

JOURNAL OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION



✓ Vol. 48 No. 6

June 1965

Theoretical aspects of adhesion

A pneumatic micro-indentation apparatus for measuring the hardness of paint coatings

The printability of paper and board

Unreacted isocyanate groups in cured polyurethane lacquers

TECHNICAL REPORT ON OCCA 17

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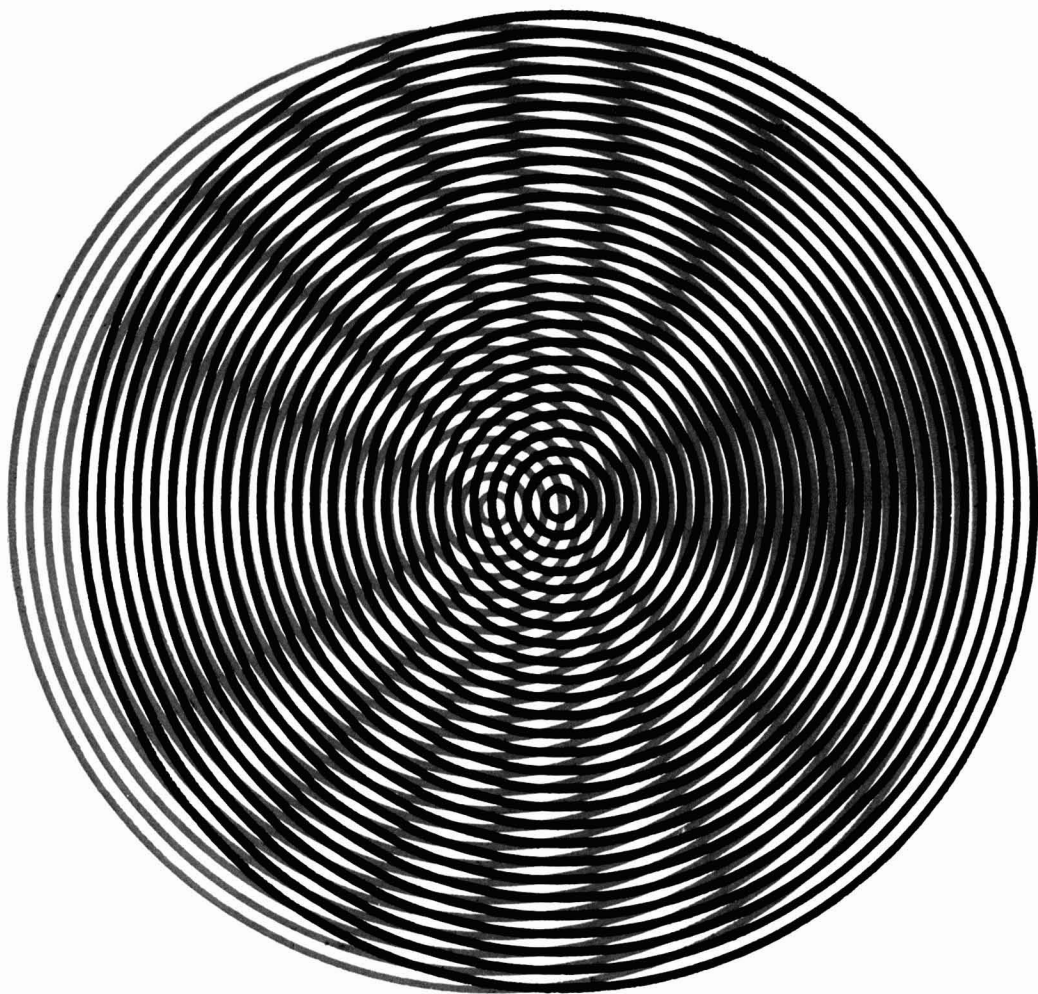
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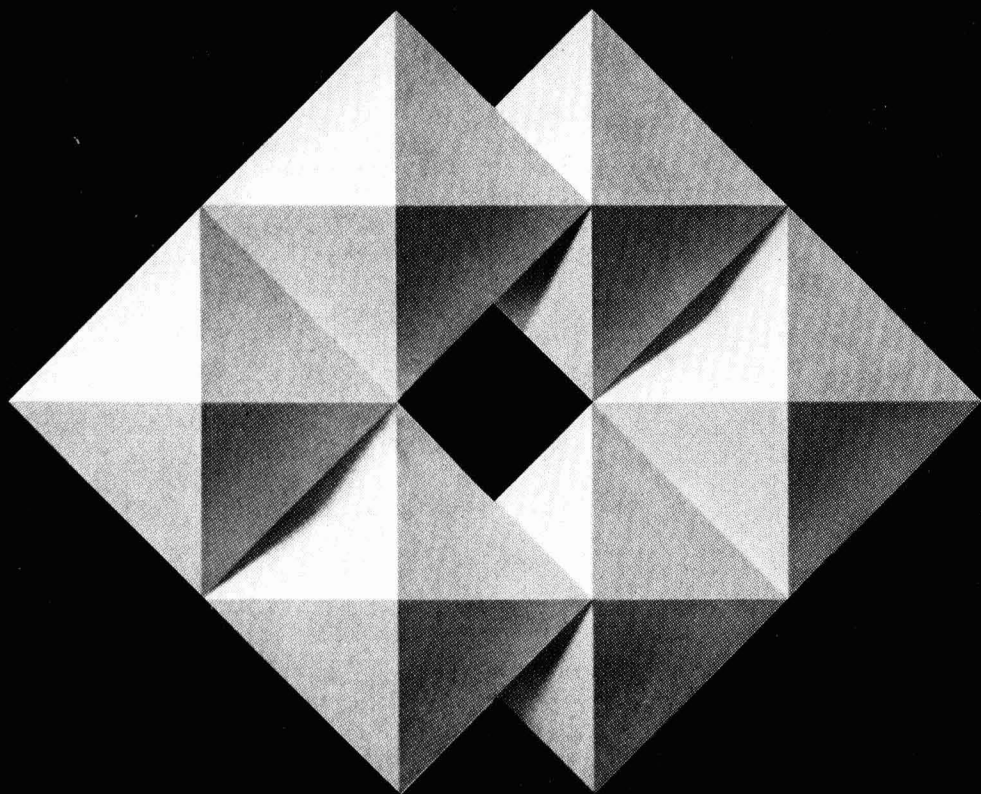
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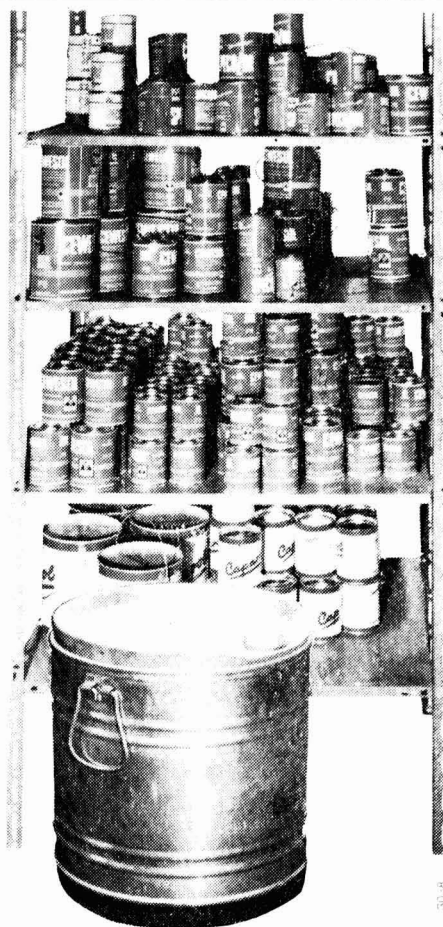
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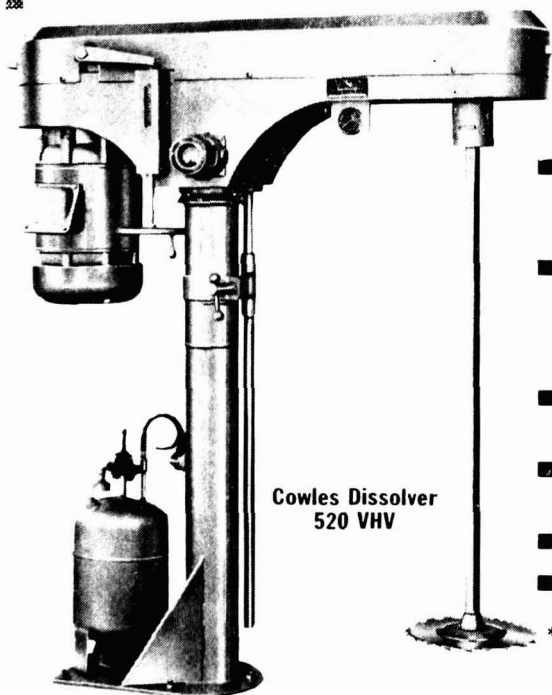
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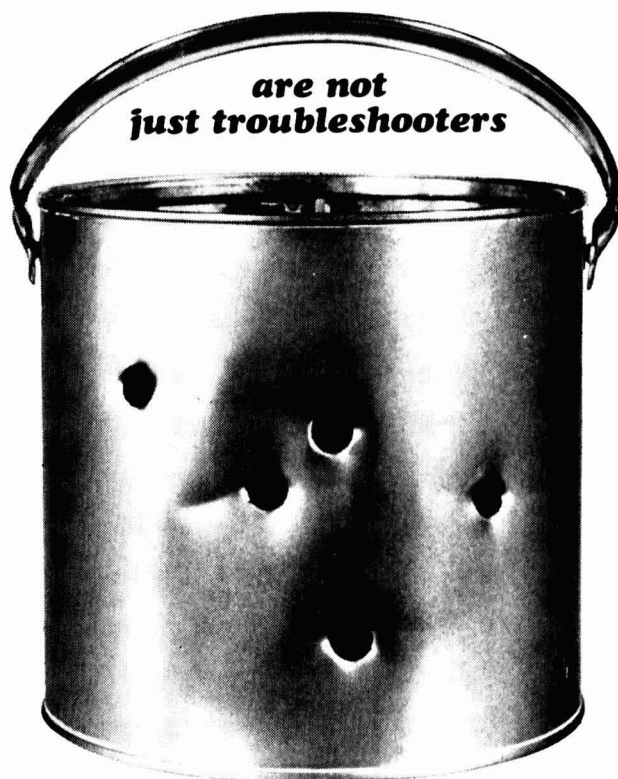
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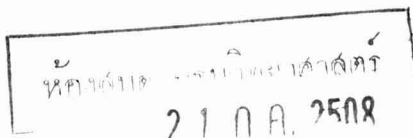
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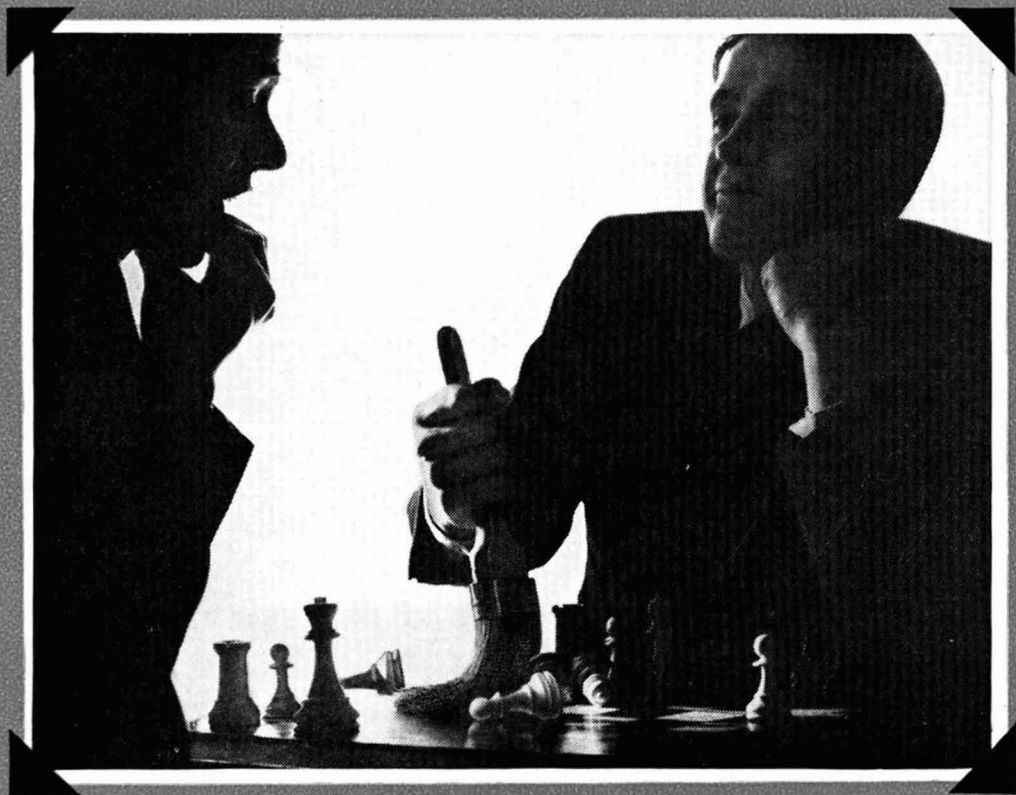
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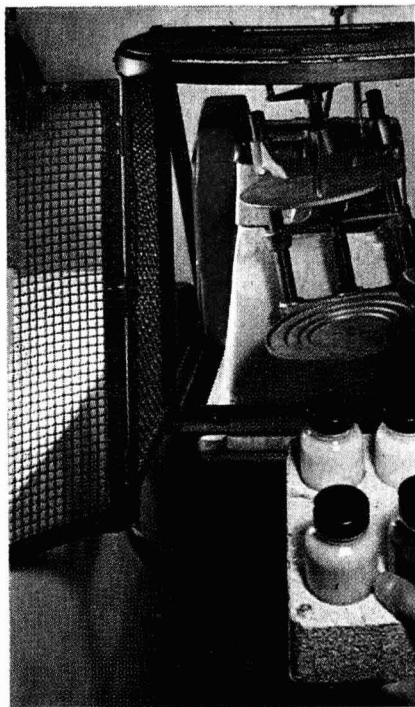


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Theoretical aspects of adhesion*

By W. J. Dunning

Chemistry Department, University of Bristol

Summary

The nature of the intermolecular forces which attract molecules to surfaces is discussed. The concept of thermodynamic adhesion is presented, but practical tests of adhesion reveal its limitations. The discrepancies found emphasise the importance of kinetics in adhesion failure and of the imperfections of present knowledge of kinetics.

Aspects théoriques d'adhésion

Résumé

On décrit la nature des forces intermoléculaires attirant des molécules vers des surfaces. Les essais pratiques de la force d'adhésion révèlent les restrictions du concept thermodynamique présenté.

Les différences entre les résultats pratiques d'une part et les résultats théoriques d'autre part font ressortir l'importance des études cinétiques en expliquant l'affaiblissement d'adhésion et elles soulignent également les imperfections de la connaissance à l'égard de la cinétique.

Haftung von Theoretischen Gesichtspunkten aus betrachtet

Zusammenfassung

Zur Diskussion steht das Problem, welcher Art die zwischenmolekularen Kräfte sind, durch deren Einwirkung Moleküle von Oberflächen angezogen werden. Das Konzept der auf thermodynamischer Grundlage beruhenden Haftung wird dargelegt; praktische Versuche zeigen jedoch, dass dieses Konzept nur in beschränktem Masse gültig ist.

Die aufgedeckten Widersprüche betonen zwar die Bedeutung der Kinetik in Bezug auf Haftungsfehler, zeigen aber auch auf, wie unvollständig diese Fehler mit ihrer Hilfe erklärt werden können.

Introduction

Molecular interaction and adhesion

There are many factors which contribute to the strength of an adhesive joint. One factor of fundamental importance is the interaction of the molecules of adhesive with the surface of the adherend. The forces across the interface originate in the interaction of molecules with each other and such forces may be classified as physical or chemical.

Of the physical interactions, the first to be considered are the London or dispersion forces which operate between any two molecules. These result from the interactions between the random motions of the electrons in the two species. The electrons of either molecule can be visualised as being polarised

* Presented before the Bristol Section, 25 September 1964

by the dipole field resulting from the instantaneous configuration of electrons and nuclei in the other molecule. For two helium atoms the energy of interaction is found to be

$$U_L = - \frac{1.4e^2 a_o^5}{R^6}$$

where e is the electronic charge, a_o is the radius of the Bohr orbit in a hydrogen atom and R is the distance between the atoms. The minus sign indicates that these London forces are attractive. Such forces operate between any molecules whether they are non-polar, polar, ionic or neutral.

When one of the molecules has a permanent dipole moment μ , this induces polarisation in the other molecule. Debye found that the energy of interaction resulting from this effect was :

$$U_{D\alpha} = - \frac{\alpha_2 \mu_1}{R^6}$$

where α_2 is the polarisability of the second molecule.

When both molecules have permanent dipole moments, μ_1 and μ_2 , each dipole endeavours to orient the other dipole against the rotational thermal motion and the energy of interaction in this case therefore depends on the temperature

$$U_{DD} = - \frac{3}{2} \frac{\mu_1^2 \mu_2^2}{KTR^6}$$

Where K = Boltzmann's constant

A special case of dipole-dipole interaction is the hydrogen bond.

When one molecule is an ion and the other a dipole, the energy of interaction is then

$$U_{ID} = - \frac{Ze \mu \cos \theta}{R^2}$$

where Ze is the charge on the ion and θ the angle between the dipole axis and R . It will be noticed that the energy falls off as $1/R^2$, so the forces here are of longer range than have been considered.

For two ions of opposite charge, the energy is inversely proportioned to the distance between them,

$$U_{II} = - \frac{Z_1 Z_2 e^2}{R}$$

and such ionic interactions are of long range.

All the interactions so far mentioned may be described as physical and are to be distinguished from chemical bonding. In chemical bonding the electrons are shared, forming a covalent bond such as obtained when two hydrogen atoms form a hydrogen molecule. When bonding occurs the attractive potential energy is generally much greater than that for physical interactions other than ionic interactions.

The forces so far mentioned are all attractive. As molecules come very close to each other, their electron clouds begin to overlap. Lennard-Jones put forward the expression

$$U_R = \frac{C}{R^{12}}$$

for the repulsive potential energy ; here C is a constant. More generally it is assumed that

$$U_R = C/R^n \text{ or } B \exp (-r/\rho)$$

where $n=5-10$ or B and ρ are constants.

The molecules are thus subject to attractive and repulsive forces, these come to equilibrium when the equilibrium separation is R_0 , at which the net potential energy U as the sum of the attractive and repulsive energies is a minimum (Fig.1).

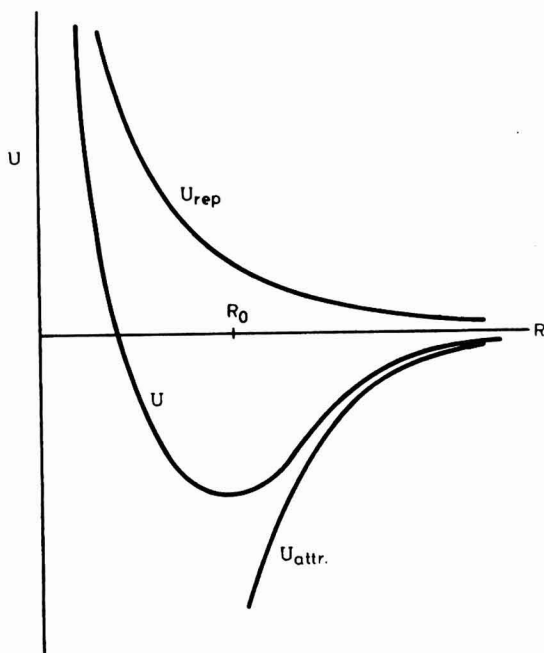


Fig. 1

So far only two molecules in isolation have been considered. In principle, at least, the total energy of interaction between two phases across the interface can be calculated. This is done by summing all the interactions between pairs of molecules (Fig. 2).

If chemical bond formation occurs, the summation is limited to those pairs which are bonded together. In the case where one phase is a metal and the other phase contains ions or dipoles, the polarisation induced in the metal is treated most conveniently as an image of the charge in the surface of the metal and the interaction can be computed accordingly (Fig. 3).

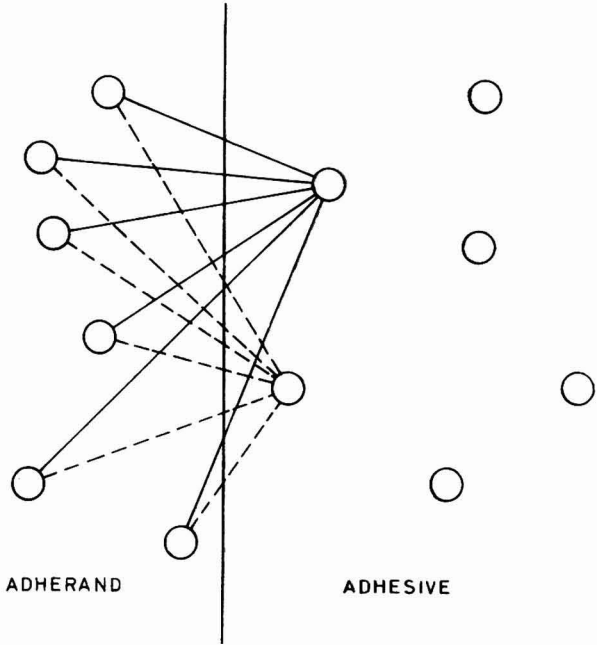


Fig. 2

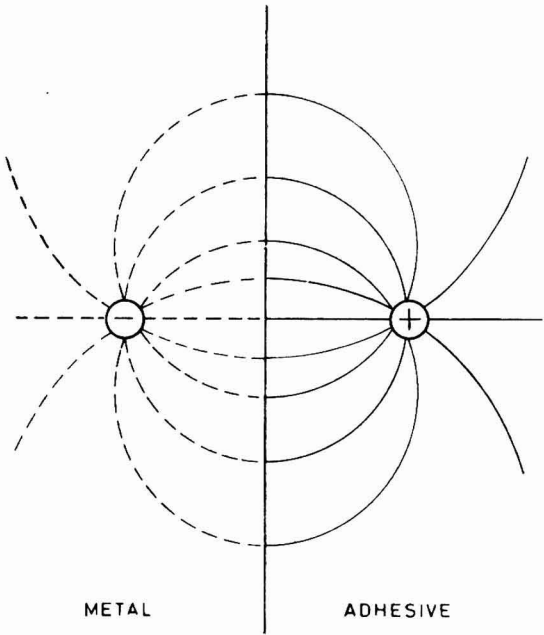


Fig. 3

In all cases, any attempt at calculating the total energy of interaction would require a fairly detailed knowledge of the structure of the interface in terms of the positions and situations of the molecules. This knowledge is very sketchy in most cases, particularly when polymeric material forms one phase.

Thermodynamic aspects of adhesion

To avoid such calculations, it is possible in certain cases to use calorimetric determinations of heats of wetting. This is particularly convenient when one phase is a solid and the other a liquid.

The process of adhesive failure may be represented as



Fig. 4

and the enthalpy of adhesion $h_{A(SL)}$ is the heat absorbed in this process per unit area of interface

$$h_{A(SL)} = h_S + h_L - h_{SL}$$

Here h_S , h_L and h_{SL} , are the enthalpies per unit area of the respective solid or liquid surfaces and the solid-liquid interface. For the liquid, h_L can be obtained from the surface tension γ_L and its temperature coefficient.

$$h_L = \gamma_L - T \left(\frac{d\gamma_L}{dT} \right)$$

The process of emersion may be represented by

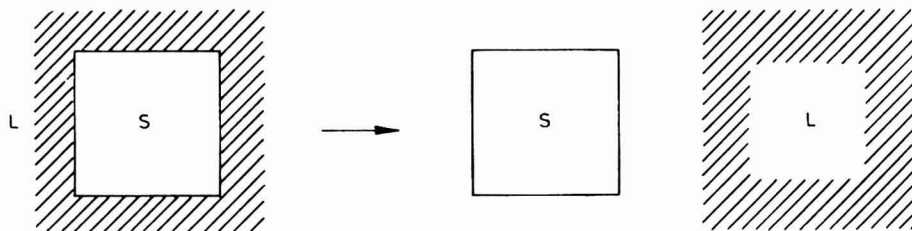


Fig. 5

The heat absorbed per unit area of interface is the enthalpy of emersion, $h_{E(SL)}$. This would be measured by finding the heat of emersion, a process represented by reversing the arrow in the diagram.

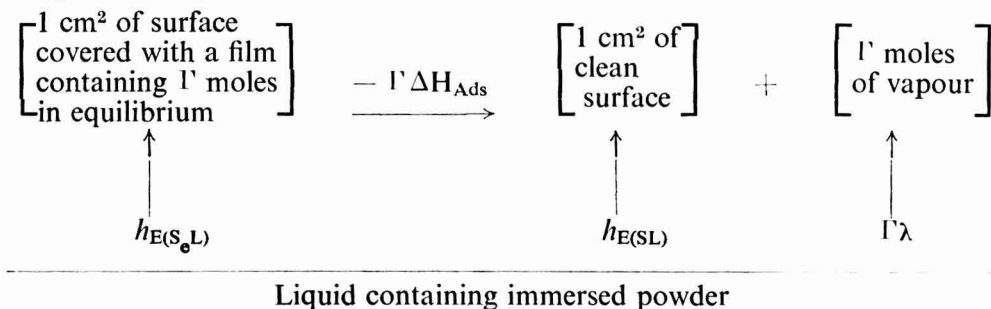
$$h_{E(SL)} = h_S - h_{SL}$$

Thus

$$h_{A(SL)} = h_{E(SL)} + h_L$$

In this way the enthalpy of adhesion has been resolved into two parts each of which may be studied independently.

How this can be done may be seen by considering the following cycle for 1 sq cm of surface.



here λ is the heat of evaporation. It can be seen that

$$h_{E(S_e L)} - \Gamma' \Delta H_{\text{Ads}} = h_{E(SL)} + \Gamma' \lambda$$

or

$$h_{E(S_e L)} - h_{E(SL)} = \Gamma' \Delta H_{\text{Ad}} + \Gamma' \lambda$$

and the relationship of enthalpies of emersion, and thus of adhesion to heats of adsorption is clear. Heats of adsorption may be used to study adhesion problems in suitable cases such as the following.

If E_L and E_G are the internal energies of a molecule in the liquid and in the vapour

$$\lambda = N_0(E_G - E_L)$$

Also

$$\Delta H_{\text{Ads}} = N_0(E_S - E_G)$$

where E_S is the internal energy per molecule in the adsorbed film. Hence

$$h_{E(S_e L)} - h_{E(SL)} = N_S(E_S - E_L)$$

If the angle of contact, θ_e , of the liquid at equilibrium with the film-covered surface is zero, it can be shown that :

$$h_{E(S_e L)} = h_L$$

implying that the outer surface of the film is equivalent in properties at the surface of the liquid and then

$$h_L - h_{E(SL)} = N_S(E_S - E_L)$$

Zettlemoyer has measured the heats of immersion of titanium dioxide in a series of butyl derivatives. For these cases he puts

$$E_S - E_G = E_W + E_\alpha + E_{\text{int}} + F\mu$$

and $E_{\text{int}} = E_L - E_G$. Here E_W is the London dispersion energy, E_α the polarisation energy and $F\mu$ the ion-dipole energy of the butyl derivatives in the electrostatic field of the rutile.

Zettlemoyer found a very good linear relation between his measured $E_S - E_L$ and the dipole moments of the derivatives (Fig. 6).

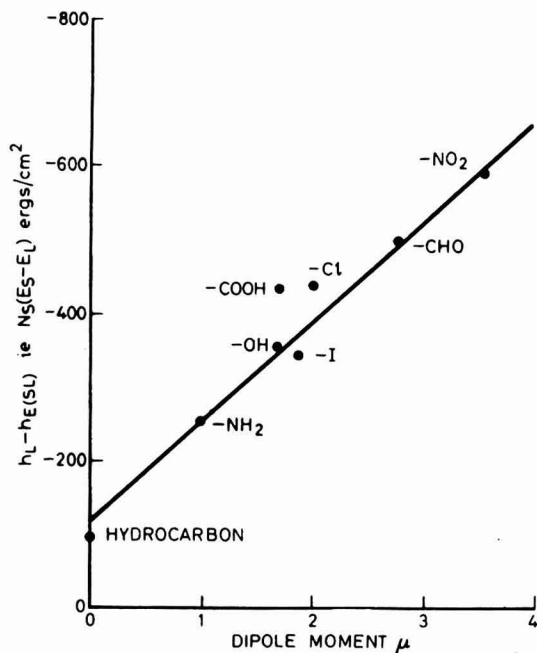


Fig. 6

The slope gives the electrostatic field at the surface of the TiO_2 and the intercept gives $E_W + E_\alpha$. Thus in favourable cases, these interaction energies can be measured.

However, energies may be only part of the problem, entropy changes may be important. In an idealised case of adhesion failure can be represented by Fig. 4 on page 513.

The work done in separating the interface may be called the work of adhesion $W_{A(SL)}$ and

$$W_{A(SL)} = \gamma_S + \gamma_L - \gamma_{SL}$$

where γ_S , γ_L , and γ_{SL} are the solid and liquid surface tensions and the solid-liquid interfacial tension. In this a clean, dry solid surface has been produced. Suppose the process is carried out on the solid surface leaving a thin film of liquid in equilibrium with the vapour

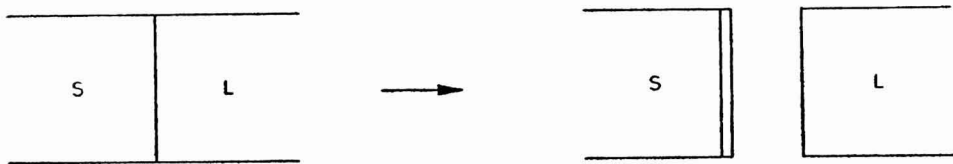


Fig. 7

The work of adhesion is now different and may be designated $W_{A(S_eL)}$ and

$$W_{A(S_eL)} = \gamma_{Se} + \gamma_L - \gamma_{SL}$$

with

$$W_{A(SL)} - W_{A(S_eL)} = \gamma_S - \gamma_{Se} - \varphi_e$$

where φ_e is the equilibrium spreading pressure of the film.

Using the Young-Dupré equation for the angle of contact

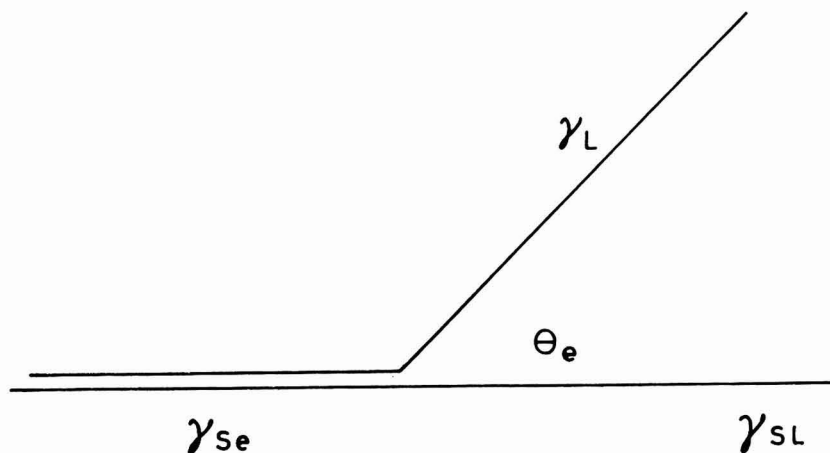


Fig. 8

$$\gamma_{Se} = \gamma_{SL} + \gamma_L (1 + \cos \theta_e)$$

whence

$$W_{A(S_eL)} = \gamma_L (1 + \cos \theta_e)$$

$$W_{A(SL)} = \varphi_e + \gamma_L (1 + \cos \theta_e)$$

Thus the work required to rupture the interface leaving the solid surface clean is greater by φ_e than the work done when the solid surface retains an equilibrium film. The difference is substantial; for n-heptane on iron $W_{A(S_eL)} = 40$ erg cm⁻², $W_{A(SL)} = 93$ ergs cm⁻². This suggests that in the ideal case rupture will occur leaving a film of adhesive.

The work of adhesion $W_{A(S_eL)}$ shows a relation with the dipole moment and polarisation

Hg/paraffins	~ 120 erg/cm ²
Aromatic hydrocarbons ..	150
Primary alcohols ..	130-160
Undecylenic acids ..	150
Bromides, iodides ..	190-213

Kinetic aspects of adhesion

Let it be assumed that the forces acting across the interface operate over a short distance say 3×10^{-8} cm. Then for n-heptane on iron

$$F = \frac{W_{A(S_e L)}}{3 \times 10^{-8}} = \frac{40 \text{ ergs}}{3 \times 10^{-8} \text{ cm}}$$

$$\sim 8 \text{ tons per sq in}$$

This is much greater than the failing loads found in practice. For example, for polythene-steel a tensile failing load of 1.16 tons/in² has been reported. It is clear that the ordinary forces of cohesion are more than adequate to account for the tensile failing load of a joint.

The discrepancy between theory and practice of an order of magnitude is of utmost significance. It leads to re-examination of the kinetic processes involved in joint failure. Suppose it is possible to apply a tensile stress uniformly over the whole interface. It has been assumed that at failure all atoms on one side of the interface move uniformly and synchronously away from those on the other side, as illustrated suggestively by

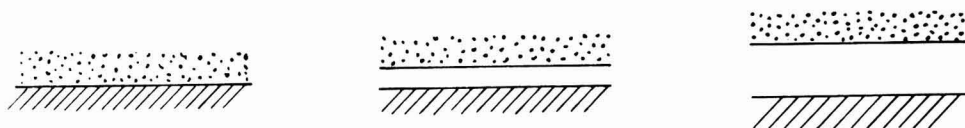


Fig. 9

This would only be possible at absolute zero. At higher temperatures, fluctuations in the relative positions of molecules would, by chance, form a small crack nucleus which would then rapidly grow in size under the stress. The

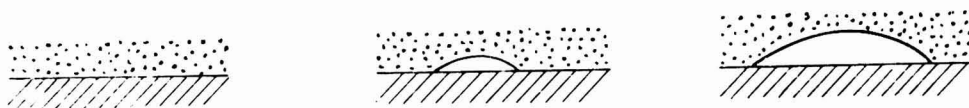


Fig. 10

nucleus would act as a point of weakness from which the interface is torn apart.

The free energy of formation of such a nucleus is ΔG^* where

$$\Delta G^* = \frac{\omega^2 E^2}{48 \sigma^4} \cdot W_A^3(S_e L)$$

here ω is a shape factor $\sim 2\pi$, and E is Young's modulus. The probability of rupture would then be proportional to

$$\exp(-\Delta G^*/KT)$$

Such a theory predicts that the probability of rupture at different interfaces would be the same when the normal stress σ satisfies

$$\sigma \propto [W_{A(S_e L)}]^{\frac{1}{3}}$$

Experiments have been done to test this theory but the results are irregular and erratic. That they are erratic suggests that adhesion failure is structure sensitive. This means that small irregularities or imperfections of the interface may

catalyse the nucleation of cracks. These imperfections may be of many sorts, small patches which are not wet as well as the rest of the surface, small pits which have not been filled completely with adhesive.

Suppose there is a small penny-shaped crack at the interface. Here there is a ready made nucleus and it is not dependant on fluctuations creating one. This crack may have happened in a number of ways, for example, from a speck of dirt, from chemical action, or by adsorption at the interface of plasticiser.

When a tensile stress σ is applied uniformly and normal to the plane of the crack

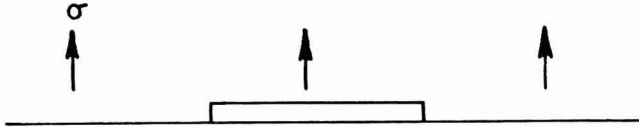


Fig. 11

the stress is concentrated in the neighbourhood of the periphery of the crack. Calculation shows that in order for the crack to propagate, the applied stress must reach a critical value given by

$$\sigma_{\text{crit}} = \sqrt{\frac{\pi E (W_{\text{ASL}})}{2 r (1 - \nu^2)}}$$

where r is the radius of the crack and ν is Poisson's ratio. If the crack is covered with an equilibrium film when $W_{\text{A}(\text{S}_\text{eL})}$ must be used and σ_{crit} will be smaller. Very often the crack will start at the interface and on extension will leave it to form a crack within the adhesive

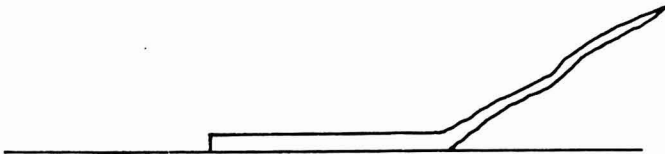


Fig. 12

This will happen since $W_{\text{A}(\text{SL})} > 2\gamma_{\text{L}}$

Only normal stresses have been considered so far. An adhesive joint must also resist shear stresses. The course of the energy curve for a molecule moving across the surface will appear like a series of

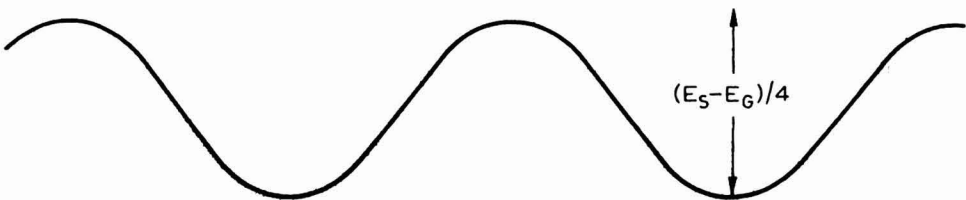


Fig. 13

peaks and troughs. Roughly the energy barrier for movement across a surface is only one quarter of the energy to remove the molecule from the surface. This implies on simple thinking that it should be easier to break a joint by shear than by tension normal to the surface. But it can be seen for normal tensions that it is unlikely that all bonds are ruptured simultaneously but that bonds break one after the other. In the same way it is unlikely that shearing failure will take place by all atoms on one side of the interface sliding in unison up and down the barrier

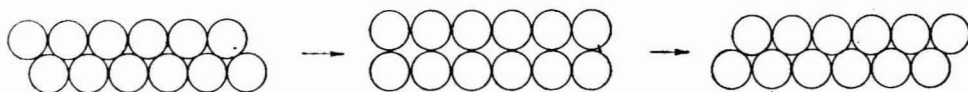


Fig. 14

The shear is more likely to take place by the movement of a dislocation.



Fig. 15

In this case the height of the barrier to movement will be less since the top layer moves like a caterpillar over the surface. Strength will now be conferred by placing obstacles in the path of the motion, surface irregularities and chemical bonds would be examples of these.

Conclusion

In conclusion it will be clear that the problem of adhesion is by no means solved. It seems that attention is moving away from thermodynamic consideration of adhesion towards considerations of the kinetics of adhesive failure and of stress concentrations at cracks and imperfections.

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A pneumatic micro-indentation apparatus for measuring the hardness of paint coatings

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Summary

This paper describes the design and construction of an improved form of micro-indentation apparatus for measuring the hardness of paint coatings. The depth of penetration of a ball ended needle under the application of a constant load is recorded as a function of time. The recovery subsequent to load removal can also be recorded. Provision is made for the temperature of the specimen to be varied from -20°C to 90°C . Results obtained with the apparatus are useful in determining the rheological state of the specimen and in following changes caused by ageing and weathering.

Un appareil pneumatique destiné à mesurer par micro-indentation la dureté des revêtements de peinture

Résumé

Cet exposé décrit le dessein ainsi que la construction d'un modèle perfectionné d'appareil à mesurer la dureté des revêtements de peinture. La profondeur de pénétration d'une aiguille à bout de bille sous l'application d'une charge constante est enregistré comme fonction de temps. On peut mesurer également la récupération du revêtement après l'enlèvement de la charge. On dispose de la possibilité de faire varier la température de l'éprouvette entre -20°C et 90°C . Les résultats que l'on obtient à l'aide de l'appareil sont utiles à déterminer l'état rhéologique de l'éprouvette et aussi à suivre les changements produits par le processus de vieillissement et par l'action des intempéries.

Pneumatisch Arbeitendes Mikro-Eindrucktiefen-Messgerät zur Bestimmung der Härte von Anstrichfilmen

Zusammenfassung

Plan und Konstruktion einer verbesserten Ausführung eines Mikro-Eindrucktiefen-Messgerätes für das Messen der Härte von Anstrichfilmen werden besprochen. Die Eindringungstiefe unter gleichbleibender Belastung von einer Nadel, an deren Ende sich eine Kugel befindet, wird als Funktion der Zeit registriert.

Die Rückbildung nach Entfernung des Gewichtes kann ebenfalls registriert werden. Vorkehrungen wurden getroffen, um die Temperatur der Probe zwischen -20 und 90°C variieren zu können. Die mit diesem Apparat erhältlichen Ergebnisse sind sowohl von Nutzen zur Bestimmung des rheologischen Zustandes der Probe, als auch um die Veränderungen zu verfolgen, die bei Alterung und Verwitterung vor sich gehen.

Introduction

The measurement of indentation hardness has been used for some considerable time in these laboratories as a method of assessing the mechanical properties of paint coatings. The method has the advantage over tensile testing on free films in avoiding the need to detach the coating from its substrate and thus allowing a much wider range of samples to be tested. Measurements were made originally with the Wallace micro-indentation tester¹, an instrument developed

for the rubber industry, but its usefulness was limited by the fact that it was being used at the limit of its sensitivity. The Wallace tester has now been largely replaced by the apparatus described herein, which is more sensitive and has the additional features of self-recording and easy temperature control.

Discussion

Basically the test consists of measuring either the depth to which a loaded "point" penetrates the sample or, alternatively, the size of the imprint left after the test has been carried out. The imprint method is, however, limited in scope by the fact that paint coatings have considerable powers of recovery. For this reason, measurement of the actual depth of penetration is favoured for tests on paint coatings, since this brings the possibility of measuring not only the total deformation under load but also the recovery when the load is removed. These measurements, particularly when obtained over a range of temperature, can give valuable information about the rheological state of the coating.

Two instruments of this kind have been used for measurements on paint, the Wallace instrument and the one described by Hoekstra and Van Laar². Both of these work on a similar principle using a combination of a mechanical micrometer and an electronic null point detector for measurement of the penetration. The Hoekstra and Van Laar instrument is considerably more sensitive than the other, but neither is adapted for recording. Other indentation apparatus used mainly in conjunction with metal testing have been described^{3, 4}.

When measuring penetrations into surface coatings, it is essential to avoid undue interference from the substrate; the total depth of penetration must be considerably less than the thickness of the coating. The limiting value that is acceptable is a function of the size and shape of the indenter and the coating thickness. For the range of spherical indenters used with this instrument a maximum indentation of 6μ was taken to be a reasonable compromise. Spherical indenters have been adopted because accurate spheres are easily available in a wide range of sizes and materials as ball bearings and the styli used with record players.

Continuous recording on paper chart of the indentation and recovery as a function of time has the considerable advantage that not only is the shape of the curve obtained meaningful, but also any instrumental or operating fault diagnosed more readily.

Paint coatings encounter a wide range of temperatures and this dictates the need for a method of rapidly varying the temperature of the specimen under test from -10°C to $+50^{\circ}\text{C}$ and sometimes beyond. Temperature control of small coated specimens can be conveniently obtained by use of a temperature-controlled stage, and the provision of suitable heating and cooling has been greatly facilitated by the availability of the compact semi-conductor devices known as *Frigistors*. Since the lower part of the temperature scale is below the dew point of the normal laboratory atmosphere, it is necessary to lower the humidity in the neighbourhood of the apparatus to avoid interference from deposits of water or frost. Current practice in these laboratories is to enclose the apparatus in a glove box and reduce the humidity to a low value with desiccants. Control of humidity at other levels has not yet been attempted.

The measurement of the small penetrations encountered in this work can be carried out by either pneumatic or electronic methods ; both have advantages and disadvantages. The advantages of a pneumatic system are that the apparatus is simpler and cheaper than an electronic one and if necessary can be used in areas of fire hazard. The electronic method is more expensive, but has the advantage that it is easier to provide range switching. The pneumatic instrument described in this paper has worked reliably for some years, but in order to cope with the very wide range of specimens encountered an electronic version is being developed.

The system of measurement used in the instrument is one used extensively in pneumatic control equipment. The primary displacement, in this case of the indenter needle, alters the gap between a flat plate (the flapper) and a small nozzle fed with a restricted air supply. The changes in pressure resulting from these movements are amplified and applied to a pneumatic recorder.

Construction

Mechanical construction

The basic instrument is shown in Fig. 1. The main chassis is a triangular shaped piece of steel plate *A*, $\frac{1}{2}$ in in thickness and 14 in long, which is supported from the base-plate *B* by means of three adjustable legs *C*, *D* and *E*. The legs *C* and *D* form the coarse and fine adjustments for raising and lowering the top plate *A* ; this is the zeroing adjustment of the instrument. The leg *C* has a single screw thread of 20 threads per inch (tpi), but *D* has a differential screw thread of 26 and 28 tpi, so that one revolution of the knurled wheel gives a movement of 20 microns at the specimen. This wheel is divided into 0.5 μ divisions and can be used for calibrating the instrument.

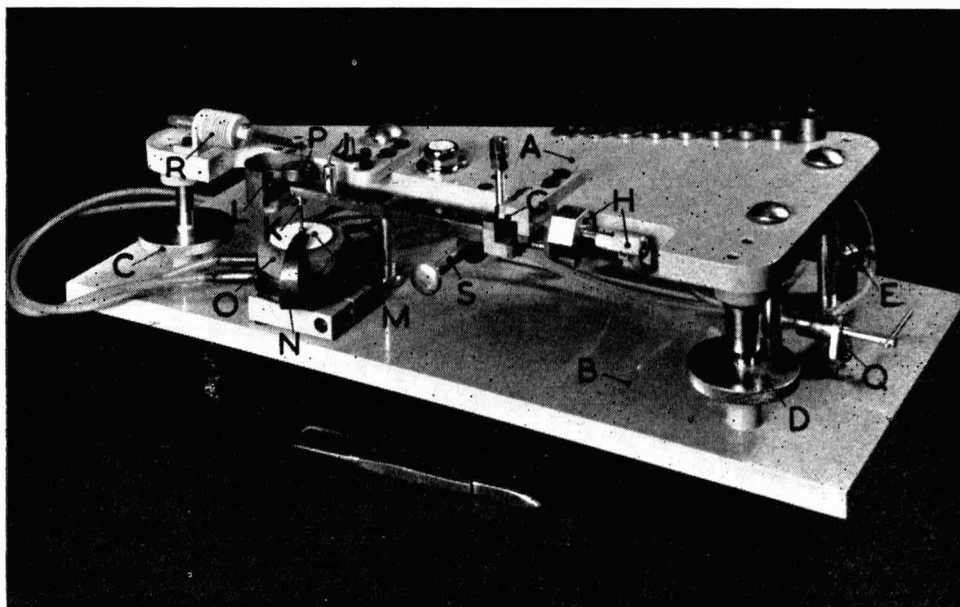


Fig. 1. The front view of the micro-indentation apparatus

The beam F is mounted on crossed flexure bearings G^5 which are made of $\frac{1}{4} \text{ in} \times 0.010 \text{ in}$ brass strip. At one end of the beam are the adjustable counter-balance weights H and at the other are the oil dash pot J , the indenter needle K and the flapper L of the flapper/nozzle system.

The specimen M is held down by a spring N on to a *Frigistor* unit O . The *Frigistor* unit⁶ is a Peltier effect device which can bring the specimen to any temperature between -20°C and 90°C in a few minutes. It requires a supply of cold water of 1 litre per minute and a low voltage DC electrical supply with a controllable output of 0-15 amp.

In operation the weight P is lowered on to the beam F pneumatically by means of the tap Q and the bellows system R^7 . A series of weights in the range 1-20 g is used with the instrument. The beam is released by turning the locking knob S .

The pneumatic measuring and recording system

The pneumatic system of the instrument is shown in the schematic diagram (Fig. 2). A supply of clean air at 20 psi enters the system at A and the proximity of the flapper B to the nozzle C determines the pressure developed in the bellows D . This operates the flapper E of a single stage amplifier with negative feed-back. The proximity of the flapper E to the nozzle F determines the pressure in the bellows G and at the recorder diaphragm H . Expansion of the bellows G by increasing pressure bends the beam J and tends to increase the separation

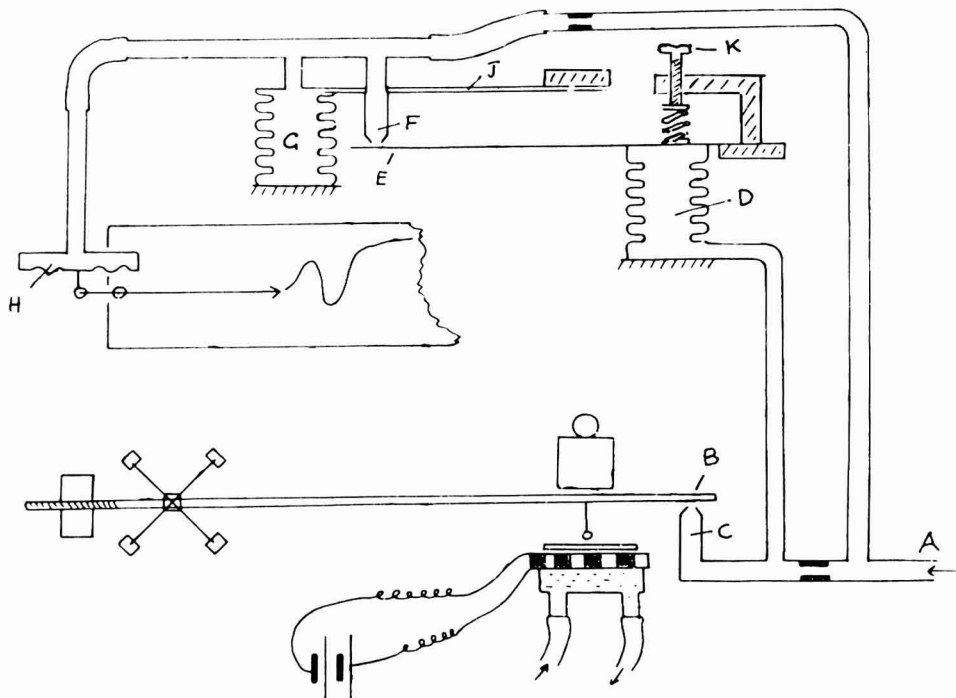


Fig. 2. A schematic diagram of the apparatus

of *E* and *F*. This applies the negative feed-back to the second stage which reduces the gain, but improves the linearity and stability of the output. The amount of negative feed-back is determined mainly by the flexibility of the beam *J*. The recorder *H* is a 0-15 psi strip chart air pressure recorder.

With this system an indenter needle movement of 6μ gives a full scale deflection on the recorder. The sensitivity of the instrument is mainly determined by the working conditions at the first stage flapper/nozzle and the amount of negative feed-back applied to the second stage. An adjustment for sensitivity is provided by the screw *K* which controls the mean separation of *E* and *F*. The amplification is sufficiently linear over the major part of the scale for most applications and a calibration graph is shown in Fig. 3.

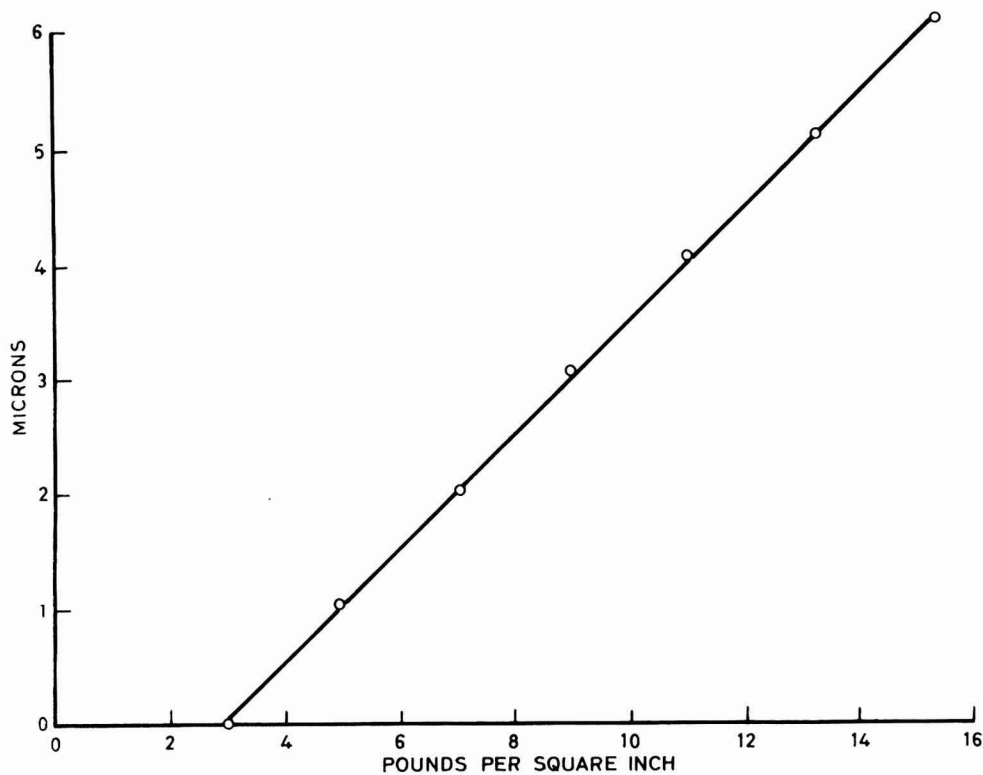


Fig. 3. The calibration graph

Fig. 4 shows the mechanical arrangement of the amplifier and carries the same letter coding as Fig. 2.

The complete apparatus is shown in Fig. 5. The instrument *A* is normally housed in a glove box so that it can be operated under conditions of low humidity. The recorder *B* is an *Arkon* 0-15 psi recorder. *C* is the power supply for the *Frigistor* unit and *D* is the Cambridge pyrometer (-50°C to $+100^{\circ}\text{C}$) for indicating the temperature of the specimen by means of a thermocouple.

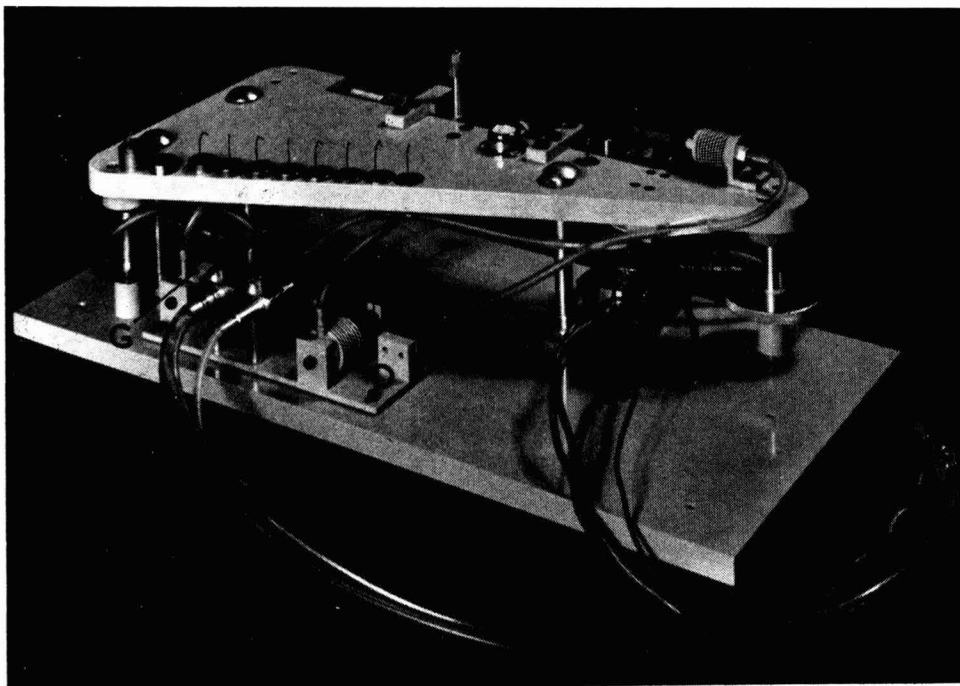


Fig. 4. The rear view of the apparatus

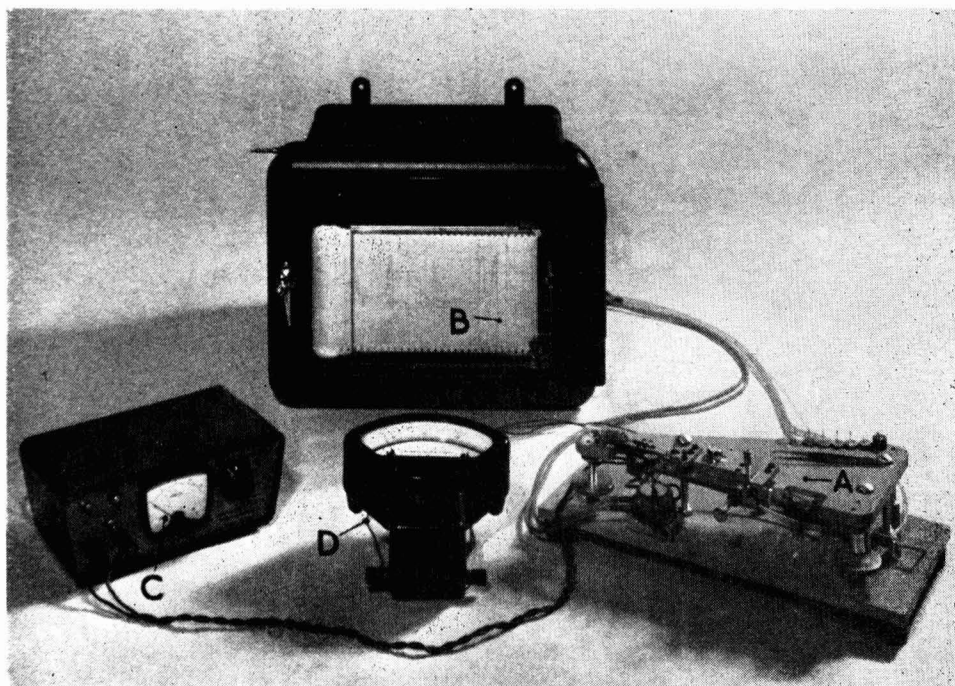


Fig. 5. The complete apparatus

Operation of the instrument

According to the estimated hardness of the specimen a suitable indenter needle is chosen and fitted to the instrument. The needles have spherical ends of steel or sapphire and vary from 0.0025 in to 0.063 in radius. The beam is unlocked and then balanced by means of the counter-balance weights. The specimen is fixed to the specimen holder and allowed to come to equilibrium for temperature and humidity. The beam is then lowered by the adjusting screws until the indenter needle makes contact with the specimen. This applies a small load of approximately 0.1 g to the specimen and opens the flapper/nozzle system. Suitable adjustment is made to the adjusting screws *C* and *D* until the recorder indicates 3 psi; this is the minor load base line. The recorder chart drive is then switched on and the load weight lowered on to the beam. Penetration is allowed to take place for some minutes or until equilibrium conditions are obtained. The load weight is then removed and the specimen is allowed to recover. The operation can be repeated at various temperatures.

Results

The instrument has been used for the investigation of the mechanical properties of many different paint compositions and some typical results are given below.

Fig. 6 shows indentation and recovery curves selected to illustrate the range of rheological states encountered in practice; (A) is a plastic film and shows no

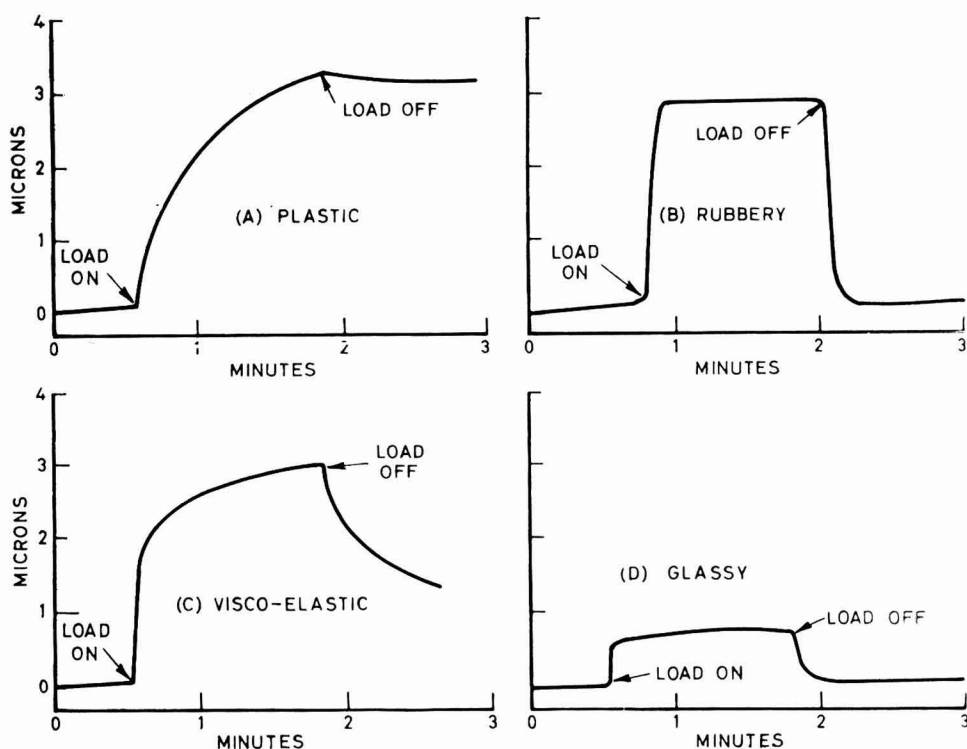


Fig. 6. Some typical indentation and recovery curves

recovery when the load is removed ; (B) is a rubbery film and shows rapid and complete recovery ; (C) is a visco-elastic film and the penetration curve shows the time dependence of the deformation ; the recovery in this case is not completed during the time of the experiment. (D) is a film in the glassy state where the penetration is much less but the recovery is rapid and complete.

Fig. 7 shows penetration curves for an air-drying alkyd finish tested at different temperatures. At the highest temperature (80°C) the film is almost completely plastic, at 40°C it is approaching a rubbery state, while at the lower temperatures the film is visco-elastic.

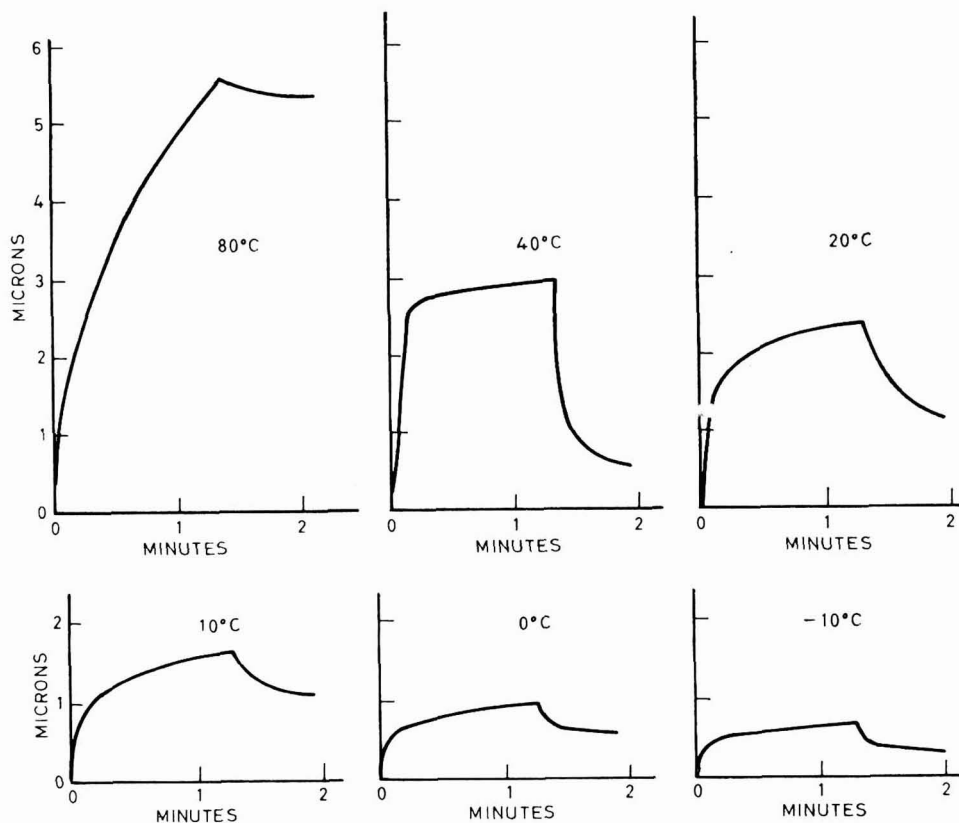


Fig. 7. Graphs showing penetration curves for an air-drying alkyd finish at different temperatures. The load weight was 6g and the indenter radius 0.008 in.

Fig. 8 shows the effect of accelerated weathering on an air-drying alkyd finish. Up to one month the film is visco-elastic at 15°C but steadily increasing in hardness. At two months the film has become very much harder and is approaching the glassy state. In this particular series the range of hardness is so large that increasing loads have been used to give easily measurable readings as the paint hardens.

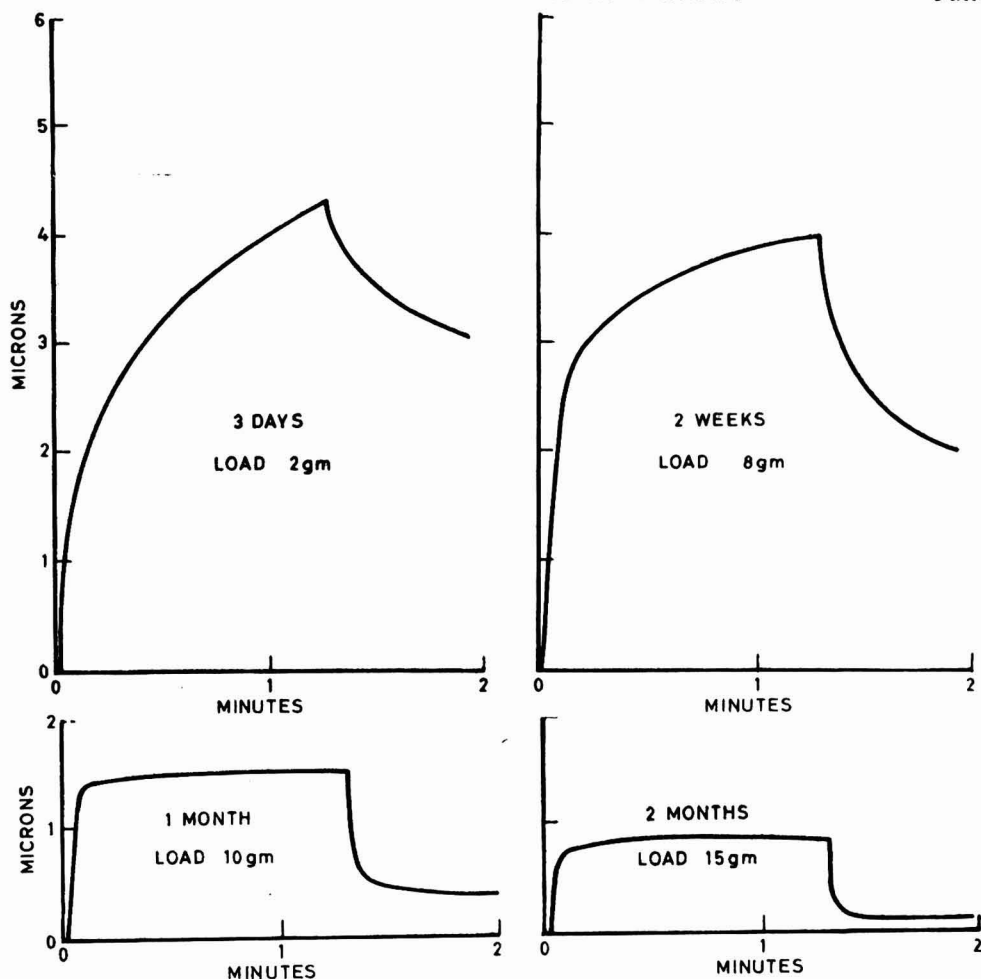


Fig. 8. Graphs showing the penetration curves for an air-drying alkyd finish subjected to accelerated weathering. The indenter radius was 0.008 in. and the test was carried out at 15 C

Acknowledgments

The authors wish to thank Dr. M. L. Steel for her enthusiastic assistance in the development of the instrument and for providing the experimental results given in this paper. Thanks are also due to Mr. N. D. P. Smith for his advice on theoretical matters and to Mr. P. G. Gordon who made the instrument described.

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The printability of paper and board*

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Summary

A large number of test procedures, mainly empirical, is available for predicting the printability of papers and boards. This paper deals in detail with three test procedures, founded on basic research, where recent work has shown the underlying principles of these ink/paper relationships. The properties investigated are surface strength, oil absorbency, and surface smoothness.

It has been shown that the stress imposed by an ink on the paper surface at separation is not due to viscosity, but tack. A method of tack measurement is outlined. Oil absorption into paper can be described by the classical physical laws for capillary penetration into porous solids. A method of test based on these principles is described, from which an absorption coefficient can be derived. An average smoothness figure, as given by the normal testers, does not adequately describe the printing behaviour of paper. To predict this behaviour it is necessary to measure pit-size distributions. A parameter from these distribution curves correlates well with gravure printability.

L'Imprimabilité de papier et de Carton

Résumé

Il existe un grand nombre d'essais, en général empirique, destiné à indiquer l'imprimabilité des papiers et des cartons. Ce texte traite en détail trois modes d'essai basés sur des recherches fondamentales, où des investigations récentes ont démontré les principes essentiels des rapports entre l'encre et le papier. On a examiné les propriétés suivantes du papier : la résistance et le lisse de sa surface ; sa prise d'huile.

On a montré que l'effort imposé—a l'instant de leur séparation—par le film d'encre sur la surface de papier n'est pas dû à sa viscosité, mais plutôt à sa nature collante. Une méthode à mesurer cette propriété de l'encre est établie. On peut décrire l'absorption d'huile par une couche de papier grâce aux lois classiques de la physique concernant la pénétration capillaire aux solides poreux. Un mode d'essai basé sur ces principes est proposé dont on peut dériver un coefficient d'absorption. Une cote moyenne de lisse—telle que donnent les appareils normales d'essai—ne décrit pas suffisamment le comportement du papier vers l'impression. Afin de le déterminer, on doit mesurer la répartition des dimensions de piqûres sur la surface du papier. Un paramètre dérivé des courbes de répartition est en bonne corrélation avec l'imprimabilité photogravurique.

Die Eignung von Papieren und Pappen zum Bedrucken

Zusammenfassung

Es gibt bereits eine grosse Zahl hauptsächlich auf praktischer Erfahrung beruhender Prüfverfahren, um die Eignung von Papieren und Pappen zum Bedrucken vorauszubestimmen. Die vorliegende Abhandlung befasst sich ausführlich mit drei Prüfmethode, die sich auf grundsätzliche Forschungsarbeiten stützen, mit deren Hilfe neuerdings die den Beziehungen von Druckfarbe und Papier zu Grunde liegenden Prinzipien aufgezeigt werden konnten. Untersucht wurden die folgenden Eigenschaften : Festigkeit der Oberfläche, Ölabsorption und Oberflächenrauheit.

*Presented before the Bristol Section on 30 October 1964

Es hat sich herausgestellt, dass der Zug, der von einer Druckfarbe im Moment der Trennung von der Paperoberfläche ausgeübt wird, nicht die Folge ihrer Viskosität, sondern des Klebgrades ist. Eine Methode wird umrissen den Klebgrad zu messen. Die Aufsaugung von Öl in das Papier kann mit Hilfe der klassischen, physikalischen Gesetze, die für kapillares Eindringen in poröse Festkörper gelten, erklärt werden. Es wird eine Prüfmethode beschrieben, die auf diesen Prinzipien beruht, mit deren Hilfe ein Absorptionskoeffizient abgeleitet werden kann. Ein mittels der üblichen Prüfgeräte erhaltener Durchschnittswert für die Rauheit von Papier gibt keine genügende Auskunft über das Verhalten beim Bedrucken. Um dieses Verhalten voraussagen zu können, ist es notwendig die Streuung der Grössengruppen der Rillen zu messen. Ein Parameter dieser Verteilungskurven stimmt mit der Bedruckbarkeit im Tiefdruckverfahren gut überein.

Introduction

The three main printing processes are letterpress, offset lithography and gravure. Because of their different methods of ink application to paper and board surfaces, different physical and chemical properties are required of these materials. For example, smoothness is far more important for gravure papers than for those used in offset lithography ; a strong surface is needed for offset paper to resist the pull of the tacky ink as it parts from the rubber blanket, whereas the low viscosity, solvent-based gravure inks exert little stress on the paper.

Rather than run through the whole gamut of printability tests, which has been done many times before, this paper will deal in detail with three areas of testing where recent research has added greatly to previous knowledge.

Picking

In offset lithography an image in a very tacky ink is offset from a flat plate to a rubber blanket and thence transferred to paper. When paper and blanket separate the force exerted on the paper surface is often greater than its surface strength. When this occurs particles of the coating layer are picked out, adhere to the blanket and produce defective prints.

It has been reported in the literature^{1, 2} that there is a simple relationship between the viscosity of a liquid and the critical printing velocity at which pick begins ; the so-called viscosity/velocity product (VVP) is constant for a given paper, being only slightly dependent on impression pressure and ink film thickness. The generally accepted (IGT) method of testing papers for picking tendency is based on this principle.

The IGT tester consists basically of two units. One is an ink distribution system, the other an apparatus for applying ink to paper under controlled conditions (Fig. 1). A given quantity of oil of known viscosity is metered on to the ink distribution system and run until it is evenly distributed over it. A thin film of oil is transferred to a small aluminium disc, which is inserted into the printing apparatus (*A*). A strip of paper to be tested is clipped on to the printing sector (*B*) and brought into contact with the inked disc under known pressure. By releasing a lever the weight (*W*) falls under gravity and, in doing so, drives the sector round, printing a film of ink on to the paper at constantly accelerating speed. When the strip is examined it will be seen that the surface has been disrupted along part of its length. By measuring the distance from the start at which disruption begins, the speed at which picking occurs can be calculated.

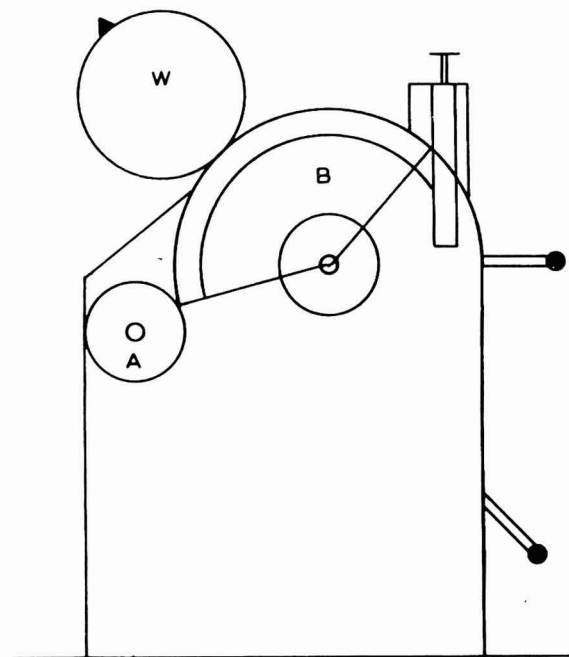


Fig. 1

In 1961, Charlesworth and Coupe³ carried out picking experiments in which a number of mineral oils, linseed oil varnishes, liquid synthetic resins and experimental inks were tested on several paper surfaces. They concluded that, whereas the VVP was approximately constant for a series of Newtonian mineral oils, there was no simple relationship over the range of oils and inks tested. Linseed oil varnishes and inks were found to require considerably higher critical velocities than mineral oils of corresponding viscosities. Picking is presumably influenced by tackiness of ink, which may be defined as the stress offered by the liquid films against splitting. Tack stress, however, is not a fundamental entity in the classical sense, but depends rather upon the method of evaluation. The PATRA Tackmeter was designed to measure this property. It is based on the same principle as the *Reed Inkometer*, but measures drag with an inductive displacement transducer instead of a sliding weight and lever system (Fig. 2).

The instrument consists essentially of a positively driven hollow brass drum (A) in contact with a steel rider roller (C) mounted on a swinging frame, pivoted about the axis of A, with a counterpoise weight at the lower end. A neoprene covered roller (B) oscillates to maintain an even ink film on A. The top end of the frame is connected to the front face of a proof ring; the back face is rigidly connected to the frame of the machine. Relative movement of the faces is measured by the transducer (E). This movement is produced by the drag of the ink film on the rider roller, which swings the frame, and is a measure of tack.

Tack stress was measured over a range of speeds on all the inks, oils and varnishes previously used for pick strength measurements by the IGT method.

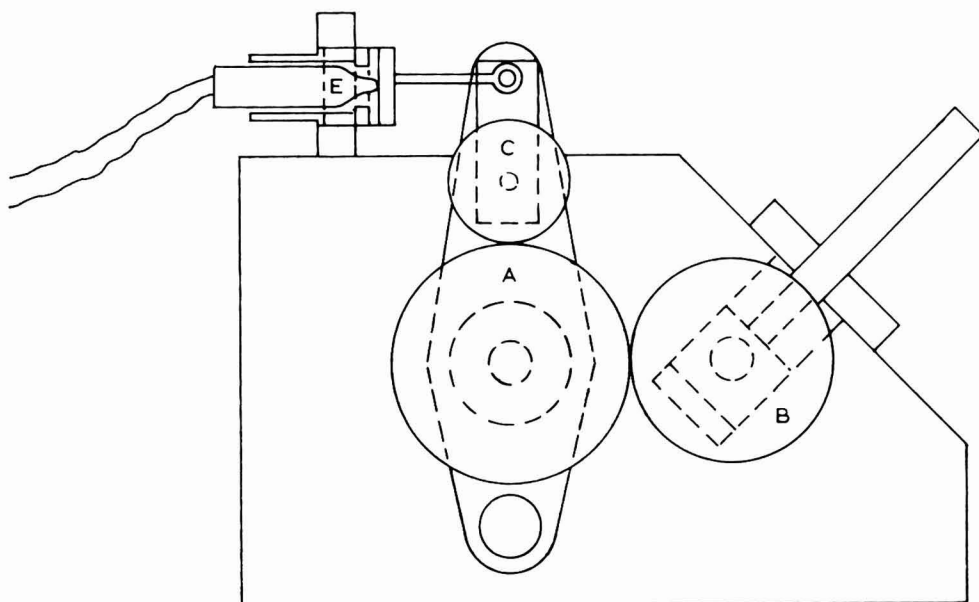


Fig. 2

For a given paper the tack stress of each liquid at the critical picking velocity was found. When this was done all points for the four different types of liquid systems lay close to a straight horizontal line (Fig. 3). Thus, for a given paper, tack stress at the moment of picking is constant, independent of the liquid

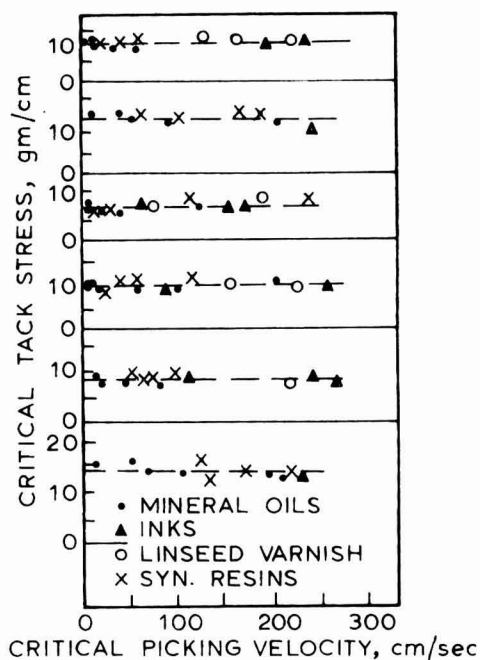


Fig. 3

used. Thus the tack stress as measured on the PATRA Tackmeter is a general criterion for assessing the tendency of a liquid to pick paper. From these measurements it is now possible to predict the top speed at which a paper could be printed with a given ink without picking, and also how far the tack of a given ink would have to be reduced to print without picking at a particular speed.

Picking resistance of paper is always higher in the machine direction than in the cross direction. This difference has been attributed to interaction among surface elements. As only a narrow band is printed at any particular time, the stress exerted on an element could be offset by the bonding strength of elements ahead and behind. As paper fibres are better orientated in the machine direction, the interaction is greater in that direction. This is a plausible explanation, but there is a more important and likely cause.

Because of the pull of the ink film, the paper emerging from the nip is carried some distance in contact with the inked blanket before being peeled off. The paper is bent as it is peeled away and, depending on the angle of bending, some of the bonds can be permanently broken so that the paper is more prone to damage by picking. The angle of take-off will vary with the bending modulus or rigidity of the paper. Rigidity is higher in the machine direction, so the bending angle at take-off is less, and picking resistance is higher.

Oil absorption

Many aspects of the final print depend on the way in which ink constituents penetrate into paper. If rapid penetration of ink vehicle occurs, there may be insufficient liquid left to form a continuous film over the pigment particles, resulting in a matt instead of a glossy finish. In severe cases insufficient vehicle may be left to bind the pigment particles to the paper, resulting in a powdery deposit which is easily rubbed off. If penetration is very slow, ink setting and drying may be retarded, leading to setting-off the wet ink film on to turner bars, other sheets in a pile, or converting machinery.

A number of test methods have been proposed to measure this property, such as the PATRA Surface Oil Absorption Test, IGT and K and N Ink tests. These tests can only be regarded as approximate as they are largely empirical, lacking a precise meaning.

Laws describing the penetration of liquids into porous systems are well established; they follow the classical case of the movement of liquids in capillaries of simple geometry. Extension to complex systems such as porous solids has been made by Kozeny⁴, Tollenaar⁵ and Hsu⁶.

These studies show that the rate of penetration depends upon the viscosity of the liquid and the pressure gradient which, in the absence of external pressure, is governed by the surface tension of the liquid and contact angle with the fibres. The only paper property involved is a geometrical parameter which takes into account pore sizes and their distribution in area and depth. This quantity is the one needed to describe the absorption characteristics of a paper independently of the liquid being absorbed. If the laws of penetration are accurate, then this quantity, derived from measurements of penetration rate by liquids of known characteristics, should be constant and independent of the liquids used.

Hawkes⁷ has carried out absorption investigations on these lines. A small, known quantity of liquid is held in a reservoir with a narrow slot in the base. This is held in close contact with a strip of paper, being drawn along it at uniform speed. A film of liquid is left on the paper, the length of track produced before the liquid is used up depending upon the nature and volume of the liquid, speed, paper roughness and absorbency. The greater the speed of paper past the slot, the smaller will be the amount of liquid absorbed ; thus a given volume produces a longer track at higher speed.

A relationship between length of track and speed can be derived theoretically, starting from Poiseuille's Law. The derived expression is as follows :

$$V/LB = R + K [(\gamma D \cos \theta)/\eta S]^{\frac{1}{2}}$$

where V = vol. of liquid

L = length of track

B = length of slot

D = breadth of slot

S = speed

and R and K are roughness and absorption coefficients respectively. From the form of the equation it follows that, if a series of observations is made relating track length to speed for a known volume of a liquid of known properties, and these values are placed in the equation, a straight line graph should be produced. If V/LB is taken as the y -axis, then the slope of the line gives a value for K and the y -axis intercept corresponds to R .

This has been done for a number of paraffin and silicone oils and straight lines have been produced. R and K have been calculated and show the same value with the various oils. Thus these two parameters are constants that describe the roughness and absorbency of paper, independent of the liquids used, showing that the physical laws of penetration into porous solids can be applied to papers.

With coated papers variations from linearity are produced as absorption proceeds from one stratum to the next. Results would be expected to differ with liquids such as water, which cause swelling of the fibres and alteration in pore structure.

The absorption characteristics of paper can now be described and should give useful information about such factors as the suitability of a paper for varnishing. This does not mean that they will necessarily predict whether inks will give a good gloss finish, as many other factors complicate the issue when pigmented systems are used. There is a need for further work in this area.

Smoothness

When a halftone illustration is printed, somewhere in the region of 30,000 dots are printed per square inch. The difficulties of doing this on a rough surface are obvious. In offset lithography, where the image is transferred from a rubber blanket, smoothness is not so important as in letterpress or gravure. In gravure printing a solvent based ink is held in etched recesses in the printing cylinder. These average about 0.005 in diameter and 0.0001-

0.002 in depth. For ink to transfer at all, a cell must contact the paper. If there are pits or depressions in the paper surface such that contact cannot occur, then no ink will be transferred in these areas, hence the speckled appearance often seen in the light tones of gravure prints.

There are a number of conventional smoothness testers in use. The most common is the Bendtsen. In this instrument air is fed into a head which has a narrow annulus at the base. If this is placed on a completely smooth surface no air can escape; if placed on a rough surface, air escapes under the annulus, the rate of air-leak measured on a Rotameter tube giving a measure of roughness. Several instruments are based on this air-leak principle.

The Chapman Tester⁸ uses an optical principle (Fig. 4). Light passes through a glass block and is incident normally on the paper sample pressed against the bottom of the block. Where the paper is in optical contact with the glass block, reflected light may be scattered in any direction. Where there is a depression in the paper surface such that optical contact does not occur, the

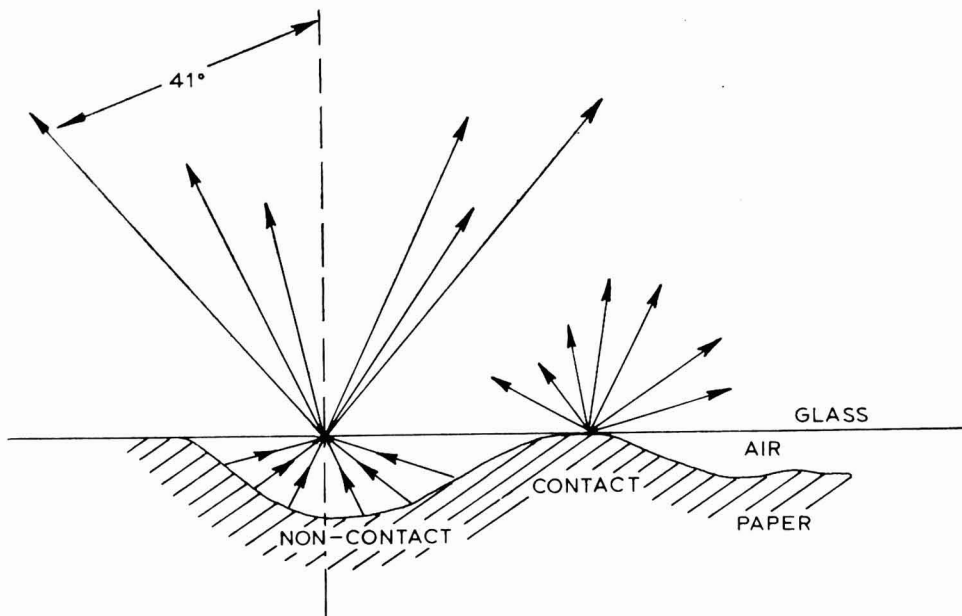


Fig. 4

incident light must traverse a layer of air before being reflected back from the paper. The reflected light is then refracted at the air/glass interface, and will be confined to a cone within the critical angle (half-angle 41° in this case). If the sample is viewed at an angle outside this cone, areas of non-contact appear black, whilst areas of contact are seen in their normal colour. By an arrangement of photocells above and below the critical angle a figure can be obtained for the percentage of surface area in contact with the glass block.

Despite the fact that surface roughness appears to be the basic cause of gravure speckle, all these tests give poor correlation with speckle tendency.

The testers all express roughness by one average figure, so two papers of very different surface contours may still appear equally rough. It seems logical that in practice some sizes of pit may have more effect on the print than others, so roughness must be described in terms of pit-size distributions before valid inferences on printing behaviour can be drawn.

This information can be obtained from a modified version of the Chapman Tester. As has been stated, by viewing below the critical angle, a picture of the paper surface can be seen, the pits showing as black areas on a white ground. Owing to the geometry of the instrument, this image is distorted. By lighting the sample from below the critical angle, and taking the image out normally to the paper surface, an undistorted image can be projected directly on to bromide paper at any convenient magnification. The areas of pits can then be measured on this print and a frequency distribution plotted (Fig. 5).

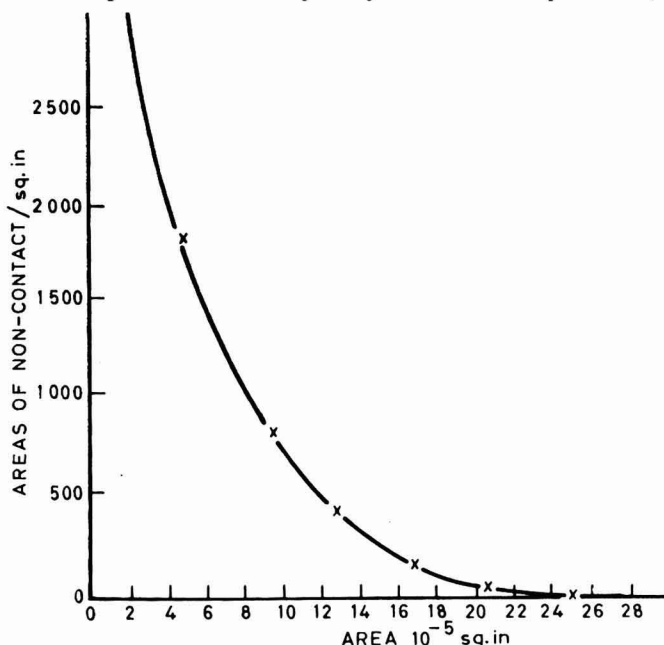


Fig. 5

This technique has been applied to a number of coated and uncoated boards, which were also printed and assessed for speckle by a panel of observers. It was found that a parameter could be calculated from the distribution curves that gave a correlation coefficient of 0.97 with panel speckle rankings (Fig. 6). This parameter is the area under the curve to the right of the point on the x -axis representing the size of a gravure cell, i.e. the probability of occurrence of pits greater than a cell. Thus it appears that conventional smoothness testers fail to predict gravure printability because the readings are influenced by numerous very small pits that have little effect on the printed result. The improvement in classification by the use of this new method can be seen by comparing Fig. 6 with Fig. 7, which shows the correlation of Bendtsen ratings with panel speckle rankings on the same series of boards.

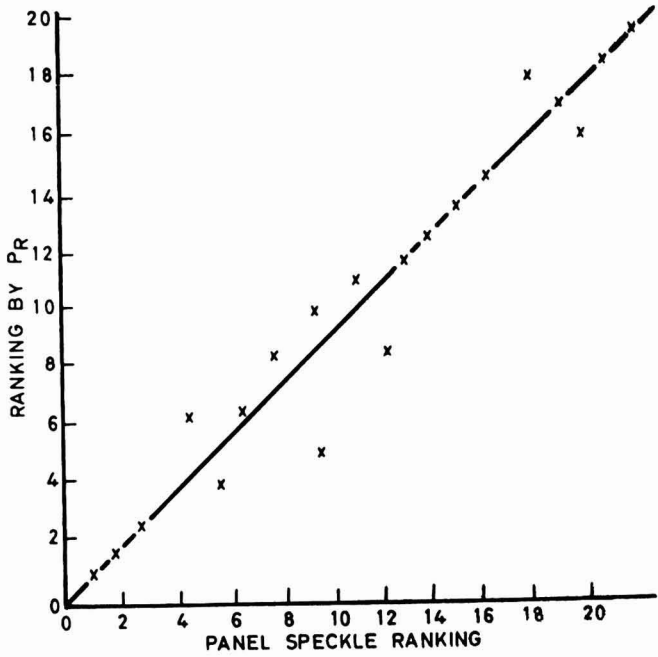


Fig. 6

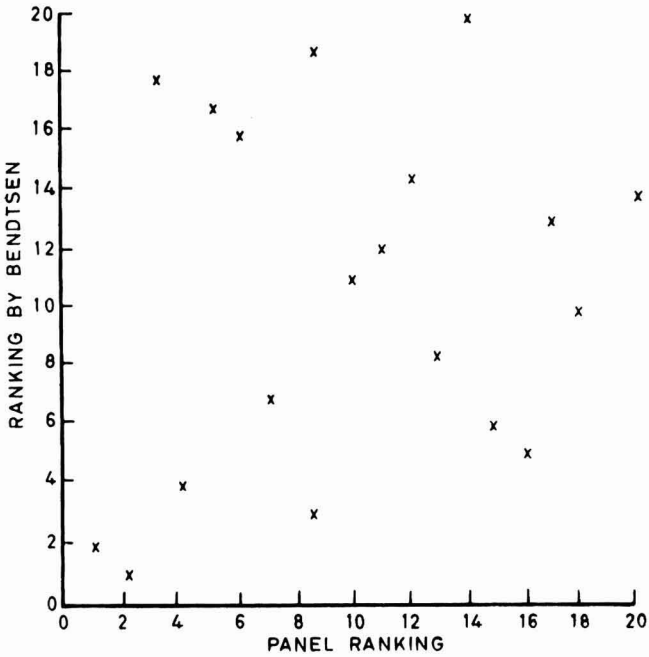


Fig. 7

This work has defined the board surface property likely to cause speckle, but is far too tedious for a quality control test. It should be possible, however, by optical scanning of the Chapman prints to make the test both simple and rapid.

Conclusions

A large number of empirical tests are used in attempts to predict the printing performance of papers and boards. Three paper properties, surface strength, absorbency and smoothness, have been discussed in detail to show the intricacy of the ink/paper relationship and the need for basic research on underlying principles before any valid test procedures can be suggested.

Acknowledgment

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Unreacted isocyanate groups in cured polyurethane lacquers

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Summary

The presence of unreacted isocyanate groups in a cured polyurethane lacquer is of some interest on account of the possibility of dust from this being inhaled when the lacquer surface is sanded.

The chemical reactions involved in polyurethane chemistry are considered and a method involving the dyestuff, malachite green, is used to show that unreacted isocyanate groups can be detected in a cured polyurethane film.

Radicales isocyanates réactifs en vernis polyuréthanes durcis

Résumé

L'existence des radicales isocyanates réactifs dans un film durci de vernis polyuréthane est d'un certain intérêt à cause de la possibilité que l'on pourrait inhaler la poussière enlevée du film pendant la ponçage.

Les réactions propres à la chimie des polyuréthanes sont remarquées. On présente une méthode se servant du vert malachite qui met en évidence des radicales isocyanates réactifs dans un film durci de vernis polyuréthane.

Nicht Umgesetzte Isozyanatgruppen in Vernetzten Polyurethanlacken

Zusammenfassung

Die Gegenwart in einem vernetzten Polyurethanlack von solchen Isozyanatgruppen, die nicht reagiert haben, ist deshalb ziemlich wichtig, weil, wenn die Lackoberfläche geschliffen wird, der dadurch entstehende Staub möglicherweise eingeatmet wird.

Die in der Polyurethan-Chemie in Frage kommenden chemischen Reaktionen werden besprochen, und eine Untersuchungsmethode wird beschrieben, in welcher der Farbstoff Malachitgrün eingesetzt wird, und mit Hilfe derer die Anwesenheit solcher Isozyanatgruppen, die in der Reaktion nicht aufgebraucht worden sind, in einem vernetzten Film nachgewiesen werden kann.

Introduction

It is known that tolylene di-isocyanate (TDI), a substance which may be present in the atmosphere when polyurethane lacquers are used, is highly irritant and may produce sensitisation reactions in very small concentrations. Recent recommendations¹ limit the safe vapour concentration of this substance to a figure as low as 0.02 ppm. Avoidance of this vapour hazard has been successfully achieved in the lacquer industry by the use of complexes of TDI, either with itself or with other substances, which are suitable for the production of polyurethane finishes, and yet show little if any vapour concentration of TDI in the atmosphere when they are used. The action of TDI presumably arises from the isocyanate groups, and this makes of importance the possibility that dust from a sanded polyurethane lacquer may contain some unreacted isocyanate groups. The exact physiological effects of such groups associated with a high molecular weight material are not known, but in view of the high reactivity of such groups, inhalation of dust containing them would appear

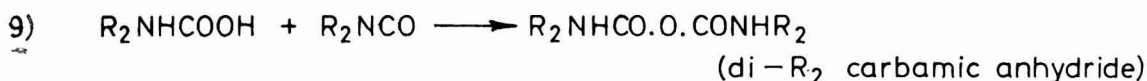
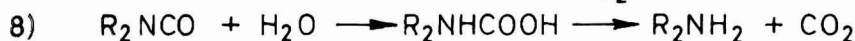
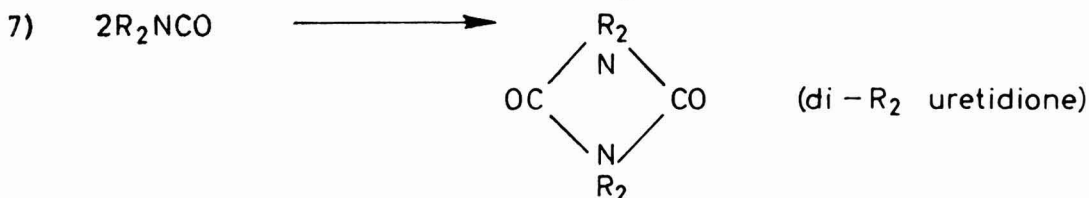
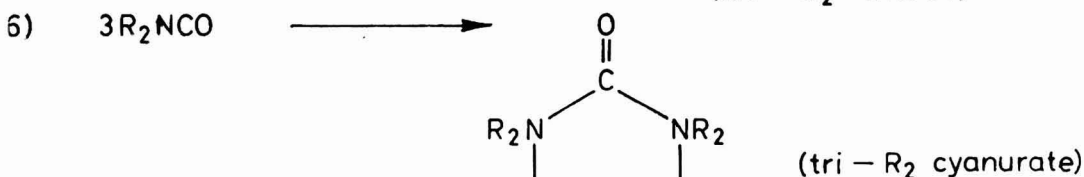
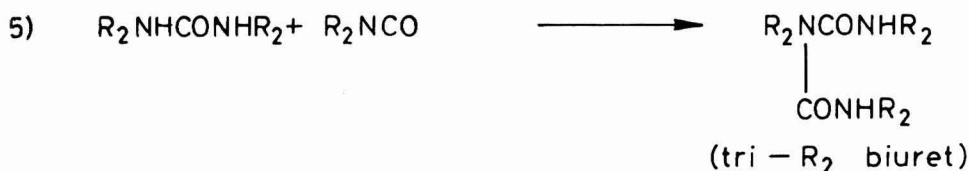
to be a practice to be avoided. It is therefore of particular interest to see whether a cured film of polyurethane lacquer contains unreacted isocyanate groups.

Polyurethane reactions

The primary reaction utilised in the curing of a two-pack polyurethane lacquer involves the production of a urethane link, —NHCOO— from hydroxyl and isocyanate groups.

(1) $\text{R}_1\text{OH} + \text{R}_2\text{NCO} \longrightarrow \text{R}_2\text{NHCOOR}_1$ (R_1R_2 urethane or R_1R_2 carbamate)

As has been pointed out by several authors, however, many other reactions may take place in the polyurethane system, these being :



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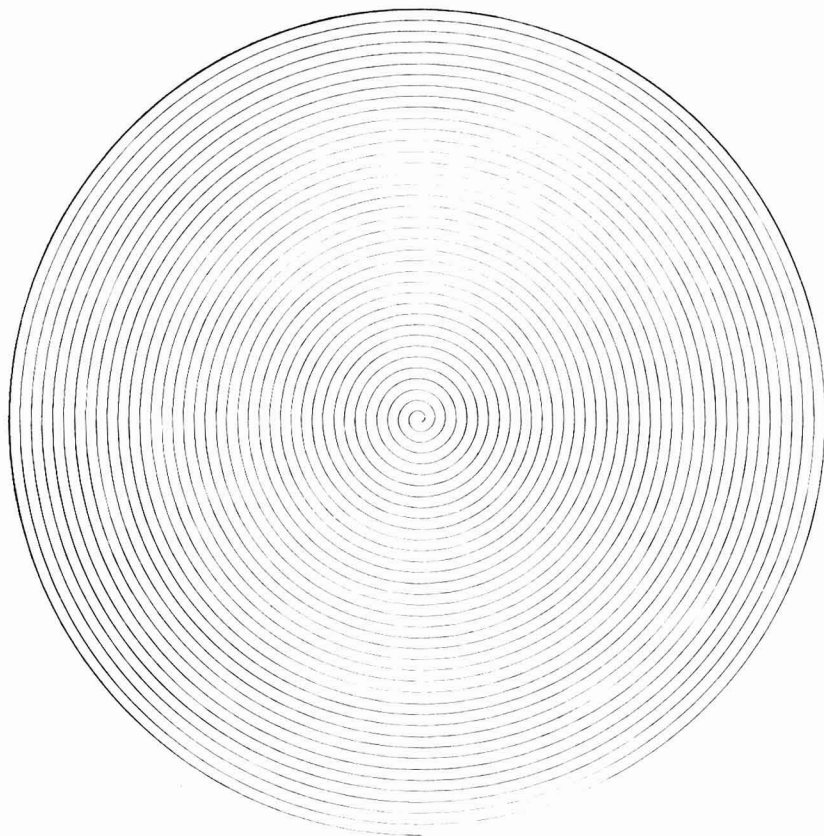
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The above indicates the possible reaction products starting with a mono-functional alcohol, R_1OH , and a monofunctional isocyanate, R_2NCO . In a lacquer, R_1OH is replaced by a polyester resin with two or more hydroxyl groups, and R_2NCO by a compound with two or more isocyanate groups. Because the primary reactants thus have a functionality greater than unity, a polymer can be formed from them. The reactions listed above show that polyurethane chemistry is complex, and although (1) above is the principal reaction in a two-pack polyurethane lacquer system, the many other reactions must be considered when looking for unreacted isocyanate groups in a cured polyurethane film.

Detection of isocyanate groups

Biuret reaction

The first reaction to be examined for the detection of isocyanate groups was the biuret reaction. Biuret, $NH_2CONH.CONH_2$, reacts with copper sulphate and sodium hydroxide to give a brilliant violet colour, and it was thought that reaction (5) above could be used for the production of a substituted biuret which would also give this colour. The polyisocyanate portion, *Suprasec KN*², of a two-pack polyurethane lacquer system was first tested, by heating urea with it for half an hour at 100°C, and then testing with copper sulphate and sodium hydroxide; no distinctive colour was, however, formed.

Diazo reaction

Reaction (3) above produces a primary amine and this can be readily identified by the diazo reaction. The use of this as a means of detecting isocyanate groups was therefore examined. Some of the polyisocyanate was refluxed with 10 per cent potassium hydroxide in methanol for 1½ hours, cooled in ice, acidified and sodium nitrite added to diazotise. On coupling with alkaline β-naphthanol solution a brilliant orange-red colour resulted, indicating the presence of a primary amine in the refluxed mixture. The same reaction was then carried out on a cured two-pack polyurethane lacquer film. This was prepared from the polyisocyanate *Suprasec KN* and the polyesters *Daltolac 9*² and *Daltolac 11*². These were used in the proportions recommended by the manufacturers, thus:

	<i>Parts by weight</i>					
<i>Daltolac 9</i>	100
<i>Daltolac 11</i>	200
Methyl ethyl ketone	550
<i>Suprasec KN</i>	680

The mixed lacquer was spread on a glass plate with an 0.008 in *Sheen* film spreader, and left for one week in a room controlled at 25°C. Flakes of the film were cut off and refluxed with 10 per cent potassium hydroxide in methanol for 1½ hours. This treatment disintegrated the lacquer film. On diazotising and coupling with β-naphthol as above an orange colour developed. A blank from the reagents alone showed no such colour. The production of this colour is a fair but by no means certain indication that free isocyanate is present in the cured lacquer film. Primary amine could have been present in the film

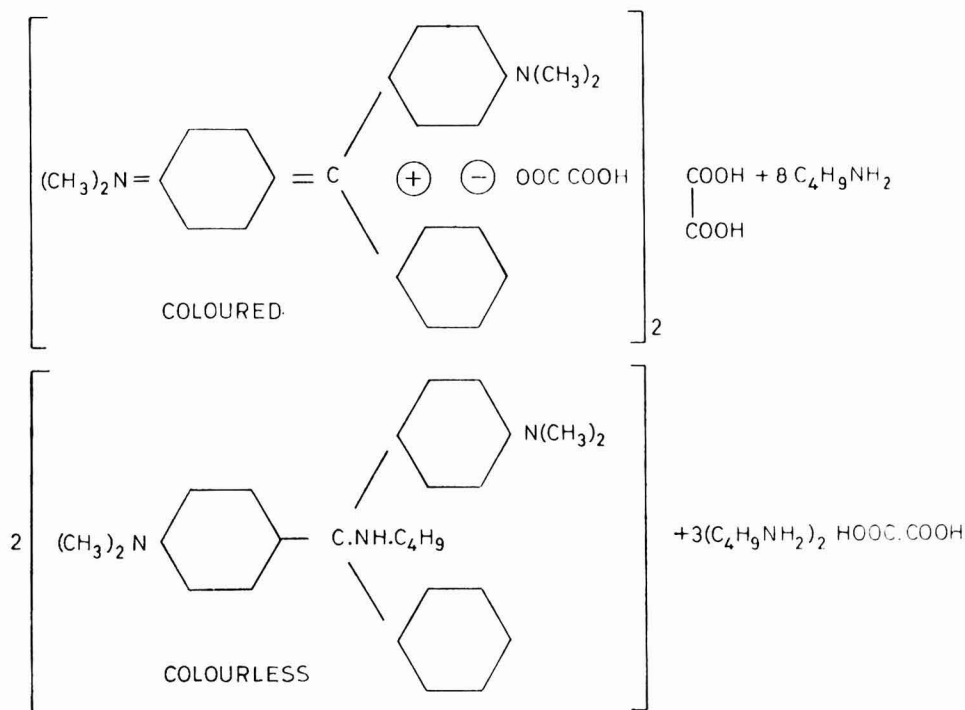
by reaction (3) taking place with moisture in the atmosphere, or in the polyester or solvent as mentioned by Lowe³, before the film was cut up and tested. The diazo reaction is used in the Marcali method for detecting volatile isocyanates in the atmosphere.

Ehrlich's reagent

Swann and Esposito⁵ and Robinson⁶ used Ehrlich's reagent for the detection of unreacted isocyanate groups. The reagent, *p*-dimethylamino-benzaldehyde, gives a bright yellow colour when tolylene 2,4-di-isocyanate or tolylene 2, 6-di-isocyanate are mixed with it in the presence of acetic acid at room temperature. However, the reagent was not particularly useful in the present case since a sample of ethyl carbamate, from which any unreacted isocyanate had been removed by hydrolysis, gave the yellow colour.

Malachite green

Kubitz⁷ describes a method for the detection and determination of traces of isocyanates in polyurethanes, involving the use of malachite green and butylamine. Malachite green, normally available as an analytical reagent as its oxalate salt $(C_{23}H_{25}N_2C_2HO_4)_2H_2C_2O_4$, reacts with butylamine thus :



This reaction involves a return from the coloured oxidised structure to the colourless *leuco* structure. Butylamine would also, of course, react with isocyanate groups according to (4) above and these two reactions provide a means for detecting and determining traces of isocyanate.

If standard amounts of butylamine, less than the amount required by the above equation, are added to a malachite green oxalate salt solution, a range

of solutions of varying optical densities are formed. With these solutions the optical density will be less, i.e. the percentage transmission greater, the greater the amount of butylamine. If a standard butylamine solution is shaken with a polyurethane containing unreacted isocyanate groups, there will be less butylamine available for subsequent reaction with the malachite green, and the increase in percentage transmission when this butylamine solution is then added to the malachite green solution will be correspondingly less. An advantage of this system of reactions is that interference from primary amines present in the polyurethane, if they dissolved in the butylamine solution and then reacted with the malachite green, would cause a greater increase in percentage transmission, hence the effect of primary amines would be to reduce the apparent content of isocyanate groups. With this method a positive isocyanate value is significant, but a negative one might not be.

Experimental

To apply the Kubitz method the following reagents were needed :

- (a) Malachite green oxalate salt, recrystallised from hot water and dried in air several days.
- (b) Tetrahydrofuran, dried over sodium and distilled.
- (c) Pyridine, containing 0.05-0.15 per cent water.
- (d) Butylamine, distilled from solid potassium hydroxide and collected from 76-78°C.

5 ml portions of a malachite green solution in pyridine were taken (0.25 g in 250 ml) and to these were added 5, 4, 3, 2, 1, 0 ml of tetrahydrofuran and 0, 1, 2, 3, 4, 5 ml of a standard solution of butylamine in tetrahydrofuran (0.0022 g in 100 ml, prepared from a solution containing 0.1084 g/100 ml diluted 1 : 50). Percentage transmission of this mixture, against a blank containing 5 ml each of tetrahydrofuran and pyridine, was measured exactly three minutes after the addition of the butylamine solution. A Pye absorptiometer, with 1 cm cells and a 610 m μ filter, was employed. Plotting $\log \frac{\text{Percentage Transmission}}{100}$ against ml of standard butylamine solution gave a straight line calibration graph.

A polyurethane lacquer of the composition previously given was prepared, spread and left for one week at 25°C. In order to obtain some uncontaminated dust from this, it was abraded with a *Permagrit* tungsten carbide file and the mixture of lacquer flakes and lacquer dust collected. A weighed amount (0.1157 g) of this mixture was shaken in a sealed flask for three hours with 15 ml of the standard butylamine solution. From this 5 ml were pipetted off, using a filter of glass wool around the tip of the pipette, 5 ml of the malachite green solution added, and after shaking, percentage transmission was measured three minutes after mixing the solution. The percentage transmission (23.0 per cent) was found to be less than that obtained (25.9 per cent) when the above procedure was followed without the addition of the lacquer film. Applying equation (4) above and using the calibration graph, it is found that this small difference in per cent transmission corresponds to 0.41 per cent free isocyanate group (—NCO) in the aged lacquer film.

Two facts need to be noted in the application of the above method. The concentration of butylamine in the standard solution slowly decreases each day and the optical density of the malachite green solution likewise decreases with time. These facts did not, however, affect the final isocyanate determination since the solutions used, with and without the lacquer film, had the same age.

Conclusions

It has been shown that the method of Kubitz is applicable to the determination of unreacted isocyanate groups in a nominally cured polyurethane lacquer film. The method gives a figure for isocyanate content of the film, which is probably on the low side due to the incompleteness of the reaction of the butylamine with the free isocyanate in the film, and also on account of the possibility of other amines being extracted from the film, which could react with malachite green.

The presence of free isocyanate in the dust abraded from a cured polyurethane film is indicated. Of particular interest is the fact that this small isocyanate content of the dust is not immediately removed by its reaction with moisture in the surrounding air, as has been often supposed.

Acknowledgments

The work described in this paper was carried out at the Furniture Industry Research Association as part of the general research programme and is published with the permission of the Director. The author also wishes to thank Mr. M. J. Merrick for his helpful discussions in the course of this work.

[Received 16 March 1965]

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PAPERS IN HAND

In addition to the papers presented to the Torquay Conference the following have also been accepted by the Honorary Editor for publication in future issues of the *Journal* :

The Photochemistry of Vinyl Chloride/Vinyl Isobutyl Ether Copolymer Part II and III by Z. Hippe *et al.*

Further Investigations of Short Oil Pentaerythritol Alkyds by H. R. Touchin.

Selection of Research and Development Projects by S. P. Rose.

Pit Corrosion in Internally Painted Cargo and Cargo/Ballast Tanks of Ocean-going Crude Oil Tankers by D. Voogel.

Phthalocyanine Blues by R. F. Hill.

Reviews

PAINT FLOW AND PIGMENT DISPERSION

By TEMPLE C. PATTON. Interscience Publishers. Pp. 479. Price £6 4s.

This book covers a field of major interest to the paint industry, including some topics such as paint flow calculations which are not normally adequately covered in books devoted to paint technology. The treatment throughout consists of a theoretical and mathematical review of each topic, followed by a number of very useful worked examples of particular problems. The book will naturally be compared with Fischer's "Colloidal Dispersions", and it covers more ground, with a somewhat different and perhaps more practical and quantitative approach.

The topics covered include rheology and viscometers of various types and a useful chapter on inter-conversion of units. The effects of resin composition and solvent on viscosity are covered in a separate chapter, including molecular weight and intrinsic viscosity considerations. There is a very good chapter on paint flow characteristics such as brushing, levelling and sagging, and a brief account of pigment settlement. Aspects of paint flow from the chemical engineering angle are covered in a chapter on piping and pump calculations.

A chapter on oil absorption and critical pigment volume concentration is followed by a further chapter on the theoretical approach to grinding and dispersion. This includes a certain amount of the surface chemistry involved in wetting such as the effects of surface tension, work of adhesion, etc., and flocculation and dispersion stability are rather briefly discussed. There follow individual chapters on the operation of the various types of mills and high speed dispersion equipment, including the sand grinder.

A chapter on solvents covers, in detail, factors such as solubility parameter followed by a rather brief account of solvent evaporation. Mill base letdown is well covered in a separate chapter. Other chapters deal with laboratory film applicators, and flow relationships of practical paints exhibiting non-Newtonian characteristics. The book concludes with a rather short chapter on defects such as flotation and flooding in the paint film, and foaming.

In a comprehensive work of this nature it is inevitable that the choice of the relative extent of coverage of the various separate topics will be a matter for the author's individual preferences. The book is in fact very well balanced ; if anything there is more about paint flow than there is about pigment dispersion, but this may be a reflection on the extent of the published literature. In particular the relation between theory and practice is well maintained, and the large number of worked examples will be of considerable value in making use of the book in the laboratory and plant. The literature is well covered, with over 300 references, most of which are quite recent. This is a good book, which will be of value both as an introduction to the field and as a work of reference to the experienced worker.

V. T. CROWL.

ORGANISCHE PHOSPHOR-VERBINDUNGEN

(Methoden der Organischen Chemie. Vol. XII. Part II). Edited by E. Müller, Stuttgart : Georg Thieme Verlag, 1964. Fourth Edition. Pp. lxxxvii+1132. Price DM 280.

Part I of Volume 12 of the new fourth edition of Houben Weyl, which described all organophosphorus compounds with at least one phosphorus-carbon bond (i.e. those known up to the end of 1961) was reviewed in the August 1963 issue of this Journal. Part II, now published, covers organic derivatives of phosphorous and phosphoric acids as well as the small number of known derivatives of hypophosphorous, hypodiphosphorous and hypophosphoric acid, and thereby completes the survey of organophosphorus chemistry.

The major part of the book, 864 pages, is devoted to derivatives of the basic types of phosphoric acids, namely pentahydroxy phosphoric acid, phosphoric acid and its sulphur and selenium analogues, imino phosphoric acid and condensed phosphoric acid. These are described according to the nature of the substituents present e.g. ester, ester halide, anhydrides with carboxylic acids, groups containing other elements such as silicon, arsenic, lead, etc., and nitrogen containing groups. A similar treatment, covering 126 pages, is accorded to all types of the organic derivatives of phosphorous acid, including their sulphur and selenium analogues.

The book maintains the excellent standard set by Part I and its treatment as regards the description of the methods of preparation, properties and reactions (including interconversions of functional groups) is, so far as could be judged, comprehensive in all these aspects up to the end of 1962. As with Part I, formulae and equations are used to illustrate the main types of reaction and there are many tables summarising details of methods, full preparative details being given for many syntheses. Where necessary attention is drawn to the hazardous nature of a particular compound or reaction. Very good indexing and a detailed contents list of 35 pages—essential features of a good reference book—should facilitate the search for particular items of information. A bibliography comprising 26 references indicates the main reviews and books on organophosphorus compounds including certain aspects, such as polymerisation and toxicity, which are outside the scope of this book.

The book will undoubtedly be of value to those who specialise in some aspect of organophosphorus chemistry, for example those concerned with the application of organophosphorus compounds as intermediates for the preparation of new flame-proofing polymers or plasticisers.

Together with Part I, it comprises the most comprehensive reference work so far available in the field of organophosphorus chemistry and commendation is due to K. Sasse, who supervised compilation of both parts, and others responsible for publication.

R. N. FAULKNER.

POLYMERS : STRUCTURE AND BULK PROPERTIES

P. MEARES. London : D. Van Nostrand & Co. Ltd. 1965. Pp. 381. Price 70s.

In the seventeen years which have elapsed since the publication of Alfrey's monograph on *Mechanical Behaviour* the physical science of polymers has so far advanced that coverage such as his, in both breadth and depth, is no longer possible in a single volume. Dr. Meares has chosen to limit the breadth of his treatment to a number of physical, mainly mechanical, properties in relation to structure. By so doing he is able, within reasonable compass, to discuss his subject in depth and with a mathematical rigour which is frequently that of classical thermodynamics.

The author takes his polymer science seriously and it is to kindred spirits that he addresses himself. In his preface he expresses the hope that the book will be useful to students of polymer science, research workers and those in industry responsible for the selection of polymers for practical applications. The first two will be particularly well suited but the last may find themselves better served by a work, such as that of Nielsen, with a more practical bias.

The first three chapters, totalling 85 pages, provide an introduction to the chemistry and structure of polymers which is a model of its kind, though the first, on the descriptive organic chemistry, of these materials is so highly condensed as to be out of tune with the rest of the book. The reader tackling the subject at this level can surely be expected to have a thorough grasp of such elementary matters and may well find their inclusion in the present volume mildly irritating.

The main work comprises ten chapters, written as substantially independent essays, on crystallinity, thermodynamics of rubberlike elasticity, statistical thermodynamics of high elasticity, practical aspects of elasticity theory, visco-elasticity, glass transitions, retarded high elasticity, diffusion of gases and vapours in polymers, and irreversible deformations. The treatment of crystallinity, glass transitions, elasticity and diffusion is as fundamental and comprehensive as one could wish. At first sight the inclusion of the chapter of diffusion of gases and vapours in polymers seems anomalous when other topics (such as electrical properties, swelling and adhesion), having equal claim to be regarded as "Bulk Properties," are omitted. It is, however, most welcome to have the field so ably reviewed by Dr. Meares who has himself made no mean contribution to the use of diffusion measurements in the study of molecular motions in polymers. The scientist employed in the surface coatings industry will find this chapter of particular value.

The chapters on visco-elasticity and irreversible deformations are somewhat sketchy by the standards of the others. One feels that much more could have been made of the interpretation of rheological phenomena in terms of current theories of the liquid state. Possibly the author has been influenced by the existence of more comprehensive works (such as that of Ferry) on these topics. Alternatively, he may have felt that his self-imposed strict standards of treatment could not be upheld in the present state of the art. Certainly he makes few concessions to empiricism, even in the chapter on practical aspects of elasticity theory, and one looks in vain throughout the book for those simple and useful, if somewhat inexact, physical pictures provided by, for example, the concept

of cohesive energy density and Smekal's *Lockerstellen* theory as it affects the relationship between the measurable strengths of primary and secondary bonds, experimental tensile strengths and the mechanism of tensile rupture. Again, the technologist seeking an interpretation of practical measurements, such as heat distortion temperature, softening point or Clash-Berg torsional modulus, in terms of fundamental principles must look elsewhere for enlightenment. These points, however, are made in an attempt to delineate the field covered by Dr. Meares's work rather than as criticisms. The book is frankly limited to scope and rigorously fundamental in approach ; as such it is first rate and eminently readable.

The index is unfortunately mediocre ; cross-indexing is at a minimum and many terms, prominent in the text, are not to be found. A random check of 20 literature references revealed no errors and this substantiates the reviewer's first impression of the excellence of the references in general. It is particularly noteworthy that about one-sixth of the references given are to literature dated 1962 and later ; there are even two references to papers published in 1964. This is an all too rare achievement and is evidence of a truly remarkable collaboration between author and publisher. If one is determined to find grounds for criticism in this connection it can only be that the author's avowed concentration on references in the English language has led to the omission of a number of others which warrant mention by any standards.

Misprints are conspicuous by their absence but one cannot but be amused by the statement on p. 69 that " the integral weight curve always increases *monotonously* with molecular weight ". There is nothing monotonous about Dr. Meares in full spate and his book is warmly recommended to, one must repeat, polymer scientists who take their subject seriously. At 70s. it provides not only knowledge but understanding at small cost by present-day standards.

A. R. H. TAWN.

ELECTRONIC STRUCTURE, PROPERTIES AND THE PERIODIC LAW

By H. H. SISLER. Pp. 120, London; Chapman & Hall, 1965. (Selective Topics in Modern Chemistry series). Price 10s. 6d.

This is a paperback, a student's small textbook, in the interesting Selective Topics in Modern Chemistry series, originally published by the Reinhold Publishing Corporation of America in 1963. The author is Head Professor of Chemistry of Florida University.

It gives an up-to-date account of the Periodic Law and its implications and tries to put over to the student the way in which the modern chemist thinks when he is investigating the fundamental properties of elements in relation to structural parameters. Broadly, attempts are made to answer three questions : (1) what is the relationship of the Periodic Law to the electronic structures of the atoms ? (2) what atomic parameters determine the kinds of bonds which atoms form with each other (how do these parameters vary with electronic structure and position in the Periodic Table) ? (3) how are the properties of substances related to the kinds of bonds uniting the atoms ?

Several of the illustrations are taken from "College Chemistry—a Systematic Approach" Sisler, Van der Werf and Davison (New York, Macmillan 1961).

R. J. COLE.

CHEMISTRY OF THE LANTHANIDES

By T. MOELLER. Pp. 117, London; Chapman & Hall, 1965. (Selective Topics in Modern Chemistry series). Price 10s. 6d.

This is another paperback textbook in the Selective Topics in Modern Chemistry series. The author is Professor of Inorganic Chemistry at Illinois University.

There has of course been a considerable rebirth of interest in the lanthanides (the name now preferred for what used to be called the "rare earths") not only as part of expanding technology but also in relation to the general renaissance in inorganic chemistry, prior to 1940, no element heavier than uranium had been positively identified. This book presents theoretical principles invoked to account for the described behaviour of this series of elements and their applications but also their limitations. Limitations of an entirely theoretical approach apply for example for yttrium and to the heavier members of the series. The author presents an essential introduction of significant matter to the student and also indicates the wisdom of applying the teaching and experience of history to the solution of new problems.

R. J. COLE.

ACIDS, BASES AND THE CHEMISTRY OF THE COVALENT BOND

By CALVIN A. VANDERWERF. Chapman & Hall Ltd. Pp. 118. Price 10s. 6d.

This small booklet in the Selective Topics in Modern Chemistry series traces the broadening of the concept of acids and bases. After the Arrhenius idea of an acid as a compound which gives hydrogen ions in aqueous solution and a base as a compound which gave hydroxyl ions, came the Bronsted-Lowry theory in which an acid is a proton donor and a base a proton acceptor. This was further modified in the Lewis concept, in which an acid is a species which can accept an electron pair and a base one which can donate an electron pair. The general application of this latter theory to the explanation of nucleophilic, considered as base displacement, and electrophilic, considered as acid displacement substitution reactions, is described. This book will be acceptable to those who require a quick, readable, introduction to the mechanism of polar reactions.

L. A. O'NEILL.

Correspondence

Pigmentation of finishes for electrodeposition—further information

SIR,—Since publication of the paper “Pigmentation of Finishes for Electrodeposition” (*JOCCA*, 1965, 48, 462), which was read to the Southern Branch of the Oil and Colour Chemists’ Association, a further examination of the effects of changing resistance of films with change in PVC has been carried out. The electrical conditions for electrodeposition were varied and a group of pigments dispersed in a water soluble resin of relatively high electrical resistance at fixed pH of 7.5, 15 per cent resin solids and temperature of 22°C were deposited at various pigment volume concentrations. For the purpose of these determinations the following pigments were used :

Tioxide R-CR
Tioxide R-SM
Red Iron Oxide *MR11*
China Clay
Mica
Whiting

In order to prepare curves which could be shown on the same scale the results obtained for such pigments as Hansa Yellow and Yellow Iron Oxide were omitted because the electrical resistance of such pigments was of a very high order and of a completely different order to those reported. The following (Fig. 1) shows the results obtained when these paints were deposited by 1 ampere per sq ft for two minutes.

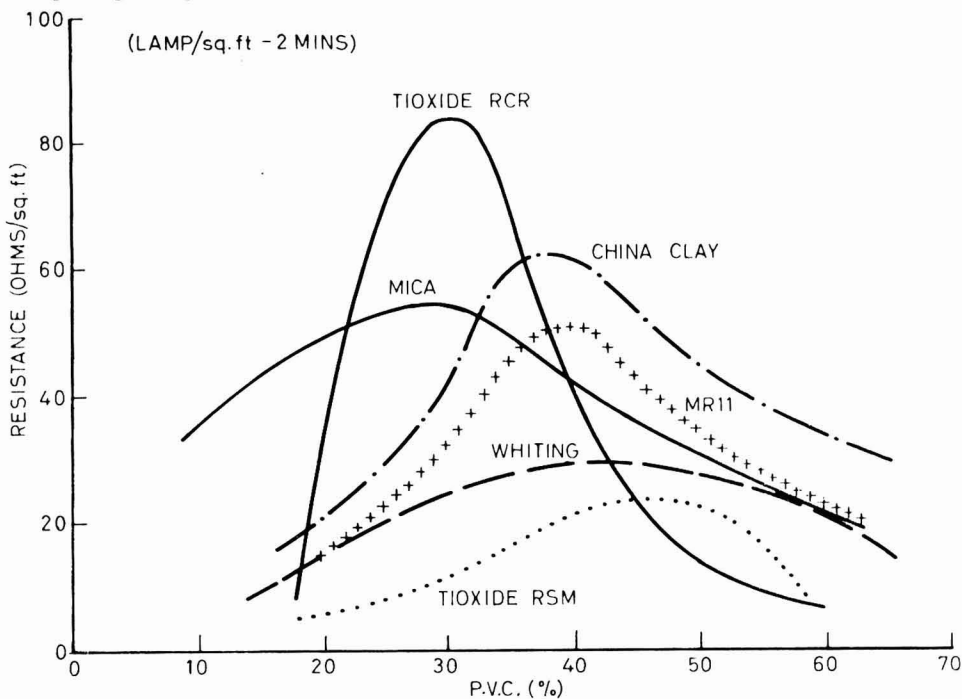


Fig. 1. Resistance/PVC relationship (1 Amp/ sq ft -2 min)

On application by 1 ampere per sq ft for two minutes the resistances were between about 20 and 80 ohms/sq ft. The *Tioxide R-CR* film had again much higher resistance than the *Tioxide R-SM* film. The extenders, mica and china clay, were similar in resistance and of about the same order as Red Iron Oxide *MR11*, whilst whiting had a relatively low resistance in this group. The same paints were then applied under conditions of fixed potential difference and Figs. 2 and 3 show the graphs which were obtained by deposition by a fixed potential difference of 60 volts for two minutes and 40 volts for two minutes respectively.

When deposited by 60 volts for two minutes the same paints had film resistance of a much higher order between about 120 and 200 ohms/sq ft. The difference between *Tioxide R-CR* and *R-SM* were again marked. Mica and china clay again had resistance of a similar order and similar to that of the Red Iron Oxide *MR11*, but whiting was found to have a resistance very much greater than that of the other two extenders. This was also greater than the resistance of *Tioxide R-CR* in this case.

If deposition was effected by a fixed potential difference of 40 volts for two minutes, under these conditions the film resistance of the whole group of pigments and extenders was reduced, but was still of a high order between about 100 ohms/sq ft and 160 ohms/sq ft. Under these conditions mica and china clay again had similar electrical resistance, but in this case of a lower order than that obtained with the Red Iron Oxide *MR11*. The difference between the resistance of *Tioxide R-CR* and *R-SM* was smaller than in previous cases, but still *R-CR* had the higher film resistance. Again under a potential difference of 40 volts, whiting had film resistance of a high order compared with the remainder of the pigments examined and this was again greater than the resistance of *Tioxide R-CR*. In all cases maximum film resistance was obtained at a pigment volume concentration of between about 30 and 50 per cent (Fig. 3).

When applied by 3 amperes per sq ft for 40 seconds the paint consisting of carbon black *Coral L* and water soluble resin had a very low film resistance at all the pigment volume concentrations examined and further trials were carried out on the selection of carbon black pigments shown below.

Carbon black	% Carbon	pH	Particle size Å	Specific electrical resistance	Surface area sq m/g
<i>Rajah Beads</i> ..	94.8	4.0	200	—	190
<i>Neospectra</i>	86.0	3.0	130	—	90
<i>Super Spectra</i> ..	92.1	4.0	130	—	970
<i>Coral L</i>	98.0	8.0	277	0.06	133
<i>FW.1</i>	96.0	6.0	118	0.20	320
<i>FW.2</i>	88.9	5.0	118	0.47	320

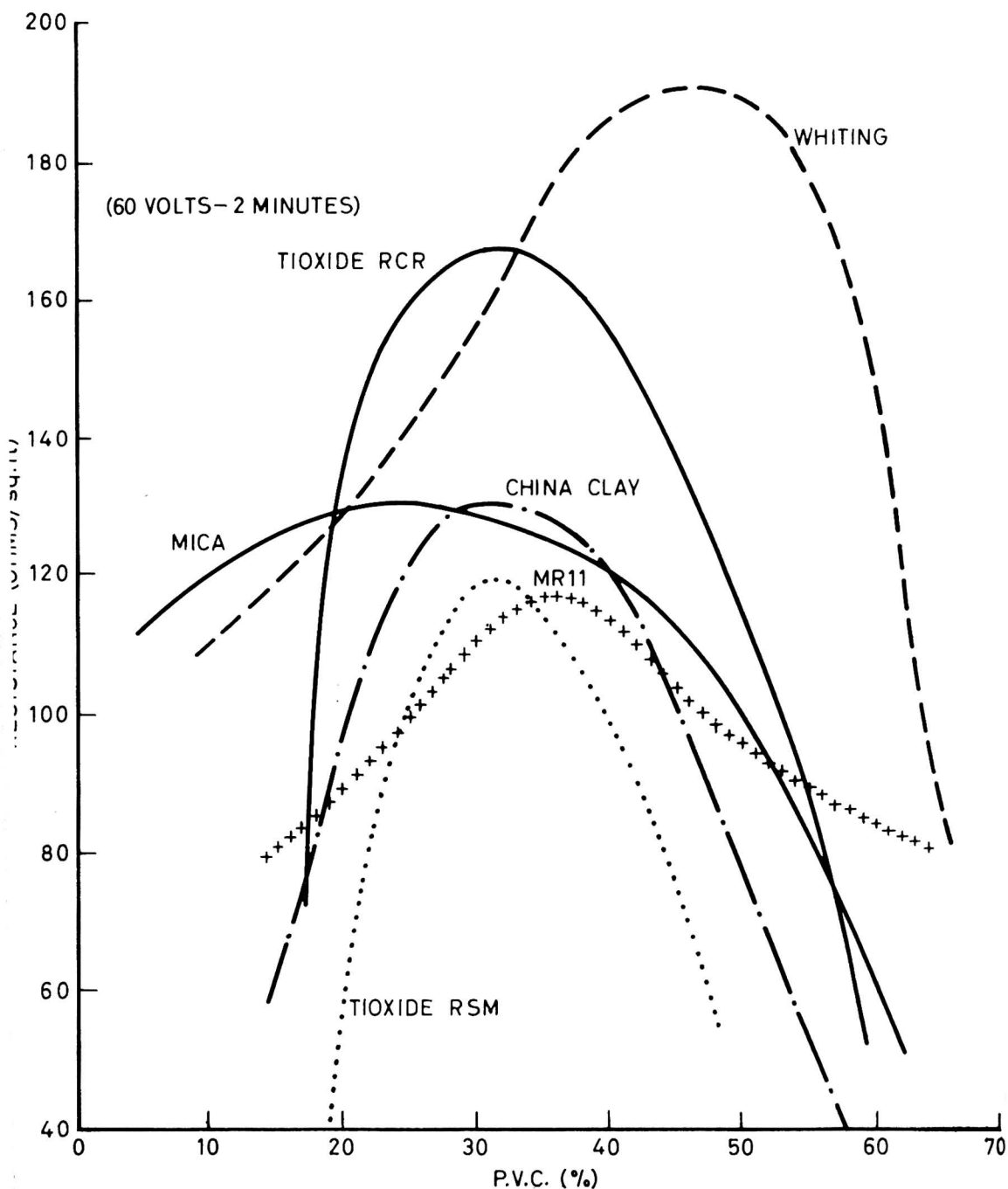


Fig. 2. Resistance/PVC relationship (60 volts -2 min)

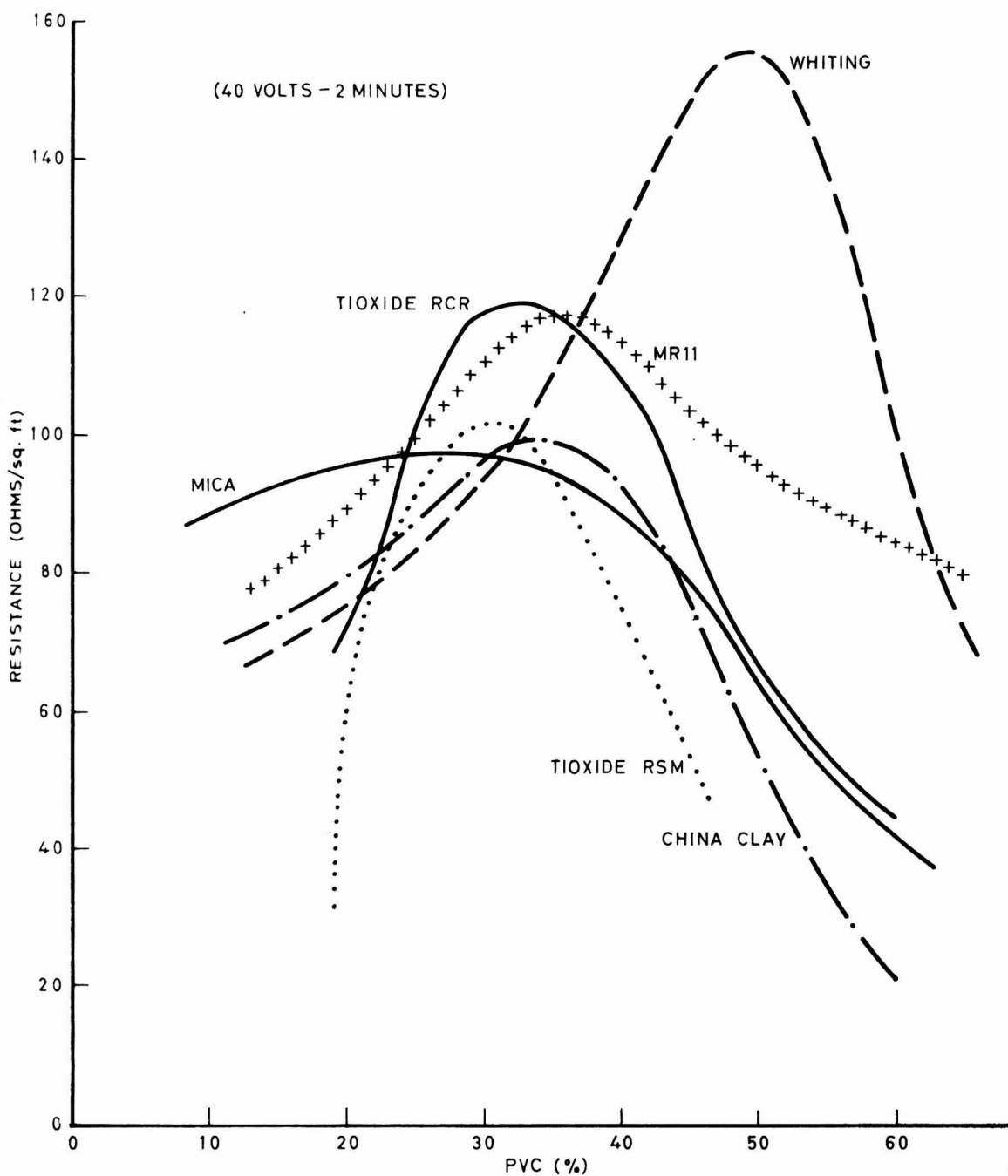


Fig. 3. Resistance/PVC relationship (40 volts -2 min)

The resistances of films of black paints at a pigment/binder ratio of 6/100 at 10 per cent solids when applied by 50 volts for one and two minutes at 22°C are shown in Fig. 4. The resistances after one minute were similar in the case of *Rajah Beads*, *Neospectra Black*, *Coral L* and *FW.2*, whereas the resistance of *Super Spectra* and *FW.1* after one minute was higher than the resistance after two minutes recorded for most other carbon black pigments. With the exception of *Coral L* and *FW.2*, the increase in resistance over the second minute was comparatively small compared with the resistance after one minute. The resistance of *Coral L* and *FW.2* after two minutes' deposition

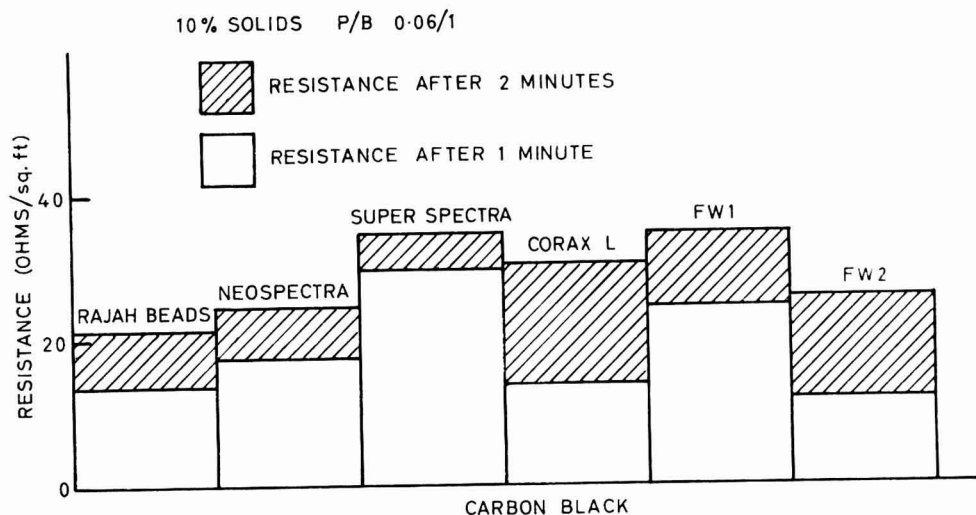


Fig. 4. Resistance of carbon blacks

was about twice the resistance obtained after one minute's deposition. On reducing the solids content of the paint to 5 per cent, the resistances shown in Fig. 5 were obtained. The resistance after one minute's deposition of all the carbon blacks was of the same order. During the second minute the *Super Spectra* and *FW.1* developed a very much higher resistance than the remainder of the pigments examined. In general the other blacks showed a smaller increase in resistance during the second minute of deposition than that obtained after the first minute.

At 5 per cent solids the resistance of all the carbon black pigments was about the same after one minute's deposition as was obtained in two minutes at 10 per cent solids content (compare Figs. 4 and 5).

The effect of pigment dispersion on film resistance was further examined by ball milling a slurry of *Ferroxite 01* in water soluble resin water at a pigment/binder ratio of 6/1. Portions of the slurry were removed at various intervals and made into paints of pigment/binder ratio of 0.5/1. The paints were diluted to 10 per cent non-volatiles and electrodeposited by 60 volts for two minutes at 22°C. As shown in Fig. 6, the film resistance increased with time of grinding up to 14 hours and then became constant. The experiment was in fact continued for two weeks, but there was no change in the film resistance after about 16 hours.

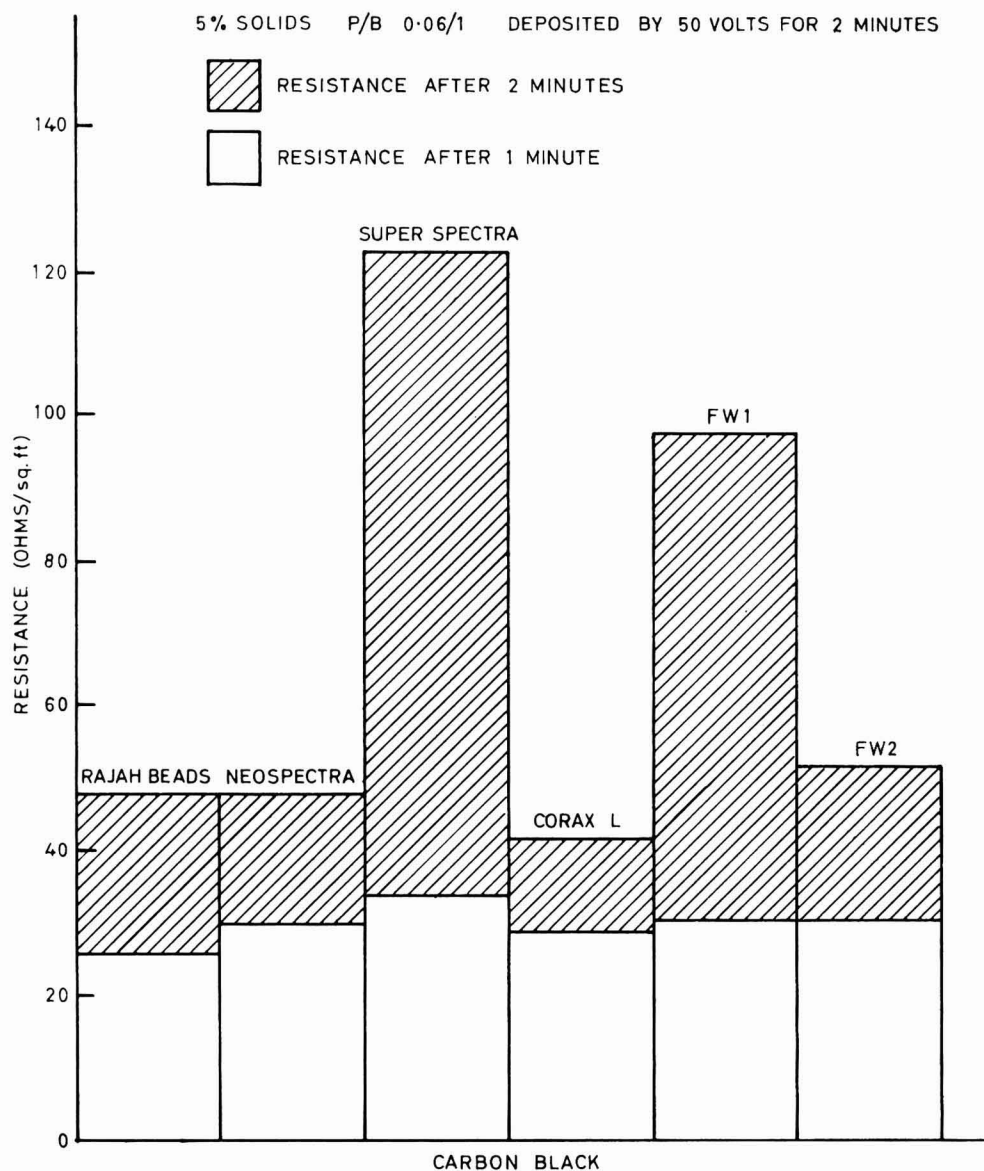


Fig. 5. Resistance of carbon blacks

These results were included in a paper presented to the Trent Valley Branch of OCCA on 25 February.

These further results confirm the earlier findings that a maximum film resistance is obtained for many pigments and extenders when paints of a pigment volume of between 30 and 50 per cent is used. It is widely held that for practical applications paints of pigment volume concentration of the order of 10 per cent are more likely to be used. Whilst the scales selected for production of the graphs illustrating change in film resistance with PVC made it difficult

to show differences at the lower PVC's, it is noticed that there are wide differences with change in pigment or extender type. Further work is being carried out to examine film resistances at the PVC's below 10 per cent.

The effect on resistance of pigment dispersion is confirmed by the ball milling exercise, the results of which are shown in Fig. 6.

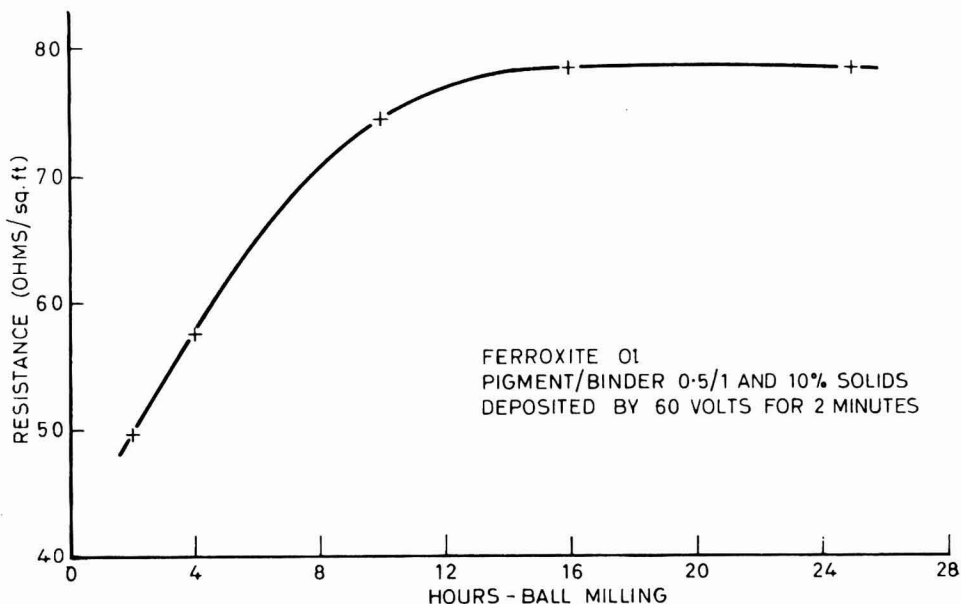


Fig. 6. Resistance/grind

L. Tasker.
J. R. Taylor.

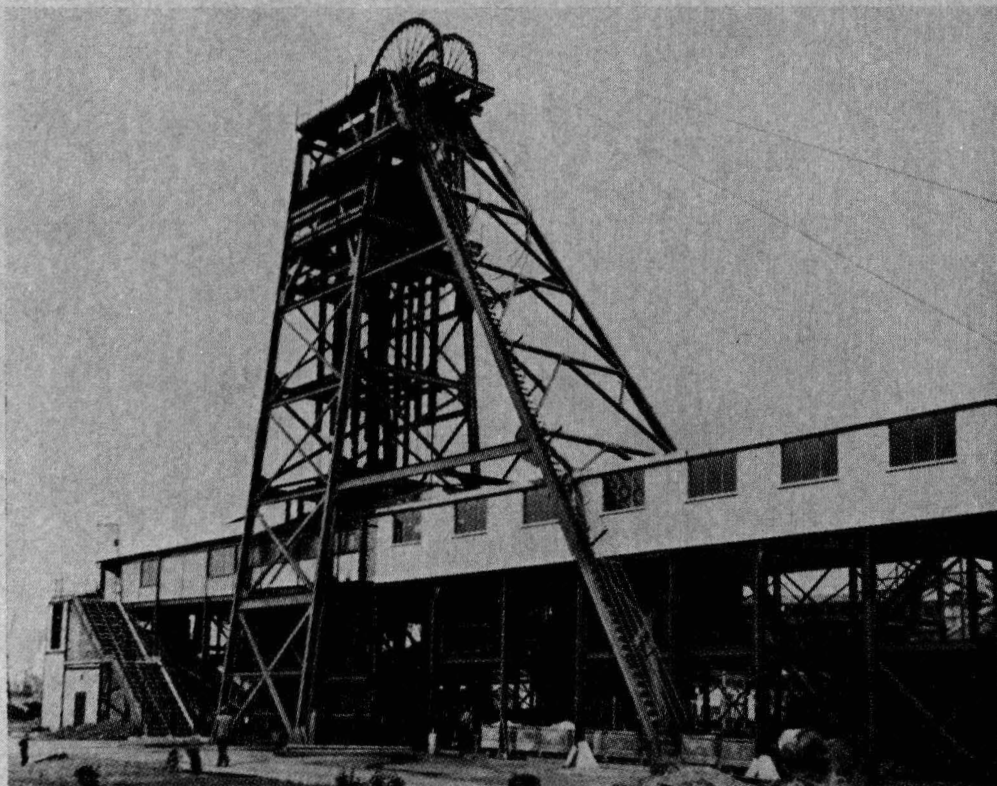
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Section Proceedings

Hull

Spectrophotometry and colorimetry—practical instrumental colour matching

The seventh ordinary meeting of the 1964-65 session was held in the Royal Station Hotel, Hull, on 1 February at 7 p.m., when the Chairman, Mr. A. J. Ford, introduced Mr. J. L. R. Landry, who gave a lecture entitled "Spectrophotometry and Colorimetry—Practical Instrumental Colour Matching."

Mr. Landry said that of the major developments in the field of colour during the last 100 years, the most significant had been made in the last three decades. Until very recently the acceptance of instrumental and conceptual advances into industry had met with limited success.

However, an analogue computer (the Davidson and Hemmendinger Colorant Mixture Computer), which was introduced in 1958, had been proved to be a valuable instrument for use in colour matching both in the laboratory and in batch control during manufacture. Its successful application arose from its ability to combine the long-established principle of successive approximation to the concepts of instrumental developments already referred to above.

This computer was now widely used in the textile, paint and plastics industries and had played a significant part in bringing to fruition the work of countless contributors to the science of colour.

The lecture was followed by a discussion during which the following took part: Messrs. E. A. Brown, A. J. Ford, C. C. Mell, A. Robinson and P. N. Willis.

A vote of thanks to the lecturer was proposed by Mr. S. A. Reed.

The use of the Daniel Flowpoint technique

On Monday 1 March 1965 the ninth ordinary meeting of the session was held in the Royal Station Hotel, Hull, at 7.15 p.m., when a paper was given by Mr. D. G. Dowling on "The use of the Daniel Flowpoint technique as a guide to methods of manufacturing paints and printing inks pigmented with titanium dioxide pigments."

The lecturer said that flowpoint curves could be arbitrarily classified into good, average and poor dispersions. The nature of the curve was influenced mainly by the medium, but might also be interdependent upon the pigment type and solvent system.

With "good dispersions," milling and problems were few, rapid pigment dispersion was achieved at good mill loadings and productivity was high. With "average dispersions," the choice of milling machinery was more restricted, effective mill loadings were lower, milling times longer and productivity reduced. With "poor dispersions," productivity was even lower due to low effective mill loadings and long milling times.

The lecture was followed by a discussion in which several speakers took part, including the following: Mr. A. J. Ford, Mr. C. C. Mell, Mr. H. Pulford and Mr. P. J. Gay.

A vote of thanks to the lecturer was proposed by Mr. P. J. Gay.

W. A. R.

Manchester

The principles and techniques of pigment dispersion

The second meeting of the session for the younger members of the Section was held at the Manchester Literary and Philosophical Society on 2 April, when Mr. H. G. Cook lectured on "The Principles and Techniques of Pigment Dispersion."

Mr. H. F. Clay, from the chair, welcomed the large audience of 85 members and visitors, and commented on the encouragement it gave to the Section Committee (many of whom were present) to continue to provide these lectures.

Mr. Cook explained that he hoped to review the subject in a general manner rather than dealing with a part in greater detail so that a perspective viewpoint could be obtained on which to add further detail. To do this he had subdivided the subject into six sections, namely :

1. Why dispersion was necessary.
2. The technological effects of achieving good pigment dispersion.
3. Measurement of degree of dispersion.
4. The dispersion process.
5. Types of dispersion machinery.
6. Aids to dispersion.

Under the first heading Mr. Cook dealt with the manufacture of pigments, the primary particle size and the sizes and formation of aggregates and agglomerates and their behaviour when they were incorporated into media.

Dealing with the technological effects of achieving good pigment dispersion, Mr. Cook dealt with the elimination of bits, the development of gloss, strength and opacity and the reduction in flow as the dispersion process proceeded and the size of the dispersed pigment mass was reduced.

Mr. Cook then commented on the various ways of measuring the degree of dispersion. Although methods such as the electron microscope, the Coulter Counter and the Disc Centrifuge were available for obtaining the particle size distribution curve, these methods were not practicable for production control and could be misleading in development work if it was not remembered that they were carried out in excessively diluted suspensions. The usual instrument used was the Hegmann gauge, but it was suggested this only gave a very rough indication of the state of dispersion and should be considered in conjunction with the results of development of gloss and strength.

Dealing with the dispersion process Mr. Cook considered the penetration and wetting of aggregates (factors rate of shear and viscosity of resin), the breakdown of aggregates (the energy factor) and the stabilisation of dispersion. The relationship of these stages to the dispersion process and the effects of media addition to millbases were described together with their effect on can stability.

Mr. Cook then explained the importance of the correct pigment/resin/solvent ratio to give the best viscosity and dispersion conditions and dealt with the requirements and characteristics of the various types of machinery used, including heavy duty mixers, triple roll mills, ball mills, sand mills and cavitation mixers.

Considering aids to dispersion, the lecturer dealt with micronised pigments, flushed pigments, dispersed pigment pastes, pigment chips and additives. He explained the necessity to balance the additional cost of treatment *versus* the possible effect of additives on the standard of dispersion achieved, the ease of achieving dispersion and the properties of the product with particular respect to gloss, opacity, can stability

and durability. The specific nature of dispersing agents for particular pigments and systems was also emphasised.

In the discussion period Mr. Cook dealt with interesting questions, including aspects of micronised spray drying, the effects of solvent wetting of pigments, the effect of heat in dispersion, the specific types of surface treatment given to particular pigments, the best dispersion techniques for mixtures of alkyd and amino resins, and the best media and solvent mixtures for obtaining stable dispersions.

In proposing a vote of thanks Mr. W. F. McDonnell expressed the thanks of the audience to Mr. Cook for presenting such a lucid, precise and concise review of the subject in such an interesting and competent manner. He hoped Mr. Cook thought the attendance was due reward for the effort he had put into the classification and presentation of the data and he was sure the Section Committee would continue to attempt to provide further lectures of the same high standard in view of the great interest shown. The audience demonstrated their wholehearted support and thanks in the appropriate manner.

W. F. MCD.

New developments in the field of polyurethane lacquers

The sixth and last technical meeting of the session was held at the Strand Hotel, Liverpool, on 12 March, with Mr. H. F. Clay in the chair, when Dr. Mennicken presented a paper entitled "New Developments in the Field of Polyurethane Lacquers."

Dr. Mennicken first described the well-known basic chemistry involved in the formation of urethanes. He discussed the preparation of non-toxic isocyanate reaction products which could be used without excessive precautions and would react with water or organic materials with free hydroxyl groups. Before passing on to the newer materials, he also reviewed the formulation and use of one-pack (moisture cured and urethane oils) and two-pack materials and commented on the excellent chemical and abrasion resistance properties of the polyurethane systems.

The lecturer then discussed in detail the aliphatic isocyanate systems which were claimed to be non-toxic and to have exceptional durability and non-yellowing properties. These claims were made as a result of five years' practical experience of the materials under a wide variety of environmental conditions. The materials used were derived from hexamethylene di-isocyanate and selected polyester resins with free hydroxyl groups. The reactivity of the materials was slow and catalysts such as organotin compounds were used in small proportions to increase the reaction rate. Dr. Mennicken explained that with these systems there were four major factors to be considered when formulating. These factors were the type and amount of catalyst, the temperature at which curing would take place, the concentration of the reactants in the solution, and, lastly, the type of solvent used, whether aromatic hydrocarbon or polar.

If these factors were considered for a particular isocyanate hydroxyl resin system, the reaction rate could be varied to give the desired compromise between pot life and curing time. It was quite possible with these systems to cure satisfactorily as low as 0°C.

The performance obtained with a typical system of this type was then described using a commercial isocyanate product of 22 per cent reactivity with a polyester phthalic anhydride resin with 8 per cent hydroxyl reactivity. Laboratory results and slides of practical performance were shown to show the outstanding durability, non-yellowing, non-chalking and chemical and solvent resistance.

The discussion that followed, after an impromptu interval, covered both the chemistry and use of the isocyanate based materials. In reply to a questioner,

Dr. Mennicken said that zinc octoate was considered to be a satisfactory catalyst from both technical and economic aspects ; the amounts used generally varied between 0.1 and 0.4 per cent on the non-volatile binder. The lecturer also stated that the improved non-yellowing properties of the aliphatic isocyanate compared with the aromatic isocyanates were considered to be at least partially due to the eventual formation of aromatic amines in the case of the aromatic isocyanate based materials, giving rise to coloured compounds as in dyestuff chemistry. Dr. Mennicken also dealt with questions on the stability problems of one-pack materials and the methods used to ensure the water content of pigments did not affect stability.

Dealing with questions on the uses and properties of the aliphatic isocyanate systems, Dr. Mennicken explained the limitations of all impervious systems on wood subjected to exterior exposure and the unfortunate necessity to treat and completely seal the complete surface if satisfactory results were to be obtained, a position which was more ideal than practical. The lecturer also explained the materials could be used over any previous coating, provided it was sufficiently resistant to the solvents used in the system. Sanding was preferred before overcoating, especially if more than one coat of the urethane system was to be applied.

In proposing a vote of thanks, Dr. G. A. Wolstenholme congratulated the lecturer on the quality of the lecture, the standard of presentation and the fluent way he had both delivered the paper and answered awkward questions. Dr. Wolstenholme explained he had been very interested in the newer aliphatic isocyanates, particularly their application and uses. He had already found that the use of isocyanates in the home had greatly contributed to domestic harmony, due to their ability to take hard knocks and resist alcohol. The large audience of approximately 120 (keeping the Liverpool meeting average well above the century) enthusiastically acknowledged their thanks and appreciation.

W. F. MCD.

Midlands

The Newton-Friend Lecture

The ulterior appearance of buildings (some effects of weathering and air pollution)

Each year the Section has one meeting where the subject chosen is likely to interest members' ladies as well as the members themselves. The 1965 Newton-Friend Lecture was given on 19 March at The Chamber of Commerce, Birmingham, by Mr. R. B. White and his subject was "The Ulterior Appearance of Buildings (Some Effects of Weathering and Air Pollution)."

Mr. White said that there is a growing tendency to replace things as soon as they become shabby and so the useful life of a building could be related to its appearance. Appearance was affected by weathering and by pollution, the rate of change depending on the climate. In London the deposit was greasy and often abrasive.

Modern buildings depend largely on surface condition for their appearance and are far more critical in this respect than classical design. Implanted surfaces, like sand-faced bricks tolerate far less surface loss than older materials, before losing their appeal. The current vogue of dispensing with cornices and other well-tried features often leads to ingress of water with consequent unsightly damage. More use could be made of colour but because of the difficulty of keeping clean this soon becomes dowdy.

The speaker then illustrated with a number of slides the effects of weathering and pollution on buildings in London. These effects he classified as fortuitous or caused by lack of precaution. Sometime the contrast between rain-washed areas and unwashed black areas accentuated desirable features and left a sense of history. In

other cases where rain-water was not properly distributed unsightly irregular patches were left. Steps to remove smoke from the atmosphere were welcome, but unless SO_2 was removed, this did not prevent decay. On the whole the public got the type of building it asked for and the architect was not entirely to blame.

The Chairman, Mr. R. D. Calvert, proposed a vote of thanks and expressed the appreciation of members and their lady guests.

L. R. S.

West Riding

Pigment dispersion and pigmentation structure

The meeting held on 25 February 1965 was held jointly with the Yorkshire Section of the Society of Chemical Industry, Colloid and Surface Chemistry Group. For this occasion the subject was "Pigment Dispersion and Pigmentation Structure," and the speakers were Mr. R. J. Cole, of the Paint Research Station, and Mr. Schwitzer.

Mr. Cole was the first speaker and in introducing the subject went to some lengths in defining the terminology he would use in presenting the concept of the process.

For a definition of particle, Mr. Cole favoured the use of "working unit" and showed electron micrographs of various pigments in a finely divided state illustrating the variety of working units.

The lecturer then turned to the process of making paint and gave a detailed description of the different stages undergone by dry pigment as it is dispersed and stabilised in the medium. The lecturer then considered the role of surface active agents in aiding the wetting and dispersion of the pigments and then keeping the dispersed pigments in a deflocculated state. In discussing the mechanism for stability, the lecturer reminded the audience of the two theories in the current vogue, *viz.* the entropic theory of adsorbed colloidal components and the Overbeck and Verwey electrical double layer theory of repulsion forces resulting from interaction of layers composed of separated positive and negative ions. Paint technologists, he said, with their experience of the excellent performance of polymerisable drying oil components, etc., have always favoured the former for non-aqueous systems. In recent years, however, evidence as to the role of electrical double layer stabilisations even for non-aqueous systems has accumulated.

Turning next to the composition of paint having optimum concentrations of constituents to give the desired performance and appearance, Mr. Cole said that only when one considered the critical pigment volume concentration could any worthwhile results be obtained. After describing results of earlier workers, he mentioned the work of Asbeck and Van Loo and the most recent method developed at Teddington for determining the CPVC.

Finally, the speaker turned to the function of the pigment in the dried film and discussed in particular the general structure effect. Two very important factors which needed further study, he said, were the effects of particle shape and chemistry of the pigment surfaces.

Mr. Schwitzer then addressed the meeting, but, as the time was very late, abandoned his talk and augmented one or two points in Mr. Cole's lecture. Of note was the clear description of what took place when pigment was wetted. He also made the point that the pigment manufacturer can, by coating the pigment, aid the ease of dispersion in paint medium.

At question time, Mr. Gray asked if Mr. Cole was convinced that a paint manufacturer wanted to disperse his pigments as apart from tinctorial power he wanted to stop settlement in the can. Settlement, Mr. Cole said, could be overcome

by using a thixotropic medium. Mr. Gilmot was still uncertain about the definition of the primary particle and thought it would vary from pigment to pigment, but would get down to a uniform size. Mr. Cole answered that electron micrographs showed that with some pigments it was easy to define the elementary particle, but others like barytes were not. However, by stating the method of grinding as the questioner inferred, would be reasonable. Mr. Miller inquired which of all the problems that faced researchers in the paint field he would like to see solved first. Mr. Cole thought that if problems relating to the pigment/surface interface and the integration of rheology and surface energy requirements were solved, this would take the paint chemist a long way in answering many other problems. Mr. N. Cochrane asked Mr. Schwitzer if he would enlarge on surfactants beneficial to pigment dispersion which did not exhibit side effects. Mr. Schwitzer replied that there was not a universal agent, but many acted quite specifically for particular systems. Metallic soaps were useful and non-ionics were good for stainers. He also mentioned that the HLB system seemed to work quite well, but stressed that the medium had quite an effect on the choice of agent.

A vote of thanks was moved by Mr. Pollard, of the Society of Chemical Industry.

L. J. W.

Information Received

(In case of difficulty regarding addresses, members and subscribers to the Journal should apply for details to the General Secretary of the Association at the address shown on the front cover)

New rubine toners

ICI DYESTUFFS DIVISION have added two new toners to their range of pigments for the printing ink industry. *Rubine Toners 4BTS* and *5BTS* are considered suitable for the formulation of improved and more economical magenta inks.

New Kronos information booklets

Four new information booklets have been issued by KRONOS TITANIUM PIGMENTS LTD. Numbered 3/E, 4/E, 16/E and 19/E, they are entitled *Measurement of the Optical Properties of White Pigments*, *Preparation and Properties of Titanium Dioxide Pigments of Uniform Particle Size*, *The Concentration Triangle* and *Do Titanium Dioxide Pigments Influence Drier Performance?* respectively.

Notes and News

17th Technical Exhibition, 1965



Featured on the Association's Information Bureau, shown above, were the forthcoming Torquay Conference, the 7th Australian OCCA Convention and the Association's publications

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The Seventeenth Technical Exhibition, as reported in last month's *Journal*, was held at Alexandra Palace on 22-26 March 1965. The change of venue meant that once again it was possible to hold the entire Exhibition under one roof. The greater space available, with adequate seating arrangements, made the Exhibition more pleasant for the visitor. A record number, estimated at 11,000, attended the Exhibition in the five days it was open, including a considerable number of visitors from 27 overseas

countries. This year there were 25 firms exhibiting for the first time and a considerable number of these were showing instruments and apparatus. In all there were 18 overseas firms exhibiting, mainly from Europe, and this in itself speaks for the international character of the Exhibition. In addition a number of overseas firms' products were displayed by agents in this country.

Technical education

The theme of the TECHNICAL EDUCATION stand this year was *Chemistry and Physics in the Study of Pigment Behaviour*, and by way of illustration a series of 12 excellent electron microscope photographs of pigments and extenders were supplied by the Paint Research Station. Also on show were various items of laboratory equipment. As usual full information on training and careers in the paint industry was available, including *More Than Meets the Eye*, written by Dr. S. H. Bell for the Paintmakers Association, which provides an excellent guide to the scientific career which the industry offers.



Photo by

Lawson & Co.

The theme of the Technical Education Stand was "Chemistry and Physics in the Study of Pigment Behaviour". Illustrated with many micrographs and working models, the Stand proved of considerable interest not only to the school parties invited to the Exhibition but also to many technical personnel

For the seventh year in succession parties of Sixth Form Science students were invited to attend the Exhibition. The numbers were rather lower than in the previous year, but 420 students from 20 schools attended over the three days, during which

short talks were given prior to the students seeing the Exhibition. The talks were given by Dr. S. H. Bell, Mr. G. L. Holbrow and Mr. A. T. S. Rudram.

As in previous years the wide variety of disciplines and expertise now employed in the surface coatings industries was exemplified by reference to the work of microscopists, microbiologists, electrochemists as well as that of chemists and physicists. The reliance now placed by many industries on surface coatings for the protection, decoration and functioning of their products was illustrated by reference to the increasing demands of the aircraft, engineering, electronics, packaging and other interests of widening importance. The students were referred in particular to the Technical Education stand and the exhibits shown there.

Clearly the talks were of considerable interest, as judged by the concentration and attention of the visiting students. They were, in general, more ready to talk about the subject and question the lecturers during the coffee break which followed the talks than ask questions at the end of the talks themselves.

Research association

The PAINT RESEARCH STATION exhibit this year had as its theme *electron microscopy*, and a number of topics from the Station's research programme were selected to demonstrate the usefulness of this modern technique. The impossibility of bringing the electron microscope and shadowing equipment to the Exhibition left the display perhaps a little bare in comparison with other years, when a wealth of apparatus has been shown. The many electron micrographs which formed the substance of the exhibit were well chosen and of excellent quality, and a series of models showing the stages in the preparation and shadowing of specimens for examination admirably demonstrated the way in which electron micrographs should be interpreted, a matter not always easy to grasp for those inexperienced in the art.

Technical press

The PAINT MANUFACTURE stand stressed the wide variety of subjects covered by the journal and the technical articles regularly included. Also on the stand was a good selection of technical books available through the publishers.

The PAINT, OIL AND COLOUR JOURNAL stand, in addition to highlighting the aspects of news coverage and regular technical features included in the journal, also provided an information service during the Exhibition. The newly published *Paint, Oil and Colour Year Book, 1965*, which was on view and which aroused the interest of overseas members, is supplied free to *POCJ* subscribers.

On the PAINT TECHNOLOGY stand a backcloth of blown-up photographs portrayed the theme "Formulation → Application," and served to set off the two major publications, *Paint Technology* and *Product Finishing*. Other publications on display included the *Paint Trade Manual of Raw Materials and Plant* and the *Finishing Handbook and Directory*.

TRANSLATION AND TECHNICAL INFORMATION SERVICES displayed a range of publications, including the new journal *Paint and Resin Patents*, and the established *Continental Paint and Resin News*, illustrating the extensive abstract, news and patent coverage of surface coatings developments at home and abroad, including Eastern Europe. Attention was also drawn to translation, searching and watching services available to meet specific needs.

Pigments

ALLIED COLLOIDS LTD. exhibited a range of pigments from BASF, including three new phthalocyanine blues, *Heliogen Blue NFB*, a non-flocculating *alpha* type, and *Heliogen Blues LBGO* and *LBGT*, both *beta* types suitable for printing inks. A new

yellow shade phthalocyanine green, *Heliogen Green 8 G*, was also on show, together with a spirit soluble basic dyestuff for use in flexographic inks, *Victoria Pure Blue FGA*. *Paliogen Red LK 7095*, a new perylene pigment, could be used in paints and plastics in place of cadmium reds.

AMALGAMATED OXIDES LTD. demonstrated the use of *Zincoli* zinc dusts in zinc rich paints as protective metal primers for atmospheric and underwater use. The uses of different pigment volume concentrations and zinc contents indicated how economies could be made by careful choice of extenders and media. The results obtained with inorganic silicates were of particular interest, although the optimum silicate ratio was of importance.

F. W. BERK & CO. LTD. exhibited their *M 50* and *DAP* pigments. The latter is claimed to prevent rust-staining. VICTOR BLAGDEN & CO. LTD. showed *Duragold* bronze powders from Claremont Polychemical Corporation, USA, having improved stain resistance and suitable for many types of media. Organic pigments from Société de Produits Chimiques et Matières Colorantes de Mulhouse on display included a series of predispersed colours for rotogravure inks and the *Chromatex* range of pigment dispersions for emulsion paints.



Photo by

Lawson & Co.

The larger area available at Alexandra Palace enabled a more spacious layout of the Exhibition. Especially welcomed by both exhibitors and visitors were the attractive seating areas around the Hall where they were able to meet their friends

BRITISH TITAN PRODUCTS LTD. display was principally devoted to the new titanium dioxide pigment, *Tioxide R.TC 5*, the first chloride process pigment commercially produced in Europe. Panels showing the exceptional brightness and cleanliness of hue were on display. Also on show was *Tioxide R.HD 6*, a new grade made by the conventional process, with improved opacity, together with technical information about the established grades of titanium dioxide.

BUSH BEACH & SEGNER BAYLEY LTD. exhibited the range of Degussa carbon blacks. CIBA CLAYTON LTD. showed the results of weathering tests on their range of *Cromophthal* pigments in stoving media. The use of *Cromophthal Bordeaux RN* together with inorganic pigments in the production of maroon and red shades was also illustrated. R. H. COLE LTD. showed the new French *Chantopac* range of micronised pigment dispersions in chlorinated rubber and polyamide resins, together with the *Sirius* range of bronze powders, giving extra brilliance in printing inks and special industrial finishes. CROXTON & GARRY LTD. showed *Black Shield* carbon black dispersions. DISPERSIONS LTD. showed, by means of paste and chip dispersions in various media, how the specialist in this field could be of assistance to the paint and printing ink manufacturer.

FARBENFABRIKEN BAYER AG showed the ease of dispersion of a new grade of titanium dioxide, *Bayertitan R.K.B.D.*, with high moisture resistance and high gloss. New micronised *M* grades of red iron oxide, of increased tinctorial strength, also possessed a lower tendency to sedimentation than conventional grades. New organic pigments now available included *Helio Fast Orange GR*, *Helio Fast Green 8 G*, and three additional benzidine yellows with good rheological properties, *Helio Yellow GWF*, and *Helio Fast Yellows GGF* and *GRF*.

The GEIGY COMPANY LTD. also had on show a completely new range of organic pigments, showing remarkably good light-fastness in full and reduced shades and good overspray properties. These were *Irgazin Yellows 2 GLT* and *3 RLT*, *Orange RLT*, and *Red 2 BLT*, all isoindolinone pigments, and *Irgazin Violet BLT*, a dioxazine pigment. Some of these pigments were also available as multipurpose stainers. Also on show were *Irgazin Red GLT* and *Violet 6 RLT*, which will become available later in the year.

British made *Philblack* was displayed by R. W. GREEF & CO. LTD. HOECHST CHEMICALS LTD. showed new quinacridone pigments, *Permanent Red E3B* and *Permanent Pink E*, which combined extreme light fastness, heat stability, and solvent resistance with previously unattainable brightness of shade. The range of hybrid benzidine types, combining the lightfastness of hansas with the strength and solvent resistance of benzidines, has been extended to the more greenish yellows with *Permanent Yellows H10G* and *FGL*. A range of predispersed pigments for printing on pvc was also displayed.

IMPERIAL CHEMICAL INDUSTRIES LTD., Dyestuffs Division, featured well presented graphs and display panels illustrating the improvements achieved in the new chromes, phthalocyanines and rubine toners. *Monastral Fast Blue FBS* was a new non-flocculating pigment of greatly increased strength, with a high rate of dispersion. Also on show were two new printing ink grades of phthalocyanines. *Rubine Toner 4 BTS*, on show with another grade, *5 BTS*, had been developed in an attempt to meet the requirements of the new CEI 12/64 magenta process ink specification. New *Supra Fast Chromes* showed distinct advances in darkening resistance.

The stand of IMPERIAL SMELTING CORPORATION LTD. was devoted to a number of technical displays illustrating various aspects of the use of their products. The effects of various proportions of zinc oxide in reducing mould growth was shown. The varying reactivity of the different grades of zinc oxide with two thickeners in pva emulsion paints had been studied. Gloss retention in relation to the particle size of the zinc oxide was the subject of another exhibit, and the effects of type of medium, zinc oxide content, pigment volume concentration, and the effects of light and ammonia on yellowing were also presented. The effect of various extenders, surface agents and thickeners in zinc dust primers was also on show.

INDUSTRIAL COLOURS LTD. showed the *Flare 600* and *610* series of fluorescent pigments for screen inks, and the *630* series for letterpress and offset. The *810* series for printing inks, lacquers and plastics was also on show. KEMISK VAERK KOEGE A/S

showed their latest range of organic pigments and pigment dispersions. The main feature was a new *Benzidine Yellow 7571* developed specifically for printing inks, with improved flow properties, strength and transparency.

KINGSLEY & KEITH (CHEMICALS) LTD. showed *Harmon* pigments from Allied Chemical Corporation. A new gold paste, *F 5870*, was compatible with both thermo-setting and thermoplastic acrylics. Blends of *F 5870* with aluminium pigments and organic reds were shown. The *Vynolour 60* series of "stir-in" pigments for vinyls, *CAB* dispersions for acrylics and nitrocellulose and *Minorga* and *Microlan* pigments for alkyd enamels were on show, together with the *Versatyl* flushed colours from Sherwin Williams.

KRONOS TITANIUM PIGMENTS LTD. presented a number of technical exhibits relating to the use of their *Titanox* and *Kronos* pigments. Drier adsorption and its effect on performance was the subject of one display. A study of the correlation between natural and accelerated weathering had also been made and would shortly be reported in a technical paper. The behaviour of titanium dioxide pigmented systems in electro-deposition was also under investigation. The stand of LAPORTE TITANIUM LTD. featured two grades of titanium dioxide pigment, *Runa RE 30* for use in high pvc emulsion paints, using pva homopolymer, acrylic copolymer and pure acrylic emulsions, which had a low demand for sequestering agents such as tetron, and *Runa RO 60* which was developed for use in glossy emulsion paints. A feature of both pigments was their low water soluble content.

PFIZER LTD., a new exhibitor this year, showed *Stay/Steel* stainless steel flake pigments developed by C. K. Williams & Co., USA, of value as protective pigments, compared with aluminium flake and micaceous iron oxides. Also on display were a range of high purity pigments recommended for electrodeposition and a range of magnetic iron oxides for use in magnetic inks.

Pigment dispersions were exhibited by REEVES & SONS LTD. These were the *Bytuco* range, dispersed in blown castor oil, and a range dispersed in an alkyd medium. Specialised and custom-made dispersions for individual requirements were also featured. SPELTHORNE METALS LTD. displayed the use of metallic lead dispersed in inert media for underwater use. The performance of metallic lead epoxy primers applied over weathered pretreatment primers was also demonstrated.

STERLING COLOUR CO. LTD., exhibiting for the first time this year, offered a number of fluorescent pigments in various shades of yellow, orange, red and green, and expect to have shortly a fluorescent blue pigment. Specialised grades were also available, incorporating optical bleaches to increase light fastness for prolonged outdoor exposure. Micronised grades, for rotogravure inks, were also available. SWADA (LONDON) LTD., in conjunction with H. Haefner & Co. Ltd., exhibited further extensions to their range of *ZO Fluorescent Concentrates*, which are now suitable for ROP news ink.

Extenders

BUSH BEACH & SEGNER BAYLEY LTD. displayed Degussa's development of hydrophobic silicas, for use with water soluble resins to improve salt spray resistance. A new product, *Silbarex 20*, consisted of a co-precipitate of barium sulphate and silica with a spherical particle shape and a size between 1 micron and 35 millimicrons, for use in stopping compounds and undercoats.

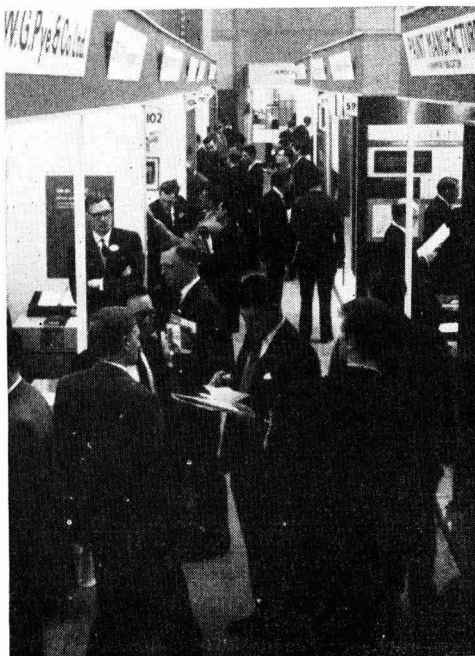
CROXTON & GARRY LTD. showed the *Omya* range of calcium carbonates, including *Vedar*, a precipitated calcium carbonate for use in pva emulsion paints, *Millicarb*, *Omya BLB 2* and *BLP 3* for matt paints. In a demonstration it was shown how *Millicarb* could replace up to 10 per cent of the titanium dioxide in a gloss paint without loss of gloss.

ENGLISH CLAYS LOVERING POCHIN & CO. LTD., exhibiting for the first time this year, showed two china clays specially developed for emulsion paints. *ECR* was specially calcined to increase its refractive index from 1.5 to about 2.0, thus making it useful as an opacifier. The introduction of *M 100* into emulsion paints improved scrubability, probably due to its wide particle size range. Weathering tests on emulsion paints containing china clays showed no blistering, cracking, or flaking and only moderate chalking even at high PVC's, with very little dirt pick-up. R. W. GREEF & CO. LTD. showed various grades of whiting from Superfine Chalks Ltd.

The stand of JOHNS-MANVILLE CO. LTD. showed filter aids, extenders and flatting agents based on diatomite, perlite, asbestos and synthetic silicates. A new synthetic silicate, *Calflo E*, was capable of absorbing several times its weight of liquid while retaining the flow properties of a powder. A/S NORWEGIAN TALC had on display the results of recent work on micro minerals, including *Microdol*, *Micro-Talc* and *Micro-Mica*, together with suggested formulations.



Photo by



Lawson & Co.

Wider corridors eased the congestion that was evident at the RHS Halls. Even so, the large number of visitors gave the space between stands a crowded appearance

Resins—emulsion polymers

BRITISH OXYGEN CHEMICALS LTD. introduced two new emulsion copolymers of vinyl acetate and butyl acrylate, *Vandike 7085* and *Vandike 7086*. These are designed for use in primers and undercoats for alkyd enamels and in highly structured emulsion paints. R. H. COLE LTD. showed the 700 series emulsions of Plastic Products Ltd., the main interest being in butyl methacrylate copolymers which could be used in tough, wear-resistant coatings for brass, copper and aluminium. The new *Elvax* emulsions also shown are of special interest in heat seal adhesives.

DUNLOP CHEMICAL PRODUCTS in a well set out display featured a new vinyl acetate/versatate copolymer emulsion, *Polimul 1175*. A series of exposure panels showed the superiority in alkali and water resistance and general durability of paints based on this material. Paints having a high gloss, approximately 80 per cent 45° EEL, were possible using mixtures of *Polimul 1160*, an alkali soluble acrylic polymer solution, with the emulsion, *Polimul 997*. HOECHST CHEMICALS LTD. showed their range of *Mowilith* emulsions, particular emphasis being placed on novelty applications such as brushable plastics and fibre containing paints. LENNIG CHEMICALS LTD. featured several new acrylic resins, including *Primal AC-61*, a 100 per cent acrylic emulsion, which is recommended for concrete floor paints.

Further technical information was made available by NATIONAL ADHESIVES LTD. on their vinyl acetate/acrylate copolymer, *National 125-2414*, and an apparatus for measuring the minimum temperature for film formation was also demonstrated together with results of tests on different types of emulsion.

SHELL CHEMICAL CO. LTD. showed latest results on the use of the vinyl ester of *Versatic 911* in copolymer latices for paints of improved durability. In a novel presentation by VINYL PRODUCTS LTD., the versatility of their *Vinamul* and *Vinacryl* emulsions in building construction was demonstrated with the aid of a section of cavity wall. Thixotropic, textured and fire-retardant paints based on these emulsions were displayed in this manner.

Resins and oils—water thinnable (other than emulsions)

BAKELITE LTD. featured a water soluble acrylic polymer, *Acrylic Resin 200*, which was particularly suitable for stoving enamels, but could also be used in primers. FREDK. BOEHM LTD., in association with Chemische Werke Albert of Wiesbaden, showed latest developments in their range of water soluble resins for stoving compositions, viz. *Hydro Alkyd L 5/3* and *Hydro Amine L 2/155* for finishing systems and *Hydro Alkyd L 8/3* for primers. Latest information from BIP CHEMICALS LTD. was available on *L 2740*, a development product designed for application by electrodeposition. BRITISH RESIN PRODUCTS LTD. gave prominence to their work in the water soluble resins field with technical data on *Epok W 1763*, suitable for pale stoving primers, and the newly developed resins *Epok WH 1762* and *WL 1762*. These latter are designed specially for electrodeposition and are of high and low electrical resistance respectively. Recent work on the effects of pigmentation on electrodeposition characteristics was presented by means of a visual aid unit. N. V. CHEMISCHE INDUSTRIE SYNRES, a newcomer to the Exhibition, showed their water soluble alkyds, *Synres D 5075* and *D 5175*, and melamine resin *Synres ME 5370*, which in combination gave high gloss stoving finishes. Emphasis was also placed on electrodeposition, and a practical demonstration showed how a one-coat finish based on *Synres WPR 264* could be applied in five seconds.

CRAY VALLEY PRODUCTS LTD. also featured electrodeposition as one of their main exhibits, the technique being demonstrated with a small German plant using *Resydrol*-based paints. Details were available on conducting primers which after electrodeposition and stoving could be given a finishing coat by the same process. A new technique for measuring "throwing-power" was also shown. DUNLOP CHEMICAL PRODUCTS DIVISION gave further technical information on the water soluble acrylic resin *Polimul 1165* introduced last year. High gloss white stoving enamels based on this resin were described, a kitchen sink unit being shown as a typical application of such materials.

NEDERLANDSE CASTOR OLIEFABRIEK "NECOF" N.V. had further information available on their water soluble cyclopentadiene treated oil, *Necowel L-2075*. This can be used as an air-drying vehicle or as the basis of baking primers applied by conventional or electrophoretic techniques. Application by the latter technique was

demonstrated, including the deposition of two-coat systems. PLASTANOL LTD. featured *Laquanol 5*, a water thinnable vinyl modified alkyd resin introduced last year, and gave more information on its use in stoving primers and finishes applied by electrodeposition. Further developments in the use of *Arolon X 1177* for car finishes of high gloss and durability were shown by SCADO-ARCHER-DANIELS N. V., and information was available from STYRENE CO-POLYMERS LTD. on *Scopasol 550*, a recently developed water soluble thermosetting acrylic resin, which can be applied by electrodeposition.

YOUNGHUSBAND STEPHENS & CO. LTD. featured new developments in their range of water soluble oils. *Wybesol 2* was now available and recommended for industrial stoving primers applied by dipping, spraying or electrodeposition. *Rothersol 2* had improved viscosity characteristics suitable for printing inks. SHELL CHEMICAL COMPANY LTD. introduced a series of water solubilised *Epikote ester* resins suitable for electrodeposition application.

Resins—unsaturated polyesters

ALLIED COLLOIDS LTD. demonstrated the use of *Ludopal U 150* as a basis for fillers and stoppers. This resin has unusual flexibility combined with good sanding properties and can be used on metal. N.V. CHEMISCHE INDUSTRIE SYNRES demonstrated compositions based on *Synresite* polyesters, also suitable as fillers for refinishing car bodies. CHEMISCHE WERKE HÜLS A.G. indicated new applications for *Vestopal LT* as a component of pvc type compositions suitable as metal primers of both air-drying and stoving types.

Resins—polyurethanes

VICTOR BLAGDEN LTD. showed a comprehensive selection of panels coated with Cargills range of polyurethane oil-based systems and some new moisture-cured types particularly suitable for coatings liable to heavy wear. N. V. CHEMISCHE INDUSTRIE SYNRES demonstrated a two-pack alkyd/isocyanate-based primer suitable for car body repairs. CROXTON & GARRY LTD. had information on *Uresol 60* and *Uresol 50*, two new one-package polyurethanes, designed for use in clear and pigmented finishes. Latest developments in the *Desmodur/Desmophen* range of polyurethane lacquers were displayed by FARBENFABRIKEN BAYER AG. A new one-component polyurethane precondensate, *Scurane VUR*, for wood finishing was shown by R. W. GREEF & CO. LTD. on behalf of Société des Usines Chimiques Rhône-Poulenc. IMPERIAL CHEMICAL INDUSTRIES LTD. (Dyestuffs Division) introduced a new polyether-isocyanate system, *Daltolac 2190/Suprasec 1160*, which had improved chemical resistance, as was demonstrated in a very effective manner by running actual resistance tests on the stand. NOVADEL LTD. showed a range of *Nourypol* and *Nouryflex* products which have been developed as the polyalcohol components for polyurethane coatings. They have low viscosities and are particularly suitable for solvent-free systems.

Resins—epoxy

Zinc rich primers based on a new high molecular weight one-pack *Araldite* resin system were exhibited by CIBA (ARL) LTD. Spray applied coatings of high viscosity *Araldite* resins were also shown and the flexibility of a new *Araldite* liquid resin demonstrated. SHELL CHEMICAL COMPANY LTD. introduced new two-pack *Epikote* formulations of outstanding hot water resistance. Improvements in the composition of *Epikote* high solids and powder coatings were also shown. A new pale-coloured hardening agent of the amine adduct type, *E.P.A. 548*, was announced by FREDK. BOEHM LTD. ANCHOR CHEMICAL CO. LTD. showed their range of curing agents for epoxy-resins, including a new anhydride, *GTMA*, and agents based on BF_3 , *Ancaflex 70* and *150*.

Resins—acrylic thermosetting (non-aqueous)

ALLIED COLLOIDS LTD. introduced a new thermosetting acrylic resin—*LR 8119*. BRITISH RESIN PRODUCTS LTD. featured thermosetting acrylics as media for car finishes and showed new developments in their range, including the new “high solids” materials *Epoks D 1120*, *D 1170* and *D 1220* and the low-bake types *Epoks D 2100*, *D 2101* and *D 2102*. CRAY VALLEY PRODUCTS LTD. also exhibited a low-bake resin, *Synolac 832 S*, which, in conjunction with a butylated melamine resin, could be cured at 120°C for 30 minutes. Panels showing the excellent gloss obtained with pigmented and polychromatic finishes based on this system were displayed. Resins which cure at 120°C/30 minutes in the presence of catalyst were shown by STYRENE CO-POLYMERS LTD. *Scopacron 80* had been specially designed for car finishes and was noted for cold-check resistance. LENNIG CHEMICALS LTD. introduced a new thermosetting acrylic polymer, *Acryloid AT-70*, designed to crosslink with epoxy resins. Information was also available on a series of experimental resins, *QR-449*, *QR-446 I*, *QR-445 A* and *QR-455*, having varying degrees of hardness and flexibility.

Resins—alkyds (non-drying)

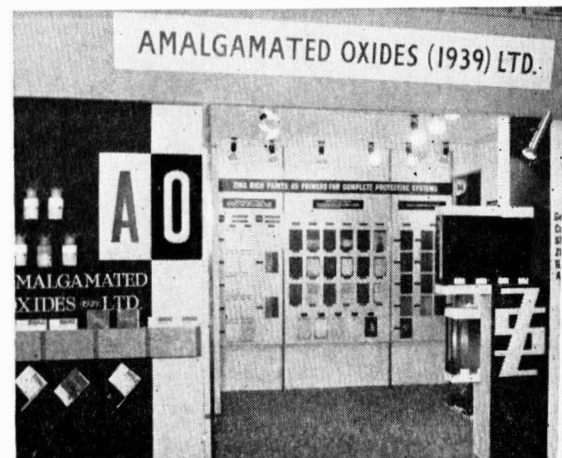
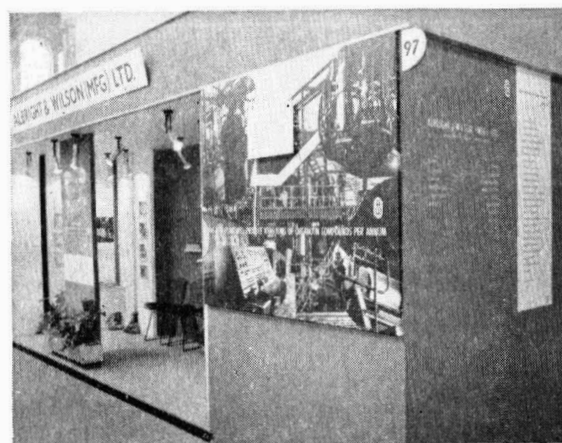
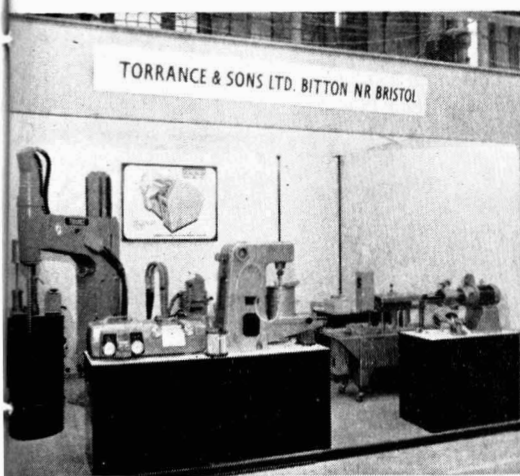
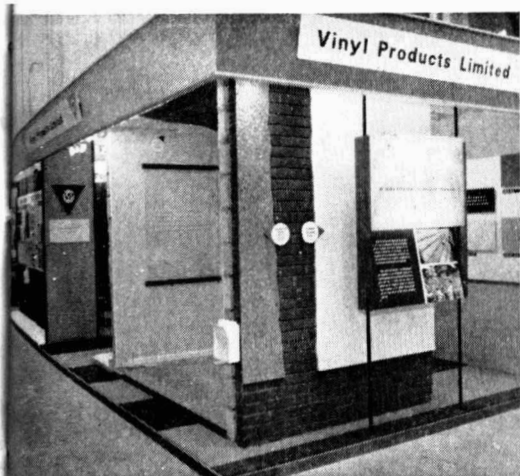
Further information was available on *Beetle resin BA 508*, a plasticising alkyd recently produced by BIP CHEMICALS LTD. for use with melamine resins. BRITISH RESIN PRODUCTS LTD. introduced a new versatic acid-based alkyd, *Epok A 6004/70*, specially recommended for use in three-component motor car finishes. KUNSTHARSHAFABRIEK SYNTHESSE N.V. highlighted the versatility of *Setal 84* as a plasticising alkyd for melamine, nitrocellulose and polyurethane systems. W. A. MITCHELL & SMITH LTD. showed a new product, *Mitchalac 241*, recommended as a plasticiser in leather finishes. SHELL CHEMICAL CO. LTD. showed panels of finishes based on their *Cardura alkyds*, the range of which has now been extended.

Resins—alkyds (drying)

CRAY VALLEY PRODUCTS LTD. have brought out a new linoleic rich thixotropic alkyd, *Gelkyd 331 W*. This material is a replacement for *330 W* of the same series and has the same rheological properties. FARBENFABRIKEN BAYER AG exhibited *Alkydal F 29*, a short-oil alkyd for industrial stoving lacquers, and *Alkydal F 68*, an extremely low viscosity alkyd for decorative paints and lacquers. R. W. GREEF & Co. showed a range of alkyd resins produced by SOAB LTD. in their new United Kingdom plant. PLASTANOL LTD. had further information on their *Plastyrol* vinyl modified alkyds, the range of which has been extended. SCADO-ARCHER-DANIELS N. V. placed particular emphasis on quick-drying resins, new products including *Scadonoval 14-X-60*, a styrenated resin, and *Scadonovols 15-ML-55* and *16-ML-50*, both vinyl-toluenated resins. A new unmodified short oil soya alkyd, *Aroplaz 6008*, which air dries in 15 minutes, was also shown. A main feature of the STYRENE CO-POLYMERS LTD. stand was a rapid-drying styrenated alkyd, *Scopol 85X*, which showed particularly good adhesion. New vinyl toluene modified alkyds, *Scopols 58 M* and *58 SP*, were also on display. MARFLEET REFINING CO. LTD. showed a series of alkyds based on their refined marine oils.

Resins—amino

BIP CHEMICALS LTD. announced the availability of three new melamine resins—*BE 667*, for use in conventional systems with alkyds; *BE 668*, a low viscosity alkylated type designed for use with thermosetting acrylic resins, and *BE 670*, a hexamethoxymethyl melamine in liquid form suitable for both water soluble and solvent-based finishes. Marproof finishes based on *BE 667* were exhibited. FREDK. BOEHM LTD. showed *Pioneer FM. 522*, a new melamine resin for acid-hardened wood finishes which was considerably more economical in use than the normal modified melamine type.



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Shown above are some of the interior designs of stands at the Exhibition

A new melamine resin etherified with iso-butanol, *Dynomin MI-10*, was exhibited by NORSK SPRAENGSTOFINDUSTRI A/S, particularly suitable for low temperature stoving finishes. Panels demonstrating the good gloss of such systems were on display.

Resins—miscellaneous

The ANCHOR CHEMICAL CO. LTD. showed a range of styrene butadiene and vinyl toluene butadiene resins manufactured by the Marbon Chemical Division of Borg-Warner Corporation in America. These included *Marbon 110T MV* resin for use in multi-colour paints. COMPAGNIE FRANCAISE GOODYEAR exhibited *Pliolite VTAC* and *VTACL*, white spirit soluble vinyl polymers suitable for eggshell and gloss finishes for exterior applications. HERCULES POWDER COMPANY LTD. introduced two new fully hydrogenated resin esters, *S 994* and *S 1057*, both of exceptional stability. KINGSLEY & KEITH (CHEMICALS) LTD. had further information on the use of *Indopol* Polybutenes and *Amopol* Polypropylenes in caulking compounds. The SHELLAC EXPORT PROMOTION COUNCIL emphasised the versatility of shellac and demonstrated its usefulness as a modifier for modern synthetic resin-based coatings. CORNELIUS CHEMICAL COMPANY LTD. showed a range of Sinclair Petrochemicals SMA resins. These are styrene/maleic anhydride copolymers and may be used as pigment dispersing aids, protective colloids in emulsion polymerisation or cross-linking agents for epoxy resins.

SURFACE COATING SYNTHETICS LTD. demonstrated the high chemical resistance of *Surcoprene*-metallic lead paints when suitably plasticised.

Chemicals

AMOCO CHEMICALS showed their new grade of isophthalic acid. *Amoco IPA-95X*, which is claimed to give improved colour to polyester resins. The use of *Isophthalic Acid-95* in producing oil free alkyds was also demonstrated. KINGLSEY & KEITH (CHEMICALS) LTD. had further information on the use of dimethylol propionic acid (produced by the Trojan Powder Company) in formulating water soluble resins. An interesting development project was described by the UNITED COKE & CHEMICALS LTD. This concerned the catalytic conversion of *p*-xylene to *terephthalonitrile*, so offering a vapour phase route to *terephthalic acid*. IMPERIAL CHEMICAL INDUSTRIES (HOC DIVISION) featured methyl vinyl ether as a new monomer for the paint industry. Information on its uses in homopolymer form and as a component of copolymers suitable for surface coatings was available.

Solvents

CARLESS CAPEL & LEONARD LTD. provided information on special petroleum fractions of low benzene content. These *Paraset* solvents are produced to meet the increasing demands of the printing ink industry for solvents of lower toxicity.

IMPERIAL CHEMICAL INDUSTRIES LTD. presented some interesting preliminary results of basic research on solvent/solute interactions, using tetracosane as a model solute. Also on show was a demonstration of dipping and airless spraying of paints using trichloroethylene as solvent. Apart from the absence of fire-risk, there are particular advantages in the use of such systems for dip-coating. The uses of dimethyl formamide and tertiary butyl glycol ether as solvents were also displayed.

J. H. LITTLE & CO. LTD. showed products available from Henkel International *Tetralin*, *Dekalin*, *Methylhexalin* and *Hexalin* were recommended as high-boiling solvents in stoving finishes to improve flow and gloss and to overcome pinholing.

SHELL CHEMICAL CO. LTD. featured a range of glycol ethers and other solvents in the *Shellsol* range. Details of evaporation rates measured using the ETSI evaporimeter were presented, together with flashpoint data.

UNITED COKE & CHEMICALS CO. LTD. showed a range of high purity benzoles, toluoles and xylols now available, with a very narrow distillation range and low sulphur content (0.6 ppm for one grade of benzole).

Additives, driers, surfactants, fungicides, etc.

A section of a boat hull fixed to the wall, with a derelict hull below, was one of the features of the ALBRIGHT & WILSON LTD. stand. This caught the eye, with the object of stimulating interest in the use of tributyl tin oxide in anti-fouling paints. The various uses of TBTO, for control of mould and algal growth, were well presented in displays on the stand, together with other chemicals supplied of interest to the paint industry.

F. W. BERK & CO. LTD. had as their principal exhibit *Phelam* mercurial fungicides, which have extremely low solubility and vapour pressure, resulting in greater persistence in the coating. These fungicides are now available packed in a water soluble *Solu-Pack* for easy and safe handling. Other products on display were *Bentone* gellants, *Dythal* lead phthalate stabilisers for organosols and *Strodex* wetting agents.

BYK-GULDEN LOMBERG GMBH, a new exhibitor, showed a range of anti-settling and wetting agents. *Byk P 104* and *P 104 S* were additives for the control of flotation and flooding in air-drying and stoving paints. *Byketol OK*, a levelling aid for stoving finishes which eliminated "solvent boiling" during stoving, was on show. CIBA CLAYTON LTD. showed *Uvitex OB*, a non-toxic fluorescent brightening agent.

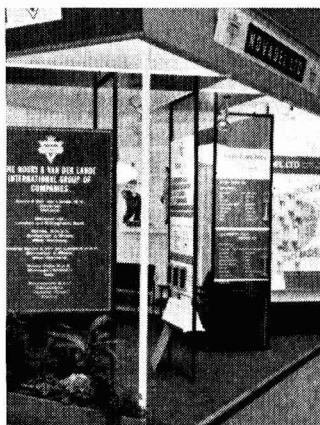
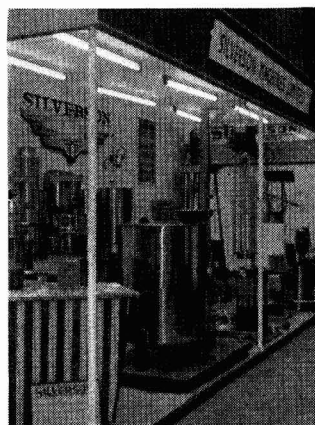
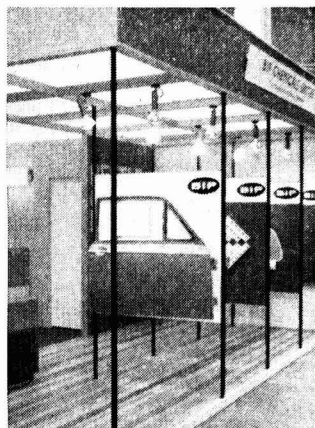
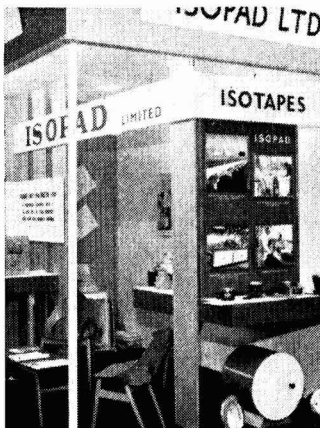
HARDMAN & HOLDEN LTD. showed the use of *Zircomplex* driers in promoting whiteness in air drying finishes. HERCULES POWDER CO. LTD. showed the use of *Natrosol* hydroxyethyl cellulose, which combined with metal complexes of titanium or zirconium to form shear-sensitive gels for nondrip emulsion paints. *Reten 763*, also on display, was a polyelectrolyte flocculant for the clarification of pigment-containing effluents. KINGSLEY & KEITH (CHEMICALS) LTD. showed *Zirco* driers, from Deutsche Advance Produktion.

Products from Henkel International were shown by J. H. LITTLE & CO. LTD., a new exhibitor. *Anti-Settling Agent 31-11*, a liquid, was recommended for use in wash primers and was claimed to be equally effective in polar and non-polar solvents, being adsorbed by the pigment. *Ceroxin* and *Ceroxin Special* were additives to improve the pattern, pattern distortion and resistance to sagging of hammer finishes. Anti-skinning agents were also displayed, together with wetting and anti-foaming agents.

NOVADEL LTD. exhibited organic peroxides, *Trigonox X 29* and *X 27*, and the well-known range of *Siccatol* driers, based on synthetic organic acids. SHELL CHEMICAL CO. LTD. also featured driers based on synthetic organic acids, *Versatic 911*, manufactured from C₈-C₁₀ olefines. TITANIUM INTERMEDIATES LTD. had on show products derived from titanium tetrachloride, illustrating a variety of uses such as modifying the rheological properties of paints, promoting adhesion of plastics, aiding dispersion and waterproofing.

Laboratory apparatus and instruments

BECKMAN INSTRUMENTS LTD., exhibiting for the first time, showed the *Beckman Model DB* double beam visible and UV recording spectrophotometer, with reflectance head, now manufactured in Scotland, which was designed for reflectance measurements over the range 280-720 millimicrons, as well as for transmission measurements, and which incorporates scale-expansion features controlled by limit switches. The CHURCHILL INSTRUMENT CO. LTD., also a newcomer to the exhibition, demonstrated the *Churchill-Metal Box Tackmeter*. Ink is applied at a predetermined film thickness to a temperature-controlled roller, with a jockey roller rotating in contact. The pull on the jockey roller at various speeds is electrically recorded and the instrument is claimed to be suitable for both control and research purposes. Another new exhibitor



Photos by

Further views of stands at the Exhibition

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was F. COPLEY & Co., showing a wide range of mainly German apparatus, including rapid weighing balances, gloss and whiteness meters, a tap density meter and a zoom stereo-microscope.

ELCOMETER INSTRUMENTS LTD. also exhibited for the first time. To complement the already well-established *Elcometer* thickness gauge for ferrous metals, the *Minitor* gauge, for use on non-ferrous metals, has been introduced. Also on show were the *Magnegage*, for accurate determination of very small up to large film thicknesses, and a simple pinhole detector. FERRANTI LTD. showed their well-known *Coaxial Cylinder* and *Ferranti-Shirley Cone and Plate Viscometers*. HERCULES POWDER CO. LTD. had on display a laboratory constructed tackmeter, working on a novel principle. ISOPAD LTD. showed a very small plastic-covered heating mantle for micro- and semi-micro work, together with normal size mantles. LIVINGSTON LABORATORIES LTD., also a new exhibitor, showed the *IDL Color Eye*, a combination colorimeter and abridged spectrophotometer (with 16 narrow band filters), which gives extensive colour information for a relatively small capital investment and which could be coupled to a computer for further calculations.

OPTICA UNITED KINGDOM LTD. was yet another new exhibitor, showing the *Optica CF4R* double-beam recording spectrophotometer, which may be used for direct transmission, diffuse transmission or reflectance in the visible and near UV. A second spectrophotometer could be used for fluorescence measurement. Also on display was the German multi-range *Rotovisko* viscometer. Also a newcomer was W. G. PYE LTD., with a particularly competent display of equipment for gas-liquid chromatography, which is now finding applications in paint laboratories. Also on show was a robust, low cost, *Model 79 pH Meter*, for laboratory and works use, the robust character being due to the pivotless taut band suspension, together with a range of spectrophotometers covering the whole spectral range from UV to IR.

RESEARCH EQUIPMENT (LONDON) LTD. once again exhibited their well-known comprehensive range of test equipment designed for the paint industry. Of considerable interest was the new *Micro-Indentation Hardness Meter*, see p. 520, to the design of Wright and Monk of ICI Paints Division, the unique feature of which was that a penetration and recovery time plot could be recorded from a normal supported paint film within a few minutes. By the use of a pneumatic sensing and recording system, a very reasonably priced instrument had been achieved. A rapid heating and cooling system incorporating a Frigistor covered a temperature range of from -20°C to $+90^{\circ}\text{C}$.

RUDOLPH MEIJERS INC., a new exhibitor, showed a range of equipment for testing printing inks. The *Tack-O-Scope*, a research and production control instrument for objective measurement of a wide range of ink properties, developed by the Institut Grafische Technik TNO, was shown, together with the IGT two-shaft *Printability Tester* and the recently introduced *Universal Printability Tester*, which will test at constant speeds of from 40-800 ft/minute and at controlled accelerating speeds.

SHEEN INSTRUMENTS (SALES) LTD. showed their range of paint-testing equipment. New developments were the *ICI Drying Time Recorder*, the *ICI Automatic Film Applicator* and a cone and plate attachment for the *ICI Rotothinner*.

UNICAM INSTRUMENTS LTD., exhibiting for the first time, showed part of their comprehensive range of spectrophotometers, covering the whole range from UV to IR as recording instruments. In addition, a manually operated instrument for the visible region 360-1,000 millimicrons was shown, together with pH meters and *Series 104* gas chromatographs.

Manufacturing equipment

F. W. BERK & CO. LTD. supplied details of their commission micronising facilities at their Stratford works. The stand of WILLIAM BOULTON LTD. effectively displayed a range of methods and techniques of increased efficiency for mixing and dispersing operations. On show were the *Podmore-Boulton Vibro-Energy Mill*, the *Boulton Vibro-Energy Screen* and the *Boulton Hi-Speed Dissolver* and information and technical data was available about other types of equipment.

R. H. COLE LTD. showed new Steatite granules for use in sand mills, together with a range of balls, lining blocks and laboratory pot mills from Steatit-Magnesia AG. Cox's MACHINERY LTD. displayed two full-size triple roll mills, the *Type 964* extra high speed triple roller mill. D. H. INDUSTRIES LTD. had on display a large variety of apparatus, including plant for media manufacture, dispersion and paint making, centrifugal clarification, filling and packing and electrodeposition of paint. The new *Sussmeyer Compact Mini-Sand Mill* had several advantages not previously available in the original design. A new pneumatic weight-operated filling unit was demonstrated and a *Sussmeyer Electrodeposition Unit* was demonstrated continuously.

ISOPAD LTD. showed a selection of their range of electric surface heaters, including a heating mantle for use in flameproof areas. This equipment is manufactured for 50, 100 and 200 litre capacity vessels and was developed in conjunction with QVF, being supplied as a complete package unit.

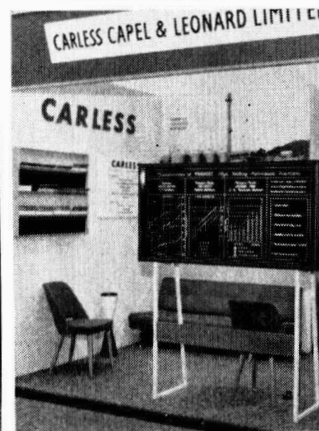
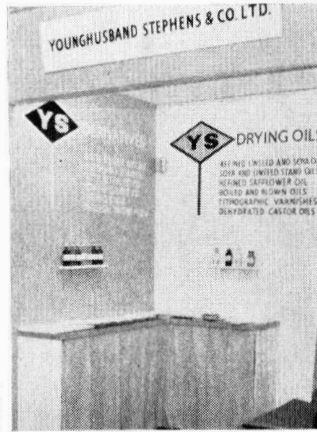
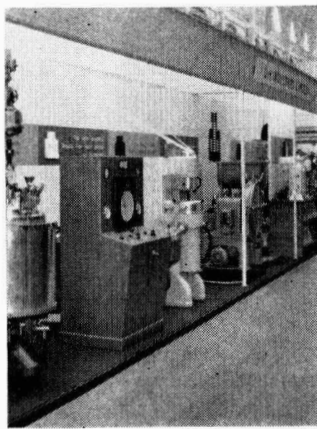
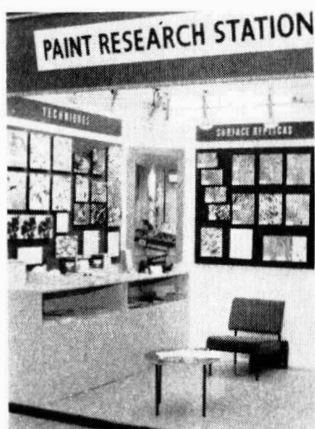
MASCHINENFABRIK HEIDENAU.V.E.B., a newcomer to the exhibition, showed a triple roll mill, *Type 813 NVS*, with hydraulic roll pressure and a hydraulic lifting device. This 13 x 32 in mill was said to handle 100-500 lb per hour of material, using 20-50 hp. MILLROOM ACCESSORIES & CHEMICALS LTD. featured the *Rotamix*, a free hanging homogenising disperser with an action designed to keep the equipment stationary within the liquid, and the *Biotomix*, a twin-headed disperser and mixer used for high viscosity materials and which is self balancing in operation. Also on show were the *Icarus* powder transporter, and high-density grinding media. The L. A. MITCHELL GROUP showed their well-known range of resin plant, mixers, extractors and heat transfer systems, etc. Spray driers are now manufactured under licence from Bowen Engineering USA. A series of extenders and granulators for handling wet filter cake before the drying operation was also of interest.

GEBRUDER NETZSCH, also present for the first time at the exhibition, showed the *Molinox Mill*, a continuously operating mill claimed to be more adaptable than the sand grinder, due to its ability to cope with media having a wide range of viscosity. Other exhibits were a double cone blender with fluid injection, incorporating an agglomerate breaker device consisting of flying chains, a planetary high speed ball mill and a vibrating sieve with vertical screens, reducing the tendency to clogging.

PREMIER COLLOID MILLS LTD. showed examples of their portable mixers and colloid mills and gave demonstrations of the larger scale equipment manufactured by their subsidiary, Chemical Engineering Premier Ltd. Emphasis was on tank-mounted side entry mixers, slow-speed agitation mixers and contra-rotating mixers, available in stainless steel fabrication. SILVERSON MACHINES LTD. had working demonstrations of their range of equipment, including an in-line mixer, coupled to a hopper feed which was capable of wetting pigments instantaneously. The machine had interchangeable heads and could be used as a disintegrator for pigment dispersion.

The exhibits of STEELE & COWLISHAW LTD. included a dry dispersion apparatus, the *Drydisperser*, suitable for dry blending a variety of materials, pigment blending, etc., a pilot size *Oblicone* vacuum drier, for blending and drying, the horizontal ribbon blade mixer, the *Mark 1A High Speed Planetary Ball Mill*, and a small scale *Cox Fluid Energy Mill*. TORRANCE & SON LTD. exhibited the *Torrance Hydraulic Cavitation Disperser* with infinitely variable speed drive. In addition, there were the *Attritor* and *Microflow* mills, the *Millmaster* laboratory triple roll mill and the *Bowers Automatic Coder and Can Closing Machine*, which may stamp codes on either top or bottom of the cans.

The WEYBURN ENGINEERING CO. LTD., showing for the first time, had a working demonstration of diaphragm metering pumps, delivering precisely determined quantities of liquids of a range of viscosities. The system consisted of a fixed actuating pump



Photos by

Further views of stands at the Exhibition

Lawson & Co.

operating a number of metering heads, which may be remotely mounted and which have adjustable deliveries. WINKWORTH MACHINERY LTD. showed examples from their range of mixers and masticators, from small scale jacketed and unjacketed laboratory

mixers to the blade of a 100 gallon heavy duty Z-blade mixer. Contra-flow blenders (4½-200 gallons), U-trough ribbon blade mixers and a twin-jar tumbler were also shown.

Acknowledgments

The Honorary Editor is indebted to the following members of the Association who gave so much of their time to assist in the reporting of the Exhibition : F. J. Acton, C. Alsop, J. R. Berry, R. A. Brett, K. D. C. Bruce, T. R. Bullett, K. W. G. Butcher, R. D. Calvert, N. Cockrane, R. Dennis, S. Duckworth, D. Fidler, T. Graham, J. R. Green, R. J. Cole, R. W. Hall, K. Hargreaves, G. L. Holbrow, A. G. Holt and colleagues, R. E. Howse, J. Jackson, A. B. Lock, W. F. McDonnell and colleagues, A. K. Miles, M. R. Mills, C. H. Morris, L. A. O'Neill, E. Redknap, F. E. Ruddick, J. F. J. Rule, P. F. Sharp, D. Soen, L. Tasker, A. R. H. Tawn, J. R. Taylor, L. J. Watkinson, R. N. Wheeler, P. J. Whitaker and I. Whittard.

The Honorary Editor particularly wishes to thank Mr. R. A. Brett and Dr. V. T. Crowl (Honorary Publications Secretary of London Section), who have collated the reports and comments received and written the final report.

London Section

Twenty-Seventh Annual General Meeting 1965

The 27th Annual General Meeting of the London Section was held on 14 April at 6.30 p.m. at the Criterion-in-Piccadilly ; with Mr. M. R. Mills in the chair and 48 members present.

Mr. R. N. Wheeler briefly presented the committee's report, and proposed its adoption. Mr. W. J. Arnot, Chairman of the Thames Valley Branch, in seconding the report, congratulated the officers and committee on a very successful year, with two new items in the programme, the Corrosion Symposium, and the start of the European Exchange lectures. Referring to the Thames Valley Branch, which had now completed its first year, he said that the Branch now had over 100 members, with an average attendance of 40-50 at each technical meeting. The Branch had now had its first paper published in the Journal, and had held its first social function, the Buffet Dance, and looked forward with confidence to the future.

Mr. C. A. Carey, Chairman of the Southern Branch, said that the new Section Programme, incorporating the Branch activities, had been a great help to

the Southern Branch in raising attendances, some members having travelled over 100 miles to attend meetings. He also referred to the joint meeting of the Branch with the Plastics Institute to be held next December, which it was hoped could aid recruitment. The committee's report was adopted unanimously.

Mr. J. E. Pooley in presenting the financial report, said that expenditure on meetings was lower this year, due to there having been one fewer meeting, and one meeting held jointly with the Plastics and Polymer Group of the S.C.I. In a very amusing speech, Mr. S. W. Kettle seconded the report, which was adopted unanimously.

The following officers of the Section were elected.

Hon. Secretary Mr. R. N. Wheeler.

Hon. Treasurer Mr. J. E. Pooley.

Hon. Publications Officer
Dr. V. T. Crowl.

Hon. Programmes Officer
Mr. A. R. H. Tawn.

Hon. Auditor Mr. W. H. Campbell.

In proposing the election of Mr. C. R. Pye as Chairman, Mr. Mills paid tribute to Mr. Pye's work for the Section over the last 12 years. Mr. A. T. S. Rudram, seconding the proposal, said that he counted himself fortunate to have been on the Committee during the period of Mr. Pye's service, and was sure that he would carry out his duties as Chairman in the same meticulous manner. Mr. Pye was elected unanimously with acclamation. Mr. W. O. Nutt proposed a vote of thanks to the retiring chairman. The past two years had been a dynamic period, with the formation of the Thames Valley branch, and the initiation of the

exchange lectures with the Continental societies, and Mr. Nutt expressed thanks to Mr. Mills not only on behalf of the Section, but also of the whole Association. A little later in the evening the following members of the Committee were declared elected :—Mr. D. C. Colborn, Dr. H. R. Hamburg, and Mr. K. Pond.

The meeting was, this year, followed by the dinner, after which four films were shown, "Surf Boats of Accra", "Donald's Off-Day", "The Home-Made Car", and "Two Laps of Honour", and were much appreciated by all present.

V.T.C.

Manchester Section

Annual General Meeting

The 41st Annual General Meeting of the Section was held in the Pavilion Suite of the Lancashire Cricket Club at Old Trafford, Manchester, on 9 April 1965 with Mr. H. F. Clay in the Chair.

After approval of the minutes of the last Annual General Meeting the Committee's Annual Report and the Financial Report were presented, discussed and adopted.

The officers of the Section were then nominated and elected as follows :

<i>Chairman</i>	Mr. H. F. Clay.
<i>Vice-Chairman</i>	Mr. I. S. Moll.
<i>Hon. Secretary</i>	Mr. H. G. Clayton.
<i>Hon. Treasurer</i>	Mr. S. Duckworth.
<i>Hon. Publications Secretary</i>	Mr. W. F. McDonnell.
<i>Hon. Research and Liaison Officer</i>	Dr. F. M. Smith.
<i>Hon. Programmes Officer</i>	Mr. C. Williams.
<i>Hon. Social Secretary</i>	Mr. M. J. Heavers.

Mr. L. Bowden and Mr. F. A. Walker were also re-elected as Hon. Auditors.

A ballot was held to fill the two vacancies on committee from the four nominations received. As a result of the ballot, Mr. W. G. Topham and Mr. G. T. Williams were elected to join the previously elected committee members, namely Mr. T. Graham, Mr. J. J. Kavanagh, Dr. D. A. Plant and Dr. G. A. Wolstenholme, and the Immediate Past-Chairman, Mr. J. Smethurst.

Under the heading of any other business, several topics were discussed including the provision of a meal after the first Liverpool meeting of the session, the wider circulation of information on Junior activities of the section, and the best way of selecting interested members for works visits. The Chairman thanked all the officers and Committee members for their efforts in the past year and hoped that they could all work together as well in the coming year. He particularly thanked Mr. Rule who was retiring from committee having served for the last three years as well as several previous occasions. He also regretted that Mr. K. W. G. Butcher was having to retire from the position of Hon. Programmes Officer for personal reasons. Mr. Clay then referred to the efficient way Mr. Butcher had carried out his duties since the position had been established during

Mr. Smethurst's term as Chairman and how he hoped the increasing attendance figures were reward for his efforts which he and the committee knew were considerable. In thanking him for his work for the section Mr. Clay was sure he had the support of all members.

In proposing a vote of thanks to the Committee, Mr. H. Smith referred to the gratifying increase in membership, published papers and junior activities and said he was sure that all would agree that these and the other activities referred to in the annual report showed that the Section's affairs were in good hands. These sentiments were wholeheartedly endorsed by the meeting. The Chairman then concluded the meeting by cordially inviting past Chairman and officers of the Section to a dinner which would follow the committee's summer committee meeting on 14 May.

After the meeting the traditional hotpot supper was held when Mr. H. Gosling, as the senior Section member present, commented on the increased numbers present and the excellent facilities and complimented the committee on their choice of venue which enabled those interested to see the fascinating exhibits of the Lancashire Cricket Club. The entertainment following the meal was again organised by Mr. J. J. Kavanagh who, together with other members, participated in supplementing the stories of the professional Irish entertainer Mr. Tony Cawley, who very topically related his tales against the building industry background and then departed to his next site for his second shift. Despite this defection, the evening's enjoyment continued and was clearly enjoyed by all.

W. F. MCD.

Midlands Section

Annual General Meeting

The 17th Annual General Meeting of the Midlands Section was held at the Parson and Clerk Hotel, Streetly, Sutton Coldfield, on Friday 9th April 1965.

After the Annual Report of the Committee and the Statement of Accounts had been received and adopted the Honorary Officers for 1965 were elected. These were as follows :—

<i>Chairman</i>	R. D. Calvert
<i>Chairman Designate</i>	C. H. Morris
<i>Hon. Secretary</i>	D. J. Silsby
<i>Hon. Treasurer</i>	D. J. Morris

Hon. Publications Secretary

L. R. Seabourne

Representative on Council

D. J. Silsby

Two new members of Committee were then elected to replace retiring members and the 1965 Committee comprises Mr. P. C. Daley, Mr. A. S. Gay, Mr. H. J. Griffiths, Mr. R. E. Howse, Mr. L. V. Jennings and Mr. G. H. Morris. Mr. F. W. Cooper and Mr. N. A. Bennett were re-elected as Honorary Auditors.

After the meeting members sat down to a "Hot-Pot Supper" and afterwards split into groups to play darts and dominoes.

L. R. S.

Newcastle Section



Photo by

Dr. T. A. Banfield

Ladies' Night

The annual Ladies' Night of the Newcastle Section was held on 26 March 1965 at the County Hotel. During the evening the Section's Chairman, Mr. J. G. N.

Smith, presented a gift to Mr. W. P. Jenkins, a founder member of the Section. In the above photograph, Mr. Jenkins (*right*) can be seen together with his wife accepting the gift from Mr. Smith.

Forgotten Aston Manor in Birmingham

Those of the Association's members who attended the Birmingham College of Advanced Technology will know that it is to be given the status of the University of Aston in Birmingham. Dr. J. Newton Friend, the senior Past President and Honorary Member of the Association, has taken the opportunity to write a short history of Aston Manor under the title of *Forgotten Aston Manor in Birmingham*. This interesting booklet gives a brief record of early sites, buildings and their history, and will surely be of interest to all those who

wish to know more of this part of Birmingham. Copies are available from Hudson's Bookshops Ltd., 116 New Street, Birmingham, 2, price 2s. 6d.

1965 Mattiello Lecture

The Federation of Societies for Paint Technology announce that the 1965 Mattiello Lecture will be given by Dr. D. L. MacAdam, of Eastman Kodak Co. The subject that Dr. MacAdam has chosen for his address is "Colour Measurement and Tolerances." The Mattiello Memorial Lecture was in-

stituted by the Federation in 1949 to commemorate the name of Dr. J. J. Mattiello, who was a prominent member of the Federation.

The Khan Rahim Bux Khan Paint Research Hall

On 21 February the foundation stone of the Khan Rahim Bux Khan Paint Research Hall was laid by Mrs. Rahim Bux Khan. The hall will form part of the buildings of the Pakistan Paint Manufacturers' Association and is expected to play an important role in the centralised paint industry of Pakistan in the training of paint technologists to meet the needs of that country.

Symposium on wetting

A symposium on the subject of "Wetting," organised by the Colloid and Surface Chemistry Group and the Bristol Section of the Society of Chemical Industry, will be held at the New School of Chemistry of the University of Bristol on 12, 13 and 14 September 1966. Topics to be discussed will probably include contact angles, wetting of porous media, wetting and non-wetting of surfaces, and wetting and non-wetting effects in dispersions.

Those wishing to submit papers or requiring further information should communicate with Dr. R. H. Ottewill, School of Chemistry, University of Bristol, Bristol.

News of Members

Mr. I. T. Smith, an Ordinary Member attached to the General Overseas Section at present with the Epoxylite Corporation, California, has been appointed Technical Manager of Epoxylite Limited.

Mr. W. Woodhall, an Ordinary Member attached to the London Section, has been appointed Deputy Managing Director of Laporte Industries Ltd.

Mr. R. H. Sudekum, an Ordinary Member attached to the London Section, has been appointed Technical Manager of the Chemicals and New Products Division of the Minnesota Mining and Manufacturing Co. Ltd.

Mr. A. McGuire, an Ordinary Member attached to the Scottish Section, has been appointed to the Board of Montgomerie, Stobo and Co. Ltd.

Register of Members

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

Ordinary Members

BROCKIE, GEOFFREY WILLIAM, 6 Floriston Road, Boronia, Victoria, Australia.

BYRNES, GEOFFREY BERNARD, B.SC., A.R.I.C., Expandite Ltd., c/o Castrol Ltd., Clayton Road, Hayes, Middlesex. *(Victorian)*
(London)

CAIN, J., 24 Chelmsford Gardens, Ilford, Essex. *(London)*

CARDER, JOHN A. H., B.SC., "Martindale," Wicket Hill, Wrecclesham, Nr. Farnham, Surrey. *(London)*

DALE, JOHN H., 5 Cample Lane, South Ockendon, Essex. *(London)*

ERNOTTE, PAUL GEORGES, 41 Avenue du Prince d'Orange, Bruxelles 18, Belgium. *(Overseas)*

HARE, PETER DENNIS, B.SC.TECH., Evington, Cavendish Park, Matlock, Derbyshire
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- HIND, GEORGE, A.R.I.C., A.C.T., 48 Chestnut Road, Quinton, Birmingham, 32.
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- LOVEDAY, JOHN H., 62 Hillingdon Street, Walworth, London, S.E.17.
(London)
- MARSH, HARRY E. S., 82 Wick Road, Homerton, London, E.9.
(London)
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- ROMELL, BORJE, Kallangsgatan 12, Goteborg V, Sweden.
(Overseas)
- ROTHWELL, GERALD W., B.SC., A.R.I.C., British Railways Research Dept., Chemical
Research Division, The Avenue, Muswell Hill, London, N.W.10.
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- SAXBY, MICHAEL F., M.A., ICI Ltd., Paints Division, Wexham Road, Slough,
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- SMITH, KENNETH ROBERT, B.SC., A.R.I.C., The New Bungalow, Waterloo Close, Waterloo,
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(Overseas)
- WILLIAMS, WILLIAM ANTHONY, B.SC., "Coppers," Bollinbarn Drive, Macclesfield,
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- WILSON, MICHAEL RICHARD, B.SC.TECH., A.R.I.C., A.M.C.T., A.M.I.CHEM.E., 18 Farm
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(Manchester)
- WRIGHT, PETER M., B.A., Shell Chemical Co. Ltd., Solvents Dept., Downstream
Building, Shell Centre, London, S.E.1.
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- ZOEPEL, CHRISTOPHER C., 5 Nicholas Lodge, St. Paul's Cray Road, Chislehurst, Kent.
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 SMYLIE, JOHN STEVEN, Flat 1, 27 Princes Road, Sale, Cheshire. (Manchester)
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 PAISLEY, AILEEN HELEN, 4 Kilmuir Road, Arden, Thornliebank, Glasgow. (Scottish)
 WOODS, WILLIAM, 63 Frank Avenue, Seaham, Co. Durham. (Newcastle)

Forthcoming Events

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

Wednesday 16 June

OCCA Council Meeting.

Thursday 17 June

NSW Section. Australian Convention, Terrigal, from 17 June to 20 June.

Monday 21 June

Scottish Section—Student Group. Works Visit to Hunsterston Atomic Power Station at 7.30 p.m.

Thursday 24 June

South Australia. Apprentice Trade School—Lecture.

Saturday 26 June

Scottish Section—Student Group. Bus outing to the Convenanters' Inn, Aberfoyle, at 5.30 p.m.



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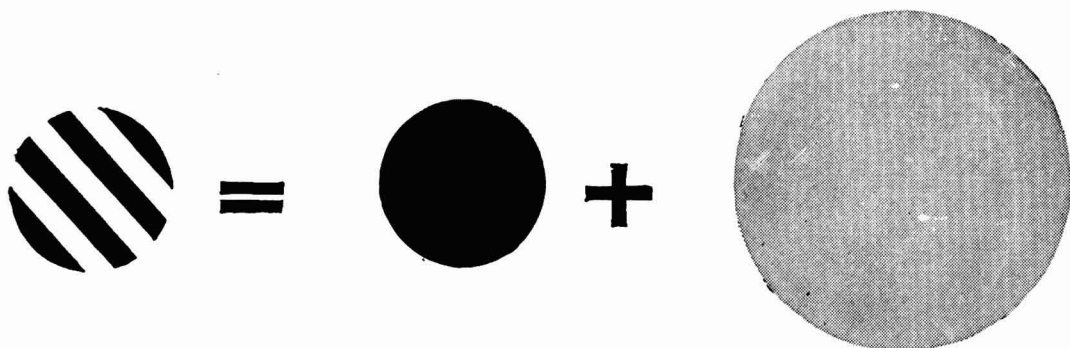
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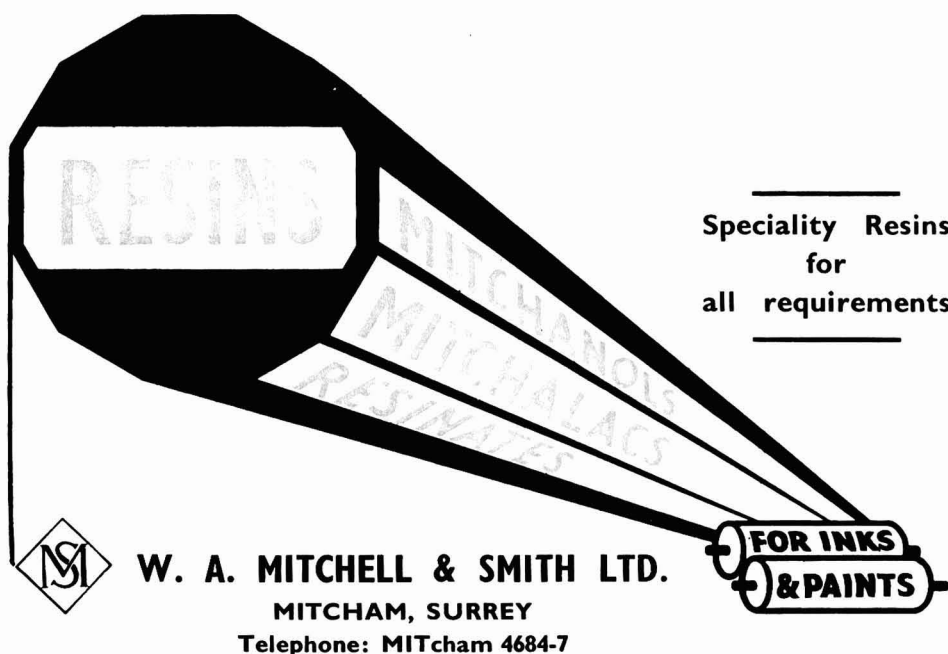
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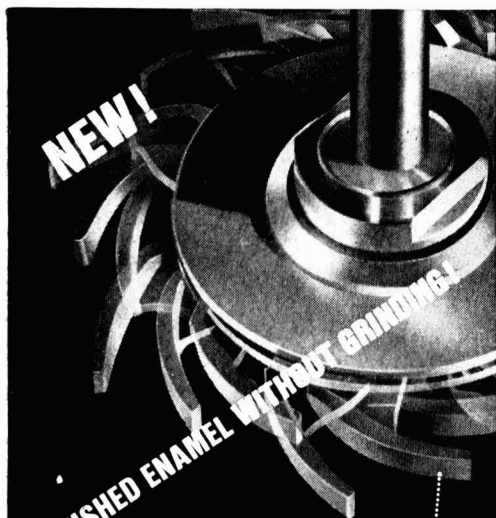
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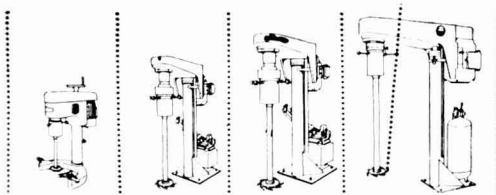
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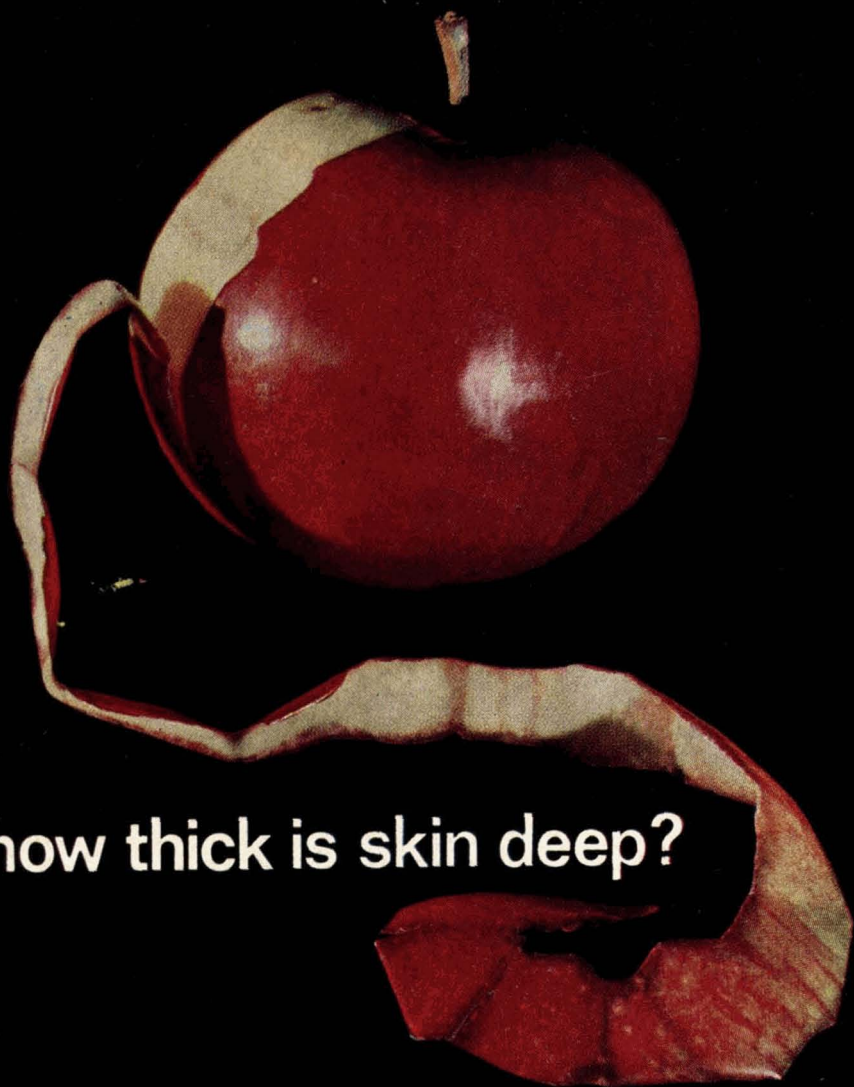
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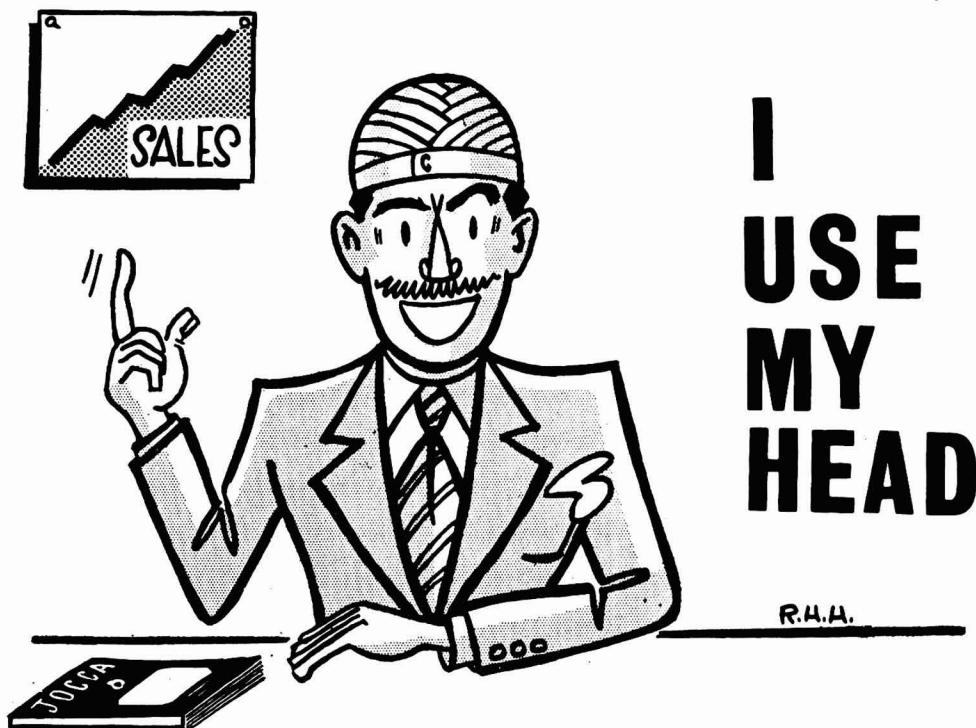
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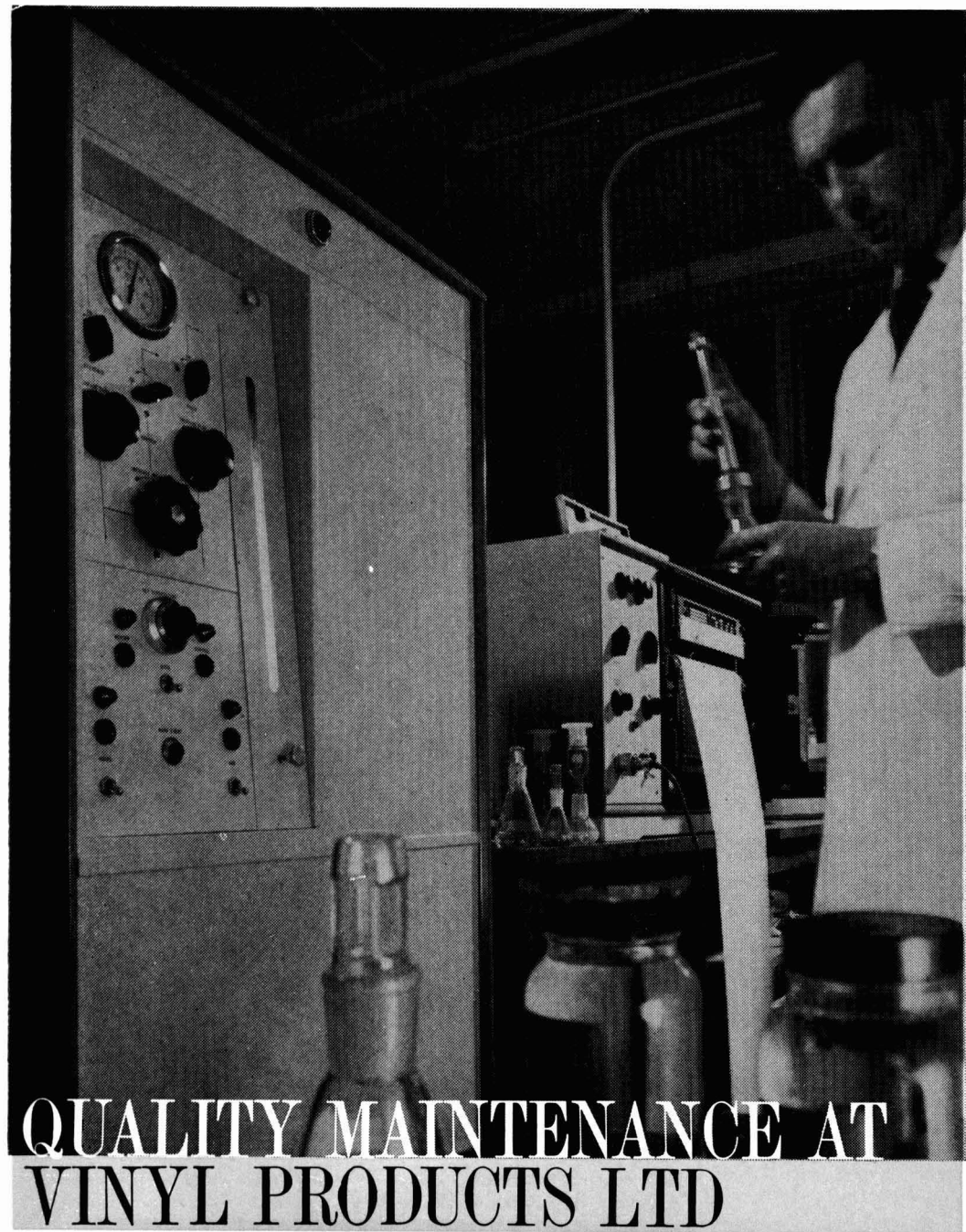
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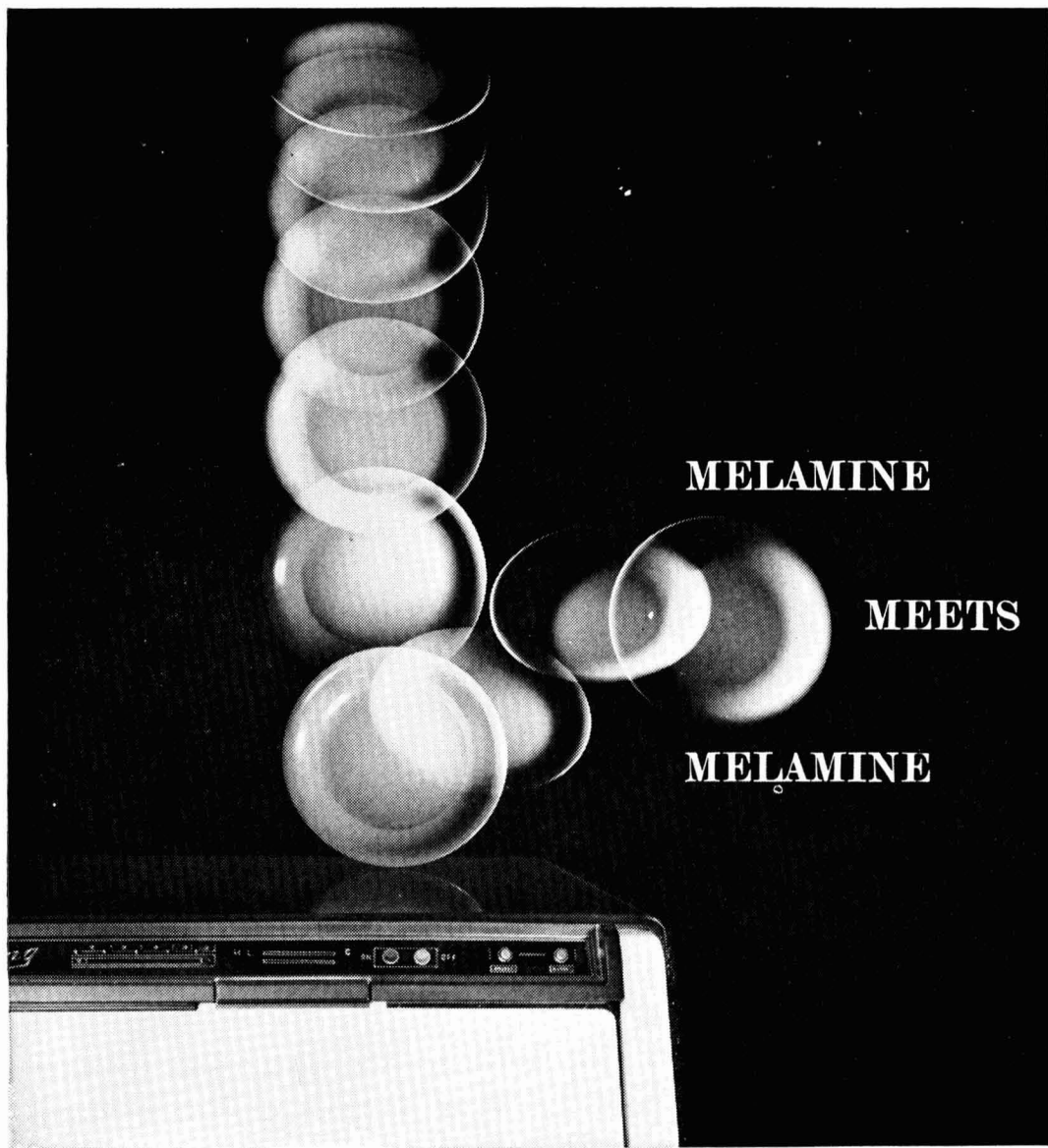
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required by Swiss paint company (near Zurich) to join development team in well-equipped laboratory. Several years' experience in the paint field desirable. Age between 24-27 preferred. Application should be made to :

**HANS DOLD & CO.
Paint and Varnish Manufacturer
8403 Wallisellen/ZH
Switzerland.**

PAINT TECHNOLOGIST, aged 22 to 26, preferably with some corrosion knowledge, required by group of Shipping Companies. Write in first instance to G. P. Acock, New Zealand Shipping Co. Ltd., Royal Albert Dock, London, E.16, giving details of age, qualifications and experience.

MANAGER OF INDUSTRIAL COATING RESEARCH AND DEVELOPMENT

LABORATORY : Applications are invited from Chemists who have had a wide experience in formulating Industrial Finishes and are familiar with modern developments. At the same time, applicants must be capable of directing a team of chemists working in this field. This situation offers a high salary, with plenty of scope for a man having the necessary qualifications, drive and initiative. Apply :—

**The Technical Director,
Arthur Holden & Sons Ltd.,
Bordesley Green Road,
Birmingham, 9.**

TECHNOLOGIST, urgently required by Lewis Berger (G.B.) Ltd., Freshwater Road, Chadwell Heath, Essex, to join small development team in expanding Automotive division. Modern well equipped laboratories. Excellent salary and conditions, previous paint experience particularly in industrial finishes desirable. Applications in writing please to Personnel Officer.

DONALD MACPHERSON & CO. LTD.

**Cock Chimney Works,
Mitcham, Surrey**

A vacancy exists in the laboratories for a Section Leader. To fill this post we require a Paint Technologist experienced in the formulation of Industrial Finishes. The successful candidate will have the opportunity to gain considerable knowledge in this field plus the opportunity of promotion within an active group of Companies.

Applications to Chief Chemist, Mitcham.

SITUATIONS VACANT

DEVELOPMENT CHEMIST
EXPANDITE LIMITED

A Member of the Castrol Group of Companies

has world-wide interests in the development, manufacture and sales of polymeric sealing and jointing compounds for buildings, roads and runways for the Motor Industry and also in anti-corrosion coatings. The Company, which is expanding rapidly, has the following vacancies in its Research and Development Laboratories in London, N.W.10.

CHEMIST, with preferably several years' experience in either printing ink or synthetic coatings or similar industry, to work on a wide variety of problems specifically associated with our Overseas Companies.

ASSISTANT CHEMIST required for work in an established laboratory on bitumen/synthetic polymer compositions for jointing compounds and similar materials. This field represents one of the major interests of the Company and materials are produced to a wide range of international specifications.

ASSISTANT, man or woman, with an interest in science, for evaluating sealing compounds. Duties will include the preparation of specimens and recording observations obtained during weathering. Previous laboratory experience would be an advantage and the ability to keep neat records is essential.

Good salaries, Staff Pension and Life Assurance Scheme and usual amenities. Apply in confidence giving adequate details to: Group Personnel Manager, Expandite Ltd., 1-9 Chase Road, London, N.W.10.

LABORATORY SUPERVISOR, urgently required by Lewis Berger (G.B.) Ltd., Freshwater Road, Chadwell Heath, Essex, to lead team in Product Control Laboratory engaged in quality control of decorative and some industrial paints. Interesting customer liaison work. Excellent salary and conditions. Please write or telephone Mrs. Brewer, Seven Kings 6030.

BUSINESS OFFERS

COMPOUNDER of chemical solutions strategically situated near the southern end of M.1 would like to discuss the possibility of custom mixing and the despatch of suitable chemical products for manufacturer who may, for example, not be conveniently situated to exploit the Midlands and South.

Products would be mixed to customer's instructions under strict control and would be despatched under customer's label. For exploratory talk in strictest confidence, please write to The Director, PO Box No 232.

Company with development work and sales potential beyond the capacity of their overworked laboratories but with ample manufacturing capacity, is prepared to develop on a fee or royalty basis original formulations for certain coatings and inks for packaging materials. Box No. 240.

MIXING CAPACITY, to customers' formulations, with heating if required.

Quality control, packing, despatching. Factory near Southend-on-Sea. Box No. 238.

EQUIPMENT WANTED

INDIAN COMPANY wishes to purchase re-conditioned Uniroll Mill 12 in x 26 in (Vickers or Torrance) and a Triple Roll Mill 12 in x 24 in. All offers to Box No. 239.

SITUATIONS WANTED

INDIAN, B.Sc. (Chem.), B.Sc. (Technology of Oils, Fats and Waxes) with two years' Industrial Experience requires immediate employment. Please write to Box No. 241.

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Based on a non-yellowing oil and recommended for rapid drying brushing enamels—

WRESINOL 502

Undercoats based on WRESINOL 502 possess extremely rapid drying combined with enamel-like flow and excellent brushability. Such undercoats may be over-coated by a gloss finish without sinkage almost any time after application.

Samples and literature are available on request



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