

CDCA-100 DYNAMIC CONTACT ANGLE TENSIO METER

Static & Dynamic Surface Tension of Coatings

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INTRODUCTION

More companies are becoming aware of dynamic measurements for surface tension and when faced with a limited budget for a Quality Control instrument should they choose dynamic or static tensiometer?

Static surface is obtained by measuring the maximum force at a liquid/gas interface on a sample where the interface is static i.e. there is no creation of new interfaces during the test. It is obtained using a force measuring device with a Du Noüy ring that is an ASTM standard test and historically it has been the basis of many companies compulsory method for determining surface tension. However when liquids reach a certain viscosity there is no doubt that rheological flow under gravity can have an effect on the ring technique, perhaps causing the lamella to break before maximum force has been reached. Elastic materials may enhance the stretching ability of the liquid and increased force may result. As such some companies now use the Wilhelmy plate with the tensiometer, which has the benefit of sitting at the surface rather than being pulled above it, thus allowing rheological effects to play out.

Regardless of whether the ring or plate is used the value obtained is a static one. When the industrial process or application involves the creation of new surfaces such as in spraying, then what relevance is the static value? The good news is that it is important, as it is the value that helps to predict wetting. The bad news is that in a dynamic process the static value may not be reached by the time the liquid hits the solid, which will then not be wetted. The following sections describe the principles behind both static and dynamic surface tension measurements with an example from a company faced with a choice between the two types of instrument for QC purposes. Would they be better opting for the static or the dynamic system? Specific examples will be made using the Camtel CIT-100 Surface & Interfacial Tensiometer for static measurements and Sita t60 Bubble Tensiometer for dynamic measurements.

PRINCIPLES OF MEASUREMENT

Du Noüy Ring – A Static Technique

The universally accepted technique for measuring the liquid/gas surface tension is by the Du Noüy ring that is a precise geometry made of Pt-Ir. International standards exist for both the liquid/gas and liquid/liquid interface, for a range of industries e.g. electrical insulation & electronics, water & environmental, rubber and surfactants, based on this technique. The methods for cleaning the ring are described in these standards but it should be noted that new health and safety rules might preclude their use. Depending on the test material, water or a 'safe' solvent should be used to remove the test liquid from the surface followed by an acetone rinse and a final clean water rinse before flaming to red heat. It is equally important that glass sample vessels must also be scrupulously clean.

The measurement simply requires the ring to be wetted by the liquid and then pulled through the interface while measuring the force exerted on the ring. The ring must sit square and parallel to the interface, as failure to do so will result in errors in the measurements. The maximum force of the vertical constituent is directly proportional to the surface tension. The force measuring sensor of the CIT-100 is an electronic balance so the weight is monitored and converted to force i.e. $1g = 9.81mN$.

The equation to calculate surface tension assumes that the contact angle of the liquid on the ring is zero hence $\cos \theta = 1$ (the condition which exists when the force vectors, as the ring is pulled out of the liquid, are vertical), see Fig.1.

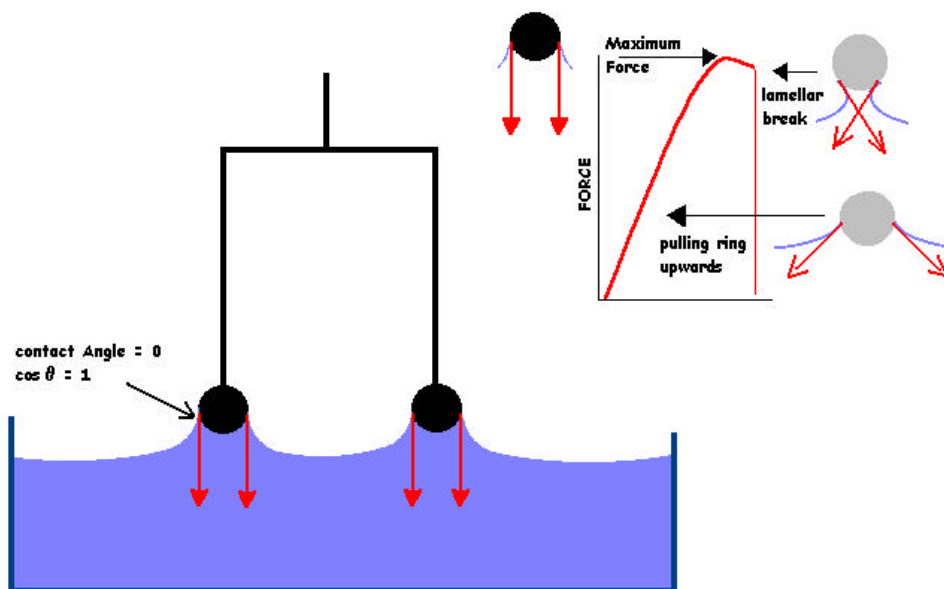


Figure 1 Schematic of Du Noüy Ring Method

The wetted length, $L = 4\pi R$, is obtained from the circumference of the inner + outer ($2 \times$ mean) radii of the ring:

$$\sigma = F/L \cos \theta \quad (1)$$

Unfortunately with this method, due to the volume of the liquid hanging from the ring as it is pulled above the surface, a correction needs to be applied:

$$\sigma = (F_{max} - F_v)/L \cos \theta \quad (2)$$

Where $F_v = gV (\rho_L - \rho_A)$

$V =$ volume of liquid at $F = F_{max}$

Work by Harkins & Jordan¹ (table of empirical values) and Zuidema & Waters² (algorithm based on ¹) allows a correction to be made for the additional volume of liquid raised above the interface:

$$F_v = 0.725 + \sqrt{\frac{1.452 * R_{aw} * ST}{(2\rho R)^2 * (P - r)} + 0.04534} - \frac{1.679}{(R/r)} \quad (3)$$

Where R is mean ring radius & r is mean wire radius

P is heavy phase density & ρ is light phase density

If surface tension needs to be measured as a function of time it can be seen from the diagram above that if surface tension decreases with time e.g. if impurities are present, then the lamella would break because the initial maximum force would be too great. Hence it is necessary to lower the ring into the liquid to relieve the force and then repeat the measurement. This sequence must be conducted to acquire a series of data points over the specified time period. Obviously every time the ring is moved it creates an 'artificial' dynamic movement of molecules within the interface which can mask naturally occurring time dependent behaviour. It is therefore normally better to use the Du Noüy ring technique for pure liquids and the Wilhelmy plate for solutions containing surfactants or impurities.

Measurements of surface tension are affected by temperature and hence literature values for pure liquids will always quote with reference to the temperature e.g. water is 72.8 at 20°C, see Fig. 2.

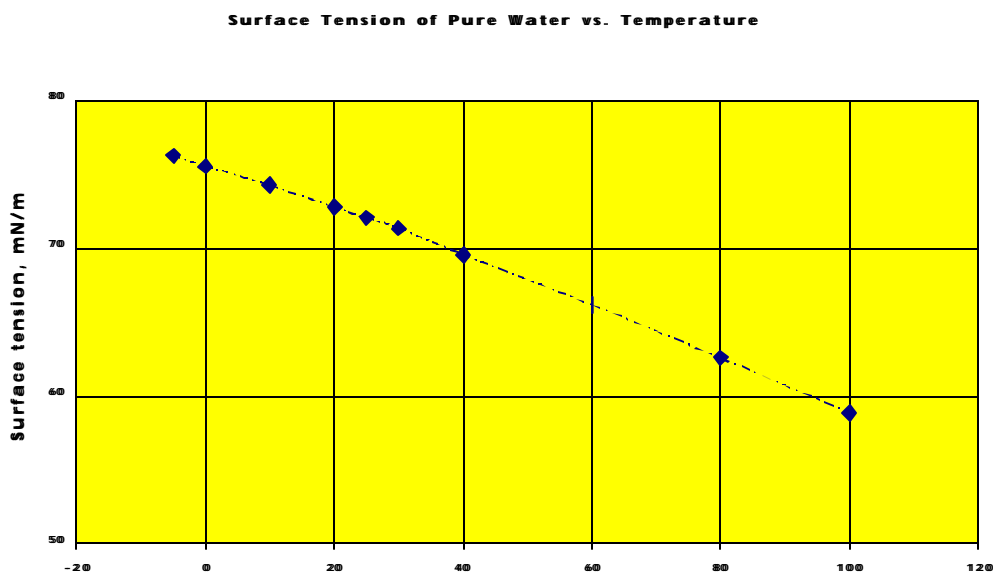


Figure 2 Effect of Temperature on Surface Tension of Water

Wilhelmy Plate – a Static Technique

An alternative geometry for measuring surface tension is the Wilhelmy plate, which is made ideally from roughened platinum but can be pre-wetted paper or glass with a hydrophilic coating. In this technique the plate is suspended at the interface and maintained in this position by a force that balances the weight of the plate and the meniscus force of the liquid acting on the lower edge of the plate. This force is proportional to the surface tension as described by Equation (1) where the wetted length is the circumference of the plate, Fig. 3.

The contact angle of most liquids against platinum is zero hence no corrections for additional forces are required. With a clean platinum plate it is easy to see the liquid 'jumping' up the plate as it is immersed into the liquid, a sign of total wetting and contact angle equal to zero.

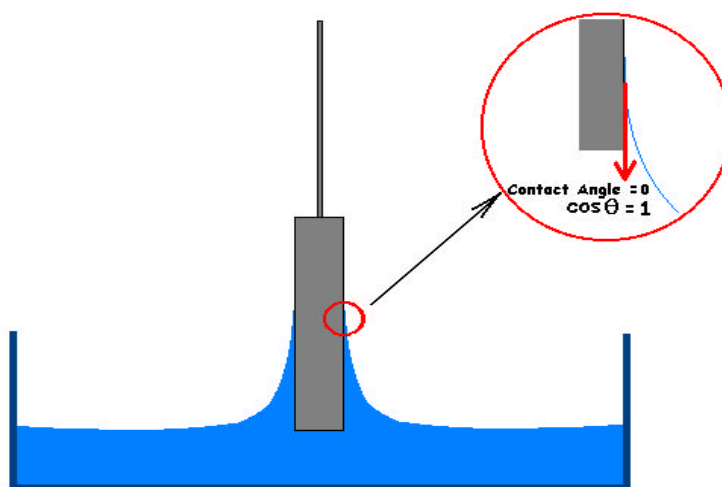


Figure 3 The Wilhelmy Plate Technique

One major difference between the ring and plate is the way in which the measurement is carried out i.e. the ring moves throughout whereas the plate is static. Therefore there is no 'artificial' disturbance of the interface and no increase in the time to reach equilibrium when using the plate method*. Any time dependent behaviour is a true effect of the sample (assuming the plate is absolutely clean) hence the plate is the recommended geometry for studying time dependent characteristics.

* When working with more viscous liquids as the plate is initially dipped into the liquid to ensure total wetting and then positioned back at the surface it takes time for a viscous material to flow from the dipped portion of the plate. This will show as an initial decrease in surface tension that will eventually plateau to a steady value once the excess liquid has flowed from the plate.

The Wilhelmy plate technique is useful for studying the time dependent behaviour of agents which affect the surface tension e.g. impurities in mineral oil. In this method it is used to monitor the time to reach equilibrium at a static boundary i.e. where the interface does not change with time.

Maximum Bubble Pressure Tensiometry – a Dynamic Technique

In real processes and applications such as spraying, the boundary between phases is not static. If a gas is used to form droplets the area of the surface constantly changes and as the surface increases space is created for new surfactant molecules to adsorb. As the function of the surfactant in this case is to lower surface tension in order to aid wetting it is imperative that these molecules reach the surface during the time of the process. The maximum bubble technique creates a dynamic surface, which enables the user to study the efficiency of individual surfactants or the synergistic effect of a blend of surfactants. Pure liquids have NO time/process related surface tension dependency.

The Sita Bubble Tensiometers use a simple method of producing gas bubbles in a liquid via a capillary at fixed or varying rates of bubble formation, Fig. 5. By sweeping the frequency of bubble formation the surface age can be changed i.e. as bubble formation increases so surface age decreases.

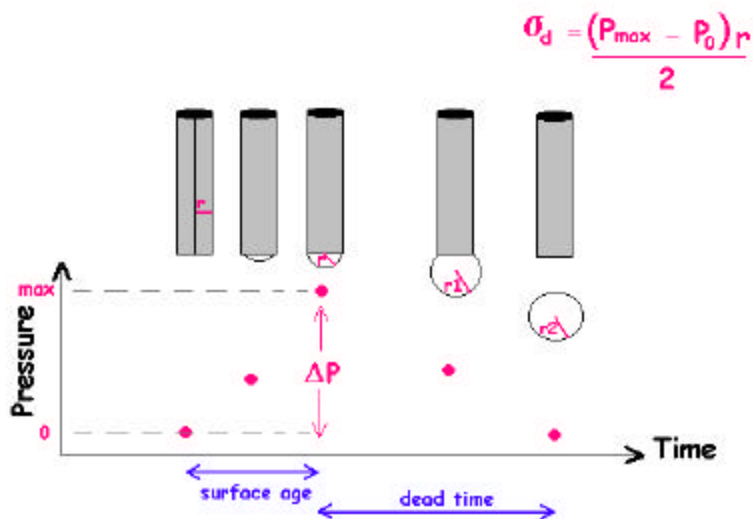


Figure 4 Maximum Bubble Frequency Technique

Dynamic surface tension is proportional to the maximum pressure obtained during the formation of a bubble that occurs at the point when the bubble radius equals capillary radius:

$$s_d = \left(\frac{P_{\max} - P_0}{2} \right) R \quad (4)$$

Where σ_d = dynamic surface tension

P_{\max} = maximum bubble pressure

P_0 = hydrostatic pressure

R = radius of capillary

'Good' surfactants or surfactant blends are those which show little if any time dependency hence they can perform their role during the lifetime of the process. 'Poor' surfactants will show a marked time dependency with the surface tension of the liquid rising to the surface tension of the solvent as the surface age decreases which in the case of aqueous liquids is ~ 72 mN/m at 25^o C.

WHY IS THE MEASUREMENT OF STATIC SURFACE TENSION IMPORTANT?

Static surface tension, which in effect is the surface energy of the liquid, is one of the parameters that describe a liquid and a contact angle describes the ability of a liquid to wet a solid. Contact angles below 90^o are required for wetting. For the liquid to adhere to the solid the surface energy of the solid must be greater than the surface energy (tension) of the liquid. Surface energy is computed from the static surface tension of pure liquids and their contact angles against the unknown solid. In general the lower the surface tension of a liquid the more likely it is to wet a solid.

The static surface tension of a liquid can be measured by ring or plate.

A first approximation to find the value of surface tension of the liquid required to wet a given solid can be obtained from the Zisman plot. This requires measuring the contact angle of a series of standard liquids, of known surface tension, on a solid to find the critical tension for wetting. By plotting the cosine of contact angles ($\cos\theta$) against surface tension of the liquids, the critical surface tension for wetting that particular solid is obtained by extrapolating the linear fit to the data to the condition $\cos\theta = 1$ (contact angle = 0), Fig 5.

If the surface energy of the substrate is known, then the liquid required to wet that solid should have a lower surface tension. Surface energies are computed from theoretical models, which require the static surface tension of the liquid used and its contact angle against the unknown solid.

Using more sophisticated force balance tensiometers such as the CCA-100 or CDCA-100 contact angles can be measured using the Wilhelmy technique. The unknown solid takes the place of the platinum plate and is immersed and retracted from the liquid. As the surface tension of the liquid is known the contact angle can be calculated by rearranging Equation 1 as follows:

$$\cos\theta = F/L\sigma \quad (5)$$

The software enables Zisman plots to be displayed and surface energies to be computed.

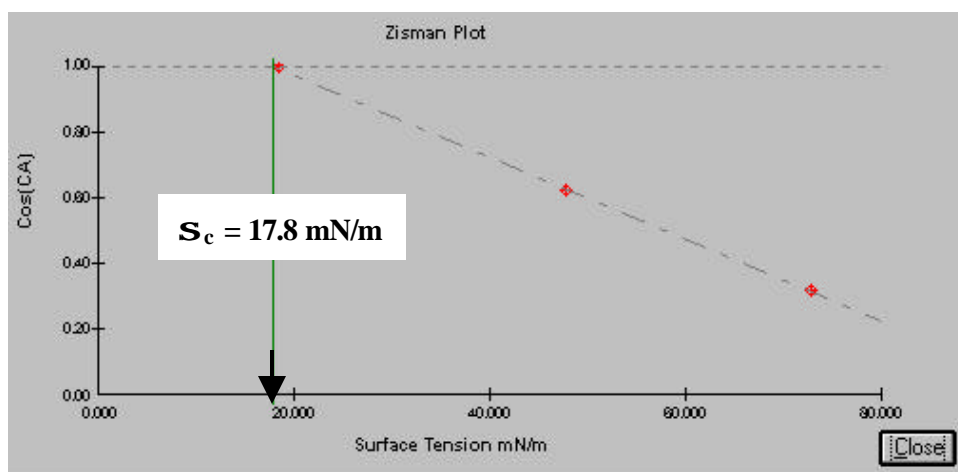


Figure 5 Example of Zisman Plot using the CDCA-100

With this information it should be possible to formulate a liquid product that will both wet and adhere to a given solid.

However as the following section reveals it is not possible to make such an assumption for any dynamic process. A further parameter is required before a successful formulation can be developed into a commercial product.

WHY IS THE MEASUREMENT OF DYNAMIC SURFACE TENSION IMPORTANT?

Environmental laws regarding the use of organic solvents have created a serious problem for the coatings industry, which used these liquids as the base for their products. Organic solvents have low surface tensions compared to water which helps in the wetting process. As a result many well-behaved commercial products have had to be re-formulated with an aqueous base. This has meant an increase in the use of surfactants to reduce the surface tension of the products.

To recap the optimum surface tension for a liquid to wet a solid is obtained by contact angle measurements, Zisman plots etc. This critical surface tension is used as the control to develop a formulation with a surface tension no greater than the control. As organic solvents are pure liquids their surface tension is time independent and historically values have been obtained with the static Du Noüy ring method. The surface tension of aqueous surfactant solutions in a dynamic situation (where new interface is constantly being created) is frequently time dependent. If the equilibrium (static) surface tension only is measured it is possible to make a product where the surface tension of the aqueous formulation is the same as that when made with organic solvents. However in the application, it can differ significantly with the result that it does not pass the QC test. Why is this? The following section describes one such application.

CASE STUDY

The surface tensions of two water-based coatings, C1 & C2, used in a spraying application were measured with the CDCA-100 using the Du Noüy ring. Water was measured as a control; see Fig. 6. Both coatings showed that the lamella did not break sharply as force decreased (as the lamella necks) but instead the force dropped gradually probably due to some rheological effect, which allowed the lamella to stretch much further before breaking.

There is not a clear maximum force value with C1, which leads to a side issue with regards to the model of tensiometer used to obtain the data. Many tensiometers are not PC controlled and cannot track the force versus time plot but take the lamella break point as the maximum force that is not correct. Other more sophisticated models do not record this data graphically, which makes it difficult to see the whole picture.

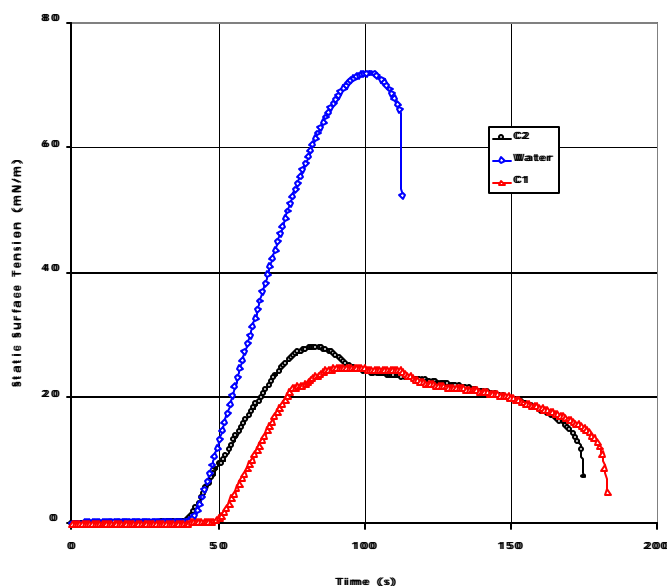


Figure 6 Static Surface Tension of Coatings using Ring Method

The same samples were tested with the plate, Fig.7 where any rheological flow effects are negligible after 40 seconds.

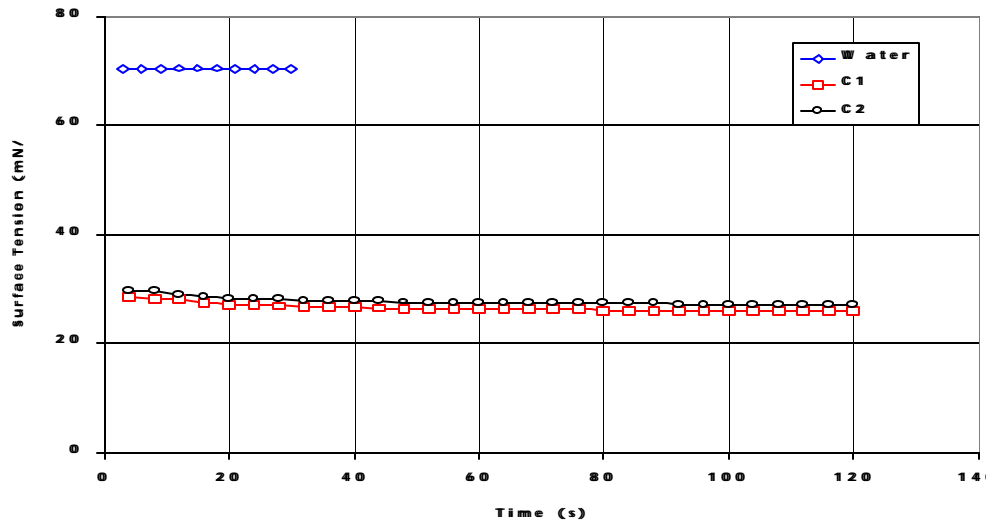


Figure 7 Static Surface Tension of Paints using Plate Method

With static surface tension below 30 mN/m both coatings fell within the accepted range of the QC test. However in the application they failed so Camtel conducted dynamic surface tension tests using the Sita t60 Bubble Tensiometer which showed why this was happening, see Fig.8.

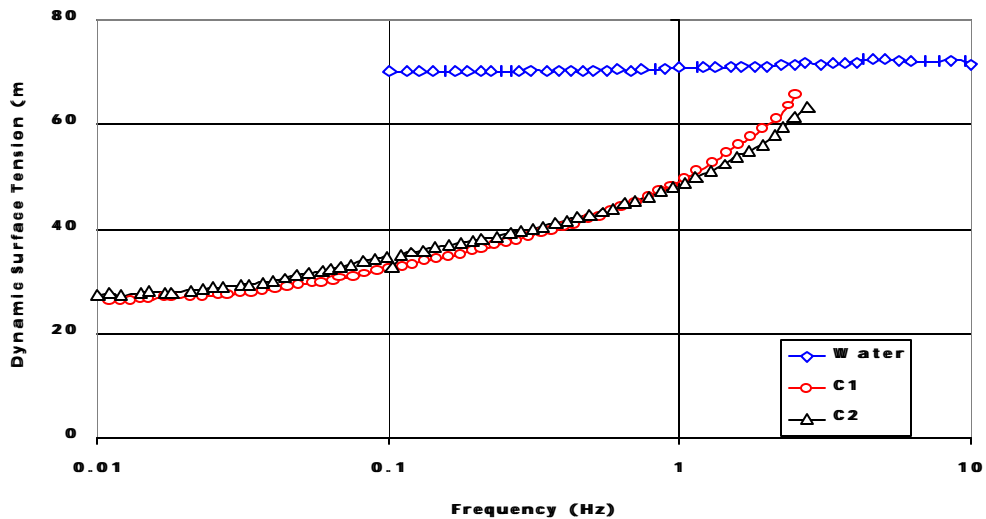


Figure 8 Dynamic Surface Tension of Paints

At time periods of 100 seconds (0.01 Hz) the bubbles are forming so slowly that the time periods are close to that of the static measurements and as such the values are in good agreement. However as the frequency of bubble formation increases so the dynamic surface tension increases. In other words the surfactant molecules are not getting to the newly formed interface quickly enough to cover it and so the surface tension rises. At time periods below 1 second the dynamic surface tension is much nearer to water, which is the base solvent of the coatings. With a pure liquid like water there are no impurities such as surfactants present and so the value of surface tension is independent of the rate of new interface formation.

The water-based coatings failed the application test because the dynamic surface tension was not time (surface age) independent.

ANSWER TO THE QUESTION

The company should invest in a Maximum Bubble Tensiometer for QC purposes, as the values obtained for longer time periods are similar to those from the static tensiometer.

Hopefully this application note shows the necessity to conduct a range of measurements to establish the critical wetting tension at least or preferably the surface energy of the substrate that is being sprayed. Static surface tension data values are required to obtain these parameters and for coatings the plate geometry is preferable to the ring. It is important at least for the R&D and formulation departments to have a quality static tensiometer preferably with the capability to measure contact angles.

The Camtel CCA-100 or CDCA-100 Dynamic Contact Angle Meter with the Sita t60 Bubble Tensiometer would make a sound investment for any coatings industry.

OTHER INDUSTRIES WITH SIMILAR NEEDS

- Agrochemicals
- Paints
- Inks
- Pharmaceuticals
- Foods
- Detergency
- Hair Care
- Surfactant Manufacturers

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