Technical Note

Washburn measurements on porous solids

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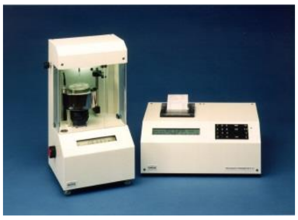

Force Tensiometer – K12

Wettability studies for porous solids including powders and fibrous materials

Scope

This technical note is intended to be an introduction for those who are interested in studying the wetting properties of porous solids including powders and fibrous materials. The note begins with a discussion of why the study of wetting is more complicated for porous solids than it is for non-porous solids. The Washburn theory is then introduced as a framework for studying the wetting of porous solids, and its mathematical detail is explained. Having established a theoretical (and mathematical) framework, the note then proceeds to discuss experimental aspects. The Krüss Force Tensiometer K12 is introduced as an instrument for automated wetting studies, and the accessories that are available for the Force Tensiometer to facilitate porous solid studies are discussed. In particular, the recent development of a new powder and fibrous material sample holder (the FL12) is highlighted. This information makes up the first two sections of this note.

Having discussed both the theoretical and the experimental aspects of porous solid wetting studies, the note proceeds to highlight six sets of wettability studies we have performed recently. Each of these sets is termed a "sample experiment" and was chosen to illustrate a certain aspect of wetting studies. Sample experiment #1 deals with the wettability of woven polyester fabric used in the composites industry. However, the discussion accompanying sample experiment #1 also deals with the possibility of misinterpreting wettability data if data analysis is done carelessly. Likewise, sample experiment #2 describes how to determine wetting of a porous paper. It also deals with the concept that solids have a characteristic "surface energy", and goes on to explain how that quantity can be defined and used. Sample experiment #3 deals with wetting a high density polyethylene membrane which has a very low surface energy. It discusses the complications of characterizing low surface energy materials. Sample experiments #4 and #5 deal with the wetting of two widely used powders – the pigment titanium dioxide and the excipient microcrystalline cellulose. However, the discussions of these experiments also deal with two very practical aspects of wettability experimentation – error analysis and the selection of proper test liquids. Sample experiment #6 shows that wetting of fibrous materials can be studied as reproducibly as the wetting of other porous materials, if experiments are properly designed. It focuses on some very common fibrous materials.

Introduction

The wetting of non-porous solid surfaces by liquids is commonly quantified by contact angle measurements. The contact angle between a liquid and a solid is the angle naturally formed when the liquid is placed on the solid surface. This is depicted in figure 1.

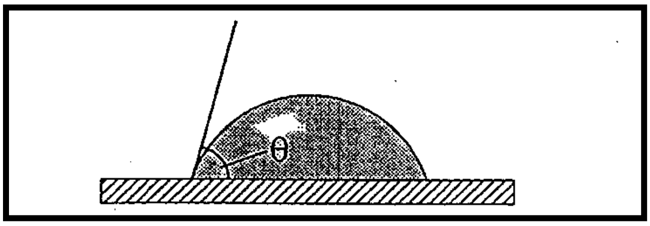

Fig. 1: contact angle on non-porous solid

Krüss offers several automated instruments which measure contact angles on non-porous solids. These instruments are fundamentally based on two techniques – the Wilhelmy (or force) method and the goniometer (or sight) method. Technical note #303 in this series compares and contrasts these two techniques and explains the difference between "advancing" (or wetting) contact angles and "receding" (or dewetting) contact angles. It is recommending reading for those who are interested in the wetting of non-porous solids.

The focus of this technical note, however, is the wettability of porous solids. If one wishes to study the wetting of porous solids such as woven textiles, prepreg composite fibers, The focus of this technical note, however, is the wettability of porous solids. If one wishes paper products, fibrous materials like cotton, or even powders like pigments, pharmaceuticals, and granulated metals, the more traditional types of contact angle measurement are largely inadequate. The contact angle of a liquid on a porous solid cannot be accurately obtained by optical inspection (the goniometer method), because the liquid will be penetrating into the pores of the solid as one is attempting to measure contact angle. This is true if the contact angle is less than 90° (the critical angle for spontaneous capillary or pore wetting). Likewise, attempts to apply the Wilhelmy method to the wetting of porous materials, including powders, are limited to the study of contact angles greater than 90°. Since the Wilhelmy method is based on measuring the force of contact between a wetting liquid and the surface of a solid, any penetration of liquid into the pores of the solid during a Wilhelmy experiment causes an error in force which is difficult, at best, and impossible at worst, to correct for. There is one notable exception to this rule. It is sometimes possible to use a goniometer as a dynamic instrument on porous solid/liquid combinations where the contact angle is less than 90°. By taking several contact angle measurements as a function of time, the rate of penetration of a liquid droplet into a porous solid may be studied. This is commonly done with coated paper products. A liquid droplet placed on the surface of a coated paper forms a contact angle which is fairly constant over some finite period of time (while the liquid is only penetrating into the surface coating). Following this time period, which may be as short as 0.01 to 0.1 seconds and as long as a few minutes, is a period during which the liquid rapidly penetrates the bulk of the paper.

There are also some situations in which it is necessary to determine contact angles of greater than 90° for liquids on porous solids. In these situations the goniometer method and the Wilhelmy method can be used. For powders, the Wilhelmy method can be used by adhering the powder to a glass microscope cover slip and running a standard dynamic contact angle experiment. The Krüss Force Tensiometer K12 is the instrument of choice for this type of measurement. Alternatively, the powder might be compressed into a "block" on which droplets could be placed for goniometer based testing. Any of a number of Krüss goniometers may be used for this type of study.

However, such situations are fairly specialized. Most people interested in wetting porous solids are working with liquids which do spontaneously penetrate into the solids (that is, have contact angles which are less than 90° on the solid). Note that the word "spontaneous", as used in this text, refers to thermodynamic and not kinetic spontaneity. In this case, "spontaneous" only means that no energy input is required to make the liquid penetrate the solid. Time, however, may be required. Suppose you take a porous solid and place it in a beaker of test liquid for some period of time. If it is evident that the liquid penetrates the solid (or simply saturates the solid, when the solid is a loose powder) during that period, then the contact angle for that liquid/solid combination is less than 90°. This is true whether the period of time you need to leave the solid in the breaker, to observe substantial penetration or saturation, is 1 second, 1 minute, 1 hour, or 1 day.

Since most studies of wetting for porous solids fall into this category, the objectives of porous solid wettability studies commonly involve understanding wetting kinetics, and quantifying the completeness of the wetting process. Investigators are usually trying to answer one or more of the following questions:

- How can I alter the nature of my wetting liquid (in terms of solute concentrations, types of solutes present, and so on) to provide for more complete and/or quicker wetting of my porous solid or powder?
- How can I alter the surface properties of my porous solid to provide for more complete and/or quicker wetting by a particular liquid?
- How is the wettability of my solid affected by various chemical and/or physical treatments which must be done to the solid for reasons other than surface modification?
- How hydrophobic and/or hydrophilic is the surface of my solid?
- What is the surface energy of my solid?
- How does surface energy relate to wettability?
- Are the surface properties of my porous solid product consistent from lot to lot?
- What level of lot to lot variability can be tolerated with my porous solid and still have it performing consistently in its application?
- What is the effect of liquid viscosity on wetting?
- What is the effect of liquid surface tension on wetting?

In order to find answers to questions like these, it is necessary to be able to accurately measure contact angles in the range of 0° to 90° on porous solids. Contact angles of greater than 90°, although obtainable by the Wilhelmy method and/or the goniometer method, are generally of little interest. If a liquid doesn't wet, it doesn't wet.

For most applications it is not important to quantify how non-spontaneous the penetration of a non-wetting liquid into the pores of the solid is. We wish to study wetting liquids. The method of choice for such studies is the Washburn method.

The Washburn Method

Washburn theory[1] indicates that if a porous solid is brought into contact with a liquid, such that the solid is not submerged in the liquid, but rather is just touching the liquid's surface, then the rise of liquid into the pores of the solid due to capillary action will be governed by the following equations:

$$t = Am^2 \qquad (1)$$

wherein t = time after the solid and the liquid are brought into contact, m = mass of liquid sucked into the solid, and A = a constant which is dependent on the properties of the liquid and the solid in question.

Specifically,

$$A = \frac{\eta}{c * \rho^2 * \sigma * cos\theta} \qquad (2)$$

wherein η = viscosity of the liquid, ρ = density of the liquid, σ = surface tension of the liquid, θ = contact angle between the solid and the liquid, and c = a material constant which is dependent on the porous architecture of the solid.

Combining equations 1 and 2, followed by rearrangement, leads to equation 3 which is the useful form of Washburn's equation.

$$cos\theta = \frac{m^2}{t} * \frac{\eta}{\rho^2 \sigma c} \quad (3)$$

In setting up a Washburn experiment, a liquid with known density (ρ), viscosity (η), and surface tension (σ) should be used. An inspection of equation 3 leads to the conclusion that if this is the case, and the mass of liquid which rises into the porous solid can be monitored as a function of time (such that m^2/t is the raw experimental data), then two unknowns remain: the contact angle of the liquid on the solid (θ) and the solid material constant (c).

However, if a Washburn experiment is performed with a liquid which is known to have a contact angle of θ = 0° (cosθ = 1) on the solid, then the solid material constant (c) is the only remaining unknown in equation 3 and can thus be determined. N-hexane is typically a good choice as the liquid for determining material constants, because of its low surface tension (18.4 mN/m) at room temperature.

Once the material constant (c) has been determined for a particular solid, a second sample of the solid can be tested for wettability by another liquid. The material constant determined by the n-hexane test is simply used in the Washburn equation, in combination with m^2/t data obtained during testing with the second liquid. This allows calculation of the contact angle between the second liquid and the solid.

Washburn adsorption experiments can be easily and automatically performed on a variety of porous materials using a Krüss Force Tensiometer K12 in combination with Krüss K121 software in the Adsorption mode. The porous solid is placed in an appropriate sample holder and suspended from the balance in the Force Tensiometer just above the surface of a test liquid. See figure 2.

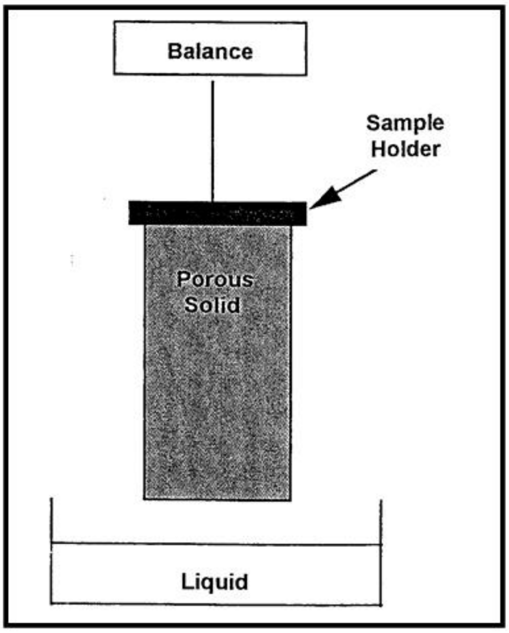

Fig. 2: sample holder

The Force Tensiometer performs the whole experiment automatically. The liquid is raised until it just touches the bottom of the porous sample. Mass versus time data is then collected as liquid penetrates into the solid. The rate and interval over which this data is collected is user selectable in the K121 software. At the end of the experiment data can be output in either graphical or tabular format. It is also automatically converted to mass^2 versus time data from which a slope is taken and used in the Washburn equation to calculate either the material constant "c" or a contact angle "θ" depending on the experiment. If a series of liquids (at least two in addition to the material constant determining liquid) is tested against any one solid, then the resultant contact angle data can be used to calculate surface energy of the porous solid. Surface energy calculations are also performed automatically by the software, and will be discussed in more detail later in this text.

The major advancement that Krüss has made to Washburn experimentation, aside from automation, involves the design of sample holders to accommodate testing on various types of porous solids – most notably powders and fibrous materials. The design of proper sample holders is of utmost importance because the Washburn equation contains two unknowns, (the material constant "c" and the contact angle "θ"). These two variables are both inherently linked and wholly independent.

The material constant for a porous solid is theoretically given by:

$$c = \frac{1}{2}\pi^2 r^5 n^2 \qquad (4)$$

where r = the average capillary radius within the porous solid, and n = the number of capillaries in the sample. From this equation it obvious that if I had two pieces of the same porous material (say pieces of fabric for example), their material constants would be the same only if they were exactly the same size (same number of capillaries (n) or pores in each). In addition, they must be held relative to the surface of the test liquid in exactly the same configuration. If they are not, then their material constants will be found to be different, because, from the point of view of the penetrating liquid, neither the average capillary radius for the pores (r) nor the number of capillaries (n) will be exactly the same.

This, however, will not affect the contact angle that the liquid forms on the pores of the fabric. In this sense, the material constant and the contact angle are independent. In other words, if I test a 2 cm x 2 cm square of woven fabric and a 1 cm x 2 cm rectangle of the same woven fabric against the same liquid, I should obtain the same contact angle from both tests, providing that I know the material constant for each sample in advance. According to the material constant definition given above, the material constant for the 2 cm x 2 cm sample will be about four times larger than the material constant for the 1 cm x 2 cm sample, however (This assumes $n_{\text{large sample}} = 2 \times n_{\text{small sample}}$).

Why, then, is it necessary to use uniform samples for multiple Washburn tests on the same solid? It is necessary because, in determining contact angles, the material constant must be known. The only way we can know the material constant of a fresh (untested) sample is to have determined it beforehand on a sample which was exactly like the fresh sample in terms of both size and placement.

For fairly rigid porous samples, such as fritted glass sieves and thick polymeric membranes, producing uniform samples is a matter of cutting the materials into rectangles or squares uniformly. To attach such samples to the balance, Krüss offers a rigid sample holder clip (model CLMP 10) which neatly holds samples with a thickness of up to 4 mm and allows a sample to be adjusted easily so that its bottom edge is parallel to the liquid's surface.

For more flexible porous solids such as papers, thin membranes, and films, the flexible sample holder (model FO12) is offered. This holder bends the flexible sample at a 45° angle along its center line perpendicular to its liquid contact edge. This gives flexible samples some added physical integrity so that the path of liquid penetration into the sample is the same from test to test. Of course, flexible samples must also be uniformly cut prior to a series of measurements.

Powders and fibrous materials require a specialized sample holder. These materials pose an additional challenge because they are not "continuous" porous materials like papers and membranes. We cannot simply cut out a rectangle of powder and clamp it to the balance. We must establish some way to pack the powder into a plug and then hold that plug together while it is being wet by the test liquid. The plug of powder should be packed tight enough that it does not "cake" and establish voids during the wetting process. The packing process must also be repeatable, so that the same material constant can be obtained for each successive test. In addition, the holder for the powder plug, which, in any scenario, will have to come into contact with the test liquid, must allow for the powder to be wet without impeding the wetting process. It would also be favorable for the holder to be relatively easy to clean (free of wet powder) at the end of each experiment. The same requirements are extended to any holder designed for fibrous materials.

Krüss has done a fair amount research on powder and fibrous material holders. Many of our current customers may be using our model PU12, which is a small glass cylinder with a fritted glass filter at one end and a means of attachment to the K12 balance at the other. With the PU12, a known quantity of powder (usually about 1 gram) is packed into the cylinder against the fritted glass filter. When liquid is brought into contact with the glass frit at the bottom of the cell, the liquid rises through the frit and then through the powder bed. Since glass has a high surface energy, the glass frit generally does not impede liquid adsorption into the powder plug (unless of course the frit becomes plugged and is not cleaned properly).

The PU12 design works quite well in a number of situations for determining contact angles on powders. However, we have realized that it does have its drawbacks. Namely, the glass frit at the bottom of the tube is difficult to clean, the whole apparatus is fragile, and it can be difficult to pack the powder into the cylinder in a highly reproducible fashion. This last problem makes it difficult to obtain a reproducible "c" factor, or material constant, for multiple experiments on the same powder. A single user, with practice, can develop his own highly reproducible powder packing method for the PU12. However, any two users would probably not pack the powder in the same manner. In addition, the PU12 is not useful for the study of fibrous materials (with the possible exception of very fine and/or very small fibers).

A new powder holder has been designed to overcome these drawbacks. The new apparatus is called the FL12. Figure 3 is a diagram of the FL12.

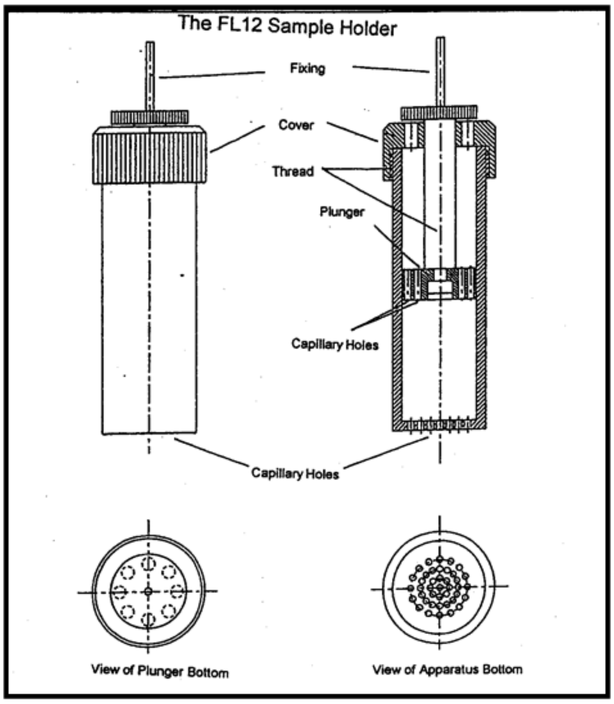

Fig. 3: FL12 sample holder

The cell is made of aluminum (less fragile than glass) and small holes in its bottom instead of a fritted glass filter (easier to clean). The cover for the cell is equipped with two screw threads. One connects it with the sample chamber while the other allows the user to guide a piston down onto the sample itself and compress it (better reproducibility in packing, and therefore "c" factor). When using the cell with powders, the following procedure can be followed:

1. Place a circle of filter paper in the bottom of the sample cell. This prevents powder from leaking out the bottom of the cell. Porosity of the filter paper to be used is governed by the nature of the powder to be tested. The finer the powder is, the finer the filter paper should be. The filter does not have to be paper, but it should be a material that is easily wet by the liquid to be tested.
2. Place a known mass of powder into the cell. This mass should be great enough that the powder is compressed a fair amount during step 4 of this procedure. If this is the case, then reproducibility of your material constants and contact angles will be dependent almost solely on your ability to weigh out the same amount of powder for each test. Thus, two users can easily achieve the same material constant on the same powder. I think this is the largest advantage of the new FL12 versus the old PU12.
3. Place a second piece of filter paper on top of the powder that you placed in the cell. This will prevent powder from rising through the holes in the piston during the compression process and/or during the experiment.
4. Screw the cover onto the sample cell and screw the piston completely down. You should have placed enough powder in the cell to provide some resistance to screwing down the piston, but not so much powder that it is impossible for you to screw the piston completely down with your fingers alone. Defining this happy medium, in terms of mass of powder used, takes a couple of tries. However, once you have it, you have a good technique to reproducibly pack powders. For most powders a good amount is in the range of 1 to 2 grams.

For fibrous materials, like cotton and fiberglass, a similar procedure should be used. Depending on how fine the fibers are, filter papers may or may not be needed.

The remainder of this note highlights the wide ranging utility of Washburn adsorption experiments by discussing some of the wettability work that has been performed in our laboratory over the past few months. The porous materials discussed include:

- Woven fabrics used in the composites industry
- Laser printer paper
- A high density polyethylene membrane support used in the water treatment industry
- A series of treated titanium dioxide (TiO2) powders, with varying degrees of hydrophobicity, which are used in the pigment industry
- Microcrystalline cellulose, which is used in the pharmaceutical industry as an excipient
- The naturally absorbent fibrous material flax
- Fiberglass insulation
- Cigarette filter fibers

Sample Experiment #1 – Woven Polyester Fabric

We have recently explored the propensity of various woven polyester fabrics to be wet by toluene and n-hexane. These fabrics are used in the composites industry as "peel ply" release liners. Their wetting properties are of interest because they must be able to be well wetted by the polymeric resin that makes up the matrix of the composite to which they are applied. The best fabric for the application would be the one that was most thoroughly wet by the resin. Tests with toluene and n-hexane were used as predictors of resin wetting behavior for a series of fabrics which had been treated in a variety of ways. The goal was save costly composite formation tests by pre-selecting the most wettable fabric. The most wettable fabric is the one that is found to have the lowest contact angle against toluene.

The fabrics were cut into 2 cm x 5 cm rectangular pieces. For both the n-hexane (material constant determining) and the toluene (contact angle determining) experiments a piece of fabric was suspended from the balance in a K12 instrument so that its 2 cm edge would be lowered into the liquid. The flexible sample holder (FO12) was used to hold the fabric samples.

Figure 4 shows some representative data from the testing. The data is in the raw form of mass^2 versus time.

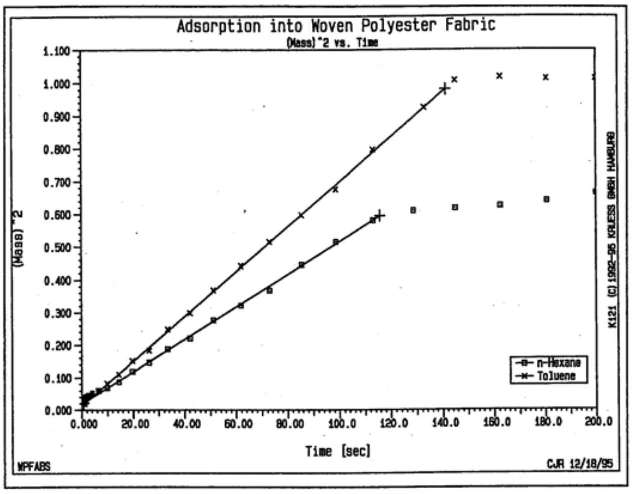

Fig. 4: Adsorption into woven polyester fabric

Note that both the n-hexane adsorption data and the toluene adsorption data are linear with a positive slope until they each reach a plateau. This is the general trend for adsorption data. Liquid rises into the pores to the solid (linear rise region in the data) until it is saturated (plateau region in the data). Also, note that the linear rise portions of both the n-hexane and the toluene data have been fit with best-fit lines. The Krüss software does this automatically. The slope of the n-hexane data was used in the Washburn equation to calculate the material constant for this particular piece of polyester fabric (which was 2.01x10-4 cm^5). The slope of the toluene data was then used to calculate contact angle of toluene on this particular polyester fabric. The contact angle with toluene was 20.2° in this case.

There is one further point of interest concerning this raw data, however. If we just view the raw data, it seems that toluene wets the fabric "better" than n-hexane. The weight of toluene rising into the fabric at any particular time is greater than the weight of n-hexane rising into the fabric at any equivalent time. In addition, at saturation, a 2 cm x 5 cm piece of the fabric has adsorbed approximately 1.0 g $\{(1.0\ g^2)^{1/2}\}$ of toluene. Only about 0.80 g $\{(0.64\ g^2)^{1/2}\}$ of n-hexane is adsorbed at saturation. All of this information appears to conflict with n-hexane having been assumed to have a contact angle of 0° on the fabric and toluene having been calculated to have a contact angle of 20.2° on the fabric. N-hexane (surface tension = 18.4 mN/m) should wet the fabric better than toluene (surface tension =28.4 mN/m). The calculated contact angle data reflects this, but studying the raw data seemingly does not. Why?

Much of the apparent conflict comes from the fact that our experiment measures the mass of liquid which rises into the pores of the solid. However, what the material constant and contact angle of a porous solid against any given liquid controls is the volume of liquid which rises into the pores as a function of time. The volume of rising liquid is, of course, the mass of rising liquid divided by the density of the rising liquid (or m/ρ in terms of the symbols used in the Washburn equation above). Note that the Washburn equation can be rearranged into the following form:

$$\cos\theta = \frac{V^2}{t} * \frac{\eta}{\sigma c} \qquad (5)$$

wherein V = the volume of liquid which has risen into the porous solid. This is actually the original form of Washburn's equation. It is simply not the form of the equation that we commonly use, since direct measurement of the volume of liquid uptake by a solid is more difficult than is direct measurement of the mass of liquid drawn up.

With this information, let's study the raw data in figure 4 again. From the two plateaus we can calculate that at saturation a 2 cm x 5 cm sample of this particular polyester fabric takes up approximately $\{1\ g^2/(0.867\ g/cm^3)^2\}^{1/2}$ = 1.15 cm^3 of toluene. The same size sample of fabric takes up approximately $\{0.64 g^2/(0.661 g/cm^3)^2\}^{1/2}$ = 1.21 cm^3 of n-hexane at saturation. In these calculations, 0.867g/cm^3 = $\rho_{Toluene}$ and 0.661 g/cm^3 = $\rho_{n\text{-}Hexane}$. On a volume basis then, n-hexane saturates the porous solid more completely than does toluene. The n-hexane also saturates the fabric more quickly. The saturation plateau is reached at approximately 115 to 120 seconds for n-hexane compared to 135 to 140 seconds for toluene. Studying the raw data in this manner eliminates our apparent conflict. The n-hexane does in fact wet the fabric more completely than does the toluene, as would be expected, and as is reflected by the contact angle data.

The point of this extended discussion concerning the first sample experiment was to provide a framework for interpretation of Washburn adsorption data. The polyester fabric data was a good example, because the raw data could be misinterpreted. We, at Krüss, like examples like this because, although our instrument is fully automated and our software automatically does Washburn calculations, we do not intend for it to be used as a magical "black box". The most useful insights into the meaning of scientific data always come from thoughtful analysis, not from automated instruments.

Similar apparent quality of wetting (raw data versus calculated data) conflicts will also be observed, but not explained in detail, throughout the series of Washburn experiment examples put forth in this text. These generally arise when two liquids with surface tensions that are very similar, but densities that are substantially different, are studied with the same solid.

One final comment on the data that we have seen so far is warranted before we proceed further. It is interesting (to me) that if we take the contact angle which was obtained for toluene wetting the fabric (20.2°) and multiply its cosine (0.9385) by the volume of n-hexane that adsorbs into the fabric at saturation (1.21 cm^3) we get a volume of 1.14 cm^3, which is nearly identical to the volume of toluene that was found to saturate the fabric 1.15 cm^3. There is probably no scientific basis for doing such a calculation. However, I find it interesting. (Note that such a calculation will be necessarily correct in the limit of a liquid which has a contact angle of 90° on the solid, since the cos(90°) = 0 and the volume of the liquid which will rise into the solid will also be 0 cm^3).

Sample Experiment #2 – Laser Print Paper

The adsorption of liquids into paper products is most notably a concern in the printing industry. To what extent an ink will penetrate a paper, or simply dry in a controlled manner on the paper's outer surface, is fundamental to printing. In addition, the longevity of a paper in terms of resistance to discoloration is often dependent on the extent to which the paper adsorbs moisture from the air.

We have recently studied the adsorption of a series of liquids into a common grade of laser printer paper by the Washburn technique. The paper was cut into 2 cm x 5 cm pieces and tested using the flexible sample holder (FO12) in the Force Tensiometer K12. Figures 5 and 6 show raw data from adsorption tests with the following liquids and in support of the following contact angle data.

Liquid	Room Temperature Surface Tension [mN/m]	Contact Angle on Laser Printer Paper [°]
n-Hexane	18.4	0 ($c=2.803x10^{-4} cm^5$)
Acetone	23.7	0
Toluene	28.4	0
Benzyl Alcohol	39.0	24.5
Ethylene Glycol	47.7	45.2
Water (distilled)	72.3	80.1

Table 1: Contact Angle Data for Laser Printer Paper

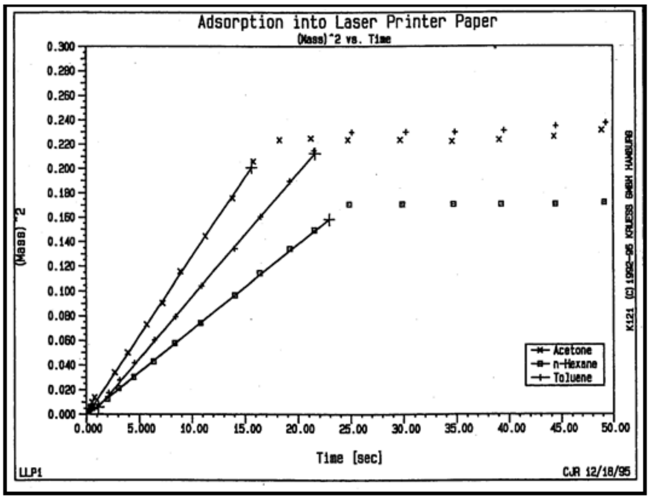

Fig. 5: Adsorption into Laser Printer Paper I

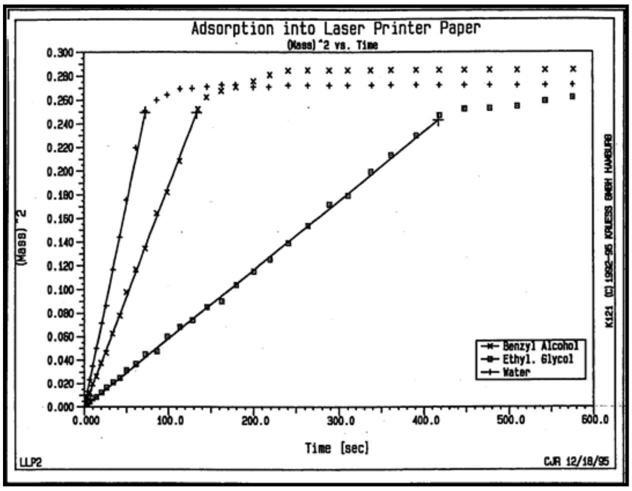

Fig. 6: Adsorption into Laser Printer Paper II

Since a series of contact angles were obtained for liquids wetting the laser printer paper, it is possible to use those contact angles to calculate "surface energy" of the paper.

The surface energy of a solid surface is conceptually the equivalent of the surface tension of a liquid. A high surface energy means that interfaces between the solid and air are not favorable in a thermodynamic sense. High surface energy solids are therefore wet extremely well by liquids, since liquid wetting eliminates solid/air interfaces in favor of liquid/solid interfaces. Low surface energy solids are correspondingly wet very poorly by most liquids. The reason for calculating the surface energy of a solid is that having this value allows you to predict how well the solid will be wet by other liquids which have not yet been tested against the solid. However, the surface energy of a solid must be calculated. It cannot be measured. In order to see why this is true, let's briefly return to the discussion of the wetting on non-porous solids.

Consider figure 7, which depicts a liquid droplet on a non-porous solid surface.

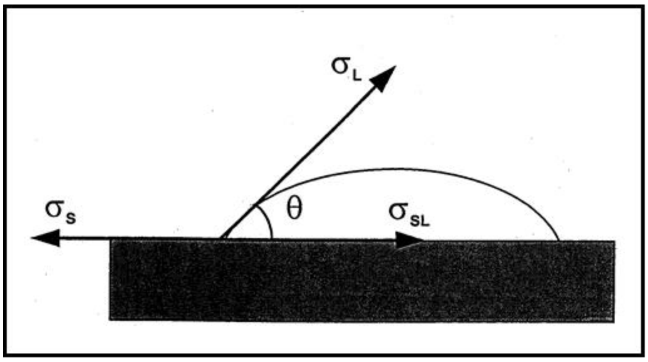

Fig. 7: liquid droplet on non-porous solid

The contact angle which the drop in figure 7 forms with the solid surface is governed by a balance of forces in the x-direction. Mathematically,

$$\theta = cos^{-1}[\frac{\sigma_S - \sigma_{SL}}{\sigma_L}] \qquad (6)$$

where θ = contact angle, σ_S = the surface tension of the solid, σ_L = the surface tension of the liquid, and σ_{SL} = the interfacial tension between the solid and the liquid.

This is Young's equation[2]. The unfortunate part of doing any contact angle work is that there is no way to deconvolute the surface tension of a solid (σ_S) from the interfacial tension between the solid and the liquid (σ_{SL}). If a liquid with known surface tension (σ_L) is placed on a non-porous solid, and the contact angle (θ) is measured, then Young's equation can be used to calculate the value (σ_S-σ_{SL}). However, the two terms cannot be separated, and thus the surface tension of a solid cannot be known. The same situation applies to contact work done on porous solids.

Fortunately, it is not necessarily the surface tension of the solid that we wish to determine. We wish to determine a characteristic value for the wettability of the solid. This characteristic value has been termed surface energy. It is now apparent that surface energy must be defined in some manner, before we can attempt to calculate it. To make matters more complicated, there is no universally agreed upon definition of surface energy. There are, however, many theories in the scientific literature regarding how surface energy should be defined. These theories range from simple to highly complex in mathematical form. Three of the most well regarded are the Zisman method[3], the Owens/Wendt method[4], and the Wu method[5].

Both the Owens/Wendt method and the Wu method are somewhat complex mathematically. The use of either involves sub-dividing the surface tension of the wetting liquid, as well as the surface energy of the solid, into polar and disperse components based on some knowledge of their chemical properties. These methods can be quite effective, and Krüss software is designed to use any of them (at the user's option) to calculate surface energies for solids based on contact angle data. However, the nature of these methods is such that, if they are individually applied to the same contact angle data, vastly different values of solid surface energy may be obtained. It is then up to the experimenter to decide which method he feels is best for his application. Individuals who are interested in a more thorough and mathematical explanation of the Owens/Wendt method and the Wu method are referred to the literature cited and to the Krüss K121 contact angle software manual. Such a discussion is somewhat beyond the scope of this text.

The Zisman method, on the other hand, is simple in mathematical form and very straightforward in terms of the information that it provides about the ability of a solid surface to be wetted. For this reason, it is more widely used than either the Owens/Wendt method or the Wu method. In order to highlight practicality of the Zisman method, we will use it to determine surface energy of the laser print paper which we have studied. However, before doing that, it is instructive to first review development of Zisman's method in a little more detail.

The problem with defining and then determining the surface energy of a solid, as related to the discussion above, is that the surface tension of the solid (σ_S) cannot be deconvoluted from the interfacial tension between that solid and a liquid (σ_{SL}), based solely on contact angle measurements. By measuring the contact angle of a liquid with known surface tension on a solid, the value (σ_S-σ_{SL}) may be obtained. However, surface energy of the solid remains undefined. Zisman's solution to this problem was to simply define surface energy of the solid as equal to the entire value (σ_S-σ_{SL}) in the limit of the contact angle approaching $\theta = 0°$. The utility of this definition becomes apparent if we consider Young's equation for the case of a liquid which has a zero contact angle on the solid in question. For θ to equal 0°, in Young's equation, the value (σ_S-σ_{SL})/σ_L must be equal to 1. In other words, (σ_S-σ_{SL}) = σ_L, or the surface energy of the solid is equal to the surface tension of an applied liquid which just has a zero contact angle on the solid. By "just" we mean that a solid's surface energy is actually defined as the being equal to the surface tension of a liquid (real or imaginary) which has the highest possible surface tension that will still allow it to wet the solid's surface with a 0° contact angle.

To determine the surface tension of this ideal liquid (and thereby the solid's surface energy) contact angle data obtained using real liquids is plotted against surface tension values for the real liquids. When such data is plotted in the form of cos(θ) versus liquid surface tension, the plot is typically linear. The data are extrapolated to cos(θ)=1 (or 0°) and surface energy of the solid is taken as the liquid surface tension at that intercept. Such a plot is called a Zisman Plot. Figure 8 shows contact angle data obtained for the laser printer paper plotted in this format.

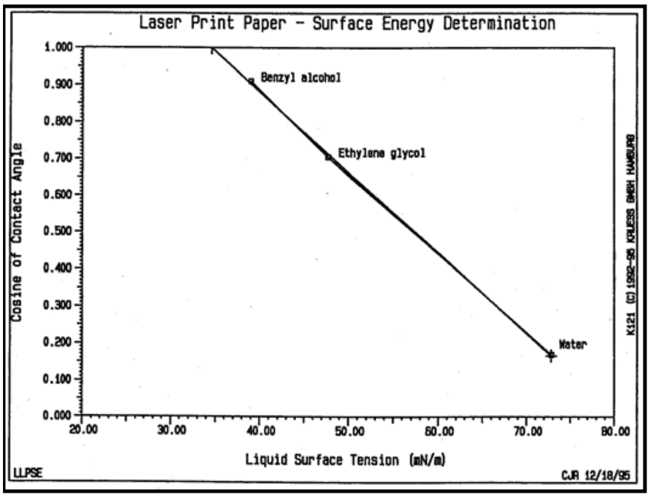

Fig. 8: surface energy determination, laser print paper

For the laser printer paper, the extrapolation to cos(θ) = 1 shows that surface energy of the paper is 34.6 mN/m. If we test liquids with surface tensions of less than 34.6 mN/m against the paper, they should all have contact angles equal to 0°. In fact, recall that we already have. We have tested acetone (surface tension =23.7 mN/m) and toluene (surface tension =28.4 mN/m) and found that they did in fact have contact angles of 0° on the paper. We also assumed that n-hexane (surface tension = 18.4 mN/m) had a contact angle of 0° on the paper. This now seems to have been a good assumption.

One additional piece of information that might be obtained from the Zisman Plot for paper is that liquids with surface tensions of greater than approximately 80 mN/m can be expected to have contact angles of greater than 90° on the paper. (The data can be extrapolated to $\cos(\theta)=0$ as well.) It is rare to deal with liquids that have surface tensions which are greater than 80 mN/m. Only concentrated aqueous salt solutions would have surface tension values this high. However, this data suggests that such liquids will not spontaneously penetrate into the laser printer paper.

Sample Experiment #3 – Adsorption into a High Density Polyethylene Membrane Support

In a manner similar to that used for the laser printer paper, we have also recently characterized wettability of a high density polyethylene (HDPE) membrane support. The support had pores in the diameter range of 10-20 microns and it was approximately 3 mm thick. It is used to support much thinner polymeric membranes which are responsible for removal of trace impurities from water. The reason for studying wettability of the membrane support and determining its surface energy, was to provide a basis for exploring what types of membranes would work most efficiently with it. The contact angle for water on the untreated support was actually found to be greater than 90°.

The support was cut into 1 cm x 3 cm strips for the wettability experiments. These samples were tested using the Force Tensiometer K12 in the adsorption mode and the rigid sample clip (CLMP10). The results of the testing are shown in Table 2 and in Figures 9 and 10.

Liquid	Room Temperature Surface Tension [mN/m]	Contact Angle on HDPE Membrane Support [°]
n-Hexane	18.4	0 ($c=1.537\times10^{-6}\,cm^{5}$)
Acetone	23.7	45.5
Toluene	28.4	57.8
Benzyl Alcohol	39.0	78.1

Table 2: Wettability Tests on a HDPE Membrane Support

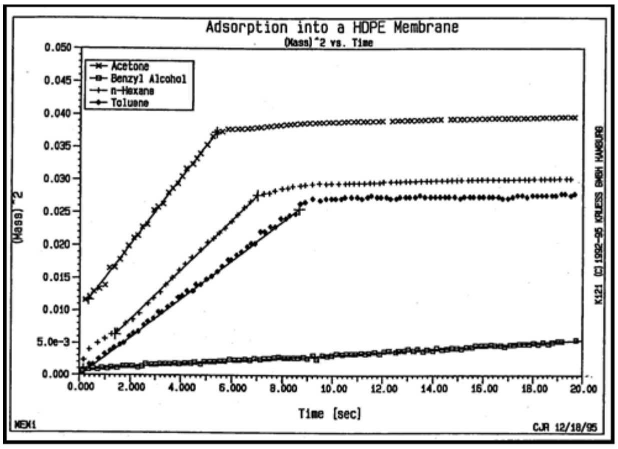

Fig. 9: Adsorption into HDPE membrane

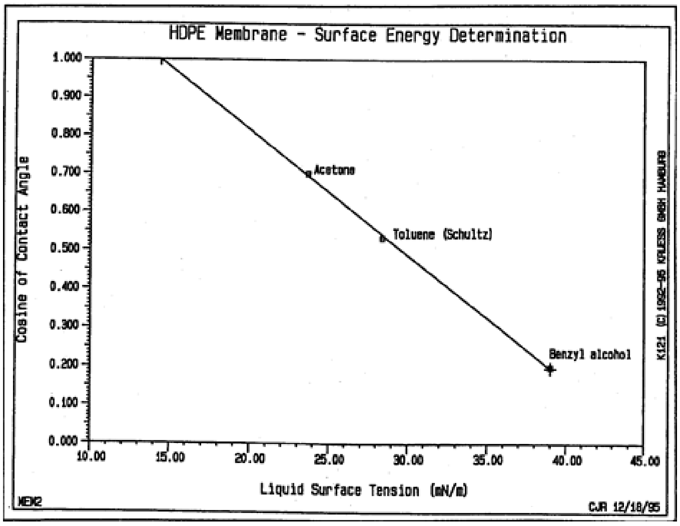

Fig. 10: surface energy determination, HDPE membrane

There are three points of interest concerning this data.

1. Figure 9 suggests that saturation of the support with benzyl alcohol is a relatively slow process. The support is saturated by n-hexane, acetone, or toluene within 10 seconds. By contrast, at 20 seconds the support is still nowhere near saturated with benzyl alcohol. It might be predicted that saturation with benzyl alcohol would take greater than 100 seconds. However, the actual experiment was terminated at 20 seconds because plenty of data had been collected by that time for the contact angle calculation. This is due to the relatively high viscosity of benzyl alcohol (η = 5.80 cP) and the high contact angle between benzyl alcohol and the support (78.1°).
2. The Zisman plot for the support (figure 10) suggests that surface energy of the support is approximately 14.4 mN/m. It should be pointed out that this number is only an estimate, however. Why?

   The value 14.4 mN/m was obtained based on contact angle values for acetone, toluene, and benzyl alcohol. Those contact angles were themselves obtained based on a material constant (c) which was in turn obtained by assuming that the contact angle of n-hexane on the support was 0°. However, if the surface energy of the support is truly 14.4 mN/m then the contact angle for n-hexane on the support would not be 0°. In fact, based on Young's equation in would be 38.5° {$\cos^{-1}(14.4/18.4)$} since n-hexane has a surface tension of 18.4 mN/m at room temperature.

   The obvious way to correct this problem is to redetermine the material constant for the support with a liquid that has a surface tension less than 14.4 mN/m, and can thus be correctly assumed to have a contact angle of 0° on the support. The contact angles for n-hexane, acetone, toluene, and benzyl alcohol could then be corrected based on the new material constant. This, however, is complicated by the fact that there are few standard liquids with surface tensions as low as 14.4 mN/m. Pentane, another easily used liquid for material constant determination, has a surface tension of 15.4 mN/m. Some fluorinated solvents do exist with surface tensions that are this low, but they are not environmentally friendly to work with.

On the other hand, it is probably not extremely important to calculate a more exact value for surface energy of the support. This data shows that the surface energy is definitely less than 18.4 mN/m (the surface tension of n-hexane), and estimates it at 14.4 mN/m. The surface is obviously very hydrophobic.

3. For water treatment (the application for this membrane support), the 90° contact angle limit is probably more important than the surface energy. Extrapolation of the Zisman plot to $\cos\theta = 0$ (contact angle = 90°) provides the information that liquids with surface tensions greater than approximately 44 mN/m will not spontaneously penetrate pores of the support. This includes liquids such as ethylene glycol (surface tension = 47.7 mN/m) and distilled water (surface tension =72.3 mN/m).

Sample Experiment #4 – Characterizing the Hydrophobicity of Treated TiO2 Powders

A major concern for pigment manufacturers is how well their pigments wet and disperse when added to various product formulations. There are basically two ways to achieve better pigment wetting and subsequent dispersion. First, the nature of the formulation can be altered to accommodate the pigment. Wetting agents (surfactants) can be added, to aqueous formulations to lower the interfacial tension between the bulk solution and the pigment. In solvent based formulations, the ratio of polar to non-polar solvent can be adjusted and dispersing aids can be used to promote wetting. Second, the nature of the pigment can be altered. Surface modifications which raise the surface energy of the pigment are generally favorable because they increase the range of liquids which will wet the pigment. Surface modification is often the option explored by pigment manufacturers, since they generally have little control over the nature of the formulations in which their pigments are used. They want to manufacture pigments which are generally more easily wetted and dispersed under a variety of conditions.

We recently had a customer who was concerned with these very issues for titanium dioxide (TiO_2) pigments. He sent six TiO_2 pigments to us which had been surface modified in various ways, and wanted us rank the samples in terms of wettability (or hydrophilicity).

So far in this note we have discussed "continuous" porous solids. This is the first sample experiment which gives us the opportunity to discuss powders. Perhaps more importantly, another thing that has not yet been discussed in this note is how to begin work on characterizing wettability of a porous solid. In the previous sample experiments we focused on details of the Washburn method. We used various common solvents as test liquids, and did not explain in any detail why those liquids were chosen for the testing.

Some contact angle work is done specifically to investigate the interaction between one or more pre-defined liquids and a solid. In these cases we do not need to search for test liquids. On the other hand, much contact angle work is done to characterize wettability (or surface energy, or hydrophobicity) of a solid. If the goal of experimentation is to determine the surface energy of a porous solid, we now know we need to study contact angles of a series of liquids against that solid. If our goal is to rank a series of solids in terms of hydrophobicity, we may be able to do this using only one test liquid. In either case, however, a characterizing liquid or set of liquids must be chosen.

The first criterion in choosing liquids for a test series is that they should not dissolve the porous solid. If they do, then Washburn experimentation cannot be effective. I purposely waited until we began a discussion of powders to make this point, because it is with powders that the solubility issue is most often a problem. If a powder is slightly soluble in a liquid (against which we want to measure its contact angle) then we can pre-saturate the liquid with the powder and proceed with the contact angle experiment. If, however, it is more than sparsely soluble, then contact angle measurement may not be possible. We would then be exploring solubility testing and not contact angle testing!

Being aware of the solubility issue, what is the second criterion for choosing a series of liquids for contact angle tests on a porous solid? Assume that we have a situation like the series of TiO_2 samples we wish to characterize. We initially know nothing about surface energies of the powders. Therefore, we have no idea which liquids will spontaneously wet the powders and which liquids will not. We said previously that liquids which do not spontaneously wet cannot be used for Washburn experimentation. So, our second objective should be to eliminate them from consideration for our series.

Now that we have boundaries regarding what liquids are not acceptable for use, we can do some educated guessing. The guessing is guided by some quick and simple experiments to determine what liquids are acceptable for use with any given solid.

To start that guessing, with virtually any porous solid, I find the following series of liquids quite useful.

Liquid	Room Temperature Surface Tension [mN/m]
n-Hexane	18.4
Acetone	23.7
Toluene	28.4
Benzyl Alcohol	39.0
Ethylene Glycol	47.7
Glycerol	63.4
Water (distilled)	72.3

Table 3: Suggested Liquids to Check Wetting

I have chosen this series for a number of reasons. First, most of these solvents are commonly found in research laboratories. Second, they are, for the most part, not extremely hazardous to the experimenter. Third, taken together, they cover the range of surface tensions for common liquids.

Many fluorinated solvents have surface tensions of less than 18.4 mN/m, but they can be hazardous. In addition, n-pentane, the highest molecular weight straight chain hydrocarbon that is a liquid at room temperature, has a surface tension of 15.4 mN/m at room temperature. It can be a good liquid for contact angle work. It is not extremely hazardous, but it is extremely volatile at room temperature. Its volatility keeps it off my list of primary test liquids. Salt solutions are the most common liquids which have surface tensions greater than that of pure water (72.3 mN/m) at room temperature. Concentrated salt solutions can have surface tensions which approach, but rarely surpass 100 mN/m. Beyond this there are only fairly exotic liquids, like mercury which has a surface tension of 484 mN/m at room temperature.

Having confined our search for test liquids somewhat, the first thing I typically do in studying wettabilities of powders (and other porous solids as well) is to simply line up a series of small beakers containing my prospective liquids and drop a small sample of each powder (or a piece of paper, if I happen to be testing paper, etc.) into each liquid. Liquids which dissolve the powder (paper, etc.) are eliminated from consideration, as are liquids which do not wet the powder within some reasonable amount of time (because those liquids have contact angles of greater than 90°) on the powder. A good set of usable test liquids can then be chosen from the liquids that were well behaved.

These simple tests, which often take no more than a few minutes, can save an experimenter from setting up Washburn experiments that don't work. It is generally best to start with distilled water. If the powder (or porous solid) wets with, but is not dissolved by, water, then use water as a test liquid. The powder will also undoubtedly wet with all of the other liquids in the series. Therefore, any of the remaining liquids that do not dissolve the solid can be used as well.

Occasionally, however, additional information beyond what test liquid might be used for contact angle tests can be gained from the initial testing. The more hydrophobic a powder is, the lower the surface tension of a liquid must be for it to spontaneously wet the powder. Therefore, if my series of liquids is used for the initial tests, along with a series of powders, sometimes powders can be distinguished from one another in terms of hydrophobicity just on the basis of these initial tests. Such was the case for the TiO_2 samples that were recently tested, mainly because they were so hydrophobic.

None of the six TiO_2 samples spontaneously wet with distilled water (surface tension = 72 mN/m) or glycerol (63 mN/m). This indicates that the contact angle of these two liquids on all of the powders is greater than 90°, and cannot be determined by the Washburn technique. Had we really wanted to know what the contact angle of these particular liquids were on the TiO_2 powders we could have determined them using the Wilhelmy method by sticking some quantity each of powder onto a solid plate (usually a glass slide) and doing dynamic contact angle experiments on the resultant coated plates. This technique was described in the background section of this note. However, for this work, we were not interested in such data. We wanted to characterize the powders with liquids which had contact angles of less than 90° on all them, if we could find such liquids.

The initial tests with ethylene glycol (surface tension = 47.7 mN/m) gave me the first indication of differences between the six TiO_2 samples. We had labeled the samples A through E. Samples A, C, and D, spontaneously wet with ethylene glycol. Sample B wet, but only very slowly. Samples E and F did not wet over the course of about two minutes. Ethylene glycol thus characterized 90° contact angles on the TiO_2 samples quite well. It also told us that samples A, C, and D, followed by B, were more hydrophilic than samples E and F. Ethylene glycol is still not low enough in surface tension to be a good test liquid for Washburn tests on all of the samples, however.

Moving to lower surface tension liquids, we did initial tests on the TiO_2 powders using benzyl alcohol (39.0 mN/m), toluene (28.4 mN/m), acetone (23.7 mN/m), and n-hexane (18.4 mN/m). All of these liquids spontaneously wet all of the powders. Therefore, no further background information was ascertained, except that any (or all) of these liquids might be used along with the Washburn technique to characterize the TiO_2 powders.

We choose to use n-hexane as the material constant determining liquid and acetone as a liquid for contact angle experimentation by the Washburn method. Since we did not necessarily need to determine the surface energy of each of the TiO_2 powders precisely, contact angle testing with acetone was sufficient. The TiO_2 powder which had the lowest contact angle with acetone could be said to be the most hydrophilic of the series, and the TiO_2 powder which had the highest contact angle with acetone could be said to be the most hydrophobic, and so on.

The FL12 powder holder was used for the experiments. The procedure described earlier for use of the FL12 with powders was strictly adhered to, and we found that 3.00 g of powder was a good amount for each test.

Raw data from some of the Washburn experiments preformed on these powders is shown in figures 11 through 13.

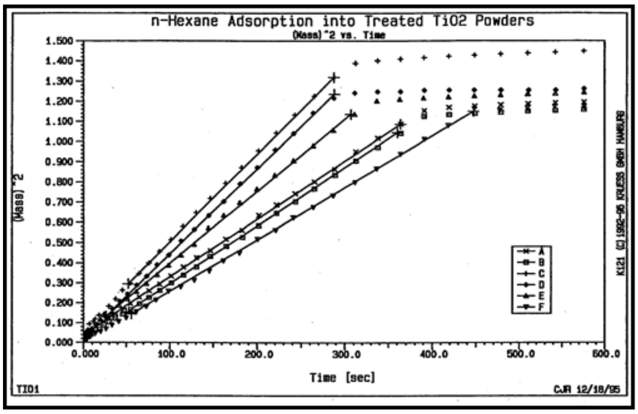

Fig. 11: n-Hexane adsorption into treated TiO_2 powders

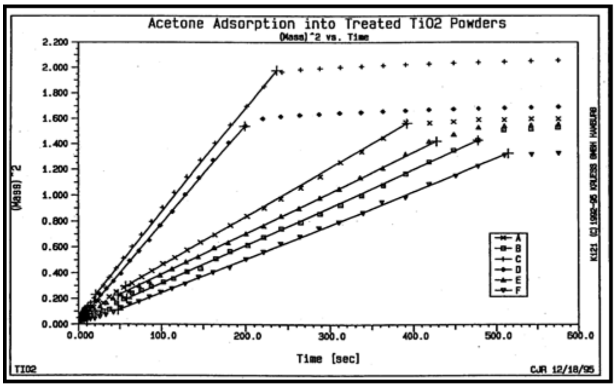

Fig. 12: acetone adsorption into treated TiO_2 powders

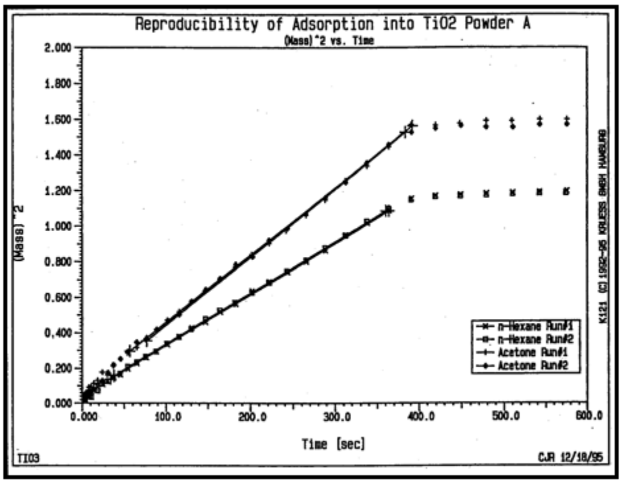

Fig. 13: reproducibility adsorption into treated TiO_2 powders

From the data in figures 11, 12 and 13 the following information regarding the powders was obtained.

TiO_2 Powder	Material constant with n-Hexane [$x10^{-6}cm^5$]	Contact Angle with Acetone [°]
A (Run #1)	1.1606	46.2
A (Run #2)	1.1676	45.8
B	1.1633	57.5
C	1.7607	11.8
D	1.7134	17.8
E	1.4451	62.4
F	1.0676	58.3

Table 4: Material Constant Determination and Acetone Contact Angles for TiO_2 Powders

There are three points that should be made about this data.

1. Data are reported from two tests with n-hexane and two tests with acetone on sample A. (The raw data from these tests is the subject of figure 13.) The purpose of this is to indicate reproducibility. We have yet to discuss data reproducibility in this application note, so we will do so now.

   It is difficult to declare a single number for the reproducibility (or precision) of Washburn adsorption data for a number of reasons. Largely, the precision is based on uniformity of the samples being tested. For continuous porous solids, "uniformity" means how similar the porous architecture of the first piece tested is to the second, and so forth. Assuming we cut such samples from the same large piece of material (for example multiple strips of paper from the same 8.5" x 11" sheet, all oriented in the same direction), this has to do with homogeneity of the sheet of paper both in terms of porosity and in terms of the surface treatment that the pores have been subjected to.

   For powders and other non-continuous porous materials sample "uniformity" means two things. First, uniformity has to do with how likely an experimenter is to get a group of powder particles of the same size distribution every time she takes a few grams of powder from a larger sample of the powder (usually a jar of powder), and how likely it is that particles she gets will have a surface treatment that is similar to that of the last particles. Obviously, a large powder sample with a narrow particle size distribution will be apt to provide more uniform small powder samples than a large powder sample with a broad particle size distribution. A widely recommended technique for obtaining representative samples of a powder is use of a spinning riffler. This device will subdivide a quantity of powder into eight or sixteen representative portions. By successive passes through the riffler a desired sample size of 1 g to 5 g can be readily obtained.

   Second, uniformity is also dependent on how reproducibly each powder sample can be packed. We have previously given some description of the advantages of the new FL12 powder holder with regard to this. In general, the FL12 has enhanced the reproducibility of Washburn experiments on powders into approximately the same range as the reproducibility achievable for continuous porous solids like papers and membranes (with which repeatable packing is at least not necessary). A good very general estimate of this reproducibility is ±2.0° for contact angle experiments and ±2% for material constant determination experiments.

   For many samples this estimate is overly conservative, however. For example, the data for TiO_2 sample A shows a material constant reproducibility of 0.6% and a contact angle reproducibility of 0.4° based on duplicate tests. Of course, for any scientific study the level of reproducibility necessary is governed by the level of detectable difference between any two systems. If the former exceeds the latter, the two systems are not differentiated by the study. This was not the case with the acetone contact angles determined on the TiO_2 powders. The closest two acetone contact angles are for samples B and F, which are 57.5° and 58.3° respectively, for a difference of 0.8°, or approximately twice the precision of this set of experiments.

2. The acetone contact angle data follows the trend developed during initial tests on the samples with ethylene glycol. However, it provides a more detailed evaluation which was necessary for our customer's work with his TiO_2 pigments. The lower the contact angle of acetone on a TiO_2 sample, the more hydrophilic the sample is. The contact angle results with acetone show the following trend.

E > F > B > A > D > C

Increasing Hydrophilicity or Surface Energy

----------------------------->

The initial test data with ethylene glycol showed.

E = F > B > A = C = D

Increasing hydrophilicity

----------------------------->

3. The third point of interest for this data involves the material constants which were determined with n-hexane. Samples A and B have very similar material constants (for 3.00 g packed plugs of each). Samples C and D also have fairly similar material constants. The material constants for samples E and F are somewhat different from all of the others. Material constants reflect the porosity of packed powder plugs, both in terms of the number of capillaries in a plug and the average radius of those capillaries. It seems that certain pairs of TiO_2 powders in the group pack very similarly. This probably indicates those powders have similar particle size distributions. We have not performed particle size analysis on these samples. Nonetheless, I point this out as a secondary piece of information that can be qualitatively obtained from Washburn experimentation on powders.

Sample Experiment #5 – Microcrystalline Cellulose Powder

We have performed Washburn experiments on a standard grade of microcrystalline cellulose, and it may be instructive to discuss that work as another example. Microcrystalline cellulose is used in the pharmaceutical industry as an "excipient". An excipient is a fairly inert substance which serves as a medium for delivery of a medicine. For example, a tablet containing 20 mg of a drug often weights 0.5 g. The 0.48 g of the tablet that is not drug is excipient. In general terms, microcrystalline cellulose is a solid diluent. It is what often makes up the majority of a pharmaceutical tablet that is not the pharmaceutical itself. How well it wets and disperses in water and other biological media is thus of some importance.

The goal of our study was to determine how well one particular grade of microcrystalline cellulose wets with water and with ethylene glycol. The study was performed using a Krüss Force Tensiometer K12 in the Adsorption mode with the FL12 powder holder. For each test, 2.00 g of microcrystalline cellulose was used. Raw data from these tests is shown in figure 14.

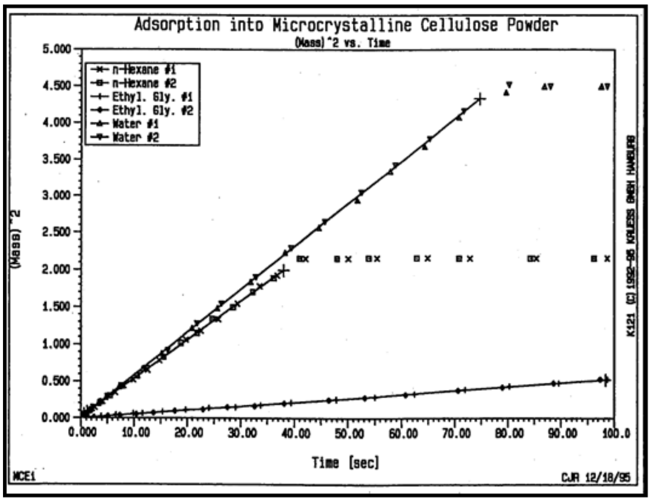

Fig. 14: adsorption into microcrystalline cellulose powder

The calculated results are as follows:

Liquid	Room Temperature Surface Tension [mN/m]	Run Number	Material Constant or Contact Angle
n-Hexane	18.4	1	$2.118x10^{-3}$ cm^5
n-Hexane	18.4	2	$2.132x10^{-3}$ cm^5
Ethylene Glycol	47.7	1	31.4°
Ethylene Glycol	47.7	2	31.6°
Water (distilled)	72.3	1	67.6°
Water (distilled)	72.3	2	66.8°

Table 5: Contact Angle Data for Microcrystalline Cellulose

A Zisman plot based on this data (not shown) indicates that surface energy of this microcrystalline cellulose is approximately 40 mN/m, and that liquids with surface tensions of greater than approximately 92 mN/m will not spontaneously wet the powder. As can be calculated from the data above, reproducibility of these experiments was 0.7% for the material constant with n-hexane, 0.8° for tests with water, and 0.2° for tests with ethylene glycol, based on duplicate experiments.

Sample Experiment #6 – Fibrous Materials

In order to demonstrate the utility of the FL12 sample holder for Washburn experiments on fibrous materials, we have studied wettabilities of three types of fibers. They were: a standard grade of fiberglass insulation, a flax-like material which serves as an absorbent within packing pads that are used to protect bottles of liquid during shipments, and cigarette filter fibers. Some of the data obtained for these three systems are shown in Table 6. Figure 15 shows data for water adsorption into each of the fibrous materials.

Fibrous Material	Wetting Liquid	Run #	Material Constant or Contact Angle
Fiberglass Insulation	n-Hexane	1	$1.172 \times 10^{-2} cm^5$
Fiberglass Insulation	n-Hexane	2	$1.161 \times 10^{-2} cm^5$
Fiberglass Insulation	Distilled Water	1	54.8°
Fiberglass Insulation	Distilled Water	2	54.7°
Absorbent Flax	n-Hexane	1	$1.634 \times 10^{-2} cm^5$
Absorbent Flax	n-Hexane	2	$1.655 \times 10^{-2} cm^5$
Absorbent Flax	Distilled Water	1	44.8°
Absorbent Flax	Distilled Water	2	44.3°
Cigarette Filter	n-Hexane	1	$1.623 \times 10^{-2} cm^5$
Cigarette Filter	n-Hexane	2	$1.632 \times 10^{-2} cm^5$
Cigarette Filter	Distilled Water	1	65.0°

Table 6: Contact Angle Data for Selected Fibrous Materials

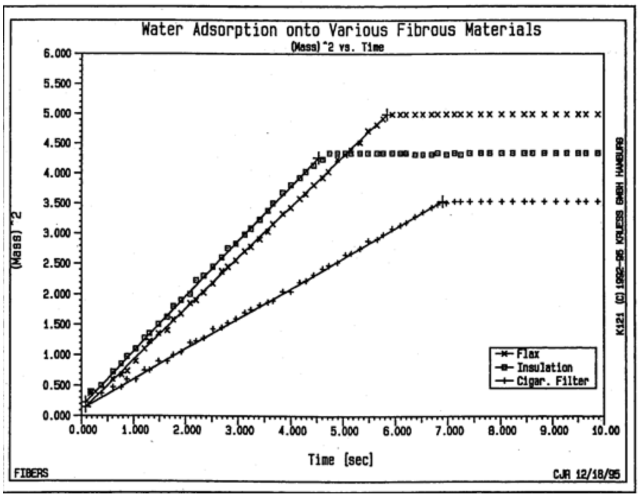

Fig. 15: water adsorption onto various fibrous materials

I think that this data makes it fairly evident that reproducibility and linearity can be achieved for Washburn experiments on packed fiber beds as well as packed powders and "continuous" porous solids. For the flax material and the cigarette filter material it is interesting to note that the material constants are very similar. This could be a function of the materials themselves being quite similar. Certainly, the packing of these two fibers into the FL12 was similar, since 2.5 grams was the amount of each used for each experiment. For the fiberglass insulation, 3.0 grams was the sample amount required for each experiment, and the material constant was much different as well. A greater mass of the fiberglass was necessary to pack the FL12 because glass is a relatively high density material, and the volume of material packed is governed by the dimensions of the FL12 itself.

The contact angle results with water are no surprise. The lowest contact angle (best wetting) was observed with the flax-like material which is supposed to be absorbent. The fiberglass wet second best, which is not unexpected because glass is known to have a fairly high surface energy. The cigarette filter material was the least wettable.

Conclusions

I hope that this technical note is both useful and instructive for individuals who are interested in studying wettabilities of porous solids. In writing it I attempted to cover both the theoretical and experimental aspects for such studies. I also tried to focus, as much as possible, on the practical aspects. I wanted to provide the reader with some idea of which experiments are necessary to answer wettability questions and, just as importantly, which experiments are not.

Experimental design issues are often difficult to treat thoroughly with in technical notes since they are largely sample dependent and cannot be generalized. I took the approach of simply sharing a handful of my own experiences in studying the wetting of porous solids (the sample experiments) and discussed the practical matters as they "fell out" of each study. I don't pretend that this was the best or only possible approach.

If you have any questions or comments about this note, or if you would like to discuss an application that you have for porous solid wettability studies, I would be happy to hear from you.

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