They're all talking about OCCA's next exhibition!

SURFEX 86

SURFEX 86

SURFEX 86

SURFEX 86

JOCCA
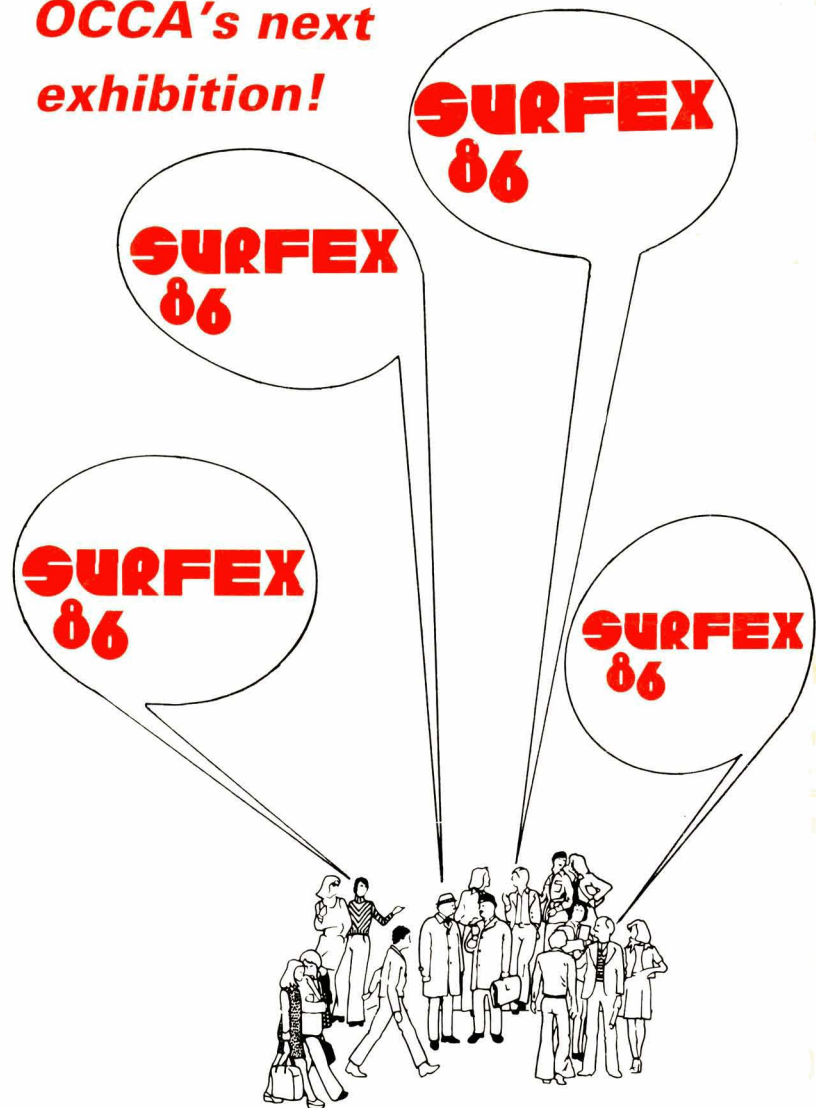
14th-15th MAY ● 1986 ● HARROGATE

In this issue:

● *Internal stress and film formation in emulsion paints*

● *Infrared studies of surface species on insoluble inorganic oxide particles immersed in liquids*

● *The adhesion of chlorinated rubber to mild steel using a blister technique*

JOURNAL of the
OIL AND COLOUR CHEMISTS' ASSOCIATION

Contents   Vol. 68 No. 11   November 1985

Transactions and Communications – Papers from the OCCA Conference

OIL AND COLOUR CHEMISTS' ASSOCIATION
Priory House, 967 Harrow Road, Wembley, Middlesex, HA0 2SF England

Let's slip into some-thing comfortable . . .
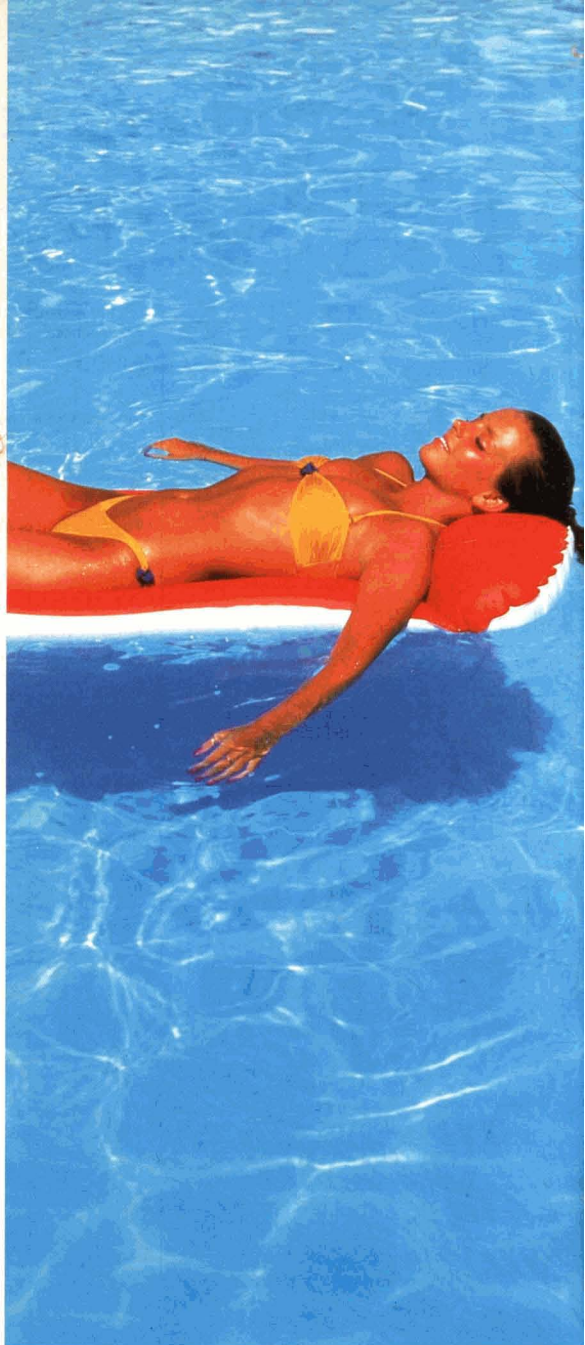
take a dip . . .

Even in Sachtleben's hallowed halls, there's more to life than white pigments and fillers, for paint and plastics. Hence our interest in the tight sweater – which wouldn't look half as comfortable if our Hombitan® TiO₂ hadn't delustered the synthetic fibre content and minimised thread breakage.

(For those not into tight sweaters, Hombitan also does a great job for the makers of light-fast printing inks.)

Time to cool off, perhaps; appropriate, isn't it, that so

hit the town . . .

and finish up with a nice barium meal

many swimming pools are purified by our Sachtoklar® water treatment formulae?

Then darkness falls – or would, if it wasn't for the brilliant light diffused by our barium sulphate technology.

At the end of the day, you must face the fact that we do not devote our entire lives to your pigments and fillers. And if you should find this an indigestible fact of life, maybe you should be sampling one of our barium meals.

iv

NOVEMBER

Internal stress and film formation in emulsion paints

D. Y. Perera

Coatings Research Institute (CoRI), B-1342 Limelette (Belgium).

Summary

The different stages occuring in the film formation of emulsion paints were examined in the light of the development of internal stress. The development of internal stress (due to coalescence, loss of volatiles) may, in addition to stress relaxation, also induce filler/binder dislocations, micro (fissures), loss of adhesion, etc; all processes which affect the film integrity.

The way in which the coating components (pigmentation, organic solvents) affect the development of internal stress, evaporation kinetics and thus film formation, was also investigated. The results obtained were explained by considering, on the one hand, the internal stress components (elastic modulus, internal strain, Poisson's ratio) and on the other hand, certain properties of fillers (specific surface area, nature of interacting sites), binders (acid/base character, Tg) and solvents (plasticizing effectiveness, molecular structure).

Introduction

In spite of the fact that film formation in emulsion paints is a complex process which is not yet completely understood, economical, ecological and technical advantages are such that interest in these products is still great. Film formation in these paints involves a number of different mechanisms which occur simultaneously or consecutively (sintering[1], capillary forces[2], diffusion[3], autohesion[4], action of polymer-air interfacial tension[5]). Among them capillary forces are considered as the main driving factor in coalescence.

Internal stress arises in a film from the moment shrinkage of the coating is prevented by coating solidifaction and adhesion to the substrate, and continues to develop as long as the tendency to shrinkage predominates over the relaxation-relief processes. For the coatings under discussion this is mainly due to coalescence and evaporation of volatiles.

Since internal stress is a direct consequence of the film formation process its determination should also provide a valid technique for investigating this process. In addition, the presence of high internal stress can affect coating integrity (loss of adhesion, microfissures[6a,7-9]). Consequently, knowledge of the development rate and magnitude of internal stress can provide valuable information concerning paint durability.

The aim of this paper is twofold: (1) to discuss the interdependence existing between film formation and the development of internal stress in emulsion paints and (2) to describe the way in which they are affected by certain composition factors. The author believes that a better understanding of these processes can facilitate further development of these paints with a view to improving their performances and to broadening their application.
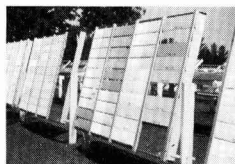
Measurement of internal stress

Two apparatus were used to measure the development of
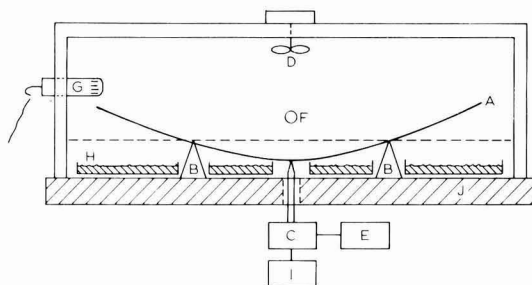
Figure 1. Outline description of the Stressmeter apparatus. A : coated flexible substrate; B : knives; C : measurement system for deflection; D : ventilator; E : command system; F : sensor for temperature regulation; G : sensor for measurement of temperature and relative humidity; H : saturated salt solution; I : recorder; J : heating/cooling system.

internal stress. Their conception is based on the plate and beam theories and the principle of measurement relies on the fact that if a paint applied on a flexible substrate is under stress, the coated substrate will curve in the direction which relieves the stress. Since the deflection can be measured and the elastic properties of the substrate are known the internal stress can be calculated[6].

In one apparatus, an elastic substrate coated on one side is vertically fixed at one end[7b, 11, 12], while in the other apparatus the elastic substrate is freely supported on two knife edges [13-15]. The latter apparatus, which we refer to as the Stressmeter[29], was developed with the assistance of Braive Instruments. Among other things, it has the advantage that the recording of the substrate deflection is automatic (see Figure 1).

Calibrated stainless steel shims were used as substrates. Adhesion of latex coatings investigated on these substrates is very good, an essential condition when using these methods.

The sensitivity of these apparatus is high enough to enable one to make accurate measurements of internal stresses as low as 0.05MPa.

Internal stress, the evaporation process and film formation

Once a liquid emulsion paint is applied on a substrate a number of physical processes, in particular the evaporation of volatiles, occur. Since the evaporation process is essential in film formation we used this process to demonstrate the interdependence between internal stress and film formation.
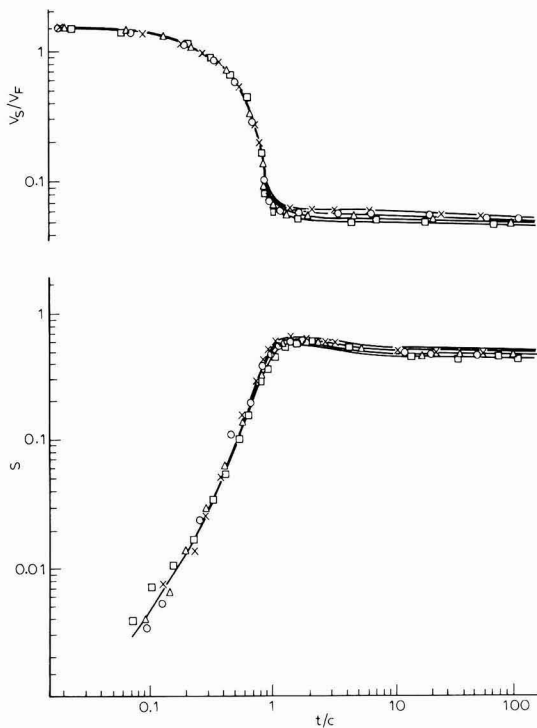
Figure 2. Above: Evaporation kinetics; V_S/V_F vs. t/c for four film thicknesses: 56 μm (X); 73 μm (O); 93 μm (△) and 107 μm (□). Below: Internal stress (S,MPa) vs. t/c for four film thicknesses: 55 μm (X); 76 μm (O); 90 μm (△) and 110 μm (□); t : time (minute); c : thickness of dry film (μm). Binder : vinyl acetate/vinyl versatate; PVC < CPVC.

Figure 3. V_S/V_F and S vs. t/c^2 (for symbols and type of paint see Figure 2).

Previous studies[16, 17] have indicated that, in general, the evaporation process takes place in two phases connected by a transition phase. Phase 1 is governed by the diffusion of volatiles through the air layer (surface resistance), and Phase 2 by the diffusion of volatiles through the film (internal diffusion resistance). Both phases are present during the transition phase (Tr).

It has been shown[17, 18] that, if evaporation kinetics experiments are carried out with films of different thicknesses and the results are expressed as V_S/V_F (or W_S/W_F) vs. t/c and V_S/V_F (or W_S/W_F) vs. t/c^2, then Phase 1 can be described as a single curve on the former plot and Phase 2 as a single curve on the latter one. V_S and W_S are, respectively, the volume and the weight of volatiles present in the film; V_F and W_F are, respectively, the volume and the weight of dry film; t=time; c=thickness of dry film.

In Phase 1 of the evaporation kinetics the mobility of the emulsion particles is great; they do not affect the evaporation process and internal stress should not develop. Since the film formation process (coalescence) does not occur instantaneously throughout the whole sample, internal stress should start to develop in the transition phase of the evaporation process and continue to increase in Phase 2 (i.e. as long as coalescence and evaporation of volatiles occur).

In order to verify these hypotheses evaporation kinetics and internal stress measurements were carried out in parallel. Some of the results obtained are given in figures 2-5 (see also references 19 and 20). These figures indicate that:

● A relatively good correlation exists between the evaporation process and the development of internal stress.
● In general, the internal stress develops in two stages. Stages 1 and 2 correspond, respectively to the transition phase and Phase 2 of the evaporation kinetics.

Two comments are however necessary for a better understanding of the processes under discussion.

The first one concerns the moment at which internal stress starts to develop. A closer examination of figures 2-5 might indicate that this happens in Phase 1 rather than in the transition phase of the evaporation process as stated above. This apparent disagreement is due (a) to the fact that coalescence does not occur simultaneously throughout the whole sample and (b) to the way in which internal stress is measured. For samples with the dimensions used in this investigation, coalescence starts at the edges and ends in the middle. Thus soon after paint application on an elastic substrate, and while the greatest part of the sample is still in Phase 1 of the evaporation kinetics, coalescence has already occured at the edges. Consequently the elastic substrate starts to deflect, indicating the presence of internal stress, before the bulk of the sample reaches the transition state.
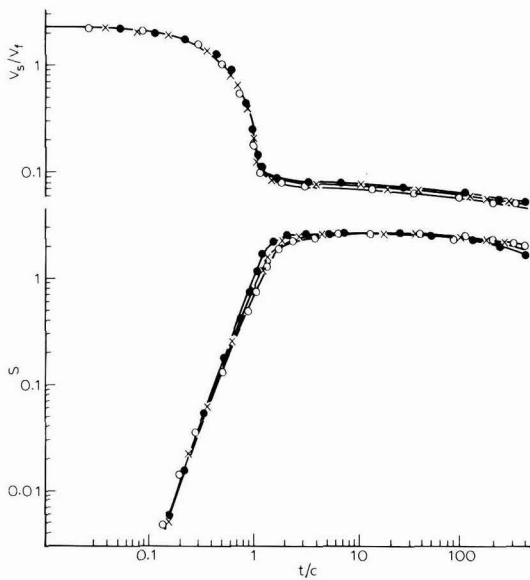
Figure 4. Above: Evaporation kinetics; V_S/V_F vs. t/c for three film thicknesses: 56 μm (●); 80 μm (X); 114 μM (O). Below: S vs. t/c for three film thicknesses: 61 μm (●); 83 μm (X); 115 μm (O). Binder: A styrene acrylic copolymer; PVC > CPVC.
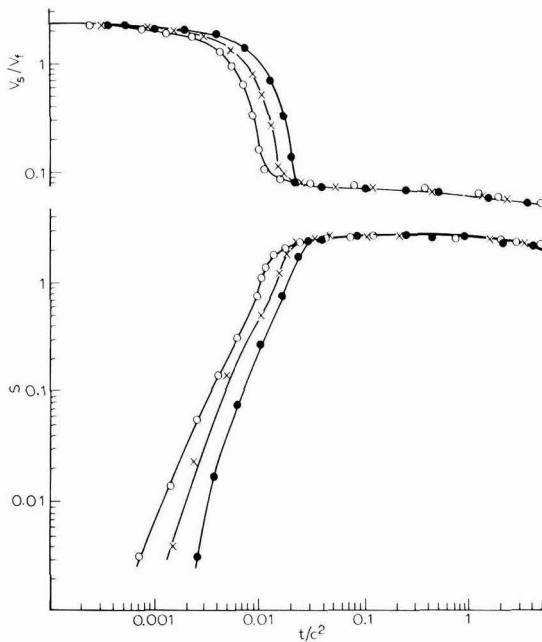
Figure 5. V_S/V_F and S vs. t/c^2 (for symbols and type of paint see Figure 4).

The second comment concerns Stage 2 of the internal stress development. In the light of the above discussions one would expect that internal stress would increase with time as long as coalescence and loss of volatiles occur. The
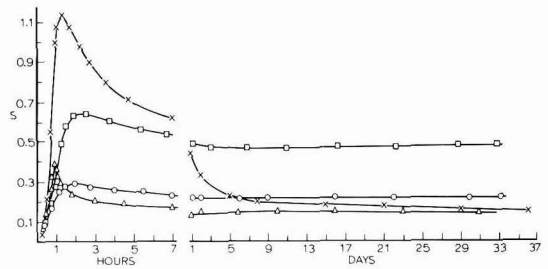
Figure 6. Internal stress (S,MPa) vs. time for four PVC's: 45% (O); 50% (□); 55% (X); 60% (△). Binder: vinyl acetate/vinyl versatate; CPVC ≈ 52%.
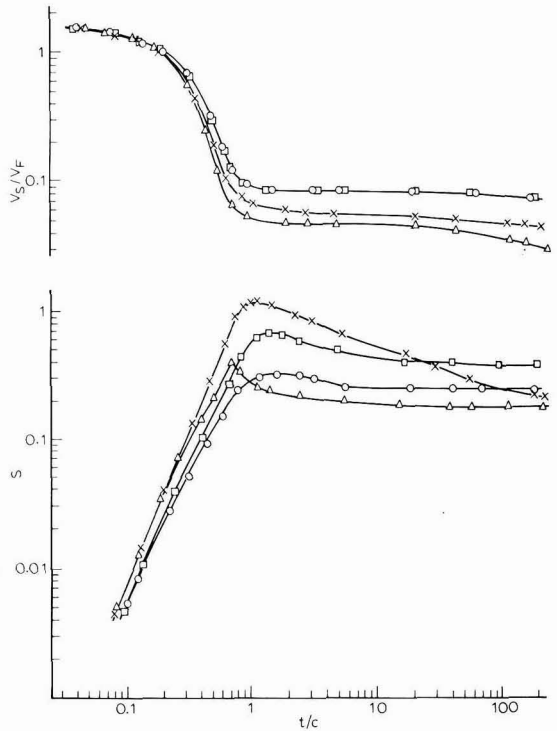
Figure 7. Above: Evaporation kinetics; V_S/V_F vs. t/c for four PVC's. Below: Internal stress (S,MPa) vs. t/c for four PVC's (for symbols see Figure 6).

results obtained (see figures 2-7, 9, 11 and 12) show, however, that this is not the case. Depending on the type of paint and composition, internal stress can increase, decrease, or first decrease and then increase; indicating that internal stress is also dependent on the mechanical properties of the paint film (viz. viscoelasticity and cohesion). As already known from previous studies[21, 22] internal stress can provoke, not only stress relaxation, but also relief mechanisms when its magnitude is sufficiently high to induce breakage of filler/binder bonds or microfissures, processes which decrease internal stress. Consequently the measured value of internal stress is a resultant of all these opposite processes which, as a function of time, can initiate the dependencies mentioned above.
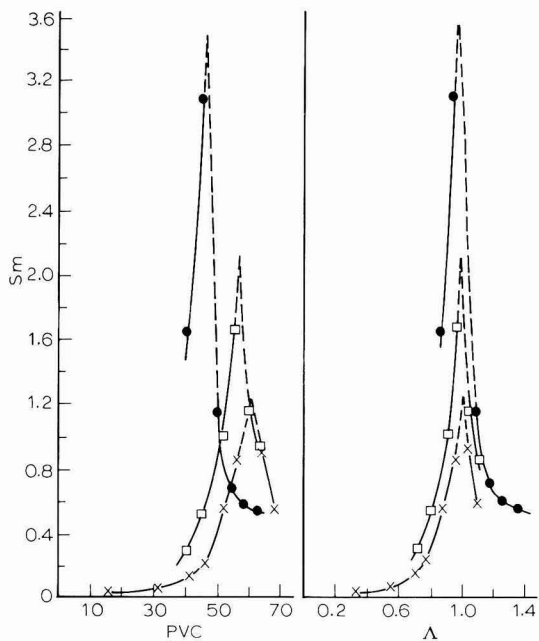
Figure 8. Maximum internal stress (Sm,MPa) vs. PVC (%) and λ (reduced PVC) for paints containing a titanium dioxide (●), a calcium carbonate (X) and their mixture ($TiO_2/CaCO_3$ in the volume ratio 1/1.5) (□). Specific surface area ($m^2.g^{-1}$) $\simeq 10(TiO_2)$ and $\simeq 2.35$ ($CaCO_3$). Binder : A styrene acrylic copolymer.

Effect of paint components on internal stress and film formation

Among the components usually present in an emulsion paint, only the effect of pigmentation and solvent(s) will be discussed in this paper.

1. Pigmentation

The effect of pigmentation on internal stress and evaporation kinetics was investigated with paints containing fillers of different type and content (i.e. Pigment Volume Concentrations, PVC).

Part of the results obtained are presented in figures 6, 7 and 8.

Figures 6 and 7 confirm again the existence of a good correlation between the development of internal stress, the evaporation kinetics and thus between internal stress and the film formation process. Although this is evident for PVC < CPVC (Critical PVC), for PVC > CPVC this might not appear so because, as a function of time, internal stress after an expected initial increase shows a remarkable decrease. As already mentioned, this decrease is attributed to relief mechanisms (filler/binder dislocations and/or formation of micro-fissures) initiated by a relatively weak filler/binder adhesion strength and/or cohesion forces with respect to the internal stress developed in the coating. These arguments are also endorsed by the fact that for PVC > CPVC (see Figure 7) the evaporation rate of volatiles increases with PVC.
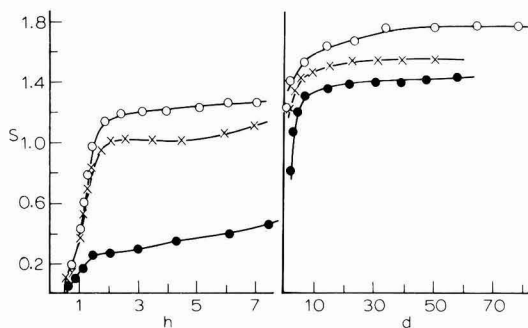
Figure 9. Internal stress (S,MPa) vs. time (h, hours; d, days). Binder : A styrene acrylic copolymer; PVC < CPVC . Texanol (O); Dalpad A (X); Dalpad A + propylene glycol (●).
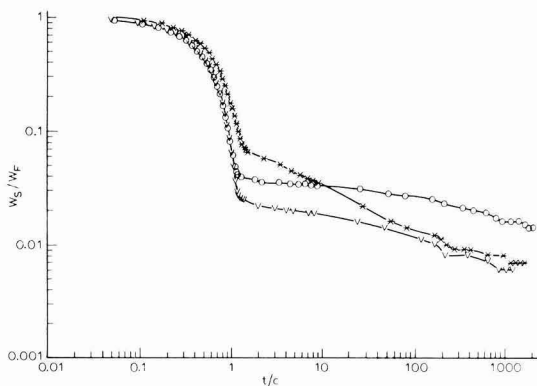
Figure 10. W_S/W_F vs. t/c (for paints' composition see Figure 9). Texanol (O); Dalpad A (V); Dalpad A + propylene glycol (*).
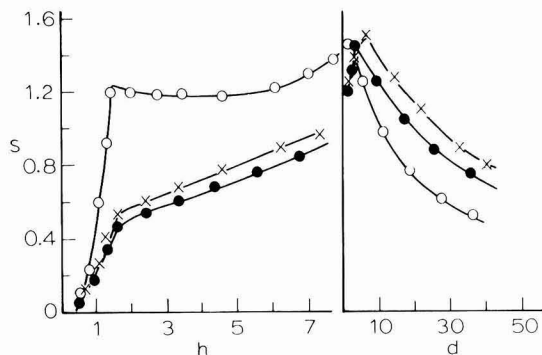
Figure 11. Internal stress (S,MPa) vs. time (h, hours; d, days). Binder : A pure acrylic; PVC > CPVC; Texanol (O); Texanol + propylene glycol (X); Dalpad A + propylene glycol (●).

Another observation resulting from evaporation kinetics measurements worth mentioning is the fact that the volume of volatiles $(V_S)^*$ present in the film when Phase 2 of evaporation process is reached decreases with increasing PVC. (* The density (d) of volatiles used in V_S-calculations was taken as equal to 1. Since the only volatiles these paints
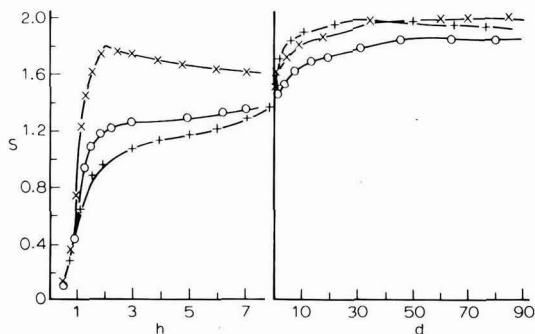
Figure 12. Internal stress (S,MPa) vs. time (h, hours; d, days). Binder : A styrene acrylic copolymer; PVC < CPVC; 5% T(X); 10% T(O); 15% T(+); T : percent Texanol by weight of binder solids.

Figure 13. W_S/W_F vs. t/c (for symbols see Figure 12).

contain are water (d=1) and Texanol (d=0.95), the resulting error is negligible with respect to changes occuring in V_S during the evaporation process.) This is probably due to the fact that, when the pigmentation level in the film is increased, the distance between emulsion particles increases and consequently higher capillary forces (obtained by the loss of volatiles) are necessary to deform the emulsion particles. This remark is in agreement with a comment made in reference 23.

Figure 8 gives the dependence of the maximum internal stress (Sm) on PVC and λ (reduced PVC, PVC/CPVC[24]) for three paints. It shows that Sm is dependent on both the pigmentation level and the type of filler. Sm increases with increasing PVC for PVC < CPVC and decreases for PVC > CPVC. The CPVC-values determined by internal stress measurements agree well with those determined by other methods (density, various mechanical properties[21, 22]).

This behaviour as already explained[21, 22] is mainly due to the elastic modulus (M), which is one of the internal stress (S) components:

$$S = \frac{M\varepsilon}{1-v} \text{ ------ (1)}$$

where ε and v are, respectively, the internal strain and Poisson's ratio.

For the PVC < CPVC, M increases with increasing PVC because the elastic modulus of an inorganic filler is in general higher than that of an organic binder, while for PVC > CPVC, M decreases as a result of the increasing film discontinuity.

The dependence of the type of filler on the internal stress magnitude is due to filler/binder interaction (reinforcing effect) which is determined by the nature, and in particular by the surface area and the acid/base character, of the binder[26].

An examination of the results obtained with paints containing a mixture of fillers indicates that, for a paint formulation having a λ ≤ 1, the maximum internal stress (S_T) and the CPVC can reasonably be predicted by [22]:
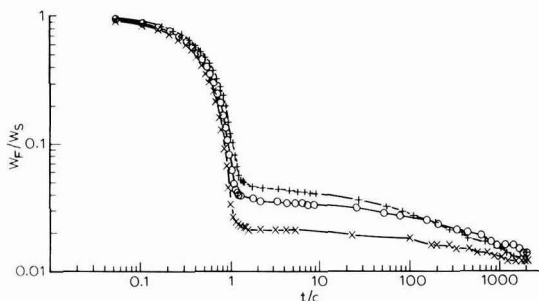
$$S_T = n_1 S_1 + n_2 S_2 + \text{ ------ (2)}$$

$$\frac{1}{(CPVC)_T} = \frac{n_1}{(CPVC)_1} + \frac{n_2}{(CPVC)_2} + \text{ ------ (3)}$$

where: $S_1, S_2, \ldots$ = maximum internal stress of single filler systems

$n_1, n_2, \ldots$ = volume fraction of fillers present in the mixture

The use of these relatively simple equations, we believe, will enable one to evaluate the maximum internal stress values and the CPVC of most commercial paints, and thus to choose more rationally the raw materials necessary to formulate paints with a low internal stress.

2. Organic solvents

Organic solvents are incorporated in a paint to modify film formation (e.g. to facilitate coalescence) and/or to improve paint applicability (rheology, drying time). They also affect internal stress.

Two aspects will be discussed in this subchapter, namely the way in which the type and the level of organic solvent influence the development of internal stress.

2.1. Type of solvent

Internal stress and the evaporation kinetics results obtained with three paints of identical composition, except for the organic solvent, are given in Figures 9 and 10. Paints 1, 2 and 3 contain, respectively, Texanol[R], Dalpad A[R] and Dalpad A and propyleneglycol.

When comparing the paints containing only one organic solvent (i.e. Paints 1 and 2), it can be seen that the paint containing Texanol developed the highest internal stress (see Figure 9).

With regard to the evaporation process (see Figure 10):

● In Phase 1 and in the transition phase, the two paints show practically the same behaviour, indicating that water evaporation is little affected by the type of solvent (in this case two coalescents).
● In Phase 2 the loss of Texanol is much slower than that of Dalpad A.

These results can be understood if the following solvent

characteristics are considered: (a) plasticizing effectiveness and (b) molar volume (Vm) and steric hindrance (SH). The plasticizing effectiveness affects the magnitude of internal stress while the other two factors affect the evaporation process. These factors are interdependent since the plasticizing effectiveness[27] increases as Vm and SH decrease.

Table 1.

Chemical formulae and molar volume of the two solvents used

	Formula	$Vm(cm^3mol^{-1})$
Texanol	CH_3 OH CH_3 $\quad\quad$ CH_3 H_3C-CH -CH- C -CH_2-O-CO-CH -CH_3 $\quad\quad\quad\quad$ CH_3	227.7
Dalpad A	$\langle O \rangle$ -OCH_2-CH_2-OH	125.2

Table 1 indicates that: Vm, SH (Texanol) > Vm, SH (Dalpad A).

Consequently the higher stress value obtained with Paint 1 is mainly attributed to the lower plasticizing effectiveness of Texanol, and the evaporation of the solvent from the film will take longer.

The presence of propylene glycol in an emulsion paint (see Figures 9 and 10) influences in particular Stage 1 of internal stress development and the transition phase of the evaporation process. The retardant effect observed is due to the fact that this solvent is much less volatile than water.

The case of a paint with a PVC close to, but above, its CPVC is illustrated in Figure 11. It can be seen that, as already discussed in a previous chapter (see Figure 4), once a certain S-value is reached, internal stress decreases with time. The importance of these results is the fact that this behaviour is independent of the type of solvent.

2.2 Solvent (coalescent) level

The effect of solvent level on internal stress (see Figure 12) and evaporation kinetics (see Figure 13) was investigated with four paints containing 0, 5, 10 and 15 per cent Texanol by weight of binder solids.

The paint containing 0 per cent Texanol is not shown in these figures, because it cracked (mudcracking) a short time after its application on the substrate.

For the paint with 5 per cent coalescent internal stress shows a strong increase in Stage 1. In Stage 2 after a small decrease internal stress continues to increase until an apparently stationary state is reached. This decrease is probably due to relaxation/relief processes occuring in the coating as a result of the relatively high internal stress developed, while the subsequent increase is due to the slow loss of volatiles (mainly Texanol) still present in the film (see Figure 13).

For the other two paints (i.e. those containing 10 per cent and 15 per cent Texanol) one can see that: (1) in Stage 1 the

higher the initial level of coalescent in the paint, the smaller the internal stress value, and (2) in Stage 2 the internal stress continues to increase slowly until an apparently stationary state is reached. Note than in Stage 2, among all the paints investigated, the one containing 10 per cent Texanol develops the lowest internal stress at "stationary state".

These results, as well as those described in references 25 and 28, indicate that an optimal level of coalescent exists for each formulation which will favour the formation of a tight continuous film developing a low internal stress.

The effect of an excessively low coalescent level on the development of internal stress was attributed to an incompletely formed film with a low film cohesion, while the effect of an excessively high coalescent level was explained by considering two of the internal stress components, namely the elastic modulus (M) and the internal strain (ε) (see Equation 1). The decrease in M as the level of coalescent increases (plasticizing effect), is compensated[28] by a higher increase in ε.

Conclusions

The measurement of internal stress alone or combined with other tests, e.g. evaporation kinetics experiments, enables one to establish the different stages of film formation, and to detect phenomena which are difficult to investigate (e.g. relaxation/relief processes occuring during film formation) by other methods.

The development of internal stress and consequently film formation is affected by paint composition [pigmentation (PVC, nature of filler), type and level of coalescing solvent]. Explanations of some of the phenomena observed are given.

Mathematical relationships are proposed to approximately predict the maximum internal stress and the critical pigment volume concentration of paints containing a mixture of fillers.

We hope that the data presented here will not only provide a better understanding of the film formation process, but will also be of value in the characterisation of raw materials (fillers, binders, organic solvents, etc.) with a view to formulating emulsion coatings developing the lowest possible internal stress.

Acknowledgments

[Received 19 February 1985

References

1. Dillon, R. E., Matheson, L. A. and Bradford, E. B., *J. Colloid Sci.*, 1951, 6, 108.

2. Brown, G. L., *J. Polymer Sci.*, 1956, **22,** 423.

3. Sheetz, D. P., *J. Appl. Polymer Sci.*, 1965, **9,** 3759.

4. Voyutskii, S. S., *J. Polymer Sci.*, 1958, **32,** 528; Polymer Reviews, vol. 4, "Autohesion and Adhesion of High Polymers" *Interscience, N. Y.*, 1963.

5. Vanderhoff, J. W., *Br. Polymer J.*, 1970, **2,** 161.

6. Corcoran, E. M., J. Paint Technology, 1969, **41,** 635.

7. Sanzharovskii, A. T., *et al, Vysokomolekularnye Soed.*, 1980, **2,** (11), (a) 1709; (b) 1698; 1703.

8. Croll, S. G., *J. Coatings Technology*, 1980, 52, No 665, 35.

9. Perera, D. Y., Proc. of Formula 81-Congress, Amsterdam (Oct. 1981).

10. Perera, D. Y. and Vanden Eynde, D., Proc. of XVI-FATIPEC Congress, May 1982, 129.

11. Nilsson, E., *Färg och Lack*, 1975, 21, 318; Saarnak, A., Nilsson, E. and Kornum, L. O., *JOCCA*, 1976, 59, 427.

12. Perera, D. Y. and Vanden Eynde, D., *J. Coatings Technology*, 1981, 53, No 677, 39.

13. Dannenberg, H., Soc. of Plastic Engineering Journal (SPE Journal), 1965, 21, No 7, 669.

14. Aronson, P. D., *JOCCA*, 1974, **57, 59** and **66.**

15. Croll, S. G., *JOCCA*, 1980, 63, 271.

16. Vanderhoff, J. W., *J. Polymer Sci.*, Symposium No 41, 1973, 155.

17. Hansen, C. M., *Ind. Eng. Chem. Prod. Res. Develop.*, 1974, 13, 150.

18. Hansen, C. M., *JOCCA*, 1968, 51, 27.

19. Perera, D. Y., *J. Coatings Technology*, 1984, 56, No 716, 111.

20. CoRI - Annual Research Report, 1982.

21. Perera, D. Y. and Vanden Eynde, D., *J. Coatings Technology*, 1981, 53, No 678, 40.

22. Perera, D. Y. and Vanden Eynde, D., *J. Coatings Technology*, 1984, 56, 717.

23. Bierwagen, G. P., *J. Coatings Technology*, 1979, **51** (658), 117.

24. Bierwagen, G. P., and Hay T. K., *Progr. Org. Coatings*, 1975, 3, 281.

25. CoRI - Annual Research Programme, 1983.

26. Toussaint, A. and D'Hont, L., *JOCCA*, 1981, 64, 302.

27. Hansen, C. M., I & EC. Products Res. Develop., 1970. 9 (3), 282.

28. Perera, D. Y. and Vanden Eynde, D., *J. Coatings Technology*, 1984, 56, 718.

29. Perera, D. Y., Proc. of XVII-FATIPEC Congress, Sept. 1984, 13.

The adhesion of chlorinated rubber to mild steel using a blister technique

Ali Elbasir*, J. D. Scantlebury; L. M. Callow

Corrosion and Protection Centre. U.M.I.S.T., P.O. Box 88, Sackville Street, Manchester M60 1QD, United Kingdom.

Summary

A novel blister technique for the measurement of the adhesion of coatings to metals is described. The technique gives a substantial improvement in reproducibility compared with other adhesion methods. The effects of film thickness on adhesion has been investigated.

Introduction

The principle of the blister technique is relatively simple. A compressed fluid is injected between the adherate (coating) and adherend (substrate) in such a way that the coating lifts off the substrate in the form of a blister. Previously, several analytical techniques have been used. The pressure in the blister as a function of blister volume and the critical pressure to initiate blistering have been employed[1,2]; alternatively, the pressure to detach the coating from the substrate[3] and the relationship between the pressure in a blister and deformation of the coating[4,5,6] have also been used to give a measure of adhesion.

The original blister test was introduced by Dannenburg[7] in 1958, where mercury or silicone oil was used as the fluid. The liquid was injected through a hole in the substrate to flow between the coating and substrate to form a blister of known size. The pressure and volume of the injected liquid were monitored, and from the pressure-volume relationship the work needed to detach the film from the substrate was calculated. As the liquid volume is proportional to the pumping time the area under the pressure-volume curve gave the work done for the de-adhesion of the system. A parallel experiment was done using a detached film to calculate the work needed to deform the coating. The difference between the values was thought to be the work needed to break the coating bond over the area of the blister. Two types of epoxy coating were applied to stainless steel and tantalum substrates. Different variables affecting the adhesion were investigated and it was shown that the surface preparation and coating thickness were the most important parameters. The same author in another paper[1] advocated the use of this apparatus for the study of different polymeric coatings on various substrates, the only limitation mentioned in his papers being that for a brittle film the technique was unsuccessful.

Hoffmann[3,4] used an apparatus similar to Dannenberg, to measure the adhesion of paint to permeable materials. The apparatus measures the pressure necessary to lift the film from the substrate. Nitrogen was used as a pressurising fluid. The measurement pressure was assumed to be equivalent to the lifting pressure if the ratio of the permeability of the substrate to that of the film is high. It was found that the apparatus could be used for the measurement of the adhesion of paints to fibrous plaster, set-gypsum plaster and permeable cement mortar, but it was not successful with asbestos cement which had too low a permeability. In another paper[8], the adhesion of different coatings to iron, brass and asbestos was studied.

Featherston[9] studied the adhesion of a polyurethane topcoat on an epoxy-polyamide primer on various types of anodized aluminium using the blister method to evaluate the surface preparation techniques and processing variables. Different anodizing and chemical treatments for aluminium alloys were investigated to optimise process variables which affect adhesion.

Disbonding of an aluminium epoxy system using the blister method has been investigated in Japan[10] where the Griffith's energy balance concept was applied to the disbonding of epoxy polymer from a rigid plate of aluminium using nitrogen gas. The critical pressure when the detachment started to grow was analysed as a function of the blister diameter. The effect of temperature on the adhesive fracture energy for brass-epoxy systems was also studied[11,12].

The use of blister method to measure the adhesion of polymer films on oxidised silicon has been discussed recently by Hinkley[2]. Polystyrene and poly (methyl methacrylate) coatings were applied to an oxidized silicon substrate and detached by nitrogen and water. The value of the critical pressure to detach the film was recorded. This method showed good reproductibility and was used to calculate the work of adhesion. Van der Meer-Lerk and Heertjes also used the blister test as part of their investigations on osmotic blistering[13,14].

In this present study, the technique has been used to study the adhesion of a chlorinated rubber lacquer onto mild steel. The technique used, differs substantially from those previously investigated in that the outer surface of the coating is clamped to a flat poly (methyl methacrylate) disc. A shallow groove is machined in the disc, thus constraining the blister to move in one direction only.

Experimental

The mild steel substrates were machined from a 50 mm rod into circular discs. The discs have three holes (3 mm diameter). These holes were plugged with PTFE prior to the application of coating. The specimens were degreased in trichlorethylene in an ultrasonic bath for 15-20 minutes, polished to a 1 micron finish and again degreased with acetone. The lacquer was prepared from chlorinated rubber (70 per cent Alloprene R40 ICI, 30 per cent chlorinated paraffin wax "Cereclor 42", in a solvent of toluene) and stored for 24 hours in a dark bottle to allow any air bubbles to be released. After the holes in the disc had been plugged, the coating was applied to the horizontal mild steel

---

*Present address: Department of Chemical Engineering, Al-Fateh University of Tripoli, Libya.
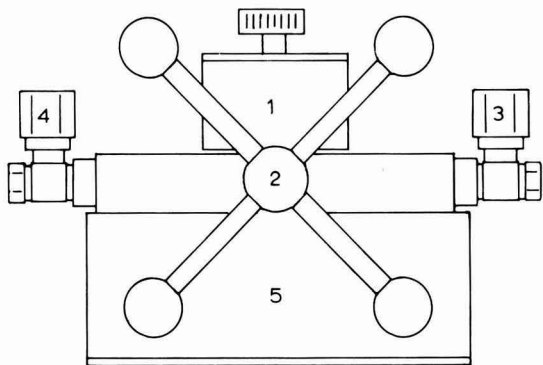
Figure 1. Side and section of Test pump. 1. Fluid reservoir; 2. Capstan; 3. Station 1, specimen holder; 4. Station 2, pressure transducer; 5. Stand.

Figure 2. Detachment distance versus time for 160 μm chlorinated rubber, at 2.07 MN m^{-2}, pressurising fluid mineral oil.

Figure 3. As Figure 2, two different thicknesses 160 μm and 360 μm.

substrates by pouring known amounts on the surface of the metal and drying by solvent evaporation for 3-4 days at room temperature. Each specimen was given several coats and the resultant thickness was measured using an Elcometer Minitector 150 type FN. The blister apparatus consisted of a Hydraulic Test Pump type T1200 (Pressurement Limited) shown in Figure 1. This pump has two outlets, one for the specimen holder, and the other for the pressure transducer. The first outlet was also used for the occasional calibration by a pressure gauge. The specimen consisted of the coated substrate and perspex cover plate which has three grooves to control the form of blister by defining its shape. Each groove could be used for one adhesion test. The steel disc and perspex cover plate were clamped together by a specimen holder. The specimen was held on stage 1 of the pump and pressure transducer was placed on stage 2. A video camera was placed above the coated specimen and the pressure transducer connected to a chart recorder prior to measurement. The operating fluid, mineral oil was introduced to the pump by filling up the liquid reservoir. Any bubbles in the fluid were removed by screwing the capstan in and out for a few minutes. After calibration, the pressure was applied at an approximately constant rate between 0.014 and 0.021 MN m^{-2}s^{-1}. The pressure was gradually increased until the working pressure of 2.07 MN m^{-2} was reached. At rapid pressure rates of 0.042 MN m^{-2}s^{-1} and at slower pressure rates, 0.0015 MN m^{-2}s^{-1}, cohesive failure of the film rather than disbonding,

took place. The blister, once initiated, grew along the groove and the resulting data was expressed as distance along the groove against time.

Results and Discussion

Several pressurising fluids were investigated. The main suggested requirements for these fluids were that the fluid should have high compressibility and that the coating should not chemically react with it. Based on these requirements, mineral oil was chosen as the operating fluid for this study.

On first applying the hydraulic pressure, the film deformed slowly and began to grow in a stepwise manner in one direction, constrained by the groove above. Very occasionally, film fracture took place during the progress of the test. This fracture could have been due to a number of possibilities including variation in adhesion, possible non-uniform thickness of the film, or changes in the mechanical properties of the film.

Figure 2 shows the results obtained using mineral oil as pressurising fluid and 160m chlorinated rubber coating on 1 μm mild steel substrate under a constant pressure of 2.07 MN m^{-2} (300 psi) for seven different specimens. In all cases

the failure was observed to be along the metal/paint interface. These results demonstrate the reproducibility obtained by the technique. The time/distace relationship is apparently linear. It is convenient to define the gradient of this curve, namely the time taken to detach a unit distance, T*, as being an indication of the adhesive strength. In this particular set of experiments this value was between 0.75 and 1.0 min mm^{-1}. Figure 3 was obtained from six specimens, three with a thickness of 160 µm and three with a thickness of 360 µm, tested at 2.07 MN m^{-2}. In both specimens the rate of growth was again approximately linear, but with the thicker film, the blister moved substantially more rapidly. In fact for the thicker film, T*, was 3.5 min mm^{-1} whereas for the thinner film T*, was 8.0 min mm^{-1}. This data seems to suggest that the adhesion of the thinner film was higher than that for the thicker.

In view of the well known lack of reproducibility of adhesion measurements, the data shown in Figure 2 shows an obvious and surprising lack of scatter. Also, the rate of progress of the blister is apparently linear. This implies that the blister velocity is not a function of how far the blister is along the groove but is determined by the specific mechanical and interfacial conditions at the tip of the advancing blister.

To what extent T*, (the time taken to advance the blister a unit distance), is a true measure of the adhesive bond between the polymer and the metal remains to be determined. There is clearly a contribution from the work necessary to separate the polymer from the metal, but there is also a contribution from the work done in deforming the coating.

The apparent increased adhesion of the thinner film compared with the thicker may be explained in several ways. The thicker coating may have had a greater internal strain and this could have effected the interfacial bonding. Alternatively, the thicker coating might have generated micro-defects at the polymer metal interface and this would have lead to reduced adhesion. Lastly, if the adhesion was due to a weak boundary layer, then it is possible that this weak boundary layer would have been altered by the presence of the thicker coating.

Clearly, much more experimental work needs to be carried out, to look at the multitude of variables associated with adhesion and to clarify those aspects already mentioned.

References

1. Dannenberg, H., *J. Appl. Polymer Sci.*, 1961, **5,** 125.
2. Hinkley, J. A., *J. Adhesion*, 1983, **16,** 115.
3. Hoffman, E., *JOCCA*, 1958, **41,** 847.
4. Malyshev, B. M. and Salganik, R. L., *Int. J. Fract. Mech.*, 1965, **1,** 114.
5. Hoffman, E. and Georgoussis, O., *JOCCA,* 1959, **42,** 267.
6. Van der Meer-Lerk, L. A. and Heertjes, P. M. *JOCCA*, 1981, **64,** 30.
7. Dannenberg, H., *J. Polymer Sci.*, 1958, **33,** 509.
8. Williams, M. L. *J. Appl. Polym. Sci.* 1969, **13,** 29.
9. Featherston, A. B., LTV Aerospace Corp., Rep. No. 2-57110/5R-3240, 1975, 71.
10. Takashi, M., Yamazaki, K., Natsume, T. and Tokebe, T., Proc. Jap. Congr. Rev, 1977, **21,** 260.
11. Takashi, M. *et al*, Proc. 16th Japan Congr. Mater, Res., 1973, 211.
12. Takashi, M. *et al*, Proc. 17th Japan Congr. Mater, Res., 1974, 192.
13. Van der Meer-Lerk, L. A. and Heertjes, P. M. *JOCCA*, 1975, **58,** 79.
14. Heertjes, P. M. and Van der Meer-Lerk, L. A., *JOCCA,* 1979, **52,** 256.

next month's issue

The Honorary Editor has accepted the following papers for publication in the December issue:

Novel corrosion inhibitors *by Z. Kalewicz*

Advances in the technology of water-based inks and coatings for the printing and packaging industries *by G. H. Hutchinson*

Formulation of solvent-based paints pigmented with titanium dioxide *by J. E. McNutt*

A jump ahead in dispersibility
BENTONE* SD-1 and BENTONE SD-2

Here are our two superdispersible rheological additives: **BENTONE SD-1** for low-polarity aliphatic and **BENTONE SD-2** for medium- to high-polarity systems. Both additives are remarkably easy to use. No need to pregel, no need for high shear, no need for a polar additive. Same outstanding performance as provided by other BENTONE products. For samples and product literature, post the coupon, write or telephone.

STEETLEY MINERALS LTD, P.O. Box 2, Gateford Hill,
Worksop, Nottinghamshire S81 8AF, Tel. (0909) 47 55 11, Telex 547 901

NL Chemicals Europe Inc., rue de l'Hôpital 31-Bte 6,
B-1000 Brussels, Tel. (02) 512 00 48, Telex 24 662

NL Chemicals

*BENTONE is a trademark of NL Industries, Inc.

STEETLEY MINERALS LTD., P.O. Box 2, Gateford Hill, | NL Chemicals Europe Inc., rue de l'Hôpital 31-Bte 6, B-1000 Brussels
Worksop, Nottinghamshire S81 8AF

Rheological additives BENTONE SD-1 □ **BENTONE SD-2** □ literature □

Please send sample □

Address:

JOCCA 11.85

On
contr

Meet Charlie on one of his quieter days.

A BP platform 110 miles off the coast of Aberdeen.

Being exposed to murderous Force 10 gales, Charlie endures the kind of laboratory conditions you cannot create in a laboratory.

A fitting test then, of 'Alloprene'.

An advanced 'Alloprene' based chlorinated rubber paint system developed by ICI, covers Charlie right up to the aerial tips.

The resin literally puts the high performance into protective coatings. Its secret? Superior impermeability.

e of our quality
l testing centres.

In simple terms, each progressive coat welds itself into the previous, creating a weather impregnable painted skin.

In Charlie's case, lasting an astonishing four years before repaint. And because it's a one pack product there are no problems with application.

For areas somewhat more confined than an oil rig exterior, 'Alloprene's' sister product 'Haloflex' comes into its own.

A water-borne coating, 'Haloflex' is touch dry within the hour, easily applied, and like 'Alloprene', puts high performance into protective coatings.

Obviously neither system is confined to the Forties.

There's hardly a metal structure on the mainland whose working life wouldn't be vastly improved by these remarkable paint systems.

Which is all you would expect, both being products of the technical expertise of ICI.

Using anything less is simply bringing the re-paint date a great deal forward.

And the added costs that come with it. So next time you're specifying a high performance paint, remember Charlie.

And rely on 'Alloprene'. BP have.

ICI

ALLOPRENE Haloflex
Put more protection into paint.

Alloprene and Haloflex are trademarks of Imperial Chemical Industries PLC

ICI MOND DIVISION, DEPT P, PO BOX 13, THE HEATH, RUNCORN, CHESHIRE WA7 4QF, ENGLAND.

'ALLOPRENE' AND 'HALOFLEX'. I'M INTERESTED, PLEASE SEND ME THE FACTS.

NAME:_____ POSITION:_____

COMPANY:_____ ADDRESS:_____

TEL. NO:_____

Reader Enquiry Service No. 399

SURFACE COATINGS

VOL 2–PAINTS AND THEIR APPLICATIONS

Prepared by OCCA Australia

Surface Coatings was first published in 1974. Since then the industry has undergone dramatic and rapid changes. For the second edition the book has been split into two volumes, the first covering raw materials and their usage, the second paints and their applications. Volume 1 was published in the autumn of 1983.

Volume 2 gives a comprehensive overview of decorative and industrial paints. Cross references to appropriate chapters in *Volume 1* are provided and the index covers both volumes. Revised and rewritten by over 80 expert contributors from industry, research institutes and universities, the books represent the most up-to-date reference available on paint technology.

Volume 2 is available in December by placing orders now (prepayment only) through the Oil & Colour Chemists' Association at £32.50 (inc. p&p in the UK) plus £3.00 for orders sent overseas by surface mail.

Volume 2 – Hardback – 480 pp.

Contents

Rheology
Formulating Principles
Paint Manufacture: Pigment
  Dispersion
Paint Manufacture: Processing
  Operations
Architectural Coatings
Heavy-Duty Protective Coatings
Anti-fouling Paints
Industrial Coatings
Automotive Coatings
Lacquers
Conversion Coatings
Powder Coatings

Ultraviolet-Cured Coatings
Printing Inks
Components and Technical Aspects
  of a Paint-Tinting System
Colour Matching (Using Computerized
  Techniques)
Testing and Quality Control
The Substrate and its Preparation
Metal Cleaning and Pretreament
The Selection of Decorative Paints
Corrosion and Prevention
Industrial Coatings: Application
  and Curing Methods
Surface Coatings Defects

Analysis of Polymeric Materials
Technical Service in the Surface
  Coatings Industry
Standardisation, Inspection and
  Accreditation in Australia
Statutory Requirements of the
  Paint Industry
Appendix: Paint Calculations
Useful Data and Conversion Tables
Glossary of Terms
List of Contributors

SURFACE COATINGS

VOL 2–PAINTS AND THEIR APPLICATIONS

To: Oil & Colour Chemists' Association
Priory House, 967 Harrow Road, Wembley, Middlesex HA0 2SF, UK

Please arrange for me to receive . . . . .copy/ies of "SURFACE COATINGS", Volume 2 Paints and their Applications at £32.50 each (inc. p&p in the UK) plus £3.00 for orders sent overseas, at the following address:
(BLOCK CAPITALS)

. . . .
. . . .
. . . .

I enclose remittance (payable to OCCA) for £ . . . .

Infrared studies of surface species on insoluble inorganic oxide particles immersed in liquids

C. H. Rochester

Chemistry Department, The University, Dundee DD1 4HN, Scotland

Summary

Infrared spectra have been recorded of surface species on rutile, silica and alumina immersed in solutions of organic solutes in carbon tetrachloride, hydrocarbons or water. The results illustrate the usefulness of infrared spectroscopy for the study of adsorption behaviour *in situ* at the solid/liquid interface.

Introduction

Surface groups and adsorbed species on powdered solids may be characterised using infrared spectroscopy[1]. The application of the technique is widespread and it has been used, for example, in studies of the surface chemistry of unsupported and supported oxides, mixed oxides, zeolites and clay minerals, glasses, supported metals and carbon. The commonest experimental method involves transmission spectroscopy with the powdered material held in the infrared beam as a pressed self-supporting porous disc. Typical results for particles of an inorganic pigment are exemplified by the spectra of rutile[2] show in Figure 1. Seven infrared bands are characterised by maxima or shoulders at 3725, 3680, 3655, 3610, 3520, 3410 and 3340 cm^{-1} and may be assigned to OH stretching vibrations of surface species. A band at 1620 cm^{-1} is due to the bending vibration of adsorbed water molecules which must also be responsible for a broad band centred at *ca.* 3400 cm^{-1} which contributed to the overall band envelope in the OH stretching region for rutile which had been evacuated at low temperatures. A high proportion of the water was desorbed by evacuation at 393 K (Figure 1 f) but some was resistant to desorption since a weak band at 1620 cm^{-1} remained even after evacuation of rutile at 623 K. Exchange experiments involving deuterium oxide confirmed that the residual water was on the surface and not in the bulk of the rutile. The other infrared bands were ascribed to six different types of surface hydroxyl group. The separate behaviour of each type of group during thermal activation is well characterised by the infrared spectra. The possible identity of the groups in terms of their existence at specific sites on the exposed crystal planes of rutile has been discussed elsewhere[2]. Even more complex are the spectra of haematite which contain eleven bands due to distinguishable types of surface hydroxyl group[3]. The relative intensities of the bands varied with changes in preparative procedure or on sintering and this is attributed to variations in external morphology of haematite particles and hence in the relative surface areas of of exposed faces. The use of deuterium oxide exchange to distinguish between surface and bulk hydroxyl groups is exemplified by infrared results for goethite[4].

Infrared spectra of acetic acid adsorbed on rutile (Figure 2) show how different modes of adsorption may be characterised and the relative reactivities of different surface groups may be monitored. Hydroxyl groups giving the bands at 3725 and 3680 cm^{-1} were more reactive than hydroxyl groups giving the maximum at 3655 cm^{-1}. In contrast hydroxyl groups giving the band at 3410 cm^{-1} were
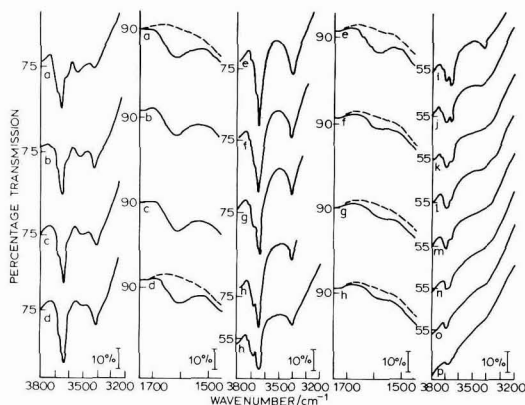
Figure 1. Spectra of rutile after (a) saturation with water vapour and evacuation at *ca.* 318 K, (b) — (p) exposure to saturated water vapour at *ca.* 293 K and a consecutive series of evacuation treatments at increasing temperatures in the range 298-663 K
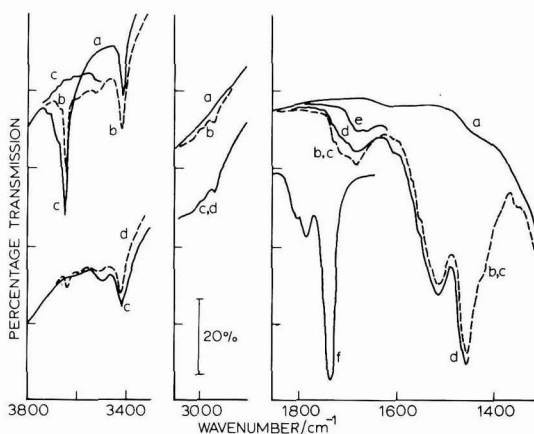
Figure 2. Spectra of rutile (a) after evacuation at 400 K, (b) in contact with acetic acid vapour, (c) with a higher acetic acid pressure, (d) and (e) after subsequent evacuation at *ca.* 306 K for 5 min and 17 h, respectively. (f) Spectrum of acetic acid vapour

unaffected by the adsorption of acetic acid. The maximum retained its intensity although some broadening did occur. Both associative and dissociative adsorption took place. A band at 1675 cm^{-1} is assigned to the (C=O) stretching vibrations of acetic acid molecules which were associatively liganded to Lewis acidic Ti^{4+} surface sites[5,6]. Two intense maxima at 1453 and 1515 cm^{-1} are due to surface acetate

Figure 3. Spectra of rutile (a) after evacuation at 400 K, (b) — (f) in contact with increasing pressures of ethyl acetate vapour

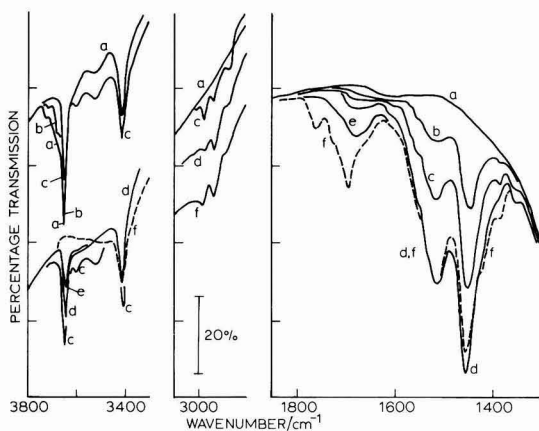ions generated by the dissociative chemisorption of acetic acid[7,8]. The same maxima appear in spectra of ethyl acetate adsorbed on rutile (Figure 3) showing that the ester is dissociated on the oxide surface to give acetate anions. Surface ethoxide ions were a second product of the chemisorption process[7]. The relative reactivities of the surface hydroxyl groups towards ethyl acetate were similar to their relative reactivities towards acetic acid.

Despite the extensive use of infrared spectroscopy in studies of the solid/gas interface the technique has been relatively little exploited in studies of the solid/liquid interface. Unambiguous information about the solid/liquid interface can only be gained if the liquid phase remains in contact with the powder during spectroscopic examination. This poses additional experimental problems, many of which have now been overcome. The present paper is aimed at illustrating, with examples drawn from our own work, the type of information which can be gained from infrared spectra of surface species at the solid/liquid interface.

Infrared cells

The design of infrared cells has been influenced by the need to be able to pretreat powdered samples thermally in particular gaseous atmospheres before the addition of liquid and by the necessity of having a short path-length of liquid in the infrared beam if spectra of surface species are to be detectable. Initial experiments used carbon tetrachloride as the predominant component of the liquid phase because of its transparency over wide regions of the spectrum. Fluorite windows are convenient because of their transparency down to *ca.* 1000 cm^{-1} and their resistance to attack by water vapour. The windows are fixed to the cell body by adhesives which precludes high temperature treatment of powders *in situ* between the windows. Cells have therefore been constructed in two sections, a base section which constitutes the optical compartment and an upper section, mounted vertically above the base, around which is wound a high temperature furnace[9]. The base section may be constructed from metal[9] or glass[10]. Powders are mounted as pressed self-supporting discs in a disc holder of glass, silica or platinum and are suspended by nylon filament or platinum wire from a winding device

which allows a disc to be raised to a position inside the furnace or lowered to between the optical windows. Cells are glassblown to a convential vacuum and gas-handling apparatus and also, via a liquid inlet, to apparatus for the purification, storage and mixing of liquids under either vacuum or an inert gas. The minimum attainable path-length in this type of cell is *ca.* 3 mm which is small enough for studies involving carbon tetrachloride.

With hydrocarbons as the main component of the liquid phase path-lengths less than *ca.* 3 mm have to be achieved. One effective way is to have a variable path-length optical compartment such that the distance between the windows can be reduced to the thickness of the disc plus holder after the disc has been lowered from the furnace section and liquid has been added[11]. An alternative is to construct the cell with silica windows sufficiently far apart (*ca.* 0.5 mm) that a disc can be placed between the windows[12]. An advantage is that no upper cell section is necessary because a furnace can be placed directly around the optical section during pretreatment of the disc and removed before the addition of liquid and spectra are recorded. A disadvantage is that silica windows are only transparent to infrared radiation above 2100 cm^{-1}. The cell shown in Figure 4 has silica windows and includes a liquid circulating system which promotes the speedy attainment of equilibrium and provides thermostat control[13]. Circulating systems have also been fitted to cells with fluorite windows and may contain a subsidiary optical compartment which allows the concentration of adsorbate at equilibrium in the liquid phase to be separately determined[11,14].
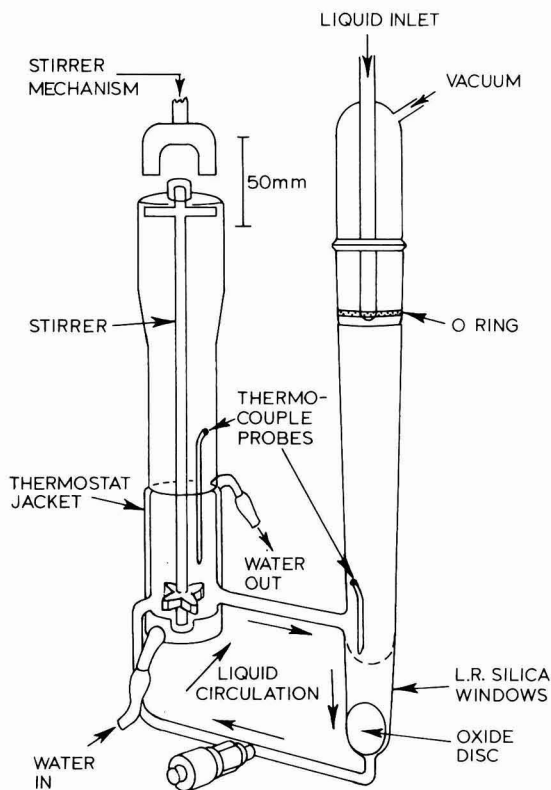

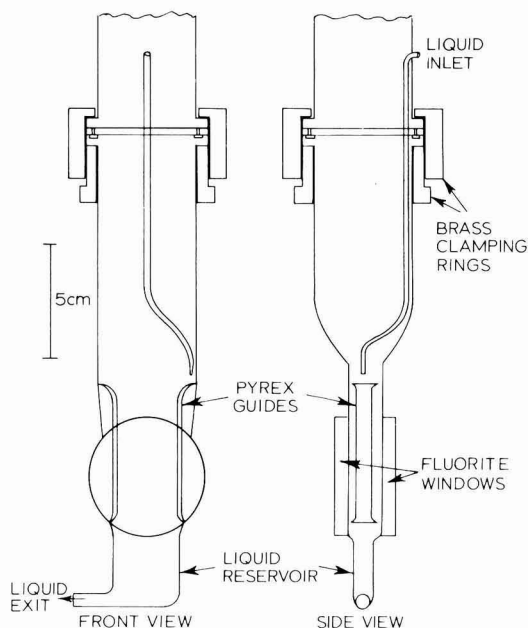**Figure 4. Infrared cell with silica windows and circulating liquid**

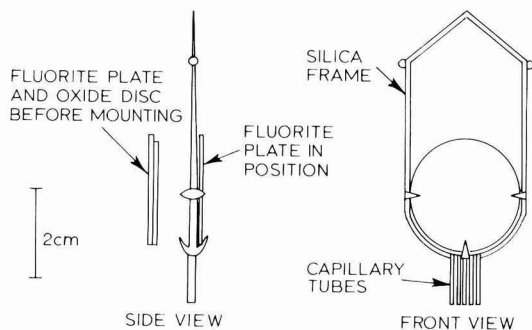Figure 5. Base section of the infrared cell with fluorite windows

Figure 6. Disc holder for the capillary rise method

An alternative method for attaining the minimum path length of liquid in contact with a powdered solid involves use of the cell base and disc holder depicted[15] in figures 5 and 6. The disc is pretreated in an upper furnace section of the cell and is then lowered until it is completely immersed in liquid in the reservoir. After equilibrium is attained the disc is raised to a position between the optical windows for spectroscopic examination. The geometry of the cell and holder are such that the capillary tubes protrude through the surface of the liquid and the disc remains wetted by capillary rise.

Details of experimental procedures leading to the recording of spectra of pressed discs of oxides in liquids or solutions are given elsewere[9-15]. It is also possible to record spectra of loose powders dispersed in liquids or solutions[16,17] although this appears less suitable than the disc technique particularly if quantitative absorbance data

are required as a function of equilibrium adsorbate concentration in solution. However, studies of dispersions of loose powders are probably more likely to be the best method if the predominant component of the liquid phase is water[16] or macromolecular adsorbates are of interest[18,19].

Results and discussion

Perturbation of surface hydroxl groups

Isolated silanol groups on silica which had been heated at 1023 K in vacuum gave an infrared band at 3750 cm^{-1} which is shifted when silica is immersed in liquids by an amount $(\Delta v_{OH}/cm^{-1})$ which depends on the strength of interaction between the silanol groups and the molecules of liquid adjacent to the silica surface[20]. Figure 7 shows spectra of silica immersed in heptane, toluene and heptane and toluene mixtures[12]. The spectra contain a constant contribution from a band at 3680 cm^{-1} due to bulk hydroxyl groups in the silica windows of the infrared cell. Silanol groups perturbed by heptane gave a maximum at 3706 cm^{-1} which implies a small shift $(\Delta v_{OH} = 44$ cm$^{-1})$ consistent with weak forces between silanol groups and heptane. Stronger interactions with toluene molecules result in a shift of 139 cm^{-1} to 3611cm^{-1}. Spectra of silica in heptane and toluene mixtures display maxima at both 3706 and 3611 cm^{-1} and a well defined isosbestic point which suggests that the extinction coefficients, half-band widths and spectral positions of the two maxima are subject to negligible change due to solvation effects over the complete range of solvent composition. Measurement of absorbance values at band maxima as a function of liquid composition therefore enables reliable fractions of the total number of surface silanol groups which are perturbed by each component of the liquid mixture to be calculated[12]. The resulting data constitute spectroscopic isotherms for the adsorption of the components of the liquid phase on to specific surface sites. The method is equally applicable for measuring spectroscopic isotherms for strongly interacting liquid or
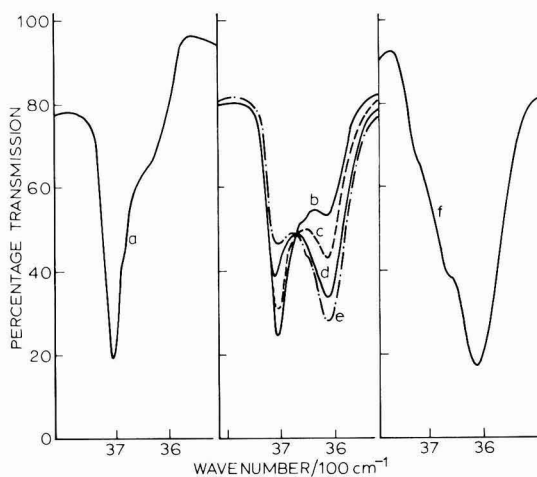

Figure 7. Spectra of silica immersed in (a) heptane, (b) − (e) heptane and toluene mixtures with mole fractions of toluene of (b) 0.067, (c) 0.132, (d) 0.194, (e) 0.313 and (f) toluene

solid adsorbates on silica. Results for the adsorption of anisoles[21] and phenols[22] on silica immersed in heptane illustrate isotherm calculations and the effects of adsorbate structure on the strength of interaction with silanol groups and hence on the spectroscopic shift $\Delta\upsilon_{OH}$. In the case of phenol, simultaneous measurement of the fractions of silanol groups perturbed and the amounts of phenol adsorbed on silica immersed in carbon tetrachloride allowed the number of isolated silanol groups to be estimated to be 2.05 nm^{-2} on the oxide surface[14].

Distinguishable behaviour of different surface sites

The band at 3655 cm^{-1} (Figure 1) in spectra of rutile which had been evacuated at 400 K shifted to 3605 cm^{-1} (Figure 8a) when rutile was immersed in heptane showing that surface hydroxyl groups responsible for the band were weakly perturbed by interaction with heptane molecules. In contrast the band at 3410 cm^{-1} did not shift when rutile was immersed in heptane. This significant difference between the behaviour of two types of hydroxyl group was also apparent from spectra of rutile in solutions of triethylamine in heptane[23]. The maximum at 3605 cm^{-1} decreased in intensity with increasing concentration of triethylamine initially because hydroxyl groups were involved in hydrogen bonding interactions with adsorbed triethylamine molecules. However, the chemisorption reaction (1).

$$OH^- + (CH_3CH_2)_3N \rightarrow {}^-OCH_2CH_3 + (CH_3CH_2)_2NH \ ..(1)$$
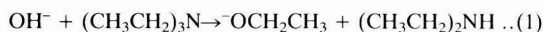
also occurred and led to the formation of adsorbed ethoxide ions and adsorbed diethylamine which was responsible for a band in the spectra at 1622 cm^{-1}. Apart from a slight broadening the band at 3410 cm^{-1} is unaffected by triethylamine. This is surprising because the bands at 3655 and 3410 cm^{-1} for rutile in vacuum had formerly been ascribed[2] to terminal (A) and bridged (B) hydroxyl groups on exposed {110} planes of rutile (Figure 9). This view must now be modifed. It is believed that hydroxyl groups giving the infrared band at 3410 cm^{-1} probably exist at sub-surface lattice sites (C or D, Figure 9) and are unperturbed by adsorbed molecules[24] despite undergoing rapid H/D exchange in the presence of deuterium oxide vapour[2]. At high triethylamine concentrations oxidative cleavage of the adsorbate was promoted by the rutile surface and led to the appearance of strong infrared bands at 1440 and 1520 cm^{-1} due to adsorbed acetate ions[23].

Isolated hydroxyl groups on silica which had been preheated at 863 K formed hydrogen bonds with the carbonyl groups of adsorbed ethyl acetate molecules on silica immersed in carbon tetrachloride[25]. Perturbation of hydroxyl groups gave a band shift from 3686 to 3440 cm^{-1} and the perturbation of carbonyl groups gave a band shift from 1747 cm^{-1} for ethyl acetate in solution to 1712 cm^{-1} for adsorbed ethyl acetate (Figure 10). Silica which had been evacuated at 453 K gave a spectrum containing the band due to isolated hydroxyl groups and additional bands at 3660 and 3550 cm^{-1} due to two types of neighbouring pairs of hydroxyl groups involved in lateral hydrogen bonding interactions between the groups in each pair[25]. Subsequent immersion in carbon tetrachloride and addition of ethyl acetate gave a new infrared band at 1688 cm^{-1} (Figure 10) which is ascribed to the (C=O) stretching vibrations of ethyl acetate molecules which are each simultaneously perturbed by two hydrogen bonds, one from each member of an adjacent pair of silanol groups. The intensities of the
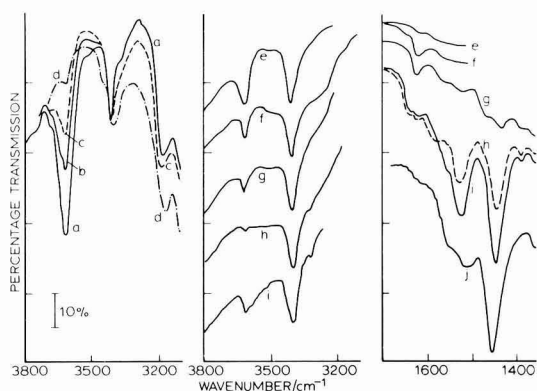

Figure 8. Spectra of rutile immersed in (a) heptane and (b) 0.015 mol %, (c) 0.025 mol %, (d) a high concentration of triethylamine in heptane. (e) As for (c) but with heptane in the blank beam of the spectrometer, (f) after a further 16 h immersion, (g) after draining and evacuation at *ca.* 306 K. (h) − (j) Spectra of rutile after immersion in a concentrated solution of triethylamine in heptane followed by drainage and evacuation at (h) *ca.* 306 K, 2 min, (i) *ca.* 306 K, 2 h and (j) 493 K, 1 h
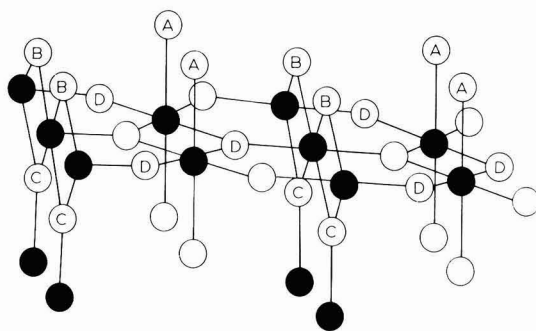

Figure 9. Angled view of the {110} surface plane of rutile. Shaded and open circles represent titanium and oxygen atoms, respectively
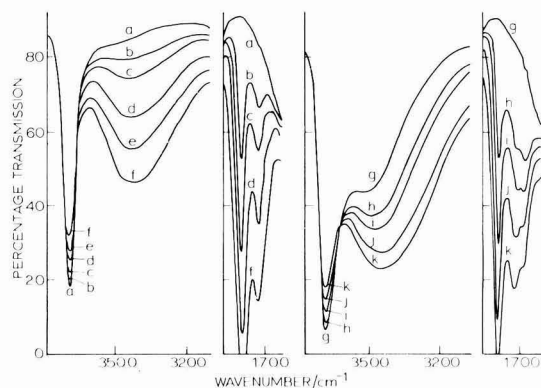

Figure 10. Spectra of silica after heat treatment at (a) − (f) 863 K or (g) − (k) 453 K, cooling and immersion in (a) and (g) carbon tetrachloride, (b) − (f) and (h) − (k) solutions containing increasing concentrations of ethyl acetate in carbon tetrachloride

maxima at 1688 and 1712 cm⁻¹ can be used to monitor the
separate extents of adsorption of ethyl acetate on to single
isolated and adjacent pair surface sites. The results for ethyl
acetate show that the stronger mode of adsorption occurs
on pair sites. The distinction between carbonyl compounds
adsorbed on single or pair sites has been particularly well
exploited in the case of cyclohexanone adsorbed on silica
immersed in 2,2,4-trimethylpentane for which the total
spectroscopic isotherm was dissected into the separate
components arising from the two modes of adsorption[26]. At
low surface coverages adsorption on pair sites
predominated in accordance with this being the stronger
mode of adsorption. However, the total number of single
sites was greater than the number of pair sites and therefore
single-site adsorption became dominant at high surface
coverages. Adsorption on isolated silanol groups was
apparently unaffected by the presence of adjacent
interacting silanol groups on silica which had been
preheated at low temperatures.

Distinguishable interactions involving particular sites

Adsorbate molecules containing more than one type of
functional group may interact with particular sites on an
oxide surface in a variety of different ways. Spectra of silica
immersed in solutions of anisole in heptane exhibit two
infrared bands which may be ascribed to isolated surface
silanol groups perturbed by hydrogen bonding interactions
with adsorbed anisole molecules. Maxima at 3610 and 3405
cm⁻¹ (Figure 11) are due to silanol groups linked by
hydrogen bonds to π-electrons in the aromatic nuclei
(structure II) and ether oxygen atoms (structure I),
respectively[21]. Studies of hydrogen bond formation
between triphenylsilanol and anisole in solution gave
similar results[27]. The solution phase reactions were of 1:1
stoichiometry and it was therefore concluded that
structures I and II represent two competing modes of
adsorption of anisole on isolated silanol group sites. The
alternative possibility of a pair of silanol groups interacting
simultaneously with each adsorbed molecule probably
occured to some extent at low coverages, but became less
significant as the coverage was increased[21,22].
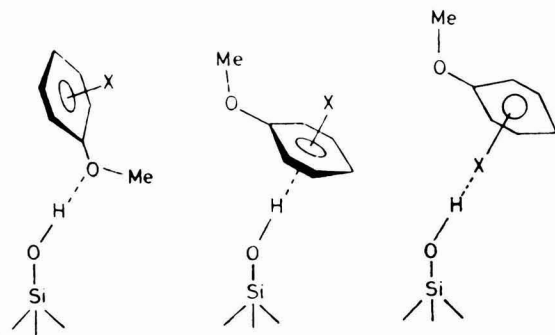
Results for a series of substituted anisoles showed that
the shifts Δv_{OH} in the position of the band due to surface
silanol groups were a function of the electronic effects of
substituent groups in the anisole ring. Figure 12c gives shifts
(measured from 3705 cm⁻¹ for silica in heptane) for silanol
groups interacting with the π-electrons of the aromatic
nuclei of aromatic hydrocarbons[21], substituted anisoles[21]
and phenols[22], ethyl benzoate[28] and benzonitrile[29] as a
function of the Hammett σ-constants[30] for all the
substituents in the aromatic ring[21]. The greater the electron

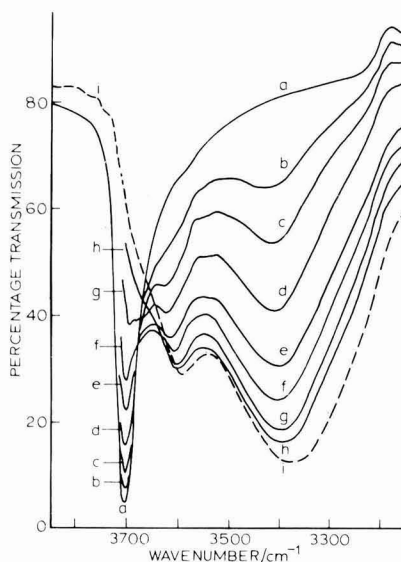**Figure 11. Spectra of silica immersed in (a) heptane, (b) − (h)
solutions of anisole in heptane at concentrations/mmol dm⁻³ of 10,
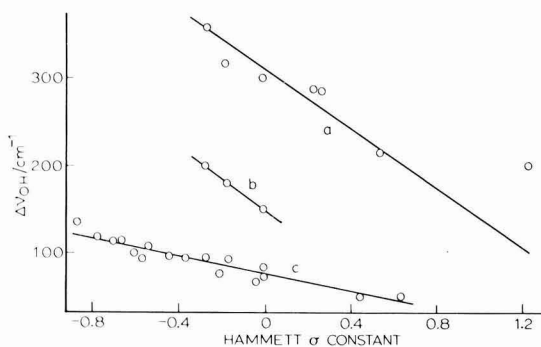19, 32, 57, 113, 305 and 764, respectively, (i) anisole**

**Figure 12. Correlations between Δv_{OH} and Hammett σ-constants
for the adsorption from liquid heptane of substituted (a) anisoles,
(b) nitrobenzenes and (c) benzenes on to isolated surface silanol
groups on silica**

density in the ring, the stronger is the interaction involving
silanol groups as hydrogen bond donors and therefore the
bigger is the shift Δv_{OH}. A similar correlation has been
observed for silanol groups interacting with the nitrogen
atoms of adsorbed substituted pyridines on silica immersed
in carbon tetrachloride[9]. The shifts for silanol groups
forming hydrogen bonds with methoxy groups in
substituted anisoles were also consistent with the
expectation that electron withdrawing substituents would
weaken the hydrogen bond and therefore give a smaller
value of Δv_{OH} Figure 12a. However, the experimental
point for 4-nitroanisole (σ = 1.24) was anomalous.
Comparison of the shift for 4-nitroanisole with Δv_{OH} for
silanol groups interacting with the nitro groups of
nitrobenzene and 4-nitrotoluene, Figure 12b shows that the
dominant mode of adsorption of 4-nitroanisole on silica in
heptane involves the formation of hydrogen bonds with the
nitro groups (structure III, X = 4-NO₂) rather than the
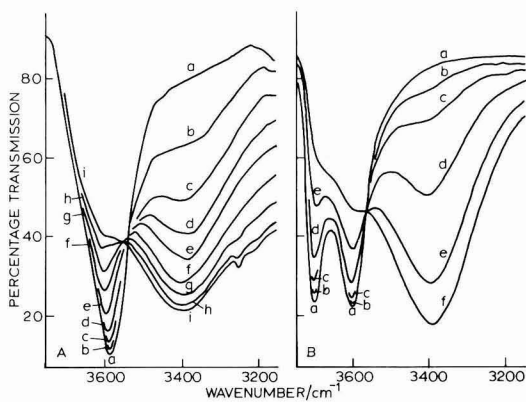methoxy groups of adsorbed molecules. The infrared data

Figure 13. (A) Spectra of silica in (a) toluene, (b) — (i) propionitrile + toluene mixtures with increasing mole fractions of propionitrile. (B) Spectra of silica in (a) a 2,2,4-trimethylpentane and toluene mixture, (b) — (f) propionitrile and 2,2,4-trimethylpentane and toluene mixtures with increasing concentrations of propionitrile and a constant mole ration of 2,2,4-trimethylpentane to toluene

therefore allows three modes of adsorption of substituted anisoles on silica to be unambiguously characterised.

Adsorption from three component mixtures

Immersion of silica in propionitrile and toluene mixtures gave spectra containing maxima at 3595 and 3395 cm^{-1} (Figure 13A) due to silanol groups perturbed by hydrogen bonding interactions with toluene and propionitrile molecules, respectively. Two bands also existed in spectra of silica in propionitrile and 2,2,4-trimethylpentane mixtures, one at 3395 cm^{-1} due to the formation of hydrogen bonds between silanol groups and cyano groups in adsorbed propionitrile and the second at 3705 cm^{-1} due to the weak perturbation of silanol groups by 2,2,4-trimethylpentane[13]. Figure 13B shows spectra of silica which had been heated in vacuum at 873 K and cooled to room temperature before immersion in mixtures of propionitrile, toluene and 2,2,4-trimethylpentane. The positions of the three maxima at 3395, 3595 and 3705 cm^{-1} were independent of the composition of the liquid phase suggesting that there were negligible solvent effects on the infrared bands. Measurements of absorbance values at the spectral positions corresponding to the three maxima allow calculation of the fractions of the total surface population of silanol groups which are perturbed by each of the three components of the liquid phase[13]. Similar results have been obtained for silica immersed in mixtures of cyclohexanone, 1,4-dimethylbenzene and 2,2,4-trimethylpentane[11]. The infrared data therefore enable a quantitative measure to be gained of the relative extents of adsorption of the constituents of three component liquid phases on to specific adsorption sites (isolated silanol groups) on the silica surface. The method is applicable providing the strengths of interaction between surface hydroxyl groups and the three individual components of the mixture, and hence the three shifts Δv_{OH}, are distinguishably different.

Adsorption from aqueous solution

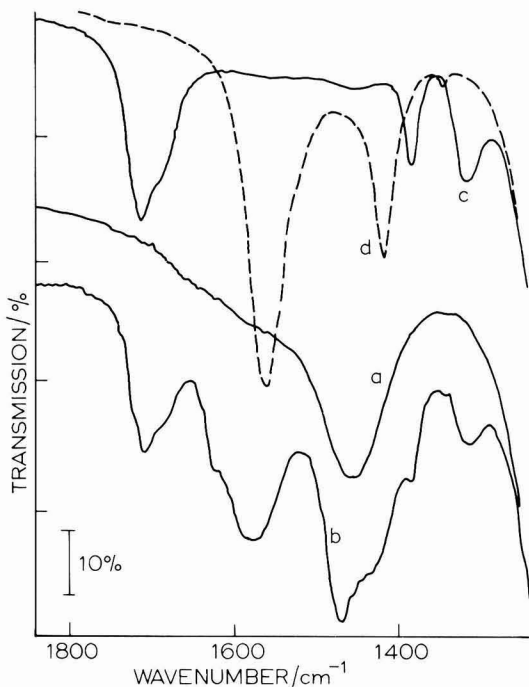Water is an extremely strong absorber of infrared radiation

Figure 14. Spectra of (a) alumina dispersed in D$_2$O, (b) alumina dispersed in a solution of acetic acid in D$_2$O, (c) acetic acid in D$_2$O, and (d) sodium acetate in D$_2$O

and therefore sols containing water as the predominant component of the liquid phase must be maintained at a low optical path length of sol in the infrared cell during spectroscopic examination. The results in Figure 14 illustrate the promise of infrared spectroscopy in this context[16]. The spectra were of systems containing deuterium oxide rather than normal water as the latter gave an intense maximum at 1645 cm^{-1} which obscured some of the spectral region of interest. Dispersions of alumina in deuterium oxide gave an infrared band at 1455 cm^{-1} assigned to the deformation vibration of HDO molecules formed by exchange between D$_2$O and surface hydroxyl groups on alumina. Dispersions of alumina in solutions of acetic acid gave spectra containing bands at 1712, 1386 and 1318 cm^{-1} which were also observed in spectra of acetic acid in deuterium oxide (Figure 14). Further maxima at 1575, 1468 and 1350 cm^{-1} and a shoulder at 1622 cm^{-1} compared with bands at 1561, 1418 and 1350 cm^{-1} in spectra of solutions of sodium acetate in deuterium oxide. The four new bands could partly be attributed to soluble aluminium acetate species formed by dissolution of alumina in the acid solution. However, replacement of the solution of acetic acid by pure solvent after adsorption had taken place clearly established that a significant contribution to the intensities of the bands arose because of adsorbed acetate species at the alumina/water interface.

The use of infrared spectroscopy for monitoring adsorption phenomena on powder surfaces in contact with water has not been very much exploited to date. However, particularly with the availability of Fourier transform infrared spectroscopy and data handling microcomputers this is an area which offers exciting prospects for future development.
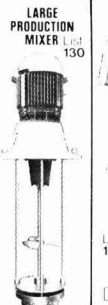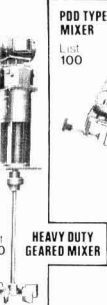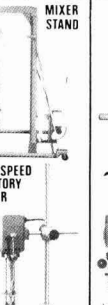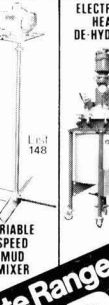
Acknowledgements

References

1. Parfitt, G. D., and Rochester, C. H., "Characterisation of Powder Surfaces" (Ed. G. D. Parfitt), *London, Academic Press*, Chap. 2. 1976.
2. Griffiths, D. M., and Rochester, C. H., *J.Chem.Soc. Faraday Trans. 1*, 1977, **73**, 1510.
3. Rochester, C. H., and Topham, S. A., *J.Chem.Soc. Faraday Trans. 1*, 1979, **75**, 1073.
4. Rochester, C. H., and Topham, S. A., *J.Chem.Soc. Faraday Trans. 1*, 1979, **75**, 591.
5. Parfitt, G. D., Ramsbotham, J., and Rochester, C. H., *Trans. Faraday Soc.*, 1971, **67**, 841.
6. Parfitt, G. D., Ramsbotham, J., and Rochester, C. H., *Trans. Faraday Soc.*, 1971, **67**, 1500.
7. Graham, J., Rochester, C. H., and Rudham, R., *J.Chem.Soc. Faraday Trans. 1*, 1981, **77**, 1973.
8. Griffiths, D. M., and Rochester, C. H., *J.Chem.Soc. Faraday Trans. 1*, 1977, **73**, 1988.
9. Griffiths, D. M., Marshall, K., and Rochester, C. H., *J.Chem.Soc. Faraday Trans. 1*, 1974, **70**, 400.
10. Buckland, A. D., Rochester, C. H., and Topham, S. A., *J.Chem.Soc. Faraday Trans. 1*, 1980, **76**, 302.
11. Buckland, A. D., Rochester, C. H., Trebilco, D.-A., and Wigfield, K., *J.Chem.Soc. Faraday Trans. 1*, 1978, **74**, 2393.
12. Rochester, C. H., and Trebilco, D.-A., *J.Chem.Soc. Faraday Trans. 1*, 1977, **73**, 883.
13. Rochester, C. H., and Yong, G. H., *J.Chem.Soc. Faraday Trans. 1*, 1980, **76**, 1466.
14. Marshall, K., and Rochester, C. H., *J.Chem.Soc. Faraday Trans. 1*, 1975, **71**, 2478.
15. Buckland, A. D., Graham, J., Rudham, R., and Rochester, C. H., *J.Chem.Soc. Faraday Trans. 1*, 1981, **77**, 2845.
16. Neagle, W., and Rochester, C. H., *J.Chem.Soc.Chem.Commun.*, 1982, 398.
17. Acosta Saracual, A. R., Pulton, S. K., Vicary, G., and Rochester, C. H., *J.Chem.Soc.Faraday Trans. 1*, 1982, **78**, 2285.
18. Fontana, B. J., and Thomas, J. R. *J.Phys.Chem.*, 1961, **65**, 480.
19. Killmann, E., and Strasser, H.-J., *Angew. Makromol, Chemie*, 1973, **31**, 169.
20. Rochester, C. H. *Adv. Colloid and Interface Sci.*, 1980, **12**, 43.
21. Rochester, C. H., and Trebilco, D.-A., *J.Chem.Soc. Faraday Trans. 1*, 1978, **74**, 1125.
22. Rochester, C. H., and Trebilco, D.-A., *J.Chem.Soc. Faraday Trans. 1*, 1978, **74**, 1137.
23. Graham, J., Rudham, R., and Rochester, C. H., *J.Chem.Soc. Faraday Trans. 1*, 1983, **79**, 2991.
24. Graham, J., Rudham, R., and Rochester, C. H., *J.Chem.Soc. Faraday Trans. 1*, 1981, **77**, 2735.
25. Cross, S. N. W., and Rochester, C. H., *J.Chem.Soc. Faraday Trans. 1*, 1979, **75**, 2865.
26. Rochester, C. H., and Trebilco, D.-A., *J.Chem.Soc. Faraday Trans. 1*, 1979, **75**, 2211.
27. Acosta Saracual, A. R., and Rochester, C. H., *J.Chem.Soc Faraday Trans 1*, 1982, **78**, 2787.
28. Cross, S. N. W., and Rochester, C. H. *J.Chem.Soc. Faraday Trans. 1*, 1981, **77**, 1027.
29. Rochester, C. H., and Yong, G. H., *Chem. and Ind.*, 1982, 101.
30. Barlin, G. B., and Perrin, D. D., *Quarterly Revs*, 1966, **20**, 75.

Discussion is encouraged at OCCA Conferences following the presentation of papers. Those who put questions were asked to fill in discussion slips with the details of their questions. Edited versions of the discussions that followed two of the papers published in the **September 1985** issue appear below: questions in ordinary roman type, answered in italic. Only those questions for which discussion slips were received are published.

The role of adhesion in corrosion protection by organic coatings

W. Funke

J. D. SCANTLEBURY: I think your emphasis on "wet adhesion" is misleading. Work, which I will refer to this morning, shows that although the adhesion falls under fully immersed conditions which in many cases is reversible; under atmospheric corrosion testing, salt spray testing, we could find no decrease in adhesion compared with the dry values?

W. FUNKE: According to our experience wet adhesion is of decisive importance to corrosion protection by organic coatings, irrespective of the fact, that after water exposure dry adhesion may be regained to some extent. Poor wet adhesion indicates that water has entered the coating/metal interface, creating the electrolyte, which is required for any electrochemical reaction. We never observed substantial under-rusting, even in case of coatings with scratches, if wet adhesion was good. Unfortunately this was not too often the case.

The reasons, why you found no correlation between conventional corrosion tests and wet adhesion may have been unsuitable experimental conditions (too short exposure time, too low temperature, too film thickness), unsuitable methods for testing wet adhesion or the fact that perhaps in some cases wet adhesion was actually good and no differentiation possible.

C. SCHOFF: Do barrier coatings really protect the substrate or do they just delay the diffusion of water, O_2 and corrosive stimulants? If the latter is true, then in wet climates or other extreme conditions barrier coatings will not give much protection since the active agents will arrive at the interface eventually. Therefore, how much use is a barrier coating in such cases?

W. FUNKE: Principally the barrier effect of an organic coating only delays diffusion of corrosive agents or stimulants to the coating/metal interface. Hence the common statement "no organic coating is impermeable"! The question is, however, how low the permeability has to be for protection

under various practical conditions. Thick film coating systems, which are successfully used in strongly corrosive environments involve no special protective mechanisms other than significantly improved barrier properties. This proves that the barrier principle functions.

Combining the barrier principle with good wet adhesion certainly gives the optimum. However, this combination makes the use of anticorrosive pigments unreasonable. If in this case such pigments act as they should, the coating/metal interface would be something like a closed chemical reaction pot which doubtless would violate generally approved requirements for good adhesion.

W. J. VAN OOIJ: I have observed that the ranking of a series of coatings, e.g. cathodic electrocoat systems on steel, in terms of their performance in salt spray tests, is duplicated in simple laboratory tests in which the coating is punctured and then placed in NaOH at pH~13. The coatings blister around the punctured site and the diameter of the blister after about one week is a measure of the performance of that same coating in salt spray tests. Similar correlations were found between blistering in acidic solutions and filiform corrosion. This would seem to suggest that in theories of "wet adhesion" the environmental, e.g. pH, should be specified. Could the author comment on this?

W. FUNKE: In the salt spray test with scribed test panels undercurrent doesn't proceed laterally from the scribe but via a stepwise process starting from the expansion of cathodic, i.e. alkaline blisters. Accordingly, the delamination conditions of the salt spray test resemble those of your test, except that in the latter delamination proceeds laterally from the punctured area and no anodic areas are present.

As far as filiform corrosion is regarded, I can hardly visualize how exposure to an acidic solution may imitate this phenomenon. However, for atmospheric corrosion acidic conditions are getting more and more important in testing organic coatings.

New developments in self-polishing antifoulings

C. M. Sghibartz

P. J. MOLES: Owing to the environmental fears associated with tributyltin compounds will we see a move towards the less toxic organotin systems such as trioctyltins and the triester tins?

C. M. SGHIBARTZ: This is an appropriate question, given the current organotin debate in this country. However, it is unfortunate that some people do not realise that banning organotins may result in switching to other biocides, which may bring unknown problems.

As far as I am aware, no clear cut case exists against organotins. It is interesting to note (European Paint and Resin News, Vol.23, No.4, April 1985, front cover) that the oyster population has steadily decreased, reaching an all time low in 1964, well before the organotins were introduced.

I think it is of paramount importance for all parties concerned to look at the situation closely and to collaborate in order to reach the correct decision. Irresponsible journalism can do a lot of damage.

The toxicity of the mentioned organotins is much lower than that of tributyl and triphenyltin derivatives used commercially today. It is unlikely to see a move towards such compounds, given their inefficiency.

The trend to use the organotins more effectively started with the launch of the "3rd Generation" will continue. The great majority of long-life antifoulings contain added organotins as boosters, in addition to cuprous oxide. As explained in the lecture, biocide release is based on migration. The exponential rate is wasteful during the first months and inefficient later on. Self-polishing paints due to the linear biocide release rate, offer more efficient systems, over longer periods of time.

The cost/performance advantage outlined is one aspect. Additionally, the organotin reduction should be welcomed by the environmentalists.

J. R. TAYLOR: It is surprising to ask if the newer type A/F compositions have good weathering properties since it is commonly accepted that A/F's are immersed in sea water, however modern supertankers have the A/F applied well above the old "boot topping line" often 20-30 feet and thus lack of cracking and crazing on exposure on return voyages to the Middle East is important?

C. M. SGHIBARTZ: *Cracking of long-life antifouling systems due to intermittent exposure to sea-water is well known. The area between load line and deep load line is often subjected to this problem.*

Self polishing paints do not crack even in these conditions, given, of course, that they were properly formulated in the first place.

At a recent symposium, arranged by the Ministry of Defence it was stated that the non-cracking characteristic of self-polishing paints is a distinct advantage over long-life antifoulings.

J. R. TAYLOR: Is it still necessary to have several qualities of A/F with these third generation A/F's for "layup" slow "steaming" and fast "steaming"?

C. M. SGHIBARTZ: *We have designed the "third generation" of self-polishing antifoulings to replace the long-life antifoulings. As stated in my lecture, they provide an overall better performance due to better biocide release control.*

Even in stationary situations they give superior performance. This can be clearly demonstrated with paints exposed for long periods. One has to remember that any "stationary" ship is subjected to water movements. Currents can have several knots, allowing polishing to take place, granted at a lower rate than on a steaming ship.

news

Essochem expands Fawley MEK solvents production

Esso Chemical Ltd has begun work on modifying its Methyl Ethyl Ketone (MEK) solvents plant at Fawley, UK. The current facility is the largest MEK plant in Europe and has been operating to its capacity of 68,000 tons per year. The expansion to 75,000 tons per year next spring will reduce Essochem's need for imports from Exxon Chemical's MEK plant in the USA and enable Essochem to satisfy increased customer demand.

In announcing the expansion, Bob Wilson, Essochem Europe's Solvents Vice President commented: "Fawley has proved to be an outstandingly competitive unit and we aim to maintain that position by continued investment in technology improvements and capacity gain".

In addition to MEK, Essochem Solvents market a wide range of hydrocarbon and oxygenated products including the Isopar, Solvesso, Exxsol D, Actrel and Exxate speciality solvents.

Anchor Chemical appointed distributor

Anchor Chemical has been appointed a distributor in the UK and Europe for the CUREZOL^R range of imidazole epoxy curing agents manufactured by Shikoku Fine Chemicals Corporation of Japan.

The CUREZOL^R range consists of both precursor imidazoles and modified imidazoles which enable the epoxy formulator to fine-tune the requirements of this latent system.

Applications for imidazole curing agents include one-pack structural adhesives for automotive and aerospace applications, potting, casting and encapsulation of electronic devices, moulding powders, powder coatings and composites.

products

New particle sizers

Malvern Instruments are to introduce new versions of their highly successful laser diffraction particle size analysers. Designed to measure particles or droplets in the range 0.5-1800 microns, they can be used for the analysis of a wide variety of samples including dry powders, suspensions and liquid sprays. A feature of the technique is that it does not require callibration or any information on density, viscosity or other physical parameters; this, combined with the simplicity of operation of the Malvern system, makes it particularly suitable for routine use as well as advanced research.

The new particle sizers, the Series 2600C and 3600E type, feature a powerful 16-bit computer/processor which has brought a significant decrease in the already short

analysis times and adds greatly to the data handling capabilities. the software of each system incorporates Malvern's exclusive Easy Sizer and Master Sizer programmes, the former making a complete analysis a simple, four keystroke procedure.

The full graphical and tabular results presentation includes size distributions in 32 size bands which can be at pre-set intervals, BS/ASTM sieve sizes or any user-selected sizes. Cumulative and frequency distributions can be plotted together and disk storage enables recalculation of data and overlay of results for comparison of different samples. Further flexibility is seen in the availability of number, length or surface area distributions in addition to the standard volume distribution.

The Series 2600C offers a modular approach enabling systems to be tailored either to specific applications or for maximum versatility. The compact and easy to use 3600E type is claimed to be optimised for highly cost effective analysis of powders and suspensions.

Reader Enquiry Service No. 32
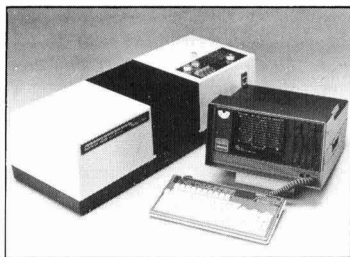
The Malvern 3600E Type particle size analyser

New adhesives system for wall coverings

Allied Colloids plc have developed a new adhesive system for the production of pre-pasted blown vinyl wall coverings. It is an addition to the Collafix adhesive range, designated PP4, that has been produced specifically to overcome the disadvantages of existing adhesives. Adhesive for pre-pasted wallpapers has been known and used for many years, but in the hear processing used for the manufacture of blown vinyl coverings disadvantages with hear stability have emerged. The new Collafix PP4 is a pre-paste single coat application polymer and is heat stable to all known process temperatures. It is not subject to bacterial attack and is claimed to offer a long shelf life on stored wall coverings.

Reader Enquiry Service No. 33

Two products launch new sundries family for retail market

Johnstone's paints have recently introduced the Universal Primer and Yacht Varnish, as first members of a new family of sundries aimed at the retail market.

The universal primer is said to meet the demands for a multi-purpose product that can be applied to wood, metal, dry plaster and masonry. It has been especially formulated with anti-corrosive pigments to inhibit rust and oils and resins to penetrate and seal absorbent substrates. It adheres strongly to the prepared surface and is said to provide an excellent key for subsequent coats.

The new primer is easy to apply with brush or roller, quick drying, and especially useful for multisurface work. Coverage varies according to substrate, with one litre yielding 7-8 m^2 on wood, 9-11 m^2 on metal and 5-9 m^2 on plaster, depending on porosity. One coat is con-sidered sufficient for most surfaces, although two are recommended for metal that has rusted badly.

Johnstone's yacht varnish is designed to protect and enhance natural wood grain. It is a clear alkyd resin-based product that gives a high build gloss finish. Suitable for exterior and interior use, it provides an exceptionally durable coating and has excellent gloss retention.

Yacht varnish can be applied to bare hard and soft woods, and surfaces that have been previously varnished or stained. Coverage is approximate 10 m^2 per litre and it is recommended that the first coat be thinned with 20 per cent white spirit. Surface drying time is two to three hours and the overcoating interval is between 16 and 24 hours.

Reader Enquiry Service No. 34

The Universal primer and yacht varnish from Johnstone's Paints.

Espa pump for solvent handling

The Espa Minox-F pump, now available from George Meller Ltd., is a stainless steel centrifugal pump available in a range of nine models, each with various motor options, to match process requirements from low to high flows. With motor sizes from 0.25 to 30 hp (0.18 to 22kw), the Minox-F range can provide flowrates from 1 to 100 m^3/h, and operate against heads up to 100 m.

The cover, impeller and swinging body are in stainless steel, the body being from 3 to 5 mm thick depending on the model, and the pump is polished both inside and out. The impeller is of precision cast open type as standard, although for high head and low flow applications requiring lower NPSH, a closed type impeller is optionally available. To suit the application, Minox-F pumps may be fitted with gland packing, or Crane, Pacific or Cyclam mechanical seals.

Reader Enquiry Service No. 35

SURFEX 86

Exhibition of raw materials and equipment for the surface coatings industries

So great has been the demand for space at Surfex 86, the new concept exhibition for the surface coatings industries to be held in Harrogate in May 1986, that as well as Hall D, space in the reception and gallery areas has almost all been reserved. Any organisation, therefore, wishing to apply for space at this prestigious event is urged to send for details of the small amount of space which can still be offered (P.O. Box 161, Wigan WN2 5TG). The West Riding Section of the Association has arranged a Dinner to take place at the Hotel Majestic, Harrogate, on the first evening of the Exhibition (14 May) and already there has been a considerable demand for tickets. Details have been printed in the members' monthly bulletin; non-members wishing to apply for tickets (£16 each inclusive of VAT) should contact Mr E. H. A. Bishop, c/o Cemontone Beaver Ltd, Woodlesford, Leeds for the appropriate form. The staff at Priory House can advise on the names of hotels in Harrogate which are prepared to offer special rates to visitors to Surfex 86 (Telex: 922670 OCCA G).

The *Official Guide* to *Surfex 86* will be printed in the April issue of *JOCCA* and will also be freely available at the entrance to the Exhibition. Admission will be free.

Advertising in the April issue will not be confined to exhibitors and other companies/organisations wishing to have details of these facilities should contact Priory House as soon as possible.

The Paint Research Association will be organising a symposium at the Hotel Majestic, Harrogate on the two days preceding the exhibition and the Association feels the opportunity to combine a visit to the Exhibition on the Wednesday and Thursday with attendance at Paint Research Association's Symposium on the preceding Monday and Tuesday will be of interest to visitors—particularly those from overseas.

Firm bookings have been received from the following exhibitors:

Allied Colloids Ltd

Alpha Chemicals/Buckman Laboratories

Samuel Banner Ltd

Baxenden Chemical Co

Blythe Burrell Colours Ltd

Boud Marketing

E. P. Bray & Co Ltd

SURFEX 86
14th-15th May 1986
Harrogate Conference Centre
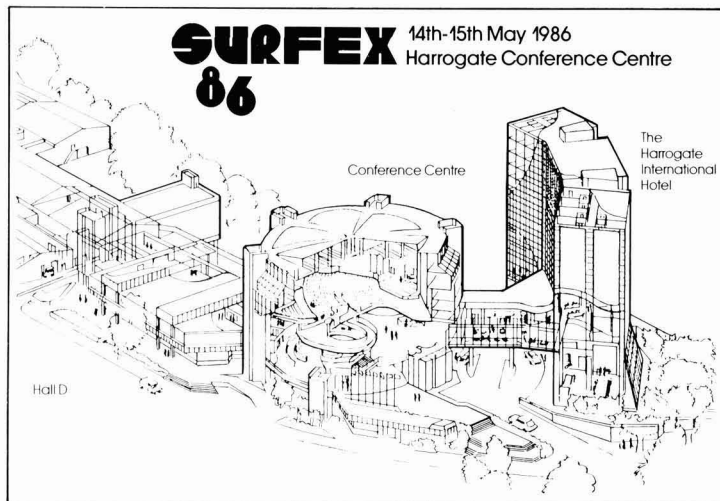
Byk Chemie GmbH
CIBA GEIGY Pigments
CIBA GEIGY Plastics
Cray Valley Products
Croda Colours Ltd
Croxton & Garry Ltd
Diamond Shamrock UK Ltd
Durham Chemicals Ltd
ECC International Ltd
Eiger Engineering Co
Elektro-Physik
Ellis & Everard
Ernstroem Minerals AB
Floridienne UK Ltd T/AS Micro Products
Foscolor Ltd
Fuel & Metallurgical Journals Ltd
John Godrich Consulting Engineers
H. Haeffner & Co Ltd
Haeffner Engineering
Harlow Chemical Co Ltd
Heubach UK Ltd
Hoechst UK Ltd
Kenroy Dispersions
Kirklees Chemicals Ltd
Kirstol Ltd
K & K Greef Ltd
Lawrence Industries Ltd
Marlow Chemicals Ltd

Mastermix Ltd
Metal Box Ltd
NL Chemicals UK Ltd
Norwegian Talc
Paintmakers' Association
Paint Research Association
Pearson Panke
Perchem
The Q-Panel Co Ltd
Red Devil
Reed Plastic Containers Ltd
Resinous Chemicals Ltd
Sandoz Products Ltd
SCM Chemicals Ltd
Scott Bader & Co Ltd
Seaton Group (Microfine)
Shear Chemicals Ltd
Sheen Instruments Ltd
Shell Chemicals UK Ltd
Siblerine Ltd
C & W Specialist Equipment
Steetley Minerals Ltd
Sun Chemicals Ltd
Tego Chemie Service
Tioxide UK Ltd
Torrance & Sons Ltd
Union Camp Chemicals Ltd
Wengain Ltd

literature

Masonry coatings and building products brochure

Glixtone Ltd. has introduced a 16-page, full-colour brochure, detailing its masonry coatings and other building products.

The company specialises in supply of coatings and other materials for the new-build, maintenance and re-furbishment markets. Glixtone produces a range of masonry coatings, including specialist coatings with anti-mould properties.

The brochure lists the full selection of products, including: conventional and anti-carbonation coatings; Wash-Perle; Heavy-Build Coatings; Wash-Lite; Medium-Build and Fine-Build Coatings; Wash-Gre, a grit-render finish; Wash-Bloc, a ready-for-use Synthetic Render; Wash Fibres; One-pack jointing compound, exterior insulation and the Wash-Ply System a check-resistant system for Plywood.

The brochure also provides advice on situations for use, techniques of application, plus a list of tools, equipment and literature.

Reader Enquiry Service No. 36

meetings

Symposium on Printing Inks

The Manchester Section of the Oil & Colour Chemists' Association are, during their Diamond Jubilee year, holding a two-day symposium entitled "Printing Inks for Packaging—Recent Changes and Future Trends".

This event will be held on Thursday and Friday, 10-11 April, 1986, at Salford University, near Manchester. A symposium dinner, overnight accommodation and a small exhibition by suppliers are all being organised.

Further information will be available from Mr M. Nixon, Winnetts Ltd., Inks Division, Demmings Works, Brookfield Road, Cheadle, Stockport SK8 2PR (Tel. 061 428 8521, Telex: 665089).

Jubilee New Zealand Convention

From Wednesday, 22 July—Sunday, 26th July, 1987, the New Zealand Section of OCCA will be holding their 25th Annual Convention.

The theme for this occasion is "Timber—its protection and decoration".

The New Zealand Section are currently calling for technical papers encompassing all aspects of this subject. And in conjunction with the Forest Institute of New Zealand a paper on "Transparent and semi-transparent coatings on Pinus Radiata", will be presented.

For further information contact: The Convention Co-ordinator, OCCA New Zealand, P.O. Box 5192, Auckland, New Zealand.

occa news

Report of Council Meeting

A meeting of the Council took place at 1.30 pm on Wednesday, 14 August 1985. at the Great Northern Hotel, King's Cross, London N1 9AN. The President (Mr F B Redman) was in the Chair and there were 26 members present.

The President extended a welcome to new members, both at home and overseas, who were serving for the first time on Council or returning after a break from former service.

The dates for Council meetings, the appointment of Council committees and the Association's representation on other organisations for the forthcoming session were agreed.

A full report and discussion on the Edinburgh Conference took place during which Council congratulated Mr J. R. Taylor (Honorary Research & Development Officer) for the excellent programme of papers and the interest aroused by them in the well-attended technical sessions. Thanks were also recorded to Mrs Anne Gibson who had taken on the task of arranging the social programme and to Mrs

Stephanie Gilliam who had also assisted. It was agreed that, in the same way as the 1985 Conference had marked the culmination of the Scottish Section's 60th Anniversary, the 1987 Conference would be held at Eastbourne (17-20 June 1987) to coincide with the London Section's 50th Anniversary.

A list showing the number of members still in arrears with 1985 subscriptions was tabled and Section Chairmen were asked to ensure that any members in arrears were reminded at Section level following reminders which had been sent from Priory House.

The Honorary Editor reported that papers from the Conference would be appearing in the *Journal* during the second half of the year. He was pleased to report to Council that the change in printers caused by the sudden liquidation of the previous printers in March had now been satisfactorily effected and all outstanding items had been successfully negotiated by the Director & Secretary with the Receiver appointed. A second monograph on "Water Borne Coatings" was now ready for printing and a third monograph by a

Past President of FATIPEC was being prepared for publication by Mr S. R. Finn, a former Honorary Editor. He also reported that Mr H. C. Worsdall was preparing a Raw Materials Index to cover the EEC and further information on this would be published in the *Journal*.

The Honorary Research & Development Officer reminded members that it was not too early to consider the subject of the 1987 Conference as it was important to provide subjects and papers which would appeal to members. He also reported that the Australian 28th annual Convention would be organised at McLaren Vale from 3-6 July 1986 and the Association had been invited to present a paper. It was agreed to put a note in the Report so that any members who were intending to be present at the Convention would be able to contact Mr Taylor.

Mr Clarke tabled a report on the progress of the Open Tech course.

The Director & Secretary reported that, in relation to the Professional Grade, two Associates had been regraded to Fellowship, five admitted as Associates and one as a Licentiate. Council noted with interest that one of the applications had been based on the New Zealand Diploma.

On the Exhibition, Mr F. Morpeth reported that all the space had been taken in Hall D and the Reception area and that some space had now been sold in a further area on the floor above leading to hospitality suites in the adjoining International Hotel.

Most of the hospitality suites had now been booked. The Official Guide to the Exhibition would be prepared as part of the April issue of the *Journal* in which exhibitors would be given free editorial space as in previous years. The West Riding Section had arranged a Dinner for the evening of Wednesday 14 May and tickets had already been purchased. Special hotel arrangements were being provided for overnight accommodation for exhibitors and visitors and this information would be appearing in the *Journal*. He had written to all Section Chairmen in UK and Ireland asking them to organise group visits if possible and to let him know the names of major companies in their areas to whom he could write. The Paint Research Association would be holding a symposium at Harrogate on the preceding two days on Coatings for Plastics and other problem substrates.

Council were saddened to learn of the death of the Honorary Member, Mr G. Copping, in June at the age of 93. It was hoped that an obituary would appear in the *Journal* in due course.

A report was received on the meeting of the ICCATCI which had met at Edinburgh and had been attended by representatives from this Association, OCCA, FATIPEC, FSCT and SLF. The three main items of report concerned the history of paint manufacture being produced by Mr Roire and a small team and it was reported that the Association had provided Mr Roire with information on this aspect. The second topic discussed concerned the FATIPEC Congress and possible Exhibition in Venice in September 1986. The last topic discussed was the Scandinavian Dictionary of Paint Terms, one version of which was in English and when this was ready details would appear in *JOCCA*.

Section Chairmen reported on their activities and the President reported on his visit to Australia and New Zealand and in particular the views expressed by the New Zealand Division.

It was reported that an order would shortly be placed for a new supply of OCCA ties. Correspondence which had been received from the Society of Dyers Colourists regarding the imminent closure of the Colour Chemistry Course at Leeds University was noted.

There being no further business, the President thanked members for their attendance and declared the meeting closed at 4.15 pm.

Jordan Award

The Jordan Award Committee now invites applications for the eighth award of £100. The rules of the Award are:

1. The Award will be made for the best contribution to the science or technology of surface coatings by a member of the Association of any nationality working in either the academic or industrial fields who is under the age of 35 at the date of the application.

2. The final date for submission of applications will on this occasion be 31 December 1986, and it is hoped to present the award at the Association's Conference in the following year.

3. The selection of the recipient of the Award will be made by the Jordan Award Committee under the chairmanship of the Association's Hon. Research and Development Officer.

4. There will be two methods of application. First, by submission of a paper describing original work by the candidate which is offered for publication in the *Journal* or has been so published during application. The alternative method will be by recommendation by a superior for work which for reasons of commercial secrecy cannot be published; in this case the candidate will be expected to submit a dissertation on a topic reating to his work and demonstrating his superior knowledge of the principles thereof. The Award is for individual merit and clear evidence of the candidate's own contribution will be required if a paper is offered under joint authorship.

5. Applications should be addressed to the Director & Secretary at the Association's offices.

News of Members

Sam Sharp retires

Mr Sam Sharp who donated the first Golf Trophy for competition at the Conference has informed us that he is now retired from Humbrol after some 30 years and 40 years in the paint industry. He is looking forward to achieving a single figure golf handicap in his retirement.

Obituary

Sam Duckworth

Mr J. E. Mitchell writes:

Members of the Association will be saddened to learn of the death of Sam Duckworth who collapsed and died whilst playing golf in Darwen on 19 September, 1985, at the age of 63.

Samuel Duckworth joined the Walpamur Company from Darwen Grammar School, eventually completing his studies by attending evening classes at Blackburn Technical College, qualifying as an Associate of the Institute of Chemistry. In November 1972 he was admitted FTSC.

During the Second World War he served as an NCO in the Royal Air Force, specialising in wireless communications.

Transferring from the research laboratories to the factory, he became production manager in Darwen and was responsible for planning the extensive modifications of the plant needed for the production of the new non-drip polyurethane gloss paint which was the spearhead of Crown Paints' marketing thrust, following the takeover of Wall Paper Manufacturers by the Reed Group.

He then joined the laboratories of the newly created Texales Division of WPM assuming responsibility for technical service between the laboratories, production units and their customers. He retired from full-time employment in 1981 and has since worked as a consultant specialising in the production of modern embossed wallcoverings.

He was always generous of his time for the Association, serving first as Hon. Treasurer to the Manchester Section 1962/69, he became Vice-Chairman 1970/72, and Chairman 1972/74 just prior to the Manchester Section Golden Jubilee Year. His service on OCCA Council is also worthy of note—member of the Finance Committee 1973/74/75, the PAC 1973/74, and Section Representative on Council 1971/72, 1973/74. In recent months he assisted at "viva" examinations of candidates for the Professional Grade.

A keen sportsman, Sam was always a tenacious competitor and when he turned from soccer to golf he quickly realised a single figure handicap! He was present at most OCCA golf events and at one time organised the golf competition at the biennial conference.

He will be sadly missed, particularly in the Manchester Section, not only for his

wise counselling over many years, but also for his exceptional skill at liar dice— which has enlivened many a long merry evening—providing the sternest challenge to allcomers to the Section social events!

Sound and penetrating in argument he will be remembered for his quiet persistent approach to the problem in hand and for his shrewd practical appreciation of all aspects of paint and wall-coverings technology.

He is survived by his widow and two children to whom we extend the deepest sympathy from the Association in their very sad loss.

Mr F. B. Windsor writes:

Sam will be sadly missed by his colleagues in the Manchester Section. We were all looking forward to his attendance at our Foundation Dinner in November to commemorate the Section's 60th Anniversary. In addition to his previous role as Chairman and Treasurer, Sam had served on the Section's Golf Committee, formed to organise the two successful annual golf events. It was in this activity that I first met Sam Duckworth. Both in committee and out on the course I began to appreciate and admire his particular and slightly dry sense of humour.

It was with that same humorous approach that he entered into the pseudo serious pastime of liar dice playing. During my initiation into this fascinating pastime I shall always recall Sam's favourite opener—Three Nines!! Even so, I always sought to sit on his left, he passed me some generous underbids. If there is a time to die, then Sam died playing one of the games he enjoyed—golf.

We shall miss him. The sympathy of the Manchester Section is extended to his wife and family.

CLASSIFIED ADVERTISEMENTS

APPOINTMENTS

INDEX TO ADVERTISERS

Further information on any of the products advertised in this Journal may be obtained by completing the Reader Enquiry Service form. The Reader Enquiry Service numbers are shown in brackets below.

OU··· LU··· OY

Tackifiers designed and tailored to meet your specific needs.

We're Oulu Oy from Finland. But that you already know. Although we're not tailors, we can dress-up your adhesives.

Do you know that :

- we put a manufacturing date on all our products, so that you know they're fresh

- our exceptionally high quality control standards ensure a uniform product that always performs the same way in your adhesives formulae

- we have our own R & D facilities - so we've no licence fees to pay, and can be more competitive

- we have our own sources of raw materials, so we don't have to shop around and wait for deliveries

- we can tailor-make a product to suit your needs, and even offer it exclusively to you

- we supply tackifiers in pastille form, ensuring minimum dust and maximum production efficiency.

But these are just a few points. We help you to be competitive, we guarantee deliveries, we can even assist you with product development. If you need stable tackifiers, fast, and backed by impeccable service - there's just one name to remember...

Oulu Oy. From Finland.

Oulu Oy

P.O. Box 196, SF-90101 Oulu 10, Finland.
Tel. 358-81-221411. Telex 32125.

The resourceful Finns