contact angle and adhesion**

*Refs. 5, 6, 11, 12*

*A resumé of published ideas and equations*

Contact angle data are often used to investigate the wetting behaviour of material surfaces in order to clarify their adhesive properties. Thermodynamic work of adhesion,  $W_A$ , of a liquid to a solid is given by:

$$W_A = \gamma_L + \gamma_S - \gamma_{SL} \dots \dots \dots (4)$$

- $\gamma_L, \gamma_S$  = surface-free energy of liquid and solid respectively
- $\gamma_{SL}$  = reduction in  $W_A$  due to interaction between solid and liquid
- = interfacial free energy

The Young equation for a liquid drop on a solid surface is:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \dots \dots \dots (5)$$

where  $\theta$  = contact angle of the drop at the solid surface, subscript  $SV$  refers to the solid-vapour interface, and similarly for  $LV$  and  $SL$ .  $\gamma_S$  and  $\gamma_{SV}$  cannot be equated, in general, because  $\gamma_{SV}$  represents the surface-free energy of the solid reduced by an amount,  $\pi$ , resulting from an adsorbed vapour layer on the solid round the liquid drop:

$$\gamma_{SV} = \gamma_S - \pi \dots \dots \dots (6)$$

$\pi$  is often called the "spreading pressure" of the saturated vapour on the solid, and its value depends on the particular vapour and solid. As the liquid and the vapour are the same material, then  $\gamma_{LV}$  must be the same as  $\gamma_L$ .

If equations (5) and (6) are combined in equation (4) the result is:

$$W_A = \gamma_{LV}(1 + \cos \theta) + \pi \dots \dots \dots (7)$$

$\pi$  is generally assumed to be very small or zero on low energy solid surfaces such as polymers<sup>11</sup>, although there is some evidence to the contrary<sup>12</sup>. On metal or metallic oxide (high energy) surfaces,  $\pi$  is usually large; on such surfaces the contact angle of organic liquids is zero and the liquid spreads readily across the solid surface. Usually  $\pi = 0$  is assumed if the liquid makes a finite contact angle on the solid.

Equation (7) shows that if the contact angle of a liquid is measured on a variety of substrates then, assuming  $\pi = 0$ , the work of adhesion for the liquid,  $W_A$ , is proportional to  $\cos\theta$ . On polymeric substrates<sup>5,6</sup> a linear relation was found between joint strength and degree of wetting ( $\cos\theta$ ). This implies a similar relation between  $\gamma_A$  and  $W_A$ . In the present paper a correlation is sought between the work of adhesion ( $\gamma_A$ ) of a polymeric solid material on different inorganic substrates and the contact angle of a liquid on those same substrates.

The differences between  $W_A$  and  $\gamma_A$  must be noted;  $W_A$  refers to the adhesion of a liquid to a solid substrate;  $\gamma_A$  is the interfacial work of adhesion of a solid to another solid where the nature of the adhesive (coating) surface adhering to the substrate is greatly different from its state when its surface energy is measured under typical conditions (in air using liquid contact angle). Consequently,  $\gamma_{LV}$  cannot be replaced in equation (7) by the measured surface energy of the adhesive and thus obtain the value for  $\gamma_A$ , although a relationship may exist<sup>5,6</sup> between it and  $W_A$ . In addition, if  $\pi$  is of significant size, there will not be a simple relation between  $W_A$  and  $\cos\theta$  for a variety of liquids and substrates, because  $\pi$  changes with each combination. It is not necessary to invoke a WBL to explain a lack of correlation between  $\gamma_A$  and  $\cos\theta$ . Similarly, there would not be a relationship between  $W_A$  and  $\gamma_A$ .

## Experimental

Ref. 13

Most of the experiments were carried out at 23°C ( $\pm 1^\circ\text{C}$ ) and 50 per cent ( $\pm 2$ ) RH.

### Spontaneous peeling

Polystyrene (Dow Styron 685) dissolved in reagent grade toluene was used as the coating because it was known to peel from various substrates at low film thicknesses. Although the thin coatings ensured rapid drying for convenience, they were not so thin that accurate thickness measurements could not be made with an Elcometer Miniteceter FN.

Coatings were formed using a draw-down blade on each substrate. The thickest film that remained attached to the substrate was considered to give the peeling thickness,  $t_p$ . Where the coating thickness varied about  $t_p$ , it was found that once peeling had been initiated it would often continue into a region where it would not naturally occur. Superior adhesion of the thin edges of a coating was sometimes responsible for the anomalous adherence of a coating thickness slightly greater than  $t_p$ . This was easily detected by gently loosening the edge of the coating with a knife or fingernail, i.e., initiating the peeling. Coating solution concentrations of 15, 25 and 35 per cent by weight of polystyrene (PS) were employed in examining the variation of adhesion with solution concentration.

Substrates used were stainless steel (SS), steel feeler

gauge stock (FGS), copper, tin, aluminium and glass. Tinplate was used for tinfoil because it provided a rigid substrate and thereby allowed the internal strain in the PS to take full effect against adhesion and not be relieved by deformation of the substrate.

All the substrates were cleaned with toluene and tissue paper immediately before use. Only for copper (which tarnished) and aluminium did the time between cleaning and coating make a significant difference in the results. The other substrates, if clean, gave consistent results whether the time before coating was about 30 seconds or as long as a week. Copper and aluminium were cleaned with a polishing paste before treatment with toluene and tissue paper. A standard procedure was adopted for cleaning each substrate because it was found that the speed and pressure used in applying the paper tissue affected the results, particularly those of the softer metals, copper and tin. This was more noticeable with contact-angle measurements. No attempt was made to prevent the formation of oxide or adsorbed water layers on the substrates. In fact, apart from the very smooth "mirror" finish of the substrates, they would represent fairly typical, clean, degreased surfaces.

Experiments were also conducted on a stainless steel substrate in a dry box to ascertain the effect of ambient humidity on adhesion. This was a gloved box maintained at 23°C and 1 per cent RH by a slight positive pressure of dry air. A desiccator was used to store the specimen for extended periods.

### Contact angle

The apparatus used for contact-angle measurements is

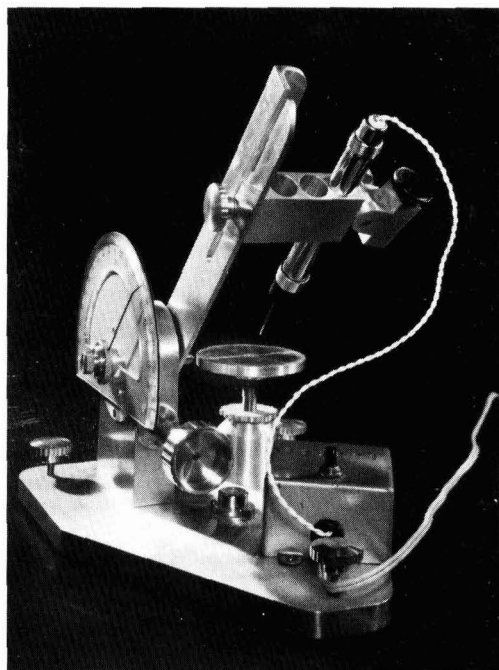


Figure 1. Apparatus for measuring contact angle

shown in Figure 1 and is essentially the same as that described by Fort and Patterson<sup>13</sup>. A narrow beam of light is directed on the junction of a liquid drop and the solid surface. The angle at which the light must be aimed to reflect upon itself is measured and the contact angle then determined by simple geometry.

The liquids used to measure contact angle were reagent grade xylene, 1-bromonaphthalene, 1-iodonaphthalene, methylene iodide (diiodomethane) and distilled water. Contact angle was measured for each of these on all the substrates and under all the conditions for which a peeling thickness was obtained. One syringe, which produced a drop diameter of 3 to 4 mm, depending on the liquid, was used throughout. For each liquid the drop size was very consistent.

The repeatability of the contact-angle measurements was within 1 degree. Contact angle varied by small but consistent amounts at different locations on the metal substrates, presumably owing to small changes in surface character. This was the main source of variability.

## Results

Ref. 8, 14, 15

The recoverable strain energy density,  $U_R$ , was  $157 \text{ kJ m}^{-3}$  for the particular PS coating used<sup>8</sup>. Thus, from peeling thickness,  $t_p$ , the interfacial work of adhesion can be calculated.

### Coating solution concentration

Glass and copper substrates gave a slightly higher peeling thickness at 15 per cent w/w concentration (27 and  $9 \mu\text{m}$ , respectively) than at 25 and 35 per cent w/w (24 and  $7 \mu\text{m}$ , respectively). The other substrates gave no systematic trend with initial solution concentration. Any difference was smaller than the range of values found for any one solution. Detecting a trend would require considerably more data and an extremely high standard of reproducibility in surface preparation.

### Spontaneous peeling thickness, $t_p$

All the results shown in Table 1 were obtained using a 25 per cent w/w solution of PS. Coatings that adhered to their substrate crazed because they were under stress. Those that peeled, frequently exhibited no damage.

Table 1  
The interfacial work of adhesion of PS to the various substrates together with some values for  $\gamma_s^d$ .

Substrate	$t_p, \mu\text{m}$	$\gamma_A, \text{J/m}^2$	$\gamma_s^d, \text{J/m}^2$
Copper	7.0	1.1	0.06
Aluminium	14.0	2.2	—
FGS	18.0	2.8	0.11
Tin	19.5	3.1	0.10
SS	22.0	3.5	0.11
Glass	24.0	3.8	—
SS (dry)	25.0	3.9	0.11

### Stainless steel (SS)

Under normal conditions (23°C and 50 RH)  $t_p$  was 22

( $\pm 2$ )  $\mu\text{m}$ . Samples of SS were heated at 100°C for two days in a dry gloved box and then coated when cool. The value of peeling thickness increased slightly in these dry conditions (1 per cent RH) to about  $25 \pm 2 \mu\text{m}$ . Upon exposure to humid air these coatings peeled further until there was no difference in  $t_p$  from those originally made under humid conditions. The normal, slight gradation in thickness allows further peeling to start under the new conditions.

### Copper

On copper, which was chosen to show no grain structure after polishing (very fine grained), the peeling thickness was determined to be  $7 \pm 1 \mu\text{m}$ .

### Tin (tinplate)

Peeling thickness was  $19.5 \pm 2 \mu\text{m}$ .

### Aluminium

Peeling thickness was  $14 \pm 1 \mu\text{m}$ .

### Glass

There appeared to be two stages in the peeling of PS films from glass. Films less than  $24 \mu\text{m}$  thick tended to craze, as did those adhering to other substrates. Above  $24 \mu\text{m}$  thickness crazing disappeared, but the films apparently remained attached to the glass. In fact, above  $24 \mu\text{m}$  thickness the films did not adhere but were held to the glass by electrostatic attraction just strong enough to exclude air from the interface and make it appear to be adhering properly. The electrostatic force was effective up to thicknesses of 60 to  $90 \mu\text{m}$  when, presumably, the film became too inflexible to mould itself to the substrate and exclude air. Within the "electrostatic" regime, a film could be peeled and replaced to look as if it were properly attached. The static charges on the film and substrate did not leak away quickly.

The value of  $24 \mu\text{m}$  was chosen to represent the spontaneous peeling thickness of PS when it is applied to glass.

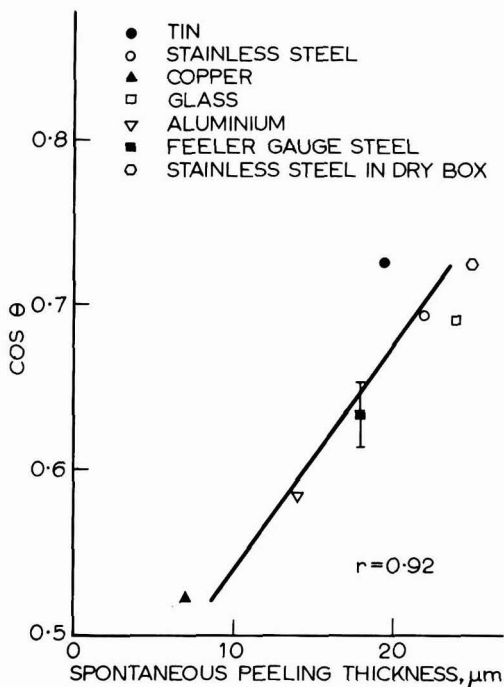
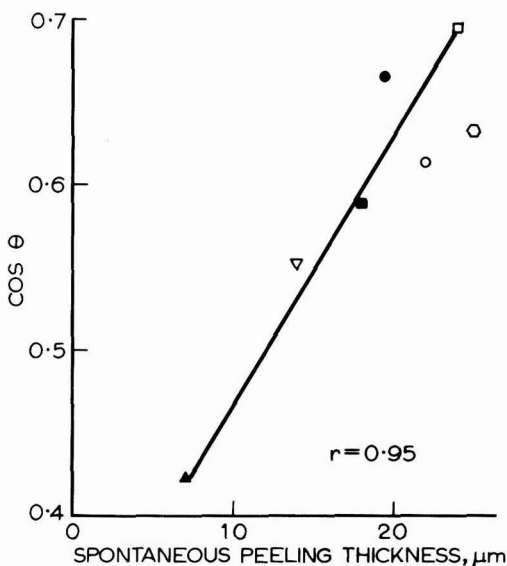
### Feeler gauge stock (FGS)

The peeling thickness<sup>8</sup> was  $18 \pm 1 \mu\text{m}$

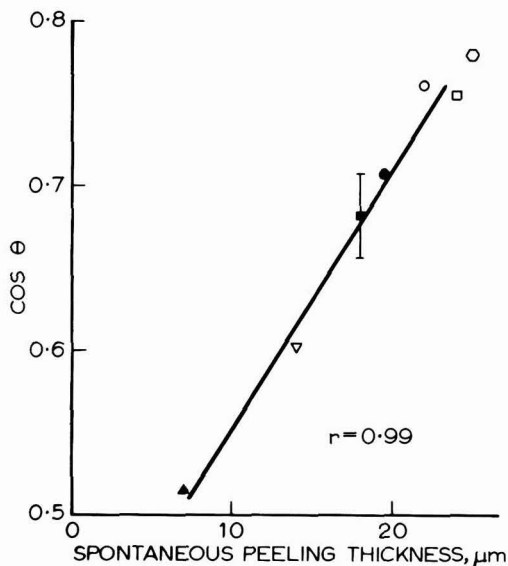
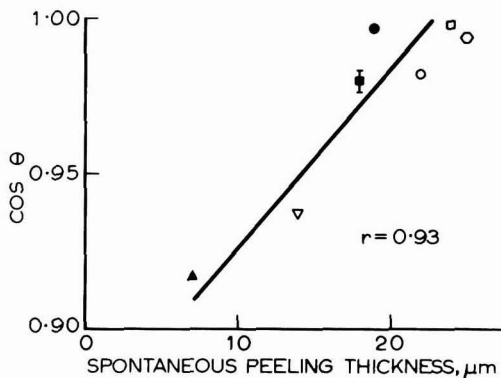
### Contact angles

Contact angle data has been used to quantify the wetting behaviour of each substrate in order to investigate its connection with the adhesion of the PS coating to the substrates. The cosine of the contact angle of each liquid on the various substrates is plotted as a function of spontaneous peeling thickness in Figures 2(a–e). The same key applies to all the graphs:  $r$  is the regression coefficient calculated for the line, including all the data measured at 50 per cent RH.

Generally, each value of  $\cos \theta$  is the average of about 50 readings on various regions of the substrates. Contact angle was found to vary systematically by one or two degrees from place to place. As  $t_p$  is measured over a larger area than contact angle and the value presented is itself the average of several determinations, it was decided that  $\cos \theta$  should be averaged over a wide area in order to correlate  $t_p$  and  $\cos \theta$ .

Figure 2(a).  $\cos$  (contact angle) for 1-iodonaphthaleneFigure 2(b).  $\cos$  (contact angle) for methylene iodide

The values of contact angle for copper are the average of approximately 70 readings, because a copper surface is softer and was more influenced by the manner of cleaning. FGS exhibited anisotropy in its contact angle. Along

Figure 2(c).  $\cos$  (contact angle) for 1-bromonaphthaleneFigure 2(d).  $\cos$  (contact angle) for xylene

its length (with the "grain") the contact angle was 2 to 4 deg lower than that across the width (the spread is indicated on the graphs). This anisotropy obviously corresponds to the way in which the strip steel is manufactured. For all subsequent calculations the average of the two directions was used. The anisotropy was not apparent, however, with methylene iodide.

Contact angles using 1-bromonaphthalene were measured on SS substrates from which PS films had just been peeled forcibly, i.e., the films were too thin to peel spontaneously. There was no difference between these contact angles and values obtained in the same places after recleaning by the standard method.

The surface energies of the liquids employed are given in Table 2. Data for 1-iodonaphthalene was obtained from Burnett and Zisman<sup>14</sup> and for the other liquids, from Fowkes<sup>15</sup>.

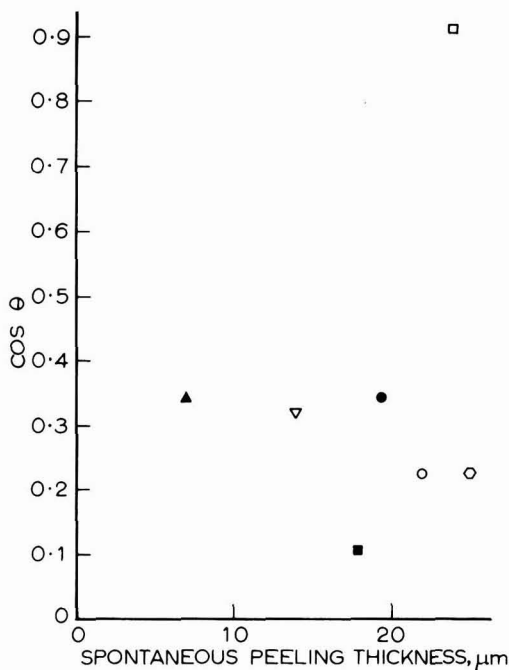


Figure 2(e). Correlation of peeling thickness with  $\cos$  (contact angle) for water

Table 2

Surface energy,  $\gamma_L$ , of the liquids used to measure contact angles together with the London dispersion force contribution,  $\gamma_L^d$ .

	$\gamma_L$ mJ/m <sup>2</sup>	$\gamma_L^d$ mJ/m <sup>2</sup>
l-bromonaphthalene	44.6	47 ± 7
l-iodonaphthalene	45.9	—
methylene iodide	50.8	48.5 ± 9
xylene	29.0	29.0
water	72.8	21.8

$$(1 \text{ mJ/m}^2 = 1 \text{ mN/m} = 1 \text{ erg/cm}^2 = 1 \text{ dyne/cm})$$

## Discussion

Ref. 1, 14–21

### Spontaneous peeling

Measurements presented here indicate that spontaneous peeling is a viable, simple, convenient and sensitive way to measure the strength of adhesion of coatings on various substrates. The results generally correlate with the wetting ( $\cos\theta$ ,  $W_A$ , etc.) of the same substrates by various liquids. This will be discussed later.

The peeling test also provides a value for a physically significant parameter, the interfacial work of adhesion,  $\gamma_A$ . Values of  $\gamma_A$  are presented in Table 1. If the measured adhesion strength were controlled by a WBL in the PS coating, no great difference would be expected in the

values of  $\gamma_A$  obtained for different substrates. A significant difference does exist, however, in the adhesion of PS to copper and steel, indicating, therefore, that the adhesion strength of PS to various substrates is not determined by any WBL in the coating.

The lack of a WBL in the PS is confirmed by contact-angle measurements taken on an SS substrate, where the adhesion was good, immediately after the peeling of a PS coating and after subsequent recleaning. As there was no difference in contact-angle value, there was no significant contamination of the SS surface by PS fragments.

It seems unlikely that WBLs on each substrate are responsible for the variation in adhesive strength. It must be concluded that the adhesion of PS to these substrates is determined by the basic forces in play across the interface.

### Work of adhesion and substrate surface energy

The PS coating was common to all the measurements of adhesion and hence an attempt was made to compare the variation in  $\gamma_A$  with the surface energy of the substrates. Surface energy values at room temperature for metals are impossible to obtain experimentally and extrapolations must be made from data on molten metals. Values quoted for the surface energy of molten metals are of the same order of magnitude as  $\gamma_A$  (1–2 Jm<sup>-2</sup>), but they show no systematic trend with  $\gamma_A$ , even when reduced to room temperature<sup>16</sup> using  $d\gamma/dT = 1.2 \text{ mJ/m}^2$ . This is not surprising when the extent of the extrapolation for most of the metals is considered.

The contribution of hydrogen bonding and polar forces to the properties of PS is very small<sup>17</sup> and it would be expected that its adhesion would be dominated by London dispersion forces, which are common to all molecules. The surface energy of PS and its dispersion interaction component,  $\gamma_s^d$ , are identical<sup>17</sup> at 43 mJ/m<sup>2</sup>. Good<sup>18</sup> has discussed the various forces between molecules. Adhesion of PS to a particular substrate may correlate better with  $\gamma_s^d$  of the substrate than with the overall value. A few values can be calculated from measurements of  $\pi$  for adsorbed vapours<sup>15</sup> at 25°C, and these are listed in Table 1. (The value given for SS and FGS is that for iron, whereas the true value for these steels may be different.) The difference in adhesion between SS and FGS demonstrates the differences in surface properties that can occur even between steels. The few values for  $\gamma_s^d$  may show the same trend as the adhesion  $\gamma_A$ , but they are rather smaller in magnitude.

Values of  $\gamma_A$  are large compared to those of  $\gamma_s^d$  or the surface tension of PS. Work supplied to overcome adhesion must not only break interfacial bonds, but also deform the PS surface and realign it to the state it must have in contact with air. Thus  $\gamma_A$  is large.

Increased adhesion was noted for glass and copper when the PS coating solution was dilute. Such a solution can flow into any surface irregularities and provide better adhesion. No corresponding effect on the other substrates was observed.

### Contact angle

The contact angle data of the liquids can be used not only to explore the nature of the interaction of the PS coating with the inorganic substrates, but also to characterise those substrate surfaces.

Interaction between PS and the substrates

It may be seen from Figure 2(a-c) that for each liquid used, except water, there is a good correlation between  $\cos \theta$  for a given substrate and adhesion of the PS coating, expressed in terms of  $t_p$ . These data are expressed as  $W_A$ , the work of adhesion of the liquids (equation 7), assuming  $\pi=0$ , and plotted as a function of  $\gamma_A$  in Figure 3. No calculation of  $W_A$  was made for water because there was no correlation between  $\cos \theta$  and adhesion. These data are similar to those presented by Mittal<sup>17</sup>, although the range in  $W_A$  is somewhat smaller. The relationship between  $\gamma_A$  and  $W_A$  may not be truly linear, but may only appear to be so for the range of data employed. Nevertheless, the correlation indicates that adhesion of the liquids is influenced by the same factors as those which determine adhesion of a solid PS coating.

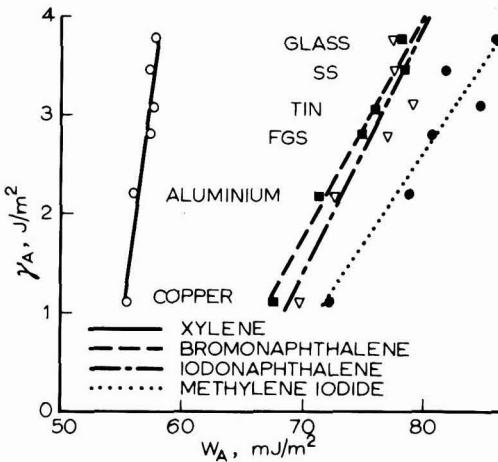


Figure 3. Variation of the interfacial work of adhesion with the adhesion of different liquids to the same substrates

The lack of correlation between  $\cos \theta$  of water and the adhesion of the PS coating indicates that the polar and hydrogen bonded water interacts with the substrates in a manner very different from that of PS.

Table 2 gives the dispersion component of the liquid surface energies,  $\gamma_L^d$ . No value for  $\gamma_L^d$  of l-iodonaphthalene could be found, but it probably approximates<sup>15</sup> to that of  $\gamma_L$ . The surface energy of PS and that of the four organic liquids is dominated by London dispersion forces. Thus, it would be expected that the adhesion properties of PS and liquid drops should correlate. They can interact with the substrates only by the common dispersion force<sup>1</sup>. This would be true even if the substrates were polar materials, since induced dipole forces in non-polar liquids tend to be weak<sup>18</sup>. The fact that coatings and adhesives which adhere well seem to be those with polar groups or hydrogen bonding (e.g., acrylates, epoxies) is worth noting; these can provide interactions in addition to the omnipresent London dispersion forces.

Critical surface tension of the substrate surfaces

Values of  $\cos \theta$  for the different liquids on a substrate can be used to calculate a value of surface tension characteristic of that substrate surface.

The method used is that of Zisman as modified by Good<sup>19</sup>, to calculate a quantity  $\gamma_C$ . This parameter is termed the "critical surface tension of wetting" and is the surface tension of a liquid that will just wet the substrate ( $\cos \theta = 1$ , or  $\theta = 0$  deg). Liquids such that  $\gamma_L < \gamma_C$  will wet the solid with zero contact angle. For low-energy solids such as polymers  $\gamma_C$  agrees very well with other determinations of the surface tension of the solid<sup>19</sup>.

$\gamma_C$  can be determined<sup>19</sup> in terms of  $\gamma_S$  and  $\gamma_L$  by using the equation:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\phi_{SL} (\gamma_S \gamma_L)^{1/2} \dots \dots \dots (8)$$

where  $\phi_{SL}$  is an interaction parameter. If  $\pi$  is assumed to be zero, then equation (8) can be substituted into equation (5), and since  $\gamma_{LV} = \gamma_L$ :

$$\cos \theta = -1 + 2\phi_{SL} \left( \frac{\gamma_S}{\gamma_L} \right)^{1/2} \dots \dots \dots (9)$$

$\gamma_C$  is deduced to be

$$\gamma_C = \phi_{SL}^2 \gamma_S$$

More complete discussions of the significance of  $\gamma_C$  and its uses can be found elsewhere<sup>19,20</sup>.

Values of  $\alpha_C$  for each substrate were obtained from a

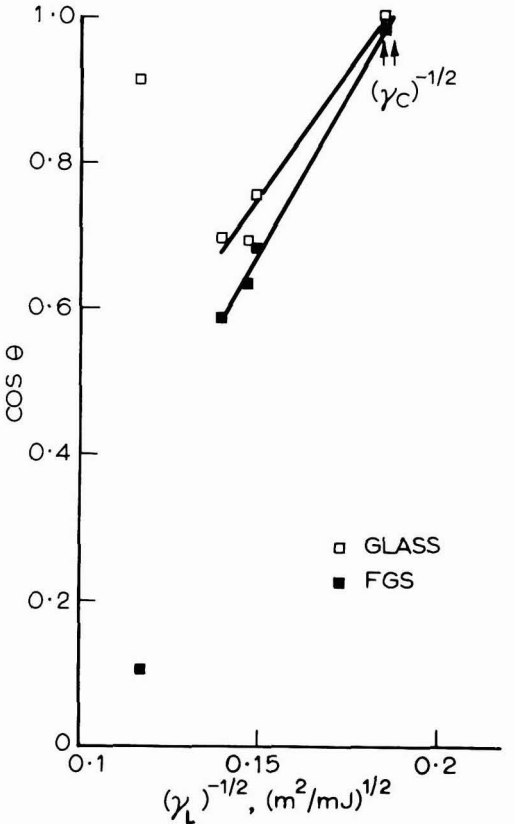


Figure 4(a). Construction used to find  $\gamma_C$  from  $\cos \theta$  and (liquid surface energy,  $\gamma_L$ )<sup>-1/2</sup>



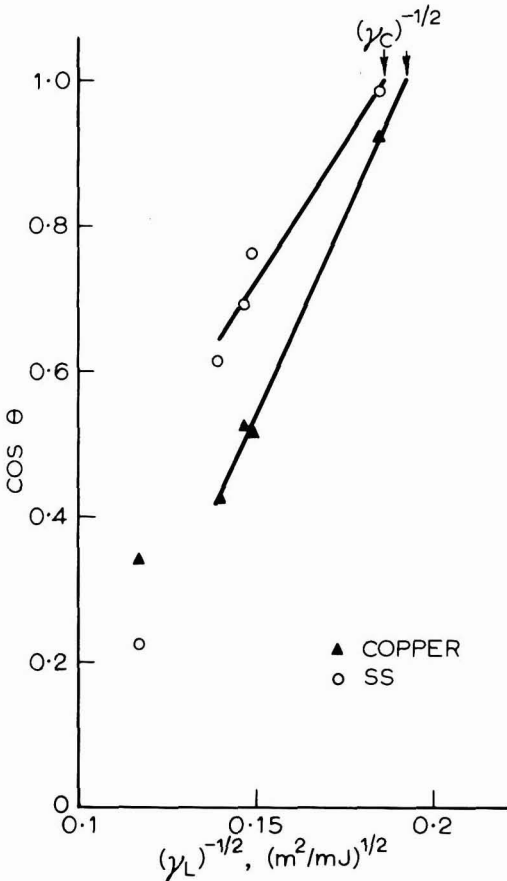


Figure 4(b). Construction used to find  $\gamma_c$  from  $\cos \theta$  vs  $(\gamma_L)^{-1/2}$  (liquid surface tension,  $\gamma_L$ )<sup>-1/2</sup>

least squares fit to graphs of  $\cos \theta$  versus  $(\gamma_L)^{-1/2}$  and calculating the value at  $\cos \theta = 1$ . Data from all these liquids, except water, were used; examples of such graphs are given in Figure 4 (where the points corresponding to water are also displayed).  $\gamma_c$  obtained by this method is shown as a function of adhesion ( $t_p$ ) in Figure 5(a).

The increased scatter in Figure 5(a) over the graphs of  $\cos \theta$  reflects the amount of manipulation the data have undergone. The magnitude of  $\gamma_c$  and the differences among the substrates are very similar to values presented elsewhere for metallic substrates<sup>14</sup>, although the experimental conditions were somewhat different in this study.

All the liquids used here should completely wet pure, clean, inorganic substrates ( $\gamma_c \approx 1 \text{ J/m}^2$ ), because their surface tensions are so much lower. This is not the case however; contact angle is non-zero, indicating that the wetting is incomplete. Further, the critical surface tension of wetting for these substrates is approximately  $30 \text{ mJ/m}^2$ , and  $\gamma_c$  does not vary much from metal to metal or glass. It has been proposed elsewhere<sup>14</sup> that the effective surface of nominally metallic substrates is determined by an adsorbed layer of water. A metallic oxide layer would also

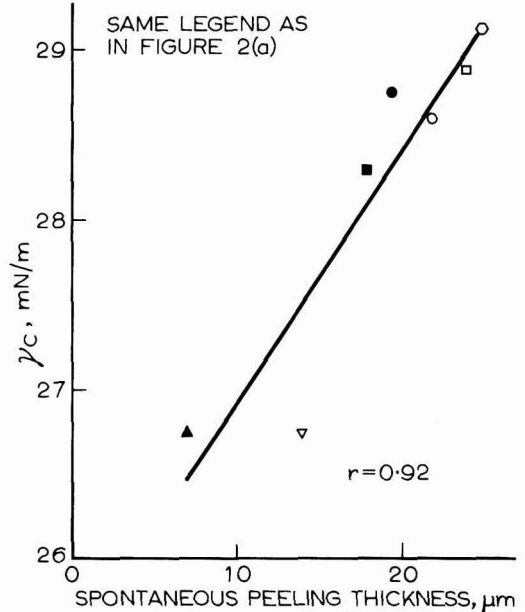


Figure 5(a). Critical surface tension,  $\gamma_c$ , measured from  $\cos(\theta)$  vs  $(\gamma_L)^{-1/2}$ , as a function of peeling thickness (adhesion)

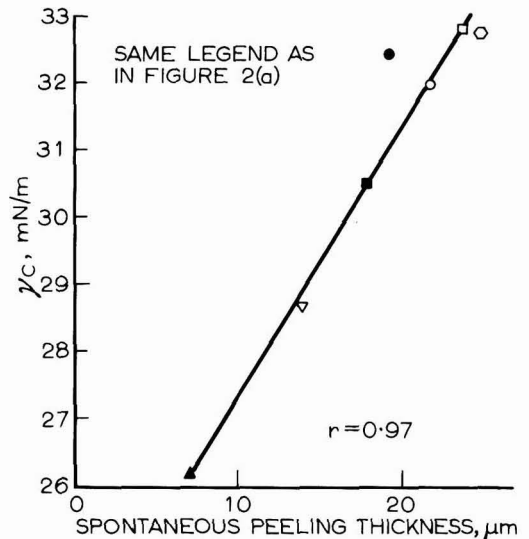


Figure 5(b). Critical surface tension,  $\gamma_c$ , measured from  $1 + \cos(\theta)$  vs  $(\gamma_L)^{-1/2}$ , as a function of peeling thickness (adhesion)

provide a high energy surface and differ according to the metal.

The results for  $\gamma_c$  presented here are consistent with this suggestion; that a layer of water, adsorbed from ambient humidity, masks the high energy surfaces and reduces them all to an almost common surface as far as their wetting properties are concerned.

The different wetting behaviour of water can now be explained if each solid surface has an adsorbed layer of water molecules. Water drops can interact via hydrogen bonding and polar forces with the water layer on the substrate surfaces, not just via London dispersion forces, as the other liquids must. The wider variation in the adhesion of the PS to the different substrates indicates that solid adhesion is not so much influenced by the common layer of adsorbed water on the substrates as are their wetting characteristics ( $\gamma_c$ ).

Values of contact angle for the liquids on SS in a dry (1 per cent RH) atmosphere were different (with the exception of water) from those obtained at 50 per cent RH (Figure 2). In dry conditions a higher value of  $\gamma_c$  results for SS, again consistent with data published elsewhere<sup>14</sup>. The contact angle measured for water drops in the otherwise dry atmosphere proved to be identical with that at 50 per cent RH. These observations support the hypothesis of an adsorbed layer of water on the substrates, the higher value of  $\gamma_c$  presumably indicating a smaller amount of water adsorbed from the drier atmosphere.

Data on wetting and adhesion for SS in dry atmospheres appear to fall on the same regression line as the data gained under humid conditions (Figures 2 and 5), and further demonstrate the connection between the two phenomena.

*Limitations on liquids with high surface energy*

Equation (9) suggests that a graph of  $(\cos \theta + 1)$  versus  $(\gamma_L)^{-1}$  should pass through the origin. Subjected to this constraint, the data  $(\cos \theta, \gamma_L)$  produce slightly different values of  $\gamma_c$ . As may be seen from Figure 5(b), these values of  $\gamma_c$  yield an excellent straight line when plotted as a function of adhesion ( $t_r$ ). Most of the values lie above that of xylene (29 mN/m), which did not completely wet the substrate, contrary to the definition of  $\gamma_c$ .

It has been pointed out<sup>19</sup> that there is only a limited range for which the expression for  $\cos \theta$ , equation (9), covers. It is:

$$\gamma_L < 2 \phi_{SL}^2 \gamma_S \dots\dots\dots (10)$$

$$\text{i.e., } \gamma_L < 2 \gamma_c \dots\dots\dots (11)$$

Care must be taken when using the point  $\cos \theta + 1 = 0$ . Although it helps to position the curve fitting, it corresponds to  $\gamma_L$  tending to infinity, and this is clearly not possible and contrary to the condition of convergence in equation (11).

Equation (11) provides another explanation of the lack of correlation between the wetting of water and adhesion.  $\gamma_c$  of the substrates is typically 29 mN/m, so that equation (11) restricts  $\gamma_L$  to less than 58 mN/m if equation (9) is to converge.  $\gamma_L$  for water is 72.8 mN/m. If there is a correlation between the wetting of a solid by water and adhesion of a PS coating to that solid, then it must be different from the correlation shown by the other liquids used, of lower  $\gamma_L$ . The same conclusion was reached in a previous section where the difference between water and the other liquids was attributed to its polar and hydrogen-bonded nature.

Other liquids with very high values of surface energy tend to be polar and hydrogen-bonded, e.g., glycerol and formamide. Equation (8) (and thus equation (9)) does not

apply to such liquids, in any case, because of the multiplicity of their interactions<sup>19,21</sup>.

There appear to be two considerations in using high energy liquids to measure wetting. Firstly, if there is a significant polar contribution to their interactions; they will tend to interact in a rather specific way with a given substrate and not correlate with measurements made with dispersion-dominated liquids. Secondly, if their  $\gamma_L$  is too large, their wetting characteristics will not match those of liquids of lower  $\gamma_L$ , irrespective of their interactions with the substrate (equation 11).

**Conclusions**

Adhesion of a PS coating, as measured by spontaneous peeling, depends to a large extent on the properties of the substrate. For example, adhesion to copper is poor whereas to SS or glass it is quite good. Because of the great differences among substrates, it seems that the adhesion strength is not determined by a WBL.

The magnitude of  $\gamma_A$  (1.1 to 3.9 J/m<sup>2</sup>) is similar to the overall surface tension of metals, but does not correlate with it. It may exhibit, however, the same trend as the dispersion component,  $\gamma_A^d$ . The large value of  $\gamma_A$  reflects not only the energy necessary to break interfacial bonds, but also work done deforming and rearranging the PS surface as it peels from the substrate.

Wetting behaviour of the substrates ( $\gamma_c$ ), determined using various liquids, correlates well with the adhesion of the PS coating. Not only is this physically significant, but it also supports the use of spontaneous peeling as a reliable and convenient method of measuring adhesion. There are only small differences in  $\gamma_c$  among substrates, confirming previously published data and supporting the hypothesis that their wetting behaviour is determined to a large extent by a layer of adsorbed water. The water, adsorbed from ambient humidity, would diminish the variation between the substrates. Results obtained from the variation of ambient humidity are also consistent with this hypothesis.

Adhesion of the PS coating showed a greater variation among substrates than did  $\gamma_c$ . Solid adhesion seems to be less dependent on any adsorbed layer of water than is wetting by liquid drops.

There is an exception to the correlation between contact-angle data and adhesion of the PS coating: water. It could not be used in the calculation of  $\gamma_c$  because of its anomalous adhesion, which has two possible explanations:

- (1) Water is a highly polar liquid, whereas the interactions of the other organic liquids and PS are mainly due to London dispersion forces. Water is capable of entering into more interactions with a substrate than are the other materials.
- (2) The surface energy of water exceeds the limit necessary necessary for the conventional formalism of contact angle and liquid adhesion to apply.

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### References

1. Wake, W. C., *Polymer*, 1978, **19** (3), 291.
2. Bikerman, J. J., "The science of adhesive joints". 2nd ed., 1978, *Academic Press*, New York.
3. Shonhorn, H. and Ryan, F. W., *J. Polym. Sci. A-2*, 1968, **6** (1), 231.
4. Good, R. J., *J. Adhesion*, 1972, **4** (2), 133.
5. Levine, M., Ilkka, G. and Weiss, P., *J. Polym. Sci. B*, 1964, **2** (9), 915.
6. Barbarisi, M. J., *Nature*, 1967, **215** (5099), 383.
7. Kitazaki, Y. and Hata, T., *J. Adhesion*, 1972, **4**, (2), 123.
8. Croll, S. G. "Adhesion loss due to internal strain". Awaiting publication in *J. Coat. Technology*.
9. Croll, S. G., *Polymer*, 1979, **20**, 1423.
10. Kendall, K., *J. Phys. D: Appl. Phys.*, 1973, **6** (15), 1782.
11. Good, R. J., *J. Colloid & Interface Sci.*, 1975, **52** (2), 308.
12. Tamai, Y., Matsunaga, T. and Horiuchi, K., *J. Colloid & Interface Sci.*, 1977, **60** (1), 112.
13. Fort, T. and Patterson, H. T., *J. Colloid Sci.*, 1963, **18** (3), 217.
14. Bennett, M. K. and Zisman, W. A., *J. Colloid & Interface Sci.*, 1968, **28** (2), 243.
15. Fowkes, F. M., "Surface chemistry", "Treatise on Adhesion and Adhesives", Vol. 1, 1967, (Ed. R. L. Patrick) *Dekker*, New York.
16. Linford, R. G., "Surface thermodynamics of solids", "Solid State Surface Science", Vol. 2, 1973, (Ed. M. Green) *Dekker*, New York.
17. Mittal, K. L., *Polym. Eng. Sci.*, 1977, **17** (7), 467.
18. Good, R. J., "Intermolecular and interatomic forces", "Treatise on Adhesion and Adhesives", Vol. 1, 1967, (Ed. R. L. Patrick) *Dekker*, New York.
19. Good, R. J., *J. Colloid & Interface Sci.*, 1977, **59** (3), 398.
20. Zisman, W. A., *J. Paint Technol.*, 1972, **44** (564), 42.
21. Gardon, J. L., *Prog. Org. Coatings*, 1977, **5** (1), 1.

# A radio tracer study of the competitive adsorption on titanium dioxide of stearic acid paired with linoleic acid and with palmitic acid

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## Summary

The simultaneous adsorption of two fatty acids from toluene on  $\text{TiO}_2$  was studied. The acids used were stearic acid, linoleic acid and palmitic acid.

For the experiments on simultaneous adsorption, stearic acid was paired with one of the others. To determine the two acids separately by titration, the use of a radioactive tracer was necessary.  $^{14}\text{C}$  stearic acid, which has the same adsorption characteristics as stearic acid, was chosen for this purpose.

The adsorption behaviour of the three single acids is the same, in the sense that they obey the Langmuir theory. However, the surface covered by each adsorbed molecule is different. For stearic acid it is  $22\text{Å}^2$ , for linoleic acid it is  $76\text{Å}^2$ , and for

palmitic acid the value is  $35\text{Å}^2$ . This indicates that the orientation of the carbon chains with respect to the  $\text{TiO}_2$  surface, as a consequence of their structure, is different for the three acids.

Therefore, if two of these fatty acids are adsorbed simultaneously, it is to be expected, because of the dynamic character of the adsorption process and because of the different orientation of the acids with respect to the surface, that in general, this adsorption cannot be described by the Langmuir isotherms calculated from those of the two individual components.

This steric hindrance has indeed been found.

## Keywords

*Raw materials for coatings pigments titanium dioxide*

*Processes and methods primarily associated with analysis, measurement or testing adsorption radio chemical method*

*raw materials used in manufacture or synthesis of ingredients for coatings stearic acid linoleic acid palmitic acid*

*manufacturing or synthesis adsorption*

## Une étude, faisant appel à un traceur radioactif, de l'adsorption relative, sur le dioxyde de titane, de l'acide stéarique jumelé avec l'acide linoléique ou l'acide palmitique

### Résumé

On a étudié l'adsorption simultanée sur le dioxyde de titane de deux acides gras à partir de leur solution en toluène. Les acides utilisés étaient stéarique, linoléique et palmitique.

Pour les expériences de l'adsorption simultanée, l'acide stéarique était jumelé avec un des autres acides. Afin de déterminer par titrage chacun des deux acides, il était nécessaire d'utiliser un traceur radioactif. L'acide stéarique  $^{14}\text{C}$  qui possède les mêmes caractéristiques d'adsorption que l'acide stéarique a été choisi pour cet emploi. Le comportement adsorptif des trois acides individuels est le même au point de vue qu'ils conforment à la théorie de Langmuir. Toutefois, l'aire de la surface occupée par chaque molécule adsorbée est différente. Pour l'acide stéari-

que il s'agit de  $22\text{Å}^2$ , pour l'acide linoléique  $76\text{Å}^2$  et pour l'acide palmitique la valeur est  $35\text{Å}^2$ . Ceci indique que l'orientation des chaînes carbonées à l'égard de la surface de  $\text{TiO}_2$  des trois acides est différente à cause de leur structure.

Ainsi, si deux de ces acides gras sont adsorbés simultanément, on doit s'y attendre en raison du caractère dynamique du processus d'adsorption et en raison de l'orientation différente des acides à l'égard de la surface, qu'en générale cette adsorption ne peut être décrite par les isothermes de Langmuir calculés à partir de ces deux constituants individuels.

Cet empêchement a été bien remarqué.

## Eine Studie der Adsorption von Stearinsäure mit Linol- und Palmitinsäure an Titandioxid mit Hilfe von radioaktiven Spurenelementen

### Zusammenfassung

Die gleichzeitige Adsorption an Titandioxid von zwei Fettsäuren in Toluollösung wurde untersucht. Stearinsäure, Linol- und Palmitinsäure wurden verwendet und zur gleichzeitigen Adsorption wurde Stearinsäure mit einer der anderen Säuren gepaart. Um die zwei Säuren separat durch Titration bestimmen zu können war es notwendig ein radioaktives Element zu

verwenden. Stearinsäure mit Kohlenstoff- $^{14}$  wurde gewählt, da diese dieselben Adsorptionseigenschaften wie normale Stearinsäure hat.

Die Adsorption aller drei Säuren ist ähnlich und folgt der Theorie von Langmuir. Die Oberfläche die von jedem adsor-

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biertem Molekül bedeckt wird ist jedoch verschieden. Für Stearinsäure ist sie 22Å, für Linolsäure 76Å und für Palmitinsäure 35Å. Das weist darauf hin, dass die Orientierung der Kohlenstoffketten in Hinsicht auf die TiO<sub>2</sub> Oberfläche als Folge ihrer Struktur für die drei Säuren verschieden ist. Wenn daher zwei dieser Fettsäuren gleichzeitig adsorbiert werden muss man wegen des dynamischen Charakters des

Adsorptionsvorganges und wegen der unterschiedlichen Orientierung der Säuren gegenüber der Oberfläche, erwarten dass im allgemeinen die Adsorption nicht durch die Langmuir Isotherme beschrieben werden kann die sich aus den Isothermen der zwei Komponenten errechnet.

Diese sterische Hinderung wurde in der Tat gefunden.

**Introduction**

*Refs. 1-7*

A number of studies<sup>1-4</sup> have shown that the adsorption behaviour of a dissolved fatty acid on titanium dioxide obeys the Langmuir theory, which is based on the existence of a monomolecular layer of the adsorbed species at the solid/liquid interface. The observed plateaus in the isotherms correspond to the completed monolayer. The Langmuir equation can be written in the form:

$$\frac{n_s}{N_s} = \frac{KkC_e}{1 + KkC_e} \dots\dots\dots (1)$$

where *n<sub>s</sub>* is the amount of fatty acid adsorbed on one gram of TiO<sub>2</sub>, *N<sub>s</sub>* is the maximum value of *n<sub>s</sub>* (surface completely covered with a monomolecular layer of fatty acid), *C<sub>e</sub>* is the equilibrium concentration of the dissolved fatty acid in mol/l, *K* is the adsorption coefficient or equilibrium constant, and *k* is a conversion factor (l/mol). It may be assumed that both *K* and *k* are constant for the systems investigated under the conditions used here. The constants *N<sub>s</sub>* and *K* can then most easily be evaluated by means of equation (2), obtained by rearranging equation (1):

$$\frac{C_e}{n_s} = \frac{1}{KkN_s} + \frac{C_e}{N_s} \dots\dots\dots (2)$$

Plotting *C<sub>e</sub>/n<sub>s</sub>* versus *C<sub>e</sub>* will give a straight line from whose slope *N<sub>s</sub>* may be calculated, and *K* can be derived from its intercept with the ordinate.

The Langmuir theory can also be applied to describe the total adsorption in systems containing more than one solute<sup>5,7</sup>. For two species (subscript 1 and 2 respectively) the adsorption isotherms are given by:

$$\frac{n_{1,s}}{N_{1,s}} = \frac{K_1kC_{e,1}}{1 + K_1kC_{e,1} + K_2kC_{e,2}} \dots\dots\dots (3)$$

$$\frac{n_{2,s}}{N_{2,s}} = \frac{K_2kC_{e,2}}{1 + K_1kC_{e,1} + K_2kC_{e,2}} \dots\dots\dots (4)$$

The purpose of the present investigation was to study the competitive adsorption of the fatty acid pairs stearic acid – linoleic acid, and stearic acid – palmitic acid on TiO<sub>2</sub>. The purpose was to determine whether the adsorption of stearic acid from solutions containing a second acid could be predicted by the equations (3) and (4), using the values of *N<sub>1,s</sub>*, *N<sub>2,s</sub>*, *K<sub>1</sub>* and *K<sub>2</sub>* obtained from the individual adsorption isotherms.

**Materials and methods**

An untreated rutile titanium dioxide pigment (Tiofine R30) with a nitrogen BET surface area of 6.4 m<sup>2</sup>/g was used in all the experiments. Stearic acid, linoleic acid and palmitic acid were obtained from Fluka AG as purissimum grade materials. <sup>14</sup>C labelled stearic acid with a specific activity of about 50 mCi/mmol, obtained from the Radiochemical Centre Amersham, was used as a tracer. The fatty acid solutions were prepared with technical grade toluene, dried on molecular sieve 5A.

Adsorption experiments were performed by dispersing 4.6 g TiO<sub>2</sub> by ultrasonic agitation (Sonicor, 40 kHz) in 10 ml of a solution of either a single fatty acid (stearic acid, linoleic acid, palmitic acid) or a pair of fatty acids (stearic acid – linoleic acid, or stearic acid – palmitic acid). In the latter cases appropriate amounts of <sup>14</sup>C stearic acid were added. After 24 hours, in which adsorption equilibrium was attained at the temperature of 21°C used, the suspensions were centrifuged until a clear supernatant liquid was obtained.

In the experiments with the single fatty acids the concentrations of these fatty acids (*C<sub>i</sub>* and *C<sub>e</sub>*) were determined by titration under nitrogen from portions of the supernatant liquid with 0.0125 M or 0.030 M ethanolic KOH, using phenolphthalein as indicator.

For the determination of the concentrations of stearic acid in the compound solutions, titration was not possible. Therefore, radioactive stearic acid was added to these compound solutions as a tracer. The adsorption of radioactive stearic acid is the same as that of non-active stearic acid. The radioactive acid was measured as follows. A two millilitre sample of the supernatant liquid was mixed with 10 ml of a scintillation solution (INSTA-GEL, Packard) in a counting vial. Counting of the <sup>14</sup>C activity was carried out with a Packard, Model 3320, Liquid Scintillation Counter. The <sup>14</sup>C activity of the initial solution was measured in a similar manner. The stearic acid equilibrium concentration *C<sub>e</sub>* was then calculated from *C<sub>e</sub>* = *C<sub>i</sub>R<sub>e</sub>*/*R<sub>i</sub>*, in which *R<sub>e</sub>* and *R<sub>i</sub>* are the counting rates of the equilibrium and the initial solution respectively.

The amount of adsorbed fatty acid per gram of adsorbent (*n<sub>s</sub>*) was calculated from *n<sub>s</sub>* = (*C<sub>i</sub>* – *C<sub>e</sub>*)*V*/*m*, where *C<sub>i</sub>* and *C<sub>e</sub>* are the initial and equilibrium concentrations of fatty acid respectively in mol/l, *V* equals the volume of the solution in litres and *m* the weight of the adsorbent in grams.

**Results and discussion**

*Refs. 2, 3*

The adsorption data for stearic acid, linoleic acid and palmitic acid are given in Fig. 1, where *n<sub>s</sub>* is plotted as a function of *C<sub>e</sub>*. In Fig. 2, *C<sub>e</sub>/n<sub>s</sub>* is presented as a function of the equilibrium concentration *C<sub>e</sub>*. It appears that the relationship between these parameters is linear showing that equation (2) is satisfied. The values of *N<sub>s</sub>* and *K* are calculated from the equations (2) so obtained. They are summarised in Table 1. The areas per adsorbed molecule calculated from the values of *N<sub>s</sub>* and the specific surface of titanium dioxide (6.4 m<sup>2</sup>/g) are also given in Table 1. The area of 22 Å<sup>2</sup> obtained for stearic acid is in close agreement with the projected area of a vertically orientated stearic acid molecule<sup>3</sup> of 20.5 Å<sup>2</sup>. This means that on the surface of TiO<sub>2</sub> completely covered with stearic acid, the molecules are orientated vertically.

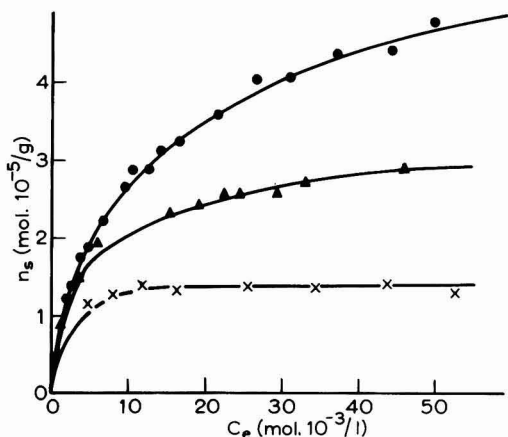


Figure 1. Adsorption isotherms of Stearic acid (o), Linoleic acid (x) and Palmitic acid (▲)

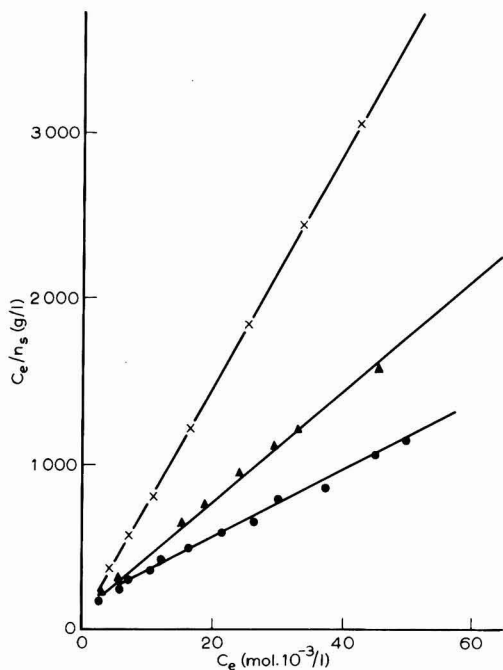


Figure 2. The relation between  $C_e/n_s$  and  $C_e$  for Stearic acid (●), Linoleic acid (x) and Palmitic acid (▲)

Again for complete coverage, one linoleic acid molecule occupies an area of  $76 \text{ \AA}^2$ , a value intermediate between the projected area of a horizontal molecule ( $87.5 \text{ \AA}^2$ ) and of a molecule with a three-point<sup>2,3</sup> attachment ( $62 \text{ \AA}^2$ ). The area of  $35 \text{ \AA}^2$  found for a molecule of palmitic acid is definitely larger than the area which a vertically orientated molecule of a saturated fatty acid would occupy. From the difference between the projected area of a perpendicularly positioned palmitic acid molecule and the experimental value it can be concluded that it is likely

Table 1  
Data pertaining to the adsorption of stearic acid, linoleic acid and palmitic acid on  $\text{TiO}_2$  from solutions in toluene

Component	$N_s$ (mol/g)	$K$	area/molecule ( $\text{\AA}^2$ )
Stearic acid	$4.9 \times 10^{-5}$	1500	22
Linoleic acid	$1.4 \times 10^{-5}$	6700	76
Palmitic acid	$3.0 \times 10^{-5}$	3000	35

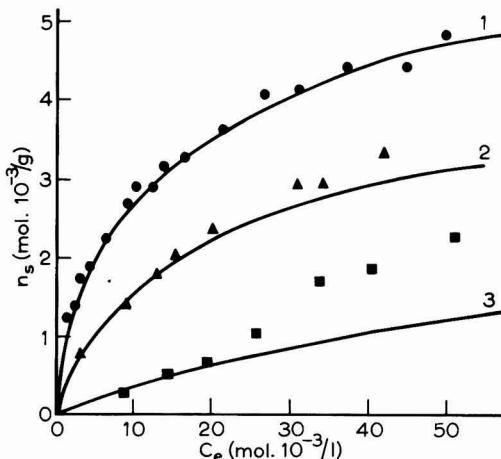


Figure 3. Measured adsorption and calculated adsorption isotherms of Stearic acid in the presence of Linoleic acid. Initial linoleic acid concentrations ( $C_i$ ) in mol/l were 1 : 0 (●), 2 :  $6.7 \times 10^{-1}$  (▲), 3 :  $35.7 \times 10^{-1}$  (■).

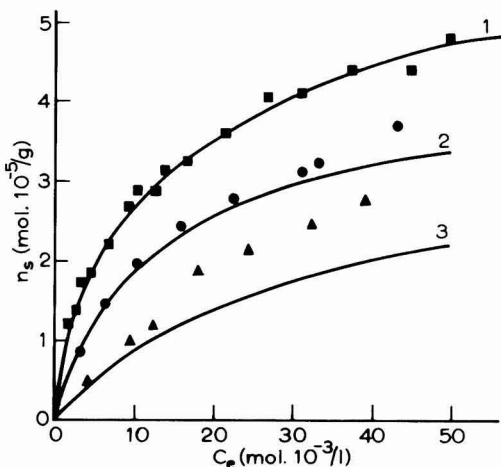


Figure 4. Measured adsorption and calculated adsorption isotherms of Stearic acid in the presence of palmitic acid. Initial palmitic acid concentrations ( $C_i$ ) in mol/l were 1 : 0 (■), 2 :  $11.8 \times 10^{-1}$  (●), and 3 :  $36.7 \times 10^{-1}$  (▲).

that the palmitic acid molecules are adsorbed in an inclined position.

Some of the adsorption data obtained for stearic acid in

the presence of different amounts of linoleic acid are given in Fig. 3. The lines in the figures for different initial concentrations of linoleic acid have been calculated by means of equations (3) and (4), in combination with the mass balances of the fatty acids. Some of the experimental data and the adsorption isotherms, calculated as above, for the fatty acid pair, stearic acid – palmitic acid, are shown in Fig. 4. Figures 3 and 4 show that there is a good agreement between the experimental and calculated values for the stearic acid adsorption at low concentrations of linoleic acid and of palmitic acid respectively. For higher concentrations of these fatty acids and particularly at higher stearic acid concentrations, the agreement between the measured and the calculated values becomes less satisfactory. As stated before, the stearic acid molecules are adsorbed in a vertical position whilst the adsorbed linoleic acid molecules are positioned more or less horizontally. This difference in orientation can play a role in the equilibrium obtained during the simultaneous adsorption of stearic acid and linoleic acid.

In this process a continuous exchange is taking place between the molecules at the  $\text{TiO}_2$  surface and the molecules in solution.

When a linoleic acid molecule is desorbed from the surface, the vacant site may be occupied by another linoleic acid molecule, but it is also possible that the vacant site may be occupied by several stearic acid molecules in a vertical position. However, when a stearic acid molecule is desorbed the situation is different. The vacant site created might again be occupied by a stearic acid molecule or it may be filled by a linoleic acid molecule not in its favourite horizontal, but in a vertical, position. In the calculations which are based on data derived from the individual adsorption behaviour of the two compounds, this difference in orientation of the linoleic acid molecules could not be taken into account. Difference in determined and calculated adsorption isotherms are, therefore, to be expected.

The extent to which the calculated stearic acid adsorption will differ from the experimental values is determined by the amount of linoleic acid molecules present at the surface of the  $\text{TiO}_2$ . Good agreement between the calculated and the measured stearic acid adsorption at low

concentrations of linoleic acid can be explained by the fact that the total amount of fatty acids was not sufficient for complete surface coverage to occur. Consequently, the molecules of linoleic acid will, in this case, be adsorbed in their favourite position. The same type of reasoning holds for the good agreement between the results of calculation and the experiments at high linoleic acid concentration, but at low stearic acid concentrations. It is obvious that only a very small amount of linoleic acid will be adsorbed in a vertical orientation. In this respect the ratio of the linoleic acid to the stearic acid concentration is of importance. The greater this ratio, the greater the probability that at a place which becomes vacant by the desorption of a stearic acid molecule, a linoleic acid molecule will be available for adsorption.

Considering the simultaneous adsorption of stearic acid and palmitic acid, the discrepancy between the experimental and calculated values for the stearic acid adsorption can be explained in the same way as given above. Some of the palmitic acid molecules in the monomolecular layer at the surface will not be able to take up their favourite position, but will have to assume a vertical position. Again the different orientation has not been taken into account in the calculation.

It can be concluded that the simultaneous adsorption of two different fatty acids whose orientation at the titanium dioxide surface is not the same, cannot, in general, be described by the Langmuir isotherms calculated from the Langmuir isotherm of the two individual components. This is due to steric hindrance.

[Received 15 December 1979]

## References

1. Sherwood, A. F. and Rybicka, S. M., *JOCCA*, 1966, **49**, 648.
2. Doorgeest, T., *JOCCA*, 1967, **50**, 841.
3. Ottewill, R. H. and Tiffany, J. M., *JOCCA*, 1967, **50**, 844.
4. Witvoet, W. C., "Engine aspecten van het dispergeerproces", Thesis, University of Technology, Delft, 1971.
5. Smith, M. L., Gordon, B. E. and Nelson, R. C., *J.Phys.Chem.*, 1965, **69**, 3833.
6. Boer, de J. H., "The Dynamical Character of Adsorption", 2nd Edition, 1968, Clarendon Press, Oxford.
7. Kennedy, P., Petronio, M. and Gisser, H., *J.Phys.Chem.*, 1971, **75**, 1975.

## Next month's issue

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

**Esters of polystyrene glycol and rosin in surface coatings** by *S. Chandra and S. Pasari*

**Effect of solvent on residual strain in clear epoxy coatings** by *S. G. Croll*

**Preservation, priming, putty and paint** by *J. J. Froggatt*

**The effect of ageing on the ease of decontamination of some paint systems** by *P. Walker and F. Cornish*

# occa meetings

## Hull

### Synthetic clays – their properties and uses

The fourth Ordinary Meeting of the Hull Section was held on 7 January 1980, when Mr B. J. R. Mayes and Mr F. D. Robinson of Laporte Industries Ltd, gave a joint lecture entitled "Synthetic Clays – their properties and uses".

The lecture was in two parts, Mr Robinson covering the technology of natural clays, followed by Mr Mayes describing and demonstrating the properties of the Laporte hydrophilic synthetic clay Laponite. (This lecture was hastily arranged following the cancellation of the original talk.)

The historical background to the development of synthetic clays was outlined with reference to the natural origins of clays from weathered volcanic debris and from the direct precipitation of clays in shallow marine basins. An example of the former is the deposit around Bath occurring in the top 2 to 3 metres of the Upper Fullers Earth Clay in the middle Jurassic. The Redhill strata is not so old, being formed in the Cretaceous Age and is a good example of direct precipitation.

Wool cleaning with clay slurries is mentioned in the Bible. Better known are the "Fullonicae" (laundries) of Roman times from which the term "Fullers Earth" originated. The development of alternative cleaning agents over the last two hundred years caused a decline in the traditional use of Fullers Earth, but new industries have developed with natural swelling clays as a basic raw material.

The chemistry of clays is that of the silicates. The principle building elements are 2 dimensional Si-O tetrahedra linked to 2 dimensional arrays of Mg or Al octahedra. Two layer structures (e.g. China Clay) and 3 layer structures (e.g. Talc, montmorillonite, bentonite etc.) predominate. The ion exchange capacity of the clay particles is directly proportional to the level of isomorphous replacement of the metal ions by ions of a lower valency. The possible combinations are legion with many hundreds occurring naturally. Natural clays are invariably contaminated with inferior material which necessitates careful processing to produce consistent products.

Mr Mayes followed by outlining the background research into the synthesis of the Laporte Laponite clay range. He demonstrated the rate of gel development and the method of neutralising the positive charge at the edge of the clay platelets to produce a water thin clay sol.

The clarity and good colour of the Laponite gels was compared with natural clay's opacity and yellow tones.

The first commercial applications of these synthetic clays were in emulsion paints where they were used to

Further information on any items mentioned below may be obtained by circling the appropriate *Reader Enquiry Service* number on the form at the back of the *Journal*. Enquiries will be forwarded to the Section concerned or may be forwarded to the lecturer.

modify the rheology. Full gel-type emulsion paints and structured paints may be produced by the addition of the clay either at the mill base stage or, alternatively, adding the clay as a sol as the last step in production.

The suspending property of Laponite is utilised in aqueous aggregate paints where the uniform suspension of large heavy aggregates is essential. Panels demonstrating the range of finishes that can be produced were shown.

The interaction of Laponite with cationic gums and certain cellulosic thickeners was ably demonstrated with an "encapsulated" Laponite/cellulosic based pigmented phase, insoluble in a Laponite sol dispersion to give a "speckled" product. This is the essence of the patents behind aqueous multi spec finishes.

Mr Mayes continued by describing the special grades of Laponite that have been developed for cosmetics and toiletries, where their structuring ability, excellent colour, clarity and chemical stability are significantly superior to those of the natural clays. Samples of the end products were demonstrated.

Finally, the use of Laponite gels as seed carriers in agriculture and horticulture was presented as the latest in a long list of potential applications that have been investigated by Laporte and established as commercially successful operations.

A very active question time followed with the vote of thanks enthusiastically proposed by Mr J. A. Hasnip.

*Reader Enquiry Service No. 21*

### China clays as opacifying extenders

The fifth Ordinary Meeting of the Hull Section complemented the Fourth Meeting since it was concerned with the properties in paint of two layer natural clay, china clay. The lecture was held on the 4 February 1980. Mr Robert McGuffog of ECC International Ltd presented a lecture entitled "China clays as opacifying extenders in paints".

After introducing the ECC Company, the lecturer ran a film showing all aspects of the mining of china clay in Cornwall. The processing steps taken to produce the range of clays that are available, with examples of their application areas were illustrated.

The lecturer continued with a statement of the particle size distribution of the various grades. He commented that the smaller the particle size, the better the opacity and brightness. Smaller sized clays also have less effect on the final film gloss. However, the coarser clays confer better scrub resistance to the film.

A hiding power comparison between china clay and chalk whitening showed china clay to be superior at all PVC levels and superior to an emulsion paint containing TiO<sub>2</sub> at a PVC of 5 per cent.

China clays of superior opacity and brightness are produced by calcination. The pre-dressed clay is calcined at 1000°C when dehydroxylation takes place accompanied by a 30 per cent weight loss. There is also some particle/particle fusion, which is claimed to lead to



better interparticle spacing in the finished paint. This is suggested as the mechanism which gives the improved opacity. A 2 per cent better brightness is also achieved in comparison with Speswhite china clay. Calcined clays are also harder, the Mohs scale value increasing from 2 to 4.

The lecturer then introduced a development calcined clay based on a smaller particle size feedstock. An improvement of 4 units in brightness, compared with the present calcined clays, had been recorded, accompanied by an opacity increase of between 2 and 7 units at PVC levels above CPVC.

Mr J. Potter proposed the vote of thanks after a lively question session by the 20 members and guests who were present.

*Reader Enquiry Service No. 22*

F.D.R.

## Manchester

### Electrodeposition: Anodic versus cathodic

The final Senior Lecture of the 1979/80 programme was presented by Dr Hans-Uwe Schenck of BASF, Ludwigshafen on 10 March 1980 at the Woodcourt Hotel, Sale. Forty members and guests were present to hear Dr Schenck deliver a lecture that was both excellent in quality and in the English language used. The lecturer has spent ten years at BASF as a resin chemist in the Plastics Laboratory followed by two years as Group Leader in Polymers and three years in Resin Chemistry. His lecture could be summarised thus:

Basic comparison of deposition mechanism of both processes.

Investigation of cathodic ED by rotating disc electrode (unpublished results).

Chemistry of binders for anodic and cathodic ED.

Comparison of anodic and cathodic ED materials used in practice

Current applications and properties.

Dr Schenck's lecture of 90 minutes covered many points including the fact that electrodeposition was a British invention of the 1930's that was developed commercially in the USA in 1960.

A lively question period followed the lecture before the vote of thanks, proposed by F. B. Windsor, was acknowledged with enthusiastic response.

*Reader Enquiry Service No. 23*

F.B.W.

## Natal

### New concepts in thixotropy

A lecture entitled "New concepts in thixotropy" was presented by Mr A. G. North of Cray Valley products.

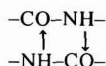
Mr North opened by conveying to the meeting good wishes from OCCA London, which were much appreciated by the members present.

In his lecture he traced the development of thixotropic alkyds from their accidental beginnings in the USA,

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# OCCA meetings

leading to the General Mills patents of 1952. T. E. Washburn had found that if dimer acids were incompletely cooked into polyamide resin, a thixotropic structure resulted which was temperature and shear sensitive. Useful resins were developed containing ca. 5 per cent polyamide on alkyd. Attempts to explain the thixotropy scientifically presume that weak hydrogen bonding forces are developed between adjacent chains thus:



Mr North listed the advantages of thixotropic paints as follows:

No hard pigment settlement; less sagging on vertical surfaces; cleanliness in use; less penetration to porous surfaces; easy brush application; and faster painting (heavier brush loading).

Paint manufacture is by standard methods, since the gelled resins liquefy under shear; viscosity has to be controlled by a high shear method such as the ICI Cone and Plate viscometer at 2500 sec<sup>-1</sup>. The thixotropy is dependent on temperature, shear rate and recovery time, and the traditional resins were fluid at 40°C. Additionally, cycling to only 35°C caused syneresis and settling out of pigments, thus making the paints unsuitable for use in the tropics. The newer resin types "Super Gelkyd" are stable to 180°C, and retain virtually full gel structure at 70°C, but the structure is history-dependent; thus the viscosity of a paint liquefied by high temperature will always be higher than one liquefied by high shear. The new types require up to 10 per cent polar solvent (e.g. Cellosolve) for full gelation, although 2.5 per cent is very effective. Due to their temperature stability they are suitable for stoving primers, and are generally compatible with chlorinated rubber.

The vote of thanks was proposed by Mr J. H. A. Smith.

*Reader Enquiry Service No. 24*

## Newcastle

### Pigment chips

The final meeting of the Newcastle Section for the 1979/80 session was held on 6 March, at St. Mary's College, Durham University. A paper on the manufacture and uses of pigment chips for the printing ink and paint industry was presented by Mr F. Morpeth, of Foscolor Limited.

Mr Morpeth started by indicating that there were two basic techniques: wet milling, which is used particularly for nitrocellulose, and dry milling, which formed the main basis of his paper.

He discussed the manufacture of chips by the dry

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milling technique which, in his company, is operated in the molten state with twin roll mills. Processing times required to disperse the pigment in the resin binder vary, depending on the pigment used. Soft pigments such as titanium dioxide, require very short milling times and the more difficult pigments would take somewhat longer but, even so, the milling times would normally not exceed 35 minutes. This technique usually employs small batch sizes but, in general, short runs are the norm for most requirements. The milled pigment is stripped off the roll, cooled in a cooling tray and usually granulated.

Mr Morpeth then went on to discuss the formulation of pigment chips, indicating the factors which affect chip formulations. These factors include pigment type and level, resin type and properties and the use of other additives, such as surfactants and plasticisers.

The advantages of chips were then outlined, emphasis being placed on improvements in gloss, transparency and strength development in comparison with other methods of pigment dispersion.

Mr Morpeth concluded by outlining the main applications for pigment chips, with particular reference to a number of applications in the printing ink industry. Other applications included wood finishes, powder coating and automotive finishes.

The meeting was concluded with a vote of thanks to Mr Morpeth proposed by Mr J. Clark, which was endorsed by the 36 members and visitors present.

A.L.

Reader Enquiry Service No. 25

# news

## Thorn uses powder finishing

Doubled output of fridges and freezers, less rejects and improved scratch-resistance have been achieved by Thorn Domestic Appliances (Electrical) Manufacturing Ltd, as a result of a switch from sprayed wet stoving paint to the application of thermoset powder coatings. Other advantages gained following the switch to powder finishing include; time, equipment and labour savings; removal of the need for flash-off zones and the elimination of problems associated with solvent in normal wet stoving paint finishing.

The area freed by removal of the wet paint plant also permitted a better and extended layout of the machine shop. The one coat powder finish replaces a two coat wet paint system.

Epoxy powder, supplied by TI Drynamels Limited, Britain's leading powder manufacturer, is used to coat flat panels for the 8,000 finished units produced at the Spennymoor plant each week.

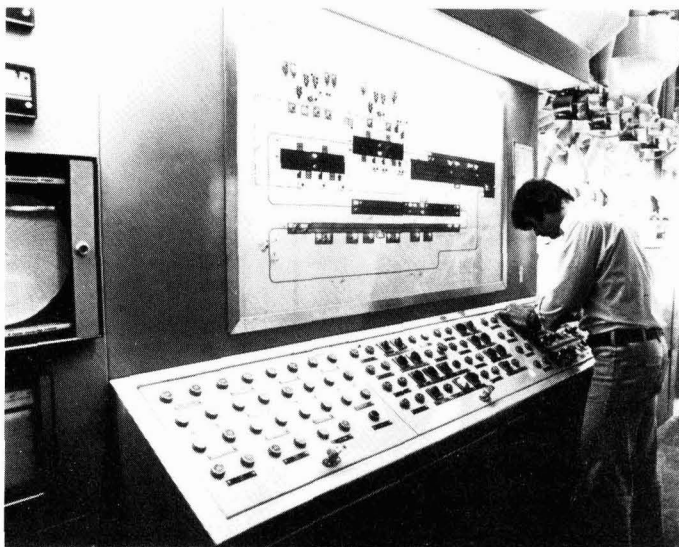
Reader Enquiry Service No. 31

## Gray-Campling Ltd

Gray-Campling Ltd, of Bournemouth, have been appointed sole concessionaires for Speeflo products in the UK. The Speeflo Manufacturing Corporation USA is one of the largest manufacturers in industrial spraying equipment in the world.

Reader Enquiry Service No. 32

Further information on any items mentioned below may be obtained by circling the appropriate Reader Enquiry Service number on the form at the back of the Journal. Enquiries will be forwarded to the organisation concerned.



The central control room of the Thorn Domestic Appliances powder coating plant

## BP phenol technology

BP Chemicals phenol-from-cumene technology has been licenced to Mitsubishi Petrochemicals Co. Ltd who will build a 100,000 ton/year phenol plant at Kashima, Japan, which is expected to come on stream in mid 1982.

The BP Chemicals phenol-from-cumene process is the leading technology for producing phenol and acetone in the world today. Mitsubishi Petrochemicals are the third Japanese company to licence the process—Mitsui Petrochemicals' first plant started up in 1958 and Mitsui Toatsu's plant in 1974.

Reader Enquiry Service No. 33

## Microbial damage of paint

Despite the good hygiene practised in most paint factories microbial contamination occasionally occurs. This can cause thinning, gassing or malodour in aqueous paints rendering them unsaleable.

Paint users can also be troubled by micro-organisms. The fungal and algal growths which can disfigure and damage ceilings and walls are well known.

Although the Paint Research Association and the paint industry have solved some of these problems, a well-attended symposium on Paint Microbiology, run by the Paint RA last year highlighted a

number of questions to which neither the Paint RA nor the 100 plus delegates had satisfactory answers.

As a result six Research Contracts were drawn up to extend existing knowledge and assist paintmakers and property owners to control the problems of microbial damage.

*Reader Enquiry Service No. 34*

### Caribbean Testing

Caribbean Testing, Inc. have set up a new outdoor weathering centre at Caguas, Puerto Rico which will help customers with performance evaluation of their paint formulations in terms of key criteria such as physical breakdown (chalking and crazing), change of colour, and resistance to fungal growth and bacterial attack.

The site of the centre in the Caguas Valley, 15 miles outside San Juan, was selected for its combination and consistency of environmental features. The climate combines high solar energy and radiation, high ambient temperature and high annual rainfall and relative humidity. As there is only two hours difference between the longest and shortest days in the year in Puerto Rico, and solar radiation is remarkably similar from season to season.

*Reader Enquiry Service No. 35*

### London agent for Janke & Kunkel

Semat (UK) have been appointed agents and distributors for the original IKA range of laboratory equipment manufactured by the German company, Janke & Kunkel. This high quality equipment consists of a range of laboratory items used for stirring, shaking, dispensing and distilling.

*Reader Enquiry Service No. 36*

## new products

### New Kremlin robot

Kremlin Spray Painting Equipment Ltd are launching the new Kremlin Programmable Robot. Kremlin states that their Programmable Robot, designed by AOIP Kremlin Robotics, takes over from where the earlier generation of robot spraying equipments leaves off.

Besides reproducing the intricate and subtle movements of a spray painter's hand, it is only the AOIP Kremlin Robotics robot that offers the following important advantages:

Triple movement teaching modes, i.e. direct teaching of the robot by the operator; teaching by a hand controller; and telecontrol teaching.

Each painting segment can be modified, resumed or re-inserted without recording the movement again.

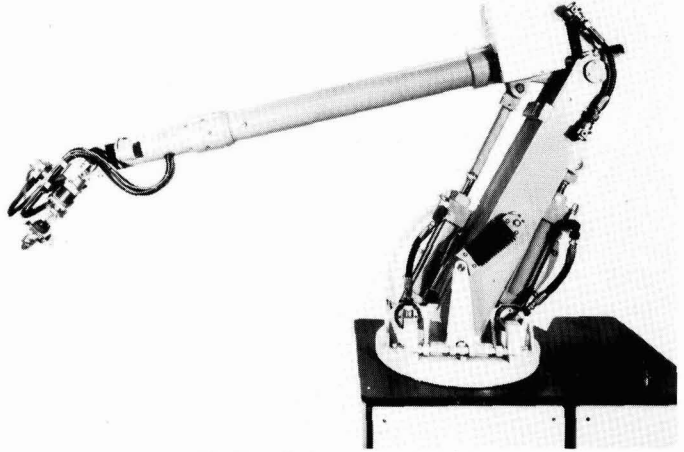
The robot is able to meet any peculiar

need such as identification by the robot itself of parts to be painted or control of colour changes.

Maintenance: a telephone connection to the manufacturer's computer will give an instantaneous tele-diagnosis.

The robot constantly assesses its own performance and operation and will indicate by an alarm any fault which develops within itself such as low or high

# news



The Kremlin Programmable Robot

oil pressure or temperature, blocked oil filter, or, for an example, an attempt by an operator to destroy a programme already protected.

There are also safety devices for equipment and operator protection, such as anti-collision protection by means of an infrared barrier along the arm.

The Kremlin Programmable Robot system is composed of the robot manipulator itself, a control cabinet, a lightweight remote control, a teaching mode structure called the "hand controller" and a hydraulic unit.

*Reader Enquiry Service No. 37*

### New air-water gun

Now introduced into the UK market is the new Hydro-Air Washer. This low cost portable air and water gun solves many cleaning problems, often eliminating the need for expensive cleaning equipment.

The gun is connected to standard air lines and normal hot or cold water supply to create a powerful penetrating force for instant washing, rinsing, sterilising, or degreasing. The nozzle is rotated to adjust the water volume and pressure of the air.

Accessories include a siphoning attachment for the application of cleaning fluids.

*Reader Enquiry Service No. 38*

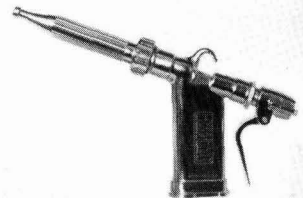
### Esso's new solvent Exsol D230/260

Esso Chemical Ltd has announced that it has further extended its range of low aromatic solvents with the introduction of Exsol D230/260, a new high boiling solvent particularly suitable for the manufacture of printing inks.

The new solvent is colourless with a high flashpoint, low evaporation rate and very low odour, and many advantages for the manufacture of pesticides and cleaning agents.

Its use in formulations to produce heat set web offset inks can help to reduce pollution, aid energy conservation and achieve greater efficiency by promoting faster machine speeds.

*Reader Enquiry Service No. 39*



The Hydro-Air Washer, a portable air and water gun

# news

## Improved Sorbina T/10 series

An improved Sorbina T/10 Series of roller coaters, with the upper and lower drums each driven independently by separate geared motors, is now being marketed in the UK by the Machinery Division of Macpherson Components Ltd.

Provision of these independent motors allows optimum control of lacquer or sealer coat application to boards and sheet materials. Provision is also made for fitting a separate geared motor to the dosing drum.

All four models in the T/10 Series have a 1400 mm working width and a working height adjustable from 20 mm to 100 mm. Speeds of the conveying and upper drums are variable between 8 and 41 metres per minute, both drums being fitted with rev. counters.

*Reader Enquiry Service No. 40*

## New drum range

A new range of storage drums, specifically designed to protect petroleum spirits, solvents and other low flash-point liquids from explosion, has been launched by Fire-Reliant Ltd.

The drums - 25l, 50l and 210l - are each filled with Explofoil, an expanded aluminium alloy mesh, which protects the contents from a wide variety of explosive hazards including impact, external heat, flashback, auto and electrostatic ignition and drum penetration by anything from a hot splinter to an incendiary bullet.

Although it completely "fills" each drum, Explofoil takes up less than one per cent of the volume, weighs only about four ounces per gallon space and retains no more than two per cent of the liquid content. It will function efficiently right up to its melting point of 1200°F.

*Reader Enquiry Service No. 41*

## New drynamels primer

A safe, weldable, steel primer with both BSC and a North of England Health Service Certificate has been introduced by TI Drynamels, Birmingham.

Based on zinc phosphate, the new primer does not emit toxic fumes during welding operations and is designed to prevent corrosion of steel components and units from initial cutting until final topcoats and finishing systems are applied.

*Reader Enquiry Service No. 42*

## New axial mixer

John Godrich Consulting Engineers have now introduced to their range of mixers the Rotojet axial mixer which, it is claimed, has been designed to give highly effective mixing and agitation without any air intake. It is particularly suitable for dissolving crystalline materials and

for mixing liquids which vary widely in specific gravity or viscosity.

A branch pipe in the stator tube can be used for adding liquids directly into the turbine. A demonstration unit is available from Ludford Mill.

*Reader Enquiry Service No. 43*

## UV-IR spectrophotometry

Incorporating several novel features, the S105 spectrophotometer is another example of a high performance, low cost, easy to operate instrument which has been added to the range available from Semat (UK).

Using a monochromator which is a plane blaze reflection diffraction grating provides a band width of less than 5 nm over an extremely versatile range from 380 to 920 nm.

The whole system is designed so that the combination of blaze grating and detector spectral sensitivity ensures that no filters are necessary over the working range.

Automatic gain setting at different wavelengths eliminates tedious resetting normally required for single beam instruments.

*Reader Enquiry Service No. 44*

## New enamel

A new enamel, Rockspeed Black, has been developed by Ault & Wiborg Paints Ltd, for the automotive components industry.

A recent market evaluation indicated that a fast drying, tough, durable material capable of withstanding severe corrosion and chemical conditions with resistance to petrol and oil, was needed. Rockspeed's formulation means it is air dry and handleable in 12 minutes which, with a one thou. film thickness over a light iron phosphate coating, withstood over 120 hours in the salt spray test.

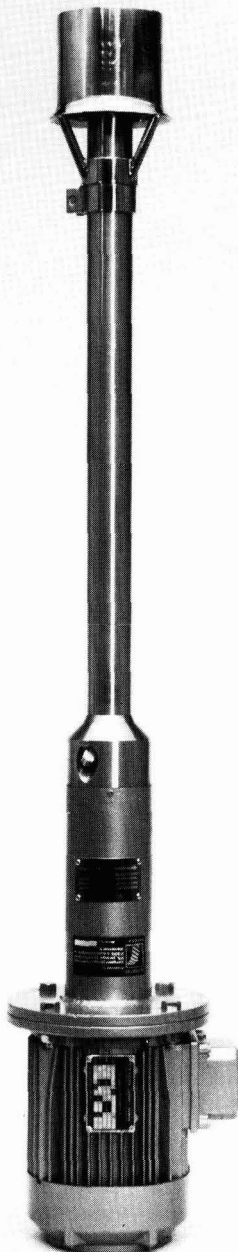
A modified alkyd resin based paint, Rockspeed is suitable for spray, electrostatic or dipping application.

*Reader Enquiry Service No. 45*

## ETFE replace ground-glass stoppers

Replacement of ground-glass stoppers by screw-caps made of "Tefzel" modified ETFE has brought savings for E. Merck, one of the world's leading suppliers of fine chemicals and pharmaceuticals.

Ground-glass stoppers have grown very expensive in recent years. After a decision to change over to an injection-mouldable plastic closure, the company tried a variety of thermoplastic materials noted for their chemical inertness. Some were nevertheless attacked by the aggressive chemicals in the glass containers; in certain cases stabilisers and other components were leached out of the plastic.



The Rotojet axial mixer which is available from John Godrich

To overcome these difficulties a PTFE disc was put inside the cap so as to prevent direct contact with the contents of the bottle. Although this measure yielded some improvement, Merck found that very small amounts of certain chemicals permeated through the PTFE and the problem persisted.

About this time Du Pont introduced "Tefzel" modified ETFE. Caps injection-moulded from this fluoropolymer were found to be suitable even for the most aggressive chemicals, including fuming nitric acid and 100 per cent sulphuric acid.

*Reader Enquiry Service No. 46*

### Water soluble thickeners

Allied Colloids Ltd, have developed a new range of water soluble thickening agents. The first three in the series have been designed specifically for the water-based adhesive and latex compounding industries, and are named Viscalex AT-11, AT-22 and AT-33.

They are supplied as low viscosity, high solids dispersions that are freeze/thaw stable.

They produce rapid and efficient thickening when added directly to an aqueous formulation. No addition of alkali is required and the Viscalex AT polymers are effective over a wide pH range e.g. pH 4.5 - 12.0.

*Reader Enquiry Service No. 47*

### New Kremlin paint pump

The new P130 paint pump system from Kremlin Spray Painting Equipment Ltd, gives a pressure of 90 psi, as opposed to a maximum of 60 psi obtained with a pressure pot system. This gives the P130 the ability to handle a much wider range of paints, lacquers, adhesives etc, (whether of thick or thin consistency) than a pressure pot.

Kremlin state that it is ideal for use with thicker materials, where better atomisation at the spray gun head can be obtained than with a pressure pot, thus saving on the amount of thinners required.

It is also said to be ideal for helping to keep in suspension those materials that have a tendency to settle out. This is achieved through the pump being equipped with a permanent circulation system which returns the unused paint to the pot.

Another advantage offered by this new versatile Kremlin pump is its ease of filling. The paint, lacquer or adhesive is simply poured into the top of a 2 litre cup without having to open clamps or bolts. Other plus points of the P130 compared to a pressure pot are that it is suitable for use with smaller quantities of materials, and only requires a mains air line for operation as it has its own built-in atomising air regulator.

*Reader Enquiry Service No. 48*

## literature

### IUPAC Recommendations

Approved recommendations 1978. Commission on nomenclature of organic chemistry. *Pure appl. chem.*, 1979, **51**, 353:

A general system for describing isotopically modified organic compounds, in both names and formulae.

Provisional recommendations 1978. Commission on nomenclature of inorganic chemistry. *Pure appl. chem.*, 1979, **51**, 1981:

The rules for the naming of isotopically modified inorganic compounds.

Provisional recommendations. Commission on macromolecular nomenclature. *Pure appl. chem.*, 1979, **51**, 1101:

This document is the first definitive statement of nomenclature for polymer stereochemistry since 1962.

Provisional recommendations. Commission on physical organic chemistry. *Pure appl. chem.*, 1979, **51**, 1725:

This glossary constitutes an attempt to describe widely accepted usage of each of an alphabetically arranged list of over 700 terms.

Provisional recommendations 1978. Commission on nomenclature of organic chemistry. *Pure appl. chem.*, 1979, **51**, 1955:

A revision of the extended Hantzsch-Widman system of nomenclature for heteromonocycles.

*Reader Enquiry Service No. 49*



The P130 paint pump system from Kremlin Spray Painting Equipment

## news

### British standards

BS 5598: Pt 7: 1980 Methods of sampling and test for halogenated hydrocarbons. Pt 7 Methods of test for methyl chloride and ethyl chloride, is now available from the British Standards Institute. *Reader Enquiry Service No. 50*

### A unique mineral thickener

Lawrence Industries announce the availability of an updated second edition of their brochure Attagel 50, a unique mineral thickener.

The booklet describes the use of a heavily micronised Attapulugus clay powder which will impart thickening, suspending and thixotropic properties to liquid systems.

The latest edition includes a new section recommending up-to-date surfactants for use in various liquids ranging from paraffins through solvents to water. *Reader Enquiry Service No. 51*

### Infrared spectroscopy atlas

This new publication contains approximately 900 pages. An important feature of the book is the fully indexed compilation of 1433 infrared spectra of materials commonly utilised in the coatings industry. Spectra include typical examples of: polymers, monomers, solvents, organic and inorganic pigments as well as common additives used in the coatings industry.

This publication also contains chapters covering: the theory of infrared spectroscopy, qualitative and quantitative analysis, instrumentation, accessories for infrared spectrophotometers, selected applications and an extensive bibliography.

*Reader Enquiry Service No. 52*

### Miniature fittings publications

Comprehensive details of the Maxam Super Speedfit push-in fittings are contained in a fully illustrated brochure published by CompAir Maxam Ltd, of Camborne, Cornwall. The company has also produced a wall chart which provides "at-a-glance" selection of the fittings available.

Super Speedfit push-in fittings enable the efficient and fast build-up of systems piped in nylon, copper, brass and steel. *Reader Enquiry Service No. 53*

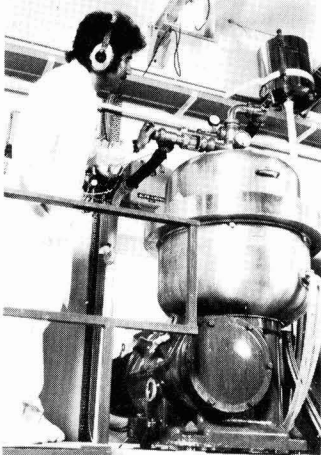
# news

## Disk-stack centrifuges

This new 20 page booklet, available free from Alfa-Laval, describes the many different types of disk-stack centrifuge currently manufactured by the company, and gives a guide to their applications in the chemical, plastics, petroleum, pharmaceutical, mineral, metals, paper, photographic, nuclear-power and associated industries.

The booklet indicates how disk-stack centrifuges can be selected and tuned to achieve desired results. Centrifuges of this type can generate separating forces exceeding 10 000 g, while the closely-stacked conical disks multiply sedimentation area as much as 100 times.

*Reader Enquiry Service No. 54*



An explosion-proof Alfa-Laval disk-stack centrifuge

## Per-compounds

"Per-compounds" cover not only the peroxides but also the hydroperoxides, peresters, and other compounds releasing oxygen or forming free radicals. In this monograph their use in polymerisation, grafting and crosslinking is considered. The principle per-compounds available commercially are listed with properties, such as a half-life table, and specific decomposition behaviour.

*Reader Enquiry Service No. 55*

## Profits in chemical industry

Profitability in the chemical manufacturing industry is greatest in companies

where capital intensity per employee is high and where employees are highly paid.

This conclusion is drawn from Management Ratios for the chemical industry, a new annual publication of business ratios produced by Dun & Bradstreet Limited, the business information company. Employees in companies with the highest capital intensity are 28 per cent better paid than those in companies with lower capital. Their improved pay is linked to higher productivity and profit generation per employee. The ratios show that a 10 per cent improvement in increased employee productivity can favourably affect profits by 30 per cent.

*Reader Enquiry Service No. 56*

## meetings, etc.

### Centenary symposium

To mark the centenary year of the Department of Colour Chemistry and Dyeing at The University of Leeds, a Centenary Symposium on Colour Chemistry has been arranged from 8 - 10 September 1980.

The scope of the symposium will be the theoretical and practical aspects of the making and application of colouring matters. Most of the lectures will be on stimulating new approaches to technological problems based on a fundamental understanding of the processes involved.

*Reader Enquiry Service No. 57*

### Plastics/paints against corrosion

Polymers are widely used these days in the fight against corrosion, both as essential components in paints and surface protectives, and also as structural replacements for more traditional materials.

A one-day conference has been organised on this theme by the Building and Construction Group of the Plastics and Rubber Institute and the London Section of the Oil and Colour Chemists' Association, entitled Plastics and Paints against Corrosion, on 12 November 1980 at Thames Polytechnic, Wellington Street, Woolwich, London SE18.

*Reader Enquiry Service No. 58*

### Symposium and new manual launch

It can be argued that the polymer system ("binder") is the most important component of a coating. The Paint Research Association (Paint RA) have organised a symposium on the subject once every two years or so.

On this occasion an entirely new team of lecturers will be present, well able to cover the field all the way from reviews of the current position on the fully established systems to an account of recent progress

in the more active fields such as powder coatings, electrodeposition, car refinishing and radiation curing.

Paint RA in the three year Technology Transfer project just completed for the Department of Industry found that many managements were facing difficulties in assessing unit costs for different methods of paint finishing, in justifying capital investment in new equipment and in choosing amongst different processes.

A manual that has been prepared for Paint RA by Value Control Ltd called Costing for Industrial Paint Finishing identifies capital and operating costs for each stage of all commonly used industrial finishing processes and sets up a framework enabling managements to calculate unit costs for various types of articles and volumes of production.

*Reader Enquiry Service No. 59*

## appointments

### The co-ordinator

To improve the effectiveness of Coates liquid inks marketing, John Saunderson has been appointed National commercial manager (liquid inks). Formerly manager of Manchester branch, he will transfer to the base factory at St Mary Cray and take up his new post on April 2 1980.



John Saunderson

### TI Drynamels

Sales and marketing function of leading U.K. industrial finishes manufacturer TI Drynamels Limited, Birmingham, has been expanded by a further seven people, a direct result of the company's recently announced investment boost. The new appointments are:

Les Brame, as sales co-ordinator, pipe coatings. Roger Hailey, as sales co-ordinator, automotive coatings. Steve Howells, as area representative for South-West England and South Wales. Ted Whinnery, as area representative for West Midlands and Central Wales. Robin Truron, as area representative, South Midlands. Steve McCafferty, as technical service representative for Scotland and Malcolm Goodman, as marketing executive.

Further information on any items below may be obtained by circling the appropriate Reader Enquiry Service number on the form at the back of the Journal.

# OCCA NEWS

## Ontario section

The Ontario Section held its fourth Annual Dinner Dance on Saturday 2 February 1980 at the "Old Mill Inn", Toronto.

The occasion was, as always, an overwhelming success in every respect.

## Newcastle Section

The Newcastle Section Annual Ladies' Night was held at the Five Bridges Hotel, Gateshead, on Friday 15 February 1980.

The dance was attended by a total of 262 people. The President of the Association, Dr Francis Smith and his wife were the principal guests of the Newcastle Section Chairman, Mr John Clark, along with the following Chairmen and their ladies: Mr G. V. G. Hill (Thames Valley), Mr J. A. Burns (Midlands) and Mr A. C. Jolly (Manchester).

The Newcastle Section of the Oil & Colour Chemists' Association was proposed by the President and the Newcastle Chairman proposed a toast to the Ladies and Guests. Dancing continued into the early hours of the morning, which appeared to arrive too soon.

F.B.W.

H.F.



Shown at the Ontario Section, Dinner Dance are the following Committee members (l-r): D. S. Wilson (Publications), R. H. Purnell (Treasurer), W. Fibiger (Immediate Past Chairman), S. Patel (Chairman), A. M. Chassels (Programmes), J. Ambury, F. Grootveld, D. Laming (Vice Chairman and Education), A. Gray (Secretary)

## Scottish Section

The Scottish Section Annual Dinner Dance took place in the Albany Hotel, Glasgow, on Friday 11 January, 1980. The evening was once again voted a great success by those attending and to those for whom this was a first time occasion the "piping" in of the haggis was an event to be remembered.

Once again an extremely good attendance was recorded and this helped to make the occasion an event to recall. Thanks must go to Mr T. Humphreys of the Scottish Section for the tremendous effort and hard work which went into the organising of this event.

A photograph of the top table personnel was included on page 180 of the April issue of JOCCA.

W.L.M.

## Manchester Section

### Informal Buffet Dance

Held, as in previous years, at the Royal Air Force Association Club, Oakfield Road, Sale, this year's date was Friday 7 March, and the dancing commenced at 8.00 p.m.

The resident musical trio, The Edelburgers, were absent due to sudden illness and were replaced by the Axis Band, a paradoxically named quartet for an RAF Club, but whose music was excellent. The varied dancing was

interrupted and welcomed by many male members, by the serving of an excellent buffet.

Further dancing was followed by a charitable digression, bottle shaped, which eventually raised £45 for the RAF wings appeal.

Dancing continued until 12.30 a.m. when the 170 members and their guests dispersed homewards by personal and arranged transport. Two Manchester members, Arthur Thornhill and David Clayton, are to be congratulated on the excellent organisation of this successful social event.



The Top Table guests at the Newcastle Section Ladies' Night

# OCCA news

## Obituary

### G. O. H. J. Delorette

It is with a profound sense of grief, that we have to announce the passing away of our friend Jürgen Delorette, Hon. Treasurer OCCA, Transvaal Section, on 9 January this year in Pretoria.

Jürgen, descendant of a Huguenot

family, was born in Berlin 1933, where his father was a well known master painter. It was thus quite natural that Jürgen became a paint chemist, starting his career in Germany in 1951. In 1958 he came to South Africa, working in Durban, where he became a member of OCCA, Natal Section.

In 1965, Jürgen returned for a year to Germany to familiarise himself with the latest methods and instruments for the testing of surface coatings, as this was the field in which he was especially interested. He returned to South Africa in 1966 to join the South African Bureau of Standards, where he worked in this special field in the Paint and Sealant Section.

In 1972, Jürgen became a South African citizen and was very proud to be accepted as a reservist in the South African army in spite of his fragile health.

He served OCCA in the past as Hon. Secretary for the Transvaal Section and was awarded Associateship in Professional Grade in 1972. Due to his heart condition, he had to retire prematurely from work at the end of September last year, but still carried on in his capacity as the Section Treasurer. Jürgen loved nature and the outdoor life, his main hobby being nature photography and it was therefore quite understandable, that South Africa became his adopted country.

Amongst friends and colleagues he was well known for his meticulous work and his typical German "Grundlichkeit"; in short, Jürgen was a real perfectionist. He will be sadly missed and we extend our most heartfelt and sincerest sympathy to his widow Ute, who also works at the SABS in the related section of Rubber and Plastics.

E.S.

# OCCA CONFERENCE 1981

17-20 JUNE 1981 - BEAUFORT HOTEL, BATH

## The venue and format

The ancient city of Bath has been chosen as the venue for the Association's next biennial Conference, which will be held from 17-20 June 1981, with headquarters at the Beaufort Hotel.

In the first century AD Bath was famous as a spa and an internationally important Roman settlement was established on the site. During the eighteenth and nineteenth centuries the remains of the Roman baths were discovered below the city. Today, the Great Bath and the adjoining Circular Bath are major historical attractions.

The theme for the Conference will be "Alternative technologies in coatings" and the technical programme will consist of four sessions, one of which will take the form of a discourse.

A social programme will be arranged for delegates' ladies which will enable them to visit local places of interest, for example the Bath Assembly Rooms. These rooms were designed by John Wood the Younger and built between 1769 and 1771. The Upper Rooms, as they were known, became the scene of continual activity ranging from public breakfasts to grand balls, and were considered to be the finest of their kind in Europe. Johann Strauss, Liszt, Madame Patti, Rubenstein and Charles Dickens were amongst the many artists who performed there in the nineteenth century.

A call for papers to be presented at the Conference is published opposite, and details of papers accepted will be published later in the year.

*Reader Enquiry Service No. 70*

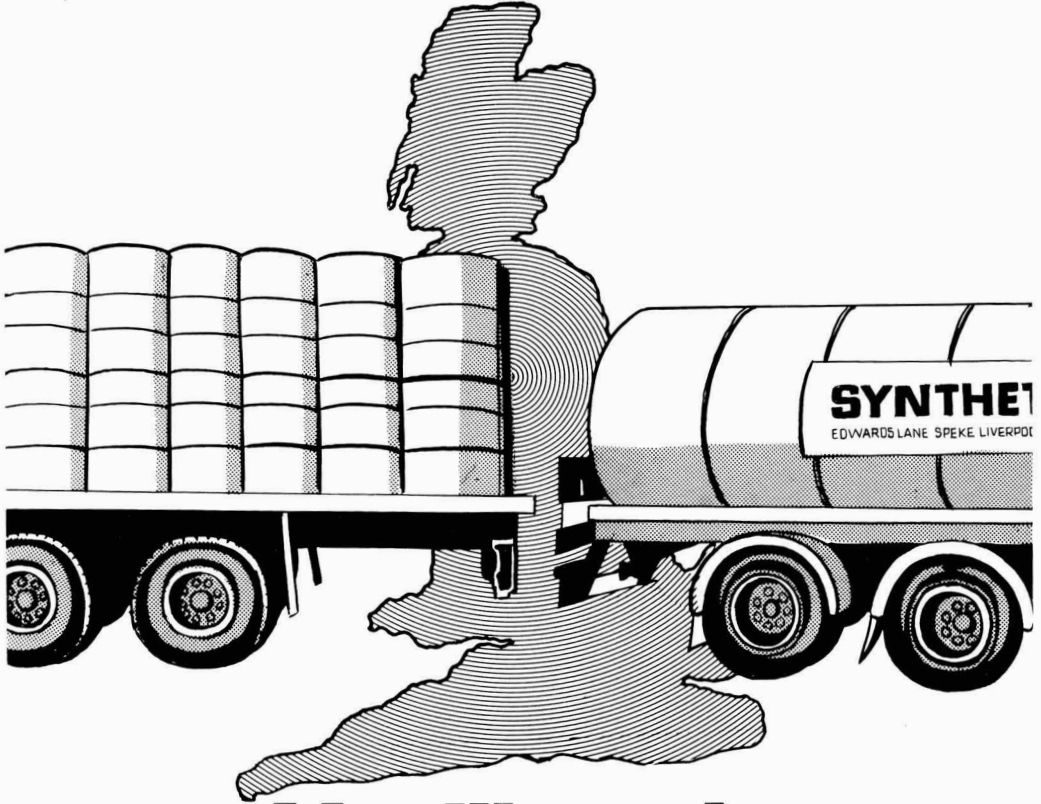
### (Left)

A view of the famous Roman Baths at Bath, which will be the venue for the 1981 Association Conference





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For registration and conference details, plus exhibitor information, contact:

**EUROCHEM 80, 232 Acton Lane,  
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# 80

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Please send me.....Show registration cards .....Conference programmes

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ER7

# OCCA CONFERENCE 1981



## Alternative technologies in coatings

### CALL FOR PAPERS

The next OCCA Biennial Conference will be held at the Beaufort Hotel, Bath from 17 – 20 June 1981 with the theme "Alternative technologies in coatings".

The future holds both opportunity and challenge for alternative technologies and topics covered by the Conference should include, EEC regulations covering the introduction of new chemicals, alternative means of obtaining opacity, the impact of microprocessors and computers on processing and application methods, high solids coatings, aqueous systems, radiation curing and powder coatings.

A departure from the usual conference format will be the inclusion of a "Discourse" session with the sub-title "Alternatives to coatings", where the use of techniques such as cathodic protection and substitution of coated items by plastics could be discussed.

The Hon. Research & Development Officer now invites offers of papers for presentation at this Conference. Anyone wishing to submit a paper for consideration should notify his intention as soon as possible to: **The Director & Secretary, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, England (Tel: 01-908 1086; Telex: 922670 OCCA G).**

# Professional Grade

At a meeting of the Professional Grade Committee held on 2 April 1980, the following Ordinary Members of the Association were admitted to the categories shown. The Section to which each member is attached is shown in brackets.

## new members

### Ordinary Members

BRAIDWOOD, CAMERON 16 Neuk Avenue, Houston, Renfrewshire, Scotland (Scottish)

CLARK, PETER MARTIN, PO Box 32211, Mobeni 4060, Republic of South Africa (Natal)

COOKE, IAIN, BSc, Hoechst (UK) Ltd, Norwich Union House, 17 Lichfield Street, Walsall (Midlands)

DIJKSTRA, MEINDERT, BSc, ICI, 1 Leyds Street, Braamfontein, Republic of South Africa (Transvaal)

DOOLEY, DAVID BRIAN, BTIC, 5 Warren Drive, Greenford, Middlesex, UB6 9ER (Thames Valley)

KAY, RALPH, BSc, PhD, CChem, FRIC, FPRI, 24 Briardene, Margery Lane, Durham DH1 4QU (Newcastle)

KLEBE, ERNST, 7 van Heerden Road, Estera-Germiston, 1407, Republic of South Africa (Transvaal)

MASON, JOHN STRATHMORE, BA, 2 Beckwith Avenue, Harrogate, North Yorkshire HG2 0BW (West Riding)

MAYNARD, NIGEL PAUL, BSc, 68 Kauri Road, Whenuapai, PO Box 1434, Auckland, New Zealand (Auckland)

MOSTERT, BERT IM, BSc, 37 Launceston Road, New Redruth, Alberton 1450, Transvaal, Republic of South Africa (Transvaal)

### Transfer from Associate to Fellow

Poborca, Stefan (Midlands)

### Associates

Kirkwood, Thomas (Scottish)

Thornton, Philip Joseph Martin (Irish)

The following elections to membership have been approved by Council. The Section to which each new Member is attached is given in italics.

NEAL, PETER CHARLES, 17 Ferndale Avenue, London E17 9EH (London)

NORTON, JOHN VICTOR, 34 Deane Avenue, Bolton BL3 5QN, Lancs. (Manchester)

POTTS, RAYMOND, 27 Rowanlea Avenue, Foxbar, Paisley, Scotland (Scottish)

### Associate Members

BREWER, MARK GREGORY, F4/17 Patterson Street, Sandringham, Auckland (Auckland)

ELVIS, ROBERT DAVID, BA, 20 Ann Court, Ellington, Castle Morpeth, Northumberland NE61 5LR (Newcastle)

LANE, LAURENCE GRAHAME, PO Box 788, Bedfordview, 2008, Republic of South Africa (Transvaal)

SHAW, JAMES CHRISTOPHER, 2 Hillfields Close, Congleton, Cheshire CW12 1NW (Manchester)

WOODBURN, DAVID KEITH, 20 Lynwood Grove, Harwood, Bolton, Lancs. BL2 3JZ (Manchester)

### Registered Students

GABRIEL, PHILIP, ICI Organics Division, Research Department, Hexagon Area, Blackney, Manchester (Manchester)

MILNE, SIMON, PO Box 539, Boksburg, 1460, Republic of South Africa (Transvaal)

RICHARDS, TUDOR, 112 Westwood Road, Sutton Coldfield, W. Midlands, B73 6UH (Midlands)

WOOLERTON, KEVIN GERARD, Undergraduate School of Colour Chemistry & Colour Technology, University of Bradford, W. Yorks. BD7 1DP (West Riding)

## occa diary

### May

#### Friday 9 May

Bristol Section: Skittles Match, at BP Chemicals, Stroud. Details to be announced.

Details are given of Association meetings in the United Kingdom and Ireland up to the end of the second month following publication and in other parts of the world up to the end of the third following publication.

#### 13 - 15 May

OCCA-32 Exhibition, at the Cunard International Hotel, Hammersmith, London W6. 09.30 to 17.30 hrs.

### June

#### Wednesday 18 June

'The maintenance and protection against corrosion of North Sea

Structures' by M. Small of Berger (UK) Ltd. Joint meeting with the Institute of Petroleum, London Branch, at 61 New Cavendish Street, London W1 commencing at 6.00 p.m.

#### Thursday 26 June

Association Annual General Meeting, at the Piccadilly Hotel, London N1, commencing at 3.00 p.m., following a luncheon and a lecture by Prof. Sir Herman Bondi on "Energy in the world".

## CLASSIFIED ADVERTISEMENTS

Classified Advertisements are charged at the rate of £4.00 per cm. Advertisements for Situations Wanted are charged at £1.00 per line. A box number is charged at 50p. They should be sent to D. M. Sanders, Assistant Editor, Oil & Colour Chemists' Association, Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF. JOCCA is published EVERY month and Classified Advertisements can be accepted up to at least the 12th, and in exceptional circumstances the 20th of the month preceding publication. Advertisers who wish to arrange for an extension of the copy deadline should contact the Assistant Editor, D. M. Sanders, at the address given above (telephone 01-908 1086, telex 922670 OCCA G).

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## Newcastle Section

**Students seminar on the fundamentals of paint technology (2 binders and paints)**

**Tuesday 9 September 1980**

Following the highly successful seminar last year it has been decided to repeat the venture with a slight change of emphasis, concentrating upon the field of resins and binders. This will allow a more in-depth treatment of the subject matter though the seminar is still intended for junior technologists employed in the paint and allied industries, or for those involved in specialised areas such as production who wish to increase their technical awareness.

The seminar will be held in the James Duff Lecture Theatre which is situated on the science site of the University of Durham.

*Applications should be sent to Mr H. Fuller, BTP Tioxide Limited, Carlton Weathering Station, Yarm Back Lane, Stockton on Tees, Cleveland TS21 1AX*

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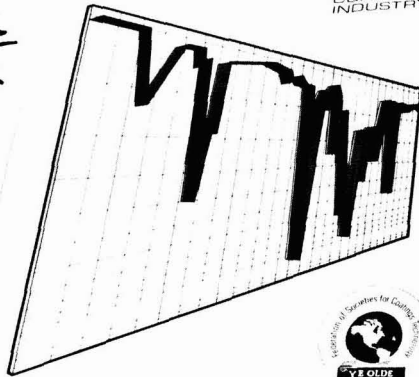
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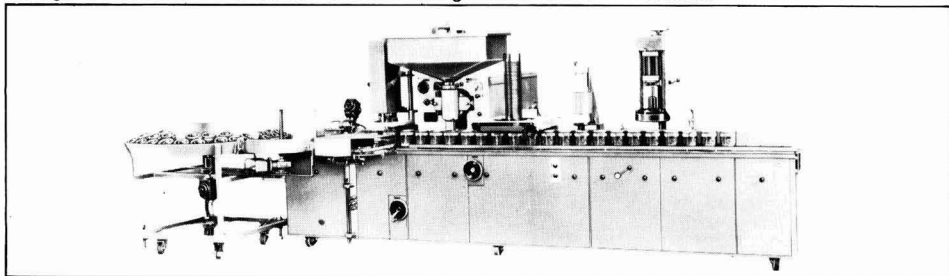
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