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A NOVEL APPROACH TO THERMAL ANALYSIS OF THIN FILMS

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A novel instrument is described called the Thin film Analyser (TFA) which quantitatively measures changes in mechanical and rheological properties of drying films in-situ on a test panel. It is based around a simple force-sensing device, capable of carrying various probes, which can be positioned in an *X-Y* plane over the panel. Temperature control is achieved by means of a heating block under the sample. By imposing a thermal gradient along the block, measurements can be obtained at a series of temperatures in a single experiment. Several applications of the TFA to the drying of curable and latex-based coatings are discussed, as well as some more specialized uses. The TFA concept represents a novel approach to the thermal analysis of thin films.

Keywords: thin films, Thin Film Analyser (TFA)

Introduction

In the coatings industry, a wide range of different tests are performed on films, during product development and for quality assurance to determine their final properties and the rate at which these properties are achieved in the field. An area of great importance is the testing of mechanical and rheological properties in drying films. Many simple and ingenious tests are currently used. Some, however, suffer from subjective interpretation and poor reproducibility. An example is the semi-automated BK test for through-film drying. This involves drawing a needle through the drying film at a known rate. While the film remains wet the needle leaves a visible trace but once it has dried the needle skates over the surface. The time of drying can, therefore, be determined by measuring the length of the line left in the coating. The end-point is seldom clear and is open to subjective interpretation, however, which often leads to poor reproducibility. The situation can be improved significantly by using a transducer to monitor the drag force on the needle. This is the basis of a cure tester marketed by Swan and Co. Ltd. Other tests are labour intensive and tedious to carry out. For example, a very common test for extent of cure is the sol-

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vent scrub test. This involves manually rubbing through the coating to the substrate with a solvent-impregnated cloth and counting the number of rubs. With a reasonable number of samples, each measured at several drying times, this can swiftly become a very tiring exercise! Other problematical areas are abrasion, wear and scrub resistance, and adhesion.

It is, of course, possible to relate mechanical properties of polymeric coatings to physical parameters such as modulus and T_g, which can be measured using established techniques such as DMA, TMA and DSC. Such techniques are playing an increasing role in research into new polymers for paints and coatings. In many situations, however, it is important to be able to measure the build-up of properties in-situ in drying films, under realistic conditions of solvent evaporation and on the appropriate substrate. In general this cannot be routinely achieved using commercially available thermal analysis instruments.

This paper describes a novel prototype instrument, the Thin Film Analyser, which automatically monitors the build-up of mechanical and rheological properties in coatings drying in-situ on a test panel, across a range of temperature. It is intended, below, to give some details of the instrument's design and to discuss a number of its applications. It is hoped that the TFA demonstrates a broader concept, that of a two-dimensional robot capable of positioning a number of different types of measuring probe over a drying film. A general-purpose thermomechanical testing station of this type would potentially be of great value for the testing of coatings. It is hoped that this paper will stimulate others to work in this area.

Description of the instrument

The Thin Film Analyser (TFA) is based on a commercial X-Y recorder in which the pen holder has been replaced by a general sensing device. Samples take the form of films spread onto standard glass or metal test panels (300×100×1–3 mm) and are placed on the modified bed of the recorder under the sensing device. Some important features of the instrument are discussed below:

a) The sensing device

The device which is currently most commonly used is shown schematically in Fig. 1. In order to minimize its weight the mechanism is constructed using hollow aluminium elements. These are jointed at low friction bearings. The probe, for example a needle in the case of scratch resistance measurements, is

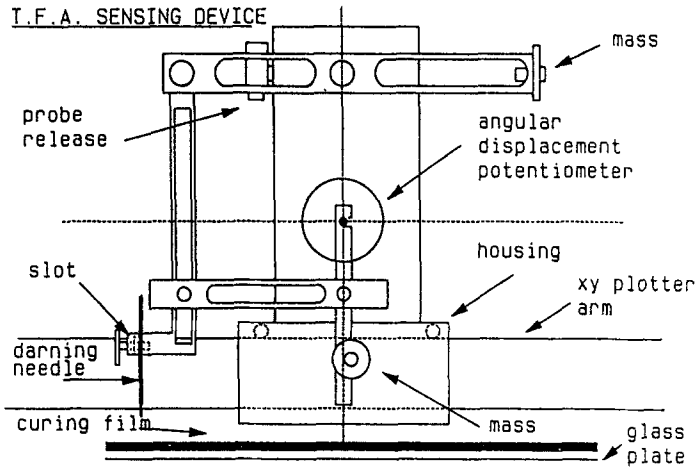

Fig. 1 Schematic diagram of the TFA sensing device

mounted in the slot indicated on the bottom left-hand side of the diagram. In order to perform a measurement the probe is first dropped down onto the film and then the housing is displaced in the '*Y*' direction along the plotter arm. As shown in Fig. 2, during this measuring stroke the probe will be displaced relative to the housing. As it is displaced from the vertical, mass 1 is raised, resulting in a lateral restoring force at the probe tip. At some critical restoring force the resistance to movement of the probe exerted by the sample may be exceeded and the probe may move across the film. This force is measured as an angular displacement of the potentiometer. The absolute restoring force can be determined by calibrating the potentiometer displacement with a known force applied to the probe using weights hung from a frictionless pulley. As shown in Fig. 3, an approximately linear relationship exists between angular displacement and force over the working range of the instrument. Often, however, a relative measurement of restoring force is adequate and results may be quoted as probe deflection, measured in volts dropped across the potentiometer. The probe can be

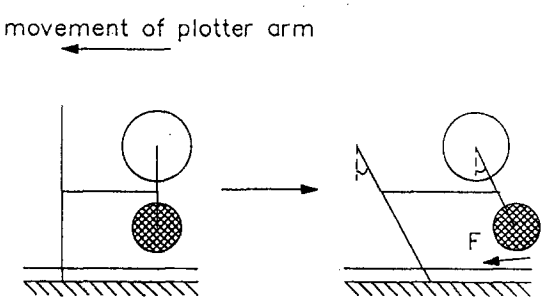

Fig. 2 Schematic view of the displacement of the probe during the measuring stroke

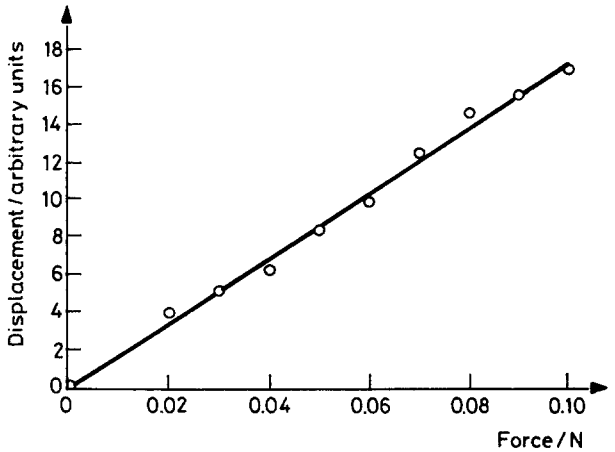

Fig. 3 Calibration curve for potentiometer displacement against true restoring force

raised and lowered from the film with a downwards force determined by mass 2 in Fig. 1.

b) Temperature control

This is achieved by means of a copper heating plate. This has a heating element at one end and a circulating water cooling coil at the other, so that a thermal gradient can be set up along the test panel. This allows measurements to be taken across a range of temperature simply by applying the probe at different '*X*' positions. This is very important feature of the instrument since, for example, it means that in one experiment the state of cure of a coating can be measured as functions of time and temperature. The temperature gradient is recorded by means of 10 spring-loaded thermocouples under the test panel. By means of a temperature controller the temperature of the hot end of the plate can be set between 30 and 100°C. The cold end is held at about 15°C using tap sub-ambient temperatures at the cold end.

c) Computer control

The instrument is automatically controlled by an IBM-compatible PC. A block diagram of the apparatus is shown in Fig. 4. A communications board in the computer is used to control the movements of the probe by the plotter. A data logger (from CIL of Worthing) collects data on the displacement of the probe during each measuring stroke and records the thermocouple readings. The controlling software is written is QUICKBASIC and BASICA. It provides the

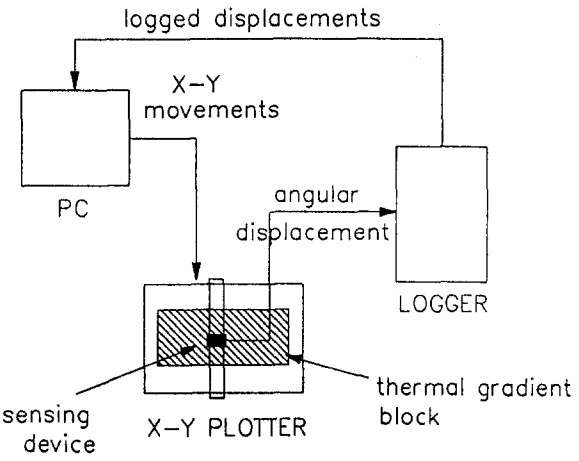

Fig. 4 Block diagram showing the components of the TFA

user with a simple language of defined functions that can be used very flexibly to programme the movements of the probe during an experiment. The probe displacement is analysed in one of several ways. In the normal scratch and viscosity modes the maximum displacement, corresponding to the maximum force, developed during the stroke is recorded. In the decay mode the displacement is measured after a set delay period after the measuring stroke is completed. As explained below, this mode extends the measuring range in order to deal with harder films. On occasions it has also proved useful to obtain more detailed data on the displacement transient during each measuring stroke.

Applications

1) Monitoring changes in viscosity during film drying

The aluminium probe used a measure the changes in viscosity of during film drying is shown in Fig. 5. During each measuring stroke the probe is drawn across the film in the *Y*-direction by a small distance (typically around 25 mm) and the maximum drag force is recorded. The carriage is then displaced in the *X*-direction and the measuring stroke is repeated successively to give a set of readings over a period of time. The drag force, divided by the wetted area of the probe, relates to a shear stress and the rate of the *Y*-displacement relates to a shear rate so that a measure of the film viscosity can be obtained. The shear regime represented by the TFA probe is complex which makes it difficult, with non-Newtonian materials, to make a quantitative comparison of readings with

other rheological techniques. It is possible, however, to calibrate the TFA against standard near-Newtonian oils of known viscosity. A typical calibration curve is shown in Fig. 6 which shows that there is a nearly linear relationship between probe displacement and viscosity.

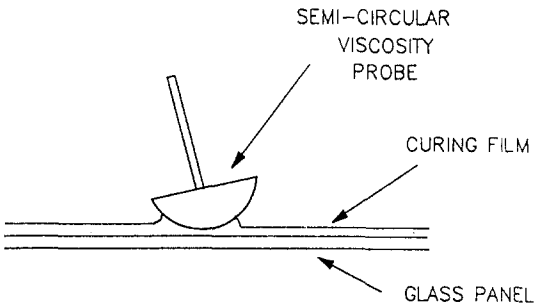

Fig. 5 The probe used to measure changes in viscosity

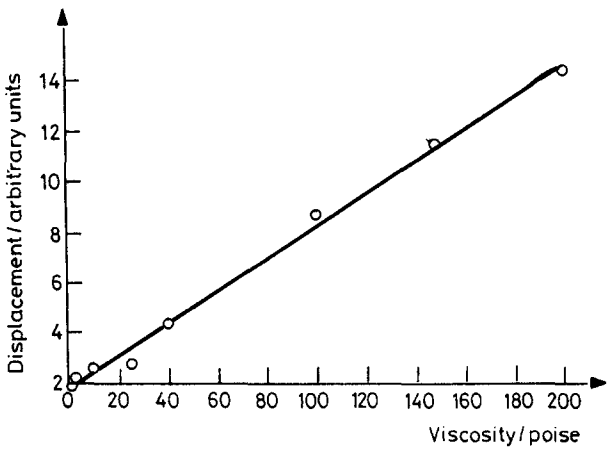

Fig. 6 Calibration curve for potentiometer displacement against viscosity of standard near-Newtonian oils

The viscosity probe is sensitive to the initial phase of film drying, over the first few minutes, during which solvent is lost. It is, therefore, useful in monitoring such phenomena as the flocculation and coalescence of polymer lattices, and the gelation of cross-linking resins. This part of the drying process is difficult to observe quantitatively by other methods. This is a critical stage during the application of many paints. It is often required that the wet film has a sufficient high viscosity immediately after application to stay on the substrate but can still flow sufficiently to remove the surface undulations resulting from brushing, spraying etc.

Figure 7 shows results for two types of household paint, a water-based emulsion paint and a white-spirit based gloss paint. It can be seen that in both cases the viscosity remains low for an initial period, after which a sharp rise occurs. This initial period is significantly longer for the gloss paint, which accounts for the greater resistance to brushmarking experienced with this type of product.

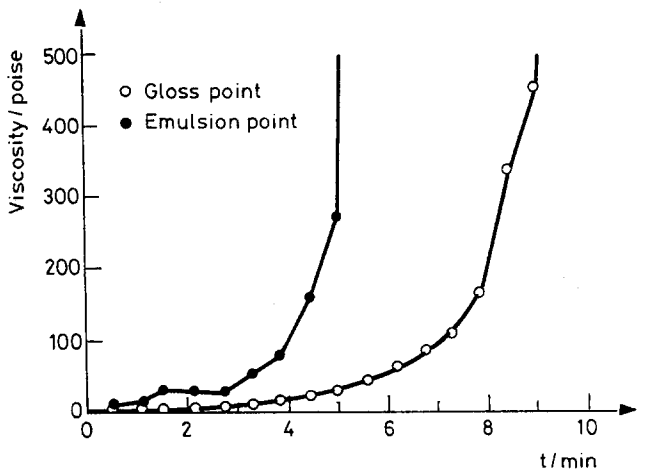

Fig. 7 Comparison of the viscosity-time profiles of drying films of an emulsion paint and a gloss paint

Another example is shown in Fig. 8 which shows results for two automotive basecoats. Figure 8*a*) shows the build up of viscosity for a sprayed film of a conventional solvent-borne product. A very rapid rise in viscosity to a limiting value occurs over the first 100 seconds as the solvent is lost. This plateau corresponds to the maximum force that the TFA can measure, i.e. instrument saturation. It can be seen that after around 300 s an apparent drop in viscosity occurs. During this part of the curve the probe has lost contact with the drying film and is skidding over the surface. In practical terms this time is the tack-free point of the paint. Figure 8*b*) shows the results of a similar experiment with a water-borne base coat. It can be seen that the build up in viscosity occurs significantly later than with the solvent-borne product.

2) Monitoring the extent-of-cure in coatings

By replacing the viscosity probe with a needle the TFA can be used to monitor the build up of the scratch resistance of coatings. This mode of operation is useful for studying the subsequent stages of film drying after most of the solvent has left the coating. For example the results can be related to the extent-of-cure

in cross-linking resins and to phenomena such as vitrification. These experiments can be done at a series of different temperatures using the thermal gradient bar.

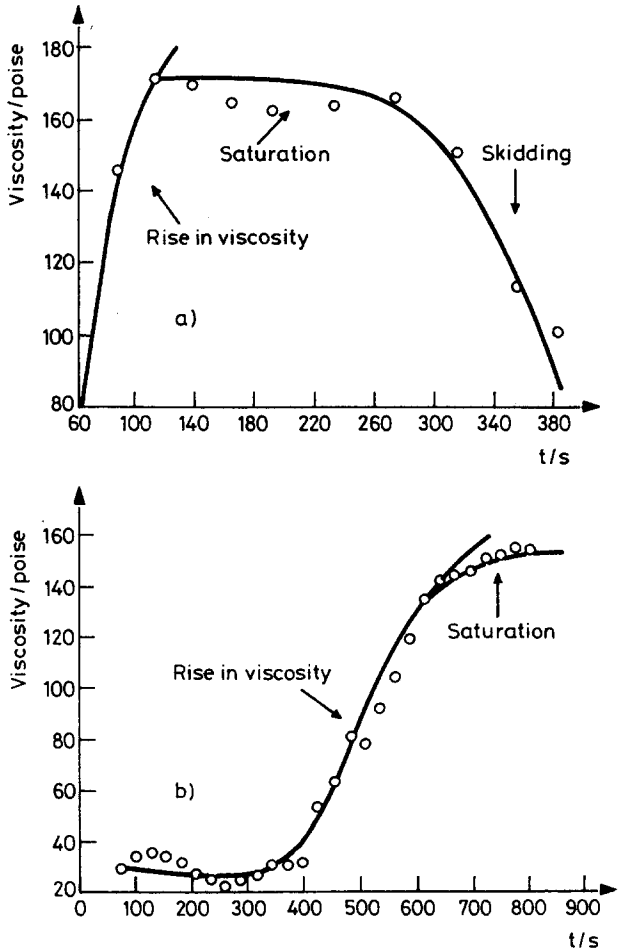

Fig. 8 Viscosity-time profiles for automotive basecoat films; *a*) solvent-borne; *b*) water-borne

Because of the viscoelastic behaviour of polymeric coating it is generally the case that the force required to scratch through the film increases with the speed of the measuring stroke. It is, therefore, possible to adjust the sensitivity of the TFA to film hardness by altering the speed. This is illustrated in Fig. 9, which shows results for a film of an alkyd-resin containing gloss paint at two different measuring speeds. The force required to scratch the coating increases as curing

progresses. The scratch resistance builds up earlier when the needle is moved with a fast stroke than with a slow stroke. An important feature of the cross-linking of this type of coating, which cures by autooxidation, is a differential reaction rate between the surface and the bulk of the film. It can be seen in Fig. 9 that both curves rise to a plateau at about 1.5 volts, which corresponds to the maximum probe deflection. It has been found that by adjustment of the masses on the sensing device and the speeds of the strokes it is possible to match the times to reach the plateau for the fast and slow stroke data with cure of the surface and through-film drying.

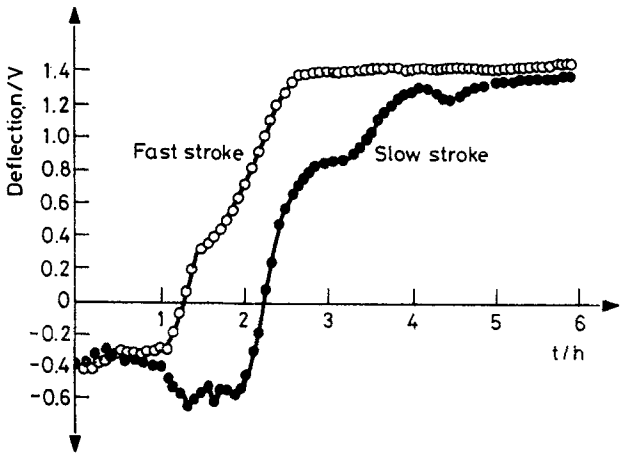

Fig. 9 The build-up in scratch resistance for fast and slow strokes, seen with a drying film of a gloss paint

In the example described above the panel was maintained at a constant temperature and scratches were made down its length to obtain results as a function of time. This test can be modified by setting up a temperature gradient along the panel so that measurements at different temperatures are obtained from scratches at different points along the *X*-direction. Results for a household gloss paint are shown in Fig. 10. Measurements were made at ten different temperatures between 20°C and 60°C, after 0, 15, 30 and 45 minutes. The data are presented as a 3-dimensional plot with scratch resistance on the *Z*-axis, temperature on the *X*-axis and elapsed time on the *Y*-axis. It can be seen that scratch resistance increases towards the top right-hand side of the figure, which shows that, as expected, the degree of cure increases with temperature and drying time. The curves at 30 and 45 minutes show a small decrease at the highest temperature. Film softening occurs here because the cross-linked polymer is close to its T_g at this temperature. This example illustrates how the TFA can provide a great deal

Table 1 Summary of the differences in functionality and T_g of the automotive topcoat formulations

Number	Functionality	T_g/°C
1	LOW	76
2	LOW	40
3	HIGH	76

of information on the cure characteristics of a coating formulation in a single, comparatively short experiment. For the coatings technologist these empirical maps of extent-of-cure versus time and temperature are useful in determining cure schedules. On a more fundamental level a refined version of the TFA might also be used to derive the TTT diagrams for cross-linking polymers pioneered by Gillham [1].

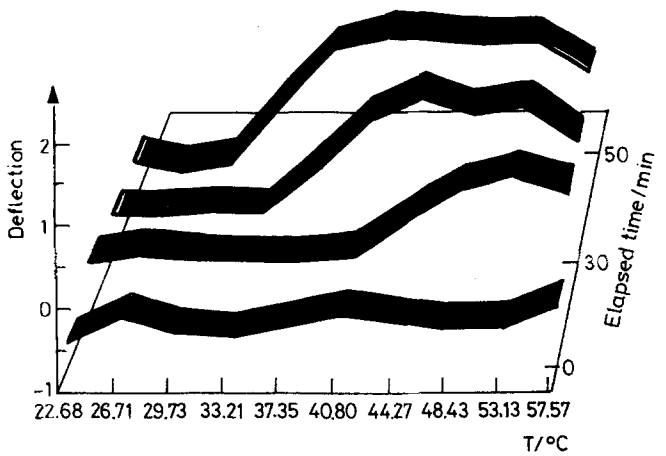

Fig. 10 3-D plot showing the results of a temperature scanning scratch test with a gloss paint

With harder coatings as used in automotive paints, for example, the limited force that can be applied by the sensing device becomes a problem with this prototype instrument. It has been found, however, that this limitation can be circumvented by modifying both the scratch and the time at which the probe deflection is measured. In this so called 'Decay' test, the probe is displaced in the *Y*-direction and then allowed to relax slowly back to an equilibrium position over a set delay period before recording the angular displacement. In effect this technique measures the minimum force required to scratch the film at an infinitesimal rate. An example of the use of the Decay test is shown in Fig. 11. Results are shown for three formulations intended for automotive topcoats. These formulations differed in their cross-linking functionality and their theoretical T_g's, as summarised in Table 1. They were measured at two different tempera-

tures on the thermal gradient bar. At 37°C it can be seen in Fig. 11*a*) that the highest functionality formulation, system 3, cures the most rapidly, followed by system 2 then system 1. The latter two formulations had the same functionality, but system 2 is closer to its T_g at this temperature, which accounts for the higher cure rate. The curves at 60°C illustrate a feature commonly seen with hard coatings on the TFA. As film cure proceeds the scratch resistance rises to the maximum deflection and then apparently decreases again. This occurs because the film becomes so hard that the needle does not penetrate at all and skids over the surface. As this skid point provides another useful piece of data on the state of cure it is often advantageous to encourage skidding by employing a blunt needle. It is interesting to note that the differences in the cure rates between sys-

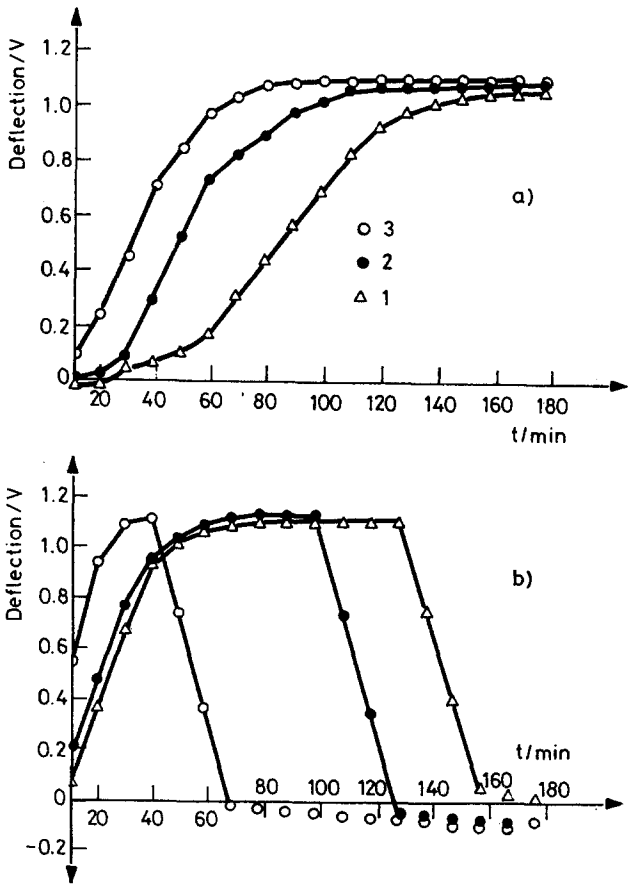

Fig. 11 Results of the decay test at two temperatures for three automotive clearcoat formulations; *a*) 37°C, *b*) 60°C

tems 1 and 2 are now smaller, since both formulations are above or close to their T_g.

3) Solvent resistance

By applying a pool of water to the test panel and scratching the film through it, it is possible to monitor its deterioration with time. This is illustrated in Fig. 12, which shows results for a series of coating formulations containing different ratios of hydrophilic and hydrophobic polymer components. It can be seen that at high levels of the hydrophobic polymer no measurable deterioration occurs during the test. As the level of the hydrophilic polymer is increased, however, the scratch resistance falls after a critical time, which gets shorter as the fraction of hydrophilic polymer increases. With due consideration for flammability hazards, in principle this technique could be used for other solvents as well as water. It could also be applied to study re-coating, that is the effect on a first coat of applying a second wet film.

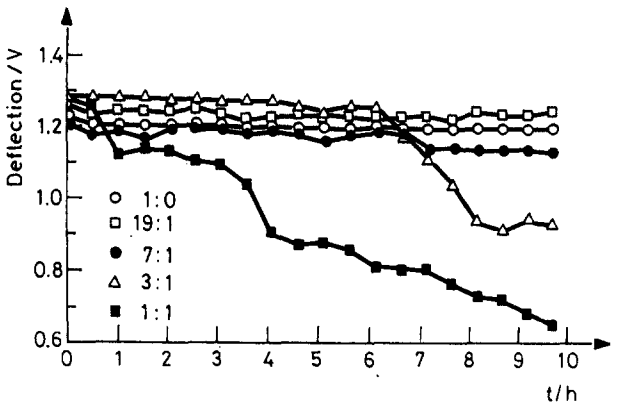

Fig. 12 Results of water resistance test on a series of coatings containing different weight ratios of hydrophilic and hydrophobic polymer components

Conclusions

A novel computer-controlled instrument, the Thin Film Analyser (TFA), has been described, which measures the build-up of viscosity or scratch resistance in a coating during film drying. It incorporates a thermal gradient heating bar for controlling the temperature of the test panel. This enables readings to be taken across a range of temperature in a single experiment. The TFA can, therefore, be used to provide a rapid empirical assessment of cure rates at different temperatures and an estimate of the T_g of the coating at different times. In providing this data on a drying film the TFA addresses an area of thermal analysis not yet

tackled by commercial instruments. The basic concept of a two-dimensional robot to position a number of different types of measuring probe on a test panel, coupled with a thermal gradient bar to control the temperature, in principle, could be extended to measure a number of other film properties. For example, for industrial testing, an abrasive pad along with a solvent jet could be used to measure scrub resistance or a chisel-type device to measure adhesion. Dielectric, optical, spectroscopic and a multitude of other types of probe can be envisaged. A vibrating probe is currently being designed that will measure both the elastic and viscous properties of a film. In principle this will allow TTT diagrams to be determined from a single experiment on one film. A method is also currently being developed for determining Minimum Film-Forming Temperatures. It is hoped that this paper will stimulate further work in this area which is of industrial importance for the development of coating and is a largely unexplored field of thermal analysis.

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References

1 G. Wisanrakkit, J. K. Gillham and J. B. Enns, J. Appl. Polym. Sci., 41 (1990) 1895.

Zusammenfassung — Es wird ein neues Gerät, ein sogenannter Dünnschichtanalysator (TFA) beschrieben, der zu quantitativen in situ Messung mechanischer und rheologischer Eigenschaften von trocknenden Filmen auf Testplatten dient. Es besteht aus einer einfachen kraftempfindlichen Vorrichtung, die verschiedene Proben tragen kann, welche in einer X-Y-Ebene über der Platte positioniert werden können. Die Temperatur wird durch einen unter der Probe befindlichen Heizblock kontrolliert. Bei Anlegen eines thermischen Gradienten entlang des Blockes können Messungen bei verschiedenen Temperaturen in einem einzigen Experiment durchgeführt werden. Es werden einige Anwendungen des TFA beim Trocknen vernetzbarer Beschichtungen auf Latexbasis beschrieben, als auch einige spezielle Anwendungen. TFA verkörpert einen neuen Weg bei der Thermoanalyse von dünnen Filmen.