ANEXOS

Anexo A: Método da gota pendente para medir tensão interfacial

Introdução

As moléculas na superfície de um líquido estão sujeitas a fortes forças de atração das moléculas interiores. A resultante dessas forças, - cuja direção é a mesma de plano tangente à superfície (em qualquer ponto desta) - atua de maneira a que a superfície líquida seja a menor possível. A grandeza desta força, atuando perpendicularmente (por unidade de comprimento) ao plano na superfície é dita tensão superficial γ.

A superfície ou interface onde a tensão existe está situada entre o líquido e seu vapor saturado no ar, normalmente a pressão atmosférica. A tensão pode também existir entre dois líquidos imiscíveis, sendo então chamada de tensão interfacial. As dimensões da tensão superficial são força por unidade de comprimento, no sistema SI = N/m.

Um dos métodos utilizados para medir tensão superficial é o método do peso da gota.

Este método, assim como todos aqueles que envolvem separação de duas superfícies, depende da suposição de que a circunferência multiplicada pela tensão superficial é a força que mantém juntas as duas partes de uma coluna líquida. Quando esta força está equilibrada pela massa da porção inferior, a gota se desprende.

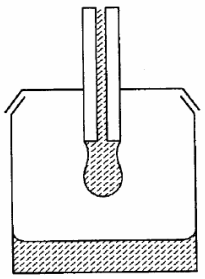

Figura A1: Método do peso da gota.

A tensão superficial é calculada pela equação

$$2\pi r\gamma = m_i g \qquad \text{(Lei de Tate)} \qquad \text{eq. A1}$$

Onde:

m_i : massa de uma gota ideal

r : raio do tubo (externo se o liquido molhar o tubo)

g : aceleração da gravidade

Na prática, o peso da gota obtido, é sempre menor que o peso da gota ideal. A razão disto torna-se evidente quando o processo de formação da gota é observado mais de perto. A figura abaixo ilustra o que realmente acontece.

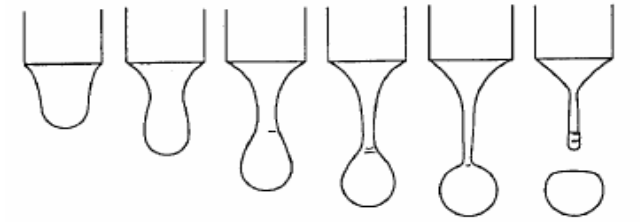

Figura A2: Fotografias de alta velocidade de uma gota caindo.

Observa-se que somente a porção mais externa da gota é que alcança a posição de instabilidade e cai. Perto de 40% do líquido que forma a gota permanece ligado ao tubo.
Para corrigir o erro causado pelo peso da gota, introduz-se na equação $\gamma = mg / 2\pi r$ um fator de correção f. Assim:

$$\gamma = \frac{mg}{2\pi r f} \qquad \text{eq. A2}$$

O fator de correção f é uma função do raio do tubo e do volume da gota. Estes valores são tabelados abaixo:

Tabela A1: Fator de correção para o método do peso da gota.

$r/V^{1/3}$	f	$r/V^{1/3}$	f	$r/V^{1/3}$	f[a]
0.00	(1.0000)	0.75	0.6032	1.225	0.656
0.30	0.7256	0.80	0.6000	1.25	0.652
0.35	0.7011	0.85	0.5992	1.30	0.640
0.40	0.6828	0.90	0.5998	1.35	0.623
0.45	0.6669	0.95	0.6034	1.40	0.603
0.50	0.6515	1.00	0.6098	1.45	0.583
0.55	0.6362	1.05	0.6179	1.50	0.567
0.60	0.6250	1.10	0.6280	1.55	0.551
0.65	0.6171	1.15	0.6407	1.60	0.535
0.70	0.6093	1.20	0.6535		

a: Os valores desta coluna são menos exatos que os das outras.

Procedimento Experimental

1. <u>Determinação do diâmetro do tubo de vidro</u>

O Diâmetro do tubo pode ser medido utilizando-se um paquímetro ou obtido a partir da massa de uma gota de um líquido padrão, cujo valor da tensão superficial seja conhecido.
A massa de uma gota de água pura a 20□C, para tubos de diferentes diâmetros, encontram-se
tabelados no quadro abaixo. Para temperaturas superiores ou inferiores a 20□C, mas não muito diferentes, pode-se usar a seguinte relação para calcular a massa da gota da água a 20□C.

Massa da gota a 20°C = massa da gota na t°C x $\frac{\gamma_{(20°C)}}{\gamma_{(t°C)}}$

Onde: γ é a tensão superficial da água nas respectivas temperaturas.

Tabela A2: Massa de uma gota de água que se desprende de tubos de diferentes diâmetros

massa da gota (g)	Raio do tubo (cm)	massa da gota (g)	Raio do tubo (cm)
0.033450	0.09946	0.90467	0.31891
0.042347	0.13062	0.091620	0.32362
0.046901	0.14769	0.096392	0.34188
0.054678	0.17750	0.096918	0.34385
0.059700	0.19666	0.09868	0.35022
0.068026	0.23052	0.10623	0.37961
0.069869	0.23790	0.10966	0.39262
0.072682	0.23135	0.11161	0.39968
0.007753	0.26802	0.11957	0.42765
0.079680	0.27605	0.12522	0.44755
0.084270	0.29423	0.12575	0.44980
0.084880	0.29694	0.14142	0.50087

2. Medidas para Obtenção da Tensão Superficial

2.1. Material:

-1 pipeta graduada de 1 ml.
-1 frasco com tampa, limpo e seco, para cada solução a ser medida.
-água destilada.
-outros solventes e/ou soluções consideradas convenientes pelo professor.
-1 tubo flexível com pinça, torneira ou seringa para controlar a velocidade de formação da gota. Inserir o tubo na extremidade superior da pipeta.

2.2. Procedimento:

1. Coloque o líquido na pipeta inserindo sua ponta no líquido e aspirando através do tubo de borracha. Regule a pinça ou a torneira de tal forma a obter uma vazão aproximada de 1 gota por minuto.
2. Recolha umas 10 gotas do líquido problema no frasco (já pesado anteriormente com a tampa). Anote o volume e a massa correspondente às gotas recolhidas.
3. Determinar o peso de uma gota.
4. Determinar o volume de uma gota.
5. Calcular $r/V^{1/3}$ e obter f utilizando a tabela 1.
6. Calcular γ através da equação 2.

2.3. Sugestões:

Tensão superficial
Além da água, outros líquidos, como soluções aquosas de n-butanol (ou outro álccol) podem ser utilizadas como material de investigação. A partir de uma solução 0,5 M de n-butanol, prepare soluções nas seguintes concentrações: 0,4M, 0,3M, 0,2M e 0,1M e meça suas respectivas tensões superficiais.

Uma outra possibilidade é preparar soluções aquosas de diferentes concentrações de um detergente tal como CTAB e fazer diversas medidas de γ para, através do gráfico de γ versus concentração de detergente, obter a concentração micelar crítica, CMC. Meça a tensão superficial de soluções de CTAB com as seguintes concentrações: (1; 2; 3; 5; 10; 20)x10-4 M.

Tensão interfacial líquido-líquido

A tensão interfacial entre dois líquidos imiscíveis pode ser medida colocando-se o líquido mais denso na pipeta graduada, mergulhando sua ponta dentro do líquido menos denso, deixando a gota do líquido mais denso crescer dentro do líquido nenos denso e obter a massa da gota por diferença de pesagem. Deve-se crescer parcialmente a gota antes de mergulhar a ponta da pipeta no líquido menos denso para que a ponta da pipeta não fique contaminada com o líquido menos denso. Neste caso, deve-se utilizar na equação 2 a massa efetiva da gota, que é a massa da gota medida na balança menos a massa do líquido deslocado (empuxo). A massa do líquido deslocado pode ser obtida multiplicando-se a sua densidade pelo volume da gota formada.

2.4. Precauções:

Limpeza é essencial em medidas de tensão superficial. Pequenas quantidades de impurezas afetam muito as propriedades superficiais. Portanto, limpe muito bem todo o material a ser usado na experiência.

Se o líquido for volátil, é necessário que as gotas sejam recolhidas em recipientes fechado. Além disto, a primeira gota deverá ser "tombada" durante aproximadamente 5 minutos para que o recipiente fique saturado nos vapores do líquido em questão.

Neste caso, é também necessário fazer duas medidas. Uma com aproximadamente 15 gotas e outra com 5 gotas.

A diferença de peso entre as duas medidas dará o peso de uma gota livre do peso do vapor. (peso 15 gotas - peso 5 gotas = peso 10 gotas sem vapor).

Trabalho Experimental:

1. Coloque água a 20□C na pipeta graduada (certifique-se de esteja bem limpa), recolha 10 gotas, pese e anote o volume . Utilizando a tabela 2, determine o raio da ponta da pipeta. Use a tabela 1 para obter o fator de correção e calcule a tensão superficial da água.
2. Meça a variação da tensão superficial com a concentração em soluções de n-butanol (ou outro álcool) em água a 20□C. Faça um gráfico da tensão superficial em função da concentração molar do álcool em água.
3. Meça a tensão interfacial entre água e um líquido menos denso que a água, tolueno (ou outro líquido imiscível com a água) a 20□C.
4. Se houver tempo, meça também a tensão interfacial entre água e um líquido mais denso que a água (clorofórmio, por exemplo).

BIBLIOGRAFIA

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2. Shaw,D.J. ; Química dos coloides e de superfícies. Editora Edgard Blucher,cap.4.
3. Daniels et al ; Experimental Physical Chemistry.

Anexo B: Tratamento matemático para obter morfologia hemisfério.

A figura A.1 apresenta a atual forma de duas fases, da partícula hemisférica, ainda com uma interface plana entre as duas fases. A notação utilizada é descrita a seguir:

r_o = radio da porção esférica da fase polimérica original.
r_p = radio da porção esférica da fase polimérica secundaria
h_o = distancia de penetração aparente da fase polimérica original dentro da fase polimérica secundaria.
h_p = distancia de penetração aparente da fase polimérica secundaria dentro da fase polimérica original.

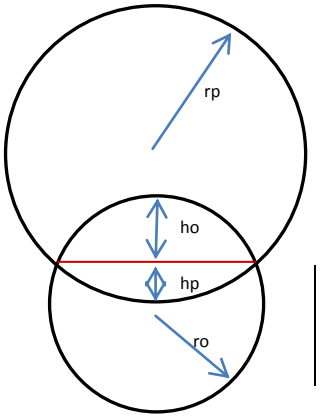


Figura B.1. Morfologia da partícula para analise hemisférico

O volume e a área interfacial desta geometria da partícula são amplamente encontrados em *standard mathematics handbooks* e são escritos como segue:

$$V_0 = (4/3)\Pi r_0^3 - (\Pi/3) h_0^2 (3r_0 - h_0) \qquad \text{Eq. B1}$$

$$V_p = (4/3)\Pi r_p^3 - (\Pi/3) h_p^2 (3r_p - h_p) \qquad \text{Eq. B2}$$

$$A_{0w} = 2\Pi\left(2r_0^2 - r_0 h_0\right) \qquad \text{Eq. B3}$$

$$A_{pw} = 2\Pi\left(2r_p^2 - r_p h_p\right) \qquad \text{Eq. B4}$$

$$A_{0p} = 2\Pi r_0 h_0 - \Pi h_0^2 = 2\Pi r_p h_p - \Pi h_p^2 \qquad \text{Eq. B5}$$

A variação de energia livre para a morfologia de hemisfério é:

$$(\Delta G)_{HS} = \gamma_{ow}\left[2\Pi\left(2r_o^2 - 2r_o h_o\right)\right] + \gamma_{pw}\left[2\Pi\left(2r_p^2 - r_p h_p\right)\right] + \gamma_{op}\left(2\Pi r_o h_o - \Pi h_o^2\right) - \gamma_{ow}\left[4\Pi\left(R_o^{'}\right)^2\right] \qquad \text{Eq. B6}$$

O radio da partícula original, $R_o^{'}$, pode ser relacionado aos parâmetros da partícula de duas fases na figura B1 por equacionar o volume do polímero original em ambas partículas.

Tais como:

$$R_o^{'} = \left[r_o^3 - \left(h_o^2 / 4 \right) \left(3r_o - h_o \right) \right]^{1/3} \qquad \text{Eq. B7}$$

Normalizando eq. (B6) pela área de superfície da partícula original, $4\prod\left(R_o^{'}\right)^2$ e usando a eq. B7 temos:

$$\left(\gamma\right)_{HS} = \left[\gamma_{ow} r_o \left(2r_o - h_o \right) + \gamma_{pw} r_p \left(2r_p - h_p \right) + \gamma_{op} h_o \left(r_o - h_o / 2 \right) \right] / \left\{ 2\left[r_o^3 - \left(h_o^2 / 4 \right) \left(3r_o - h_o \right) \right]^{2/3} \right\} - \gamma_{ow}$$

Eq. B8

Tomando o limite como ϕ_p tende a zero (o que causa que r_p, h_p e h_o sejam zero) dando $\left(\Delta\gamma\right)_{HS} = 0$ como deve ser.

Para calcular $\left(\Delta\gamma\right)_{HS}$ via a eq. B8 para varias frações de volume, ϕ_p, pode-se relacionar r_o, r_p, h_p e h_o com ϕ_p, existe algum número de combinações destes r s e h s para um dado ϕ_p o qual pode conformar a forma geométrica da figura B1, porem, somente uma destas combinações estará em estado de equilíbrio termodinâmico de menor energia. Esta condição é determinada por um processo de tentativa e erro, no qual muitos diferentes valores das r s e h s são utilizados (note que para um ϕ_p dado existem restrições sobre os valores de r_p e h_p uma vez que r_o e h_o são selecionados). O calculo de rendimento mais baixo da energia interfacial para um ϕ_p selecionado é tomada como representante da combinação apropriada de r s e h s. $\left(\Delta\gamma\right)_{HS}$ é logo facilmente calculada via a eq. B8 e o processo é repetido para outro valor de ϕ_p.

***Anexo C**:* Norma ASTM D7490-08, método do *test standard* para medir a tensão de superfícies de revestimentos sólidos, substratos e pigmentos.

Designation: D7490 – 08

Standard Test Method for Measurement of the Surface Tension of Solid Coatings, Substrates and Pigments using Contact Angle Measurements[1]

This standard is issued under the fixed designation D7490; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes a procedure for the measurement of contact angles of two liquids, one polar and the other nonpolar, of known surface tension on a substrate, pigment (in the form of a disk), or cured or air dried coating in order to calculate the surface properties (surface tension and its dispersion and polar components) of the solid.

1.2 The total solid surface tension range that can be determined using this method is approximately 20 to 60 dynes/cm.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

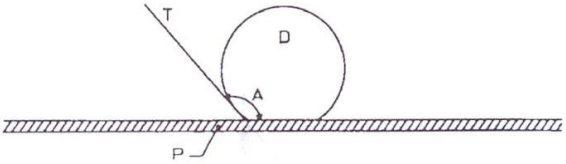
D5725 Test Method for Surface Wettability and Absorbency of Sheeted Materials Using an Automated Contact Angle Tester

D7334 Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement

3. Terminology

3.1 *Definitions:*

3.1.1 *contact angle*, *n*—the interior angle that a drop makes between the substrate and a tangent drawn at the intersection between the drop and the substrate as shown in Fig. 1; this is the angle formed by a liquid at the three phase boundary where a liquid, gas (air) and solid intersect.



A = contact angle
D = drop of liquid
P = specimen
T = tangent at specimen surface

FIG. 1 Measuring Angle of Contact

3.1.2 *dispersion component*, *n*—the component of solid surface tension that is related to intermolecular attraction caused by nonpolar dispersion forces.

3.1.3 *polar component*, *n*—the component of solid surface tension that is related to polar forces, such as hydrogen bonding and ion-dipole forces.

3.1.4 *solid surface tension*, *n*—the surface tension of a solid surface; this parameter cannot be measured directly, but must be determined by extrapolation of polymer melt or solution data to 100 % solids or by contact angles with liquids of known surface tension.

3.1.5 *surface energy*, *n*—excess free energy of surface molecules compared to those of the bulk material; arises from unbalanced molecular cohesive forces at a surface that cause the surface to contract and behave like a film or membrane (units are energy/unit areas such as joules/cm^2).

3.1.6 *surface tension*, *n*—the force necessary to break the surface of a film of a given length (units are force/length, such as dynes/cm or newtons/m); the same numerically as surface energy, but different units.

4. Summary of Test Method

4.1 Contact angles of drops of distilled water and diiodomethane (methylene iodide) are measured on the surface of interest. The two values are then substituted into two separate expressions of the Owens-Wendt-Kaelble equation (one for each liquid). This results in two equations in two

[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.23 on Physical Properties of Applied Paint Films.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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unknowns, which are then solved for the dispersion and polar components of surface tension. The sum of the components is the surface tension of the solid.

5. Significance and Use

5.1 The method described in this standard is based on the concept that the total free energy at a surface is the sum of contributions from different intermolecular forces, such as dispersion, polar and hydrogen bonding. There are other techniques that employ three components (dispersion, polar and hydrogen bonding). These methods are further complicated by needing three to five test liquids and are not practical for routine testing. This method uses contact angles of two liquids to provide data for the calculation of two components, dispersion, γ_s^d, and polar, γ_s^p.

5.2 Dispersion and polar component data, along with the total solid surface tension, are useful for explaining or predicting wetting or adhesion, or both, of coatings on pretreatments, substrates and other coatings. Low solid surface tension values often are a sign of contamination and portend potential wetting problems. High polar components may signal polar contamination. There is evidence in the literature that matching of polar components of topcoats and primers gives better adhesion.[3]

5.3 Solid surface tensions of pigments, particularly the polar components, may be useful in understanding dispersion problems or to provide signals for the composition of dispersants and mill bases. However, comparison of pigments may be difficult if there are differences in the roughness or porosity, or both, of the disks prepared from them.

5.4 Although this technique is very useful in characterizing surfaces, evaluating surface active additives and explaining problems, it is not designed to be a quality control or specification test.

6. Interferences

6.1 The following factors may interfere with results:

6.1.1 Dirt, fingerprints or other contamination on the surface being tested. Contact angles are very sensitive to surface contamination.

6.1.2 A rough or porous test surface such that drops sink in rapidly. Such surfaces are most likely found with pigment disks or sanded coatings.

6.1.3 A curved test surface such that angles are difficult or impossible to measure.

6.1.4 Low humidity (<40 % RH) when water is the test liquid such that the contact angle changes rapidly.

7. Apparatus

7.1 *Goniometer*—An instrument consisting of a controlled light source, a stage to hold the test specimen, and a microscope or camera for viewing of the drop on the specimen is required. An automated instrument for measuring angle of contact and a method for using it can be found in Test Method D5725.

7.2 *Hypodermic Syringe*—A syringe, such as a 1-mL hypodermic, equipped with a No. 27 stainless steel needle, capable of providing 100 to 200 drops from 1 mL, is suitable for use with water-like liquids. More viscous liquids may require a needle of different size.

8. Reagents and Materials

8.1 *Water*—Type II reagent water (distilled) in accordance with Specification D1193.

8.2 *Diiodomethane*—reagent grade or better.

9. Preparation of Specimens

9.1 If the part or panel of interest is too large to fit on the stage, then test specimens should be cut to a size appropriate for the instrument being used. They shall be cut in such a way as to be thoroughly representative of the sample.

9.2 The areas tested shall not contain visible blemishes or defects and shall not be touched with the fingers or contaminated in any other way.

9.3 If contamination or improper handling is suspected, the specimen may be rinsed with water or washed with laboratory detergent and water. However, cleaning may affect the results and must be noted on the report.

9.4 Pigment specimens shall be in the form of disks prepared in a press such as those used to prepare KBr disks for infrared analysis.

10. Procedure

10.1 Test the specimens at a standard temperature of 23 ± 2°C and at a relative humidity ≥50 %, unless otherwise agreed upon.

10.2 Set up the goniometer and level the stage according to the manufacturer's instructions.

10.3 Measure contact angles of water and diiodomethane on the specimen of interest as described in Practice D7334 or the manufacturer's literature for the instrument being used.

10.4 Make two angle measurements (one on each drop edge) of each of three drops on the specimen. If the contact angles on two edges are significantly different, the values should be eliminated and the test repeated. The contact angle for the specimen shall be the average of the six angles measured.

10.5 Water contact angles must be measured rapidly (within 30 s of depositing the drop) to avoid changes in angle as the water evaporates. A humidity chamber may be used to reduce the rate of evaporation.

11. Calculation

11.1 This method is based on the Owens-Wendt-Kaelble equation:[4,5]

$$\frac{\gamma_l\,(1 + \cos\theta)}{2} = [(\gamma_l^d\gamma_s^d)^{1/2} + (\gamma_l^p\gamma_s^p)^{1/2}] \quad (1)$$

[3] Imai, T. *Organic Coatings Science and Technology*, G. D. Parfitt and A. V. Patsis, eds, Vol. 6, Marcel Dekker, New York, 1984, p. 301.

[4] Schoff, C. K., "Wettability Phenomena and Coatings" in *Modern Approaches to Wettability: Theory and Applications*, M. E. Schrader and G. Loeb, eds. Plenum Press, New York, 1992, p. 375.

[5] Pierce, P. E. and Schoff, C. K., *Coating Film Defects*, 2nd Edition, Federation of Societies for Coatings Technology, Blue Bell, PA, 1994 .

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where:

θ = the average contact angle for the test liquid on the test specimen,

γ_l = the surface tension of the test liquid in dynes/cm, and

γ^d *and* γ^p = the dispersion and polar components of the liquid and the solid, also in dynes/cm.

However, since this method specifies two liquids of known surface tension (distilled water = 72.8, diiodomethane = 50.8) and known dispersion and polar components (distilled water γ^d= 21.8, γ^p= 51.0; diiodomethane γ^d= 49.5, γ^p= 1.3), all in dynes/cm), we can use these numbers to simplify the O-W-K equation and turn it into two expressions, one for water and the other for diiodomethane (denoted as i):

$$72.8\,(1 + \cos\theta_w)/2 = [(21.8\,\gamma_s^d)^{1/2} + (51.0\,\gamma_s^p)^{1/2}] \quad (2)$$

$$50.8\,(1 + \cos\theta_i)/2 = [(49.5\,\gamma_s^d)^{1/2} + (1.3\,\gamma_s^p)^{1/2}] \quad (3)$$

Next, let us further simplify the equations by calculating the square roots of the values for the dispersion and polar components of the two test liquids and placing them outside the parentheses. This gives the working equations when water and diiodomethane are used as the test liquids.

$$(36.4)(1 + \cos\theta_w) = [4.67\,(\gamma_s^d)^{1/2} + 7.14\,(\gamma_s^p)^{1/2}] \quad (4)$$

$$(25.4)(1 + \cos\theta_i) = [7.03\,(\gamma_s^d)^{1/2}] + 1.14\,(\gamma_s^p)^{1/2}] \quad (5)$$

11.2 Determine the cos θ value for each liquid from the contact angles.

11.3 Write two expressions, one for water, and the other for diiodomethane based on working Eq 4 and Eq 5 in 11.1. This will result in two equations in two unknowns (the unknowns being the dispersion and polar components of the solid surface, γ_s^d and γ_s^p, respectively).

11.4 Solve for the two unknowns (see Appendix X1 for a sample calculation).

11.5 Add the dispersion and polar component values together to give the total surface tension.

12. Report

12.1 Report the following information:

12.1.1 Identification of the specimen,

12.1.2 Average contact angles for each of the two liquids on the specimen,

12.1.3 Dispersion and polar components of solid surface tension and the total solid surface tension, and

12.1.4 If the specimen was cleaned in any way, this must be noted.

13. Precision and Bias

13.1 *Precision*—The precision of this method has not been determined by interlaboratory testing, but estimates of precision of measurements on substrates and coatings can be made based on experience with the method. Variability of measurements on pigments is expected to be greater due to differences in roughness and porosity.

13.1.1 *Repeatability (substrates and coatings)*:

13.1.1.1 *Contact Angle*—Two contact angle results (each the overall average of two measurements made on each of three drops) obtained by the same operator should be considered suspect (or as an indicator of the presence of localized contamination) if they differ by more than 2°.

13.1.1.2 *Dispersion and Polar Components*—Two values, each based on three drops of each test liquid, obtained by the same operator should be considered suspect (or as an indicator of the presence of localized contamination) if they differ by more than 5 dynes/cm.

13.1.2 *Reproducibility*—These measurements rarely if ever are carried out on the same specimen in two different laboratories. therefore, reproducibility is unknown and probably will be impossible to establish with any certainty.

13.2 *Bias*—It is not possible to determine bias for this method because of the lack of availability of a standard substrate whose surface can be expected to remain constant long enough for comparisons to be made with it.

14. Keywords

14.1 adhesion; contact angles; dispersion and polar components of solid surface tension; solid surface tension; wetting

APPENDIX

(Nonmandatory Information)

X1. SAMPLE CALCULATION FOR DISPERSION AND POLAR COMPONENTS OF SOLID SURFACE TENSION AND TOTAL SOLID SURFACE TENSION

X1.1 The following data were collected during root cause analysis work on a problem involving poor wetting/dewetting of a topcoat over a primer, particularly when the primed surface was aged.[4] Contact angles with distilled water and diiodomethane were measured on an aged specimen, the same after washing with a detergent solution, and on a control, a very similar primer know to give adequate wetting. Results are shown in Table X1.1.

TABLE X1.1 Averaged Contact Angles and Cosine Values for Problem and Control Primers

Specimen	Water Contact Angle, θ	Cos θ	Diiodomethane Angle, θ	Cos θ
Aged problem primer	63°	0.454	46°	0.695
After washing	72°	0.309	30°	0.866
Control	73°	0.292	36°	0.809

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X1.1.1 Let us consider O-W-K working equations Eq 4 and Eq 5 for water and diiodomethane that are shown in 11.1:

$$(36.4)(1 + \cos\theta_w) = [4.67\,(\gamma_s^d)^{1/2} + 7.14\,(\gamma_s^p)^{1/2}]$$

$$(25.4)(1 + \cos\theta_i) = [7.03\,(\gamma_s^d)^{1/2} + 1.14\,(\gamma_s^p)^{1/2}]$$

Now, we need to change two equations in two unknowns to a single equation with one unknown. To accomplish this, we multiply both sides of the first equation by 7.03/4.67 and subtract the second equation above from this new equation:

$$(54.8)\,(1 + \cos\theta_w) = [7.03\,(\gamma_s^d)^{1/2} + 10.75\,(\gamma_s^p)^{1/2}]$$

$$-\ \underline{\{(25.4)\,(1 + \cos\theta_i) = [7.03\,(\gamma_s^d)^{1/2} + 1.14\,(\gamma_s^p)^{1/2}]\}}$$

$$(54.8)\,(1 + \cos\theta_w) - (25.4)\,(1 + \cos\theta_i) = 9.61\,(\gamma_s^p)^{1/2}$$

For the aged problem primer, the water contact angle was 63°, so $\cos\theta_w = 0.454$, and the diiodomethane contact angle was 46°, $\cos\theta_i = 0.695$. Therefore, the expression resulting from the subtraction becomes

$$(54.8)(1.454) - (25.4)(1.695) = 79.7 - 43.0 = 36.7 = 9.61\,(\gamma_s^p)^{1/2}$$

Therefore, $\gamma_s^p = (36.7/9.61)^2 = 14.5$ dynes/cm. This is the polar component of the primer.

We then can substitute this value into either of the two equations and calculate γ_s^d, the dispersion component of the primer. For example, using the working equation for water:

$$(36.4)(1.454) = [4.67\,(\gamma_s^d)^{1/2} + (7.14)(14.5)^{1/2}]$$

$$52.9 = 4.67\,(\gamma_s^d)^{1/2} + 27.1$$

$$\gamma_s^d = [(52.9 - 27.1)/4.67]^2 = 30.5\ \textit{dynes/cm}$$

The sum of these two values gives the total solid surface tension, which in this case is 45.0 dynes/cm.

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