

Alkanolamine

on Adhesion of Waterborne Coatings

Additives are incorporated into coatings for specific reasons (e.g., viscosity modification, surface tension modification, biocidal effects, etc.), but the influence of most additives goes significantly beyond their primary function. The influence of neutralizing alkanolamines on adhesion is one example of this kind of peripheral effect (sometimes referred to as an off-diagonal effect). Comparative waterborne coating formulations that differ only in their alkanolamine content have markedly different adhesion properties on plastics, and the degree of difference is sufficient to warrant more detailed examination.

Introduction

Understanding and improving the adhesion of waterborne coatings to various substrates is an important area of industrial research. One significant aspect of adhesion examined in this work relates to the infiltration of a liquid coating into the microscopic pores and irregularities of a surface prior to drying/curing. Such permeation is a prerequisite for good anchor-type adhesion of the coating to the surface. Some simple equations involving contact angles and interfacial tensions can be derived to show the relationship between surface activity and surface permeation, and these equations have been developed herein to the point where they provide a good intuitive understanding of the mechanism of adhesion. More detailed and exact mathematical treatments of surface tension and microscopic adhesion are also given in the literature.¹⁻³ The model described herein has been developed to provide a useful model for understanding some of the more important forces involved in anchoring a coating to a surface via infiltration and in mating a coating to a substrate via general adhesive bonding.

This derivation starts by considering a simple hemispherical pore on a solid surface. We imagine that the pore is covered with a liquid coating formulation such that a pocket of air is trapped inside the covered pore. Gravity works to dislodge the bubble while surface tension may be working either with gravity to dislodge the bubble or against gravity attempting to keep the bubble lodged. The influence of the surface tension depends on the nature of the solid and liquid involved. Using an energy balance approach, we have derived an equation for the maximum contact angle allowable for a coating to permeate pores on a solid surface. The results are approximate, but the equation does illustrate why consideration of the surface tension is important when optimizing a coating formulation.

A Simple Equation for Predicting Adhesion

Consider the plastic surface with a hemispherical pore irregularity shown in Figure 1. Then coat the surface with a thin layer of an uncured/undried liquid coating, as shown in Figure 2. We assume that the coating has trapped a hemispherical pocket of air in the pore and that this trapped air now has the option of either escaping by rising up through the coating or staying where it is. If the air escapes, then the coating will flow into the pore and anchor itself to the surface. If the air does not escape, then the coating will have poor adhesion to the surface. The purpose of the following equation is to provide a model for predicting whether or not the bubble will escape. We will develop the model by first considering the total energy change that will occur if the bubble is expelled from the pore. Figure 3 shows the bubble escaping.

The only two components necessary for consideration of the energetic driving force of bubble expulsion are surface tension and gravitational potential.

FIGURE 1 | Representation of a surface with a hemispherical pore.

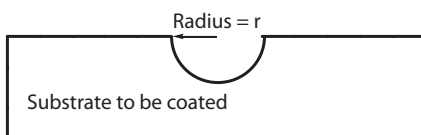


FIGURE 2 | Representation of a surface covered with a thin layer of liquid coating.

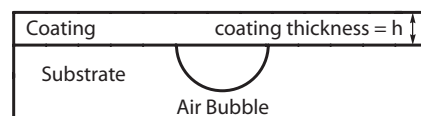
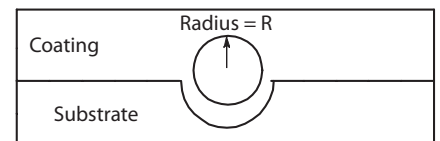


FIGURE 3 | The bubble escaping through the coating. The thickness of the coating has been exaggerated to illustrate the spherical bubble.



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Influence to Plastics

The total energy of surface tension for the bubble lodged in the pore is (γ_{SA} = surface tension of substrate to air, γ_{LA} = surface tension of liquid coating to air, γ_{LS} = surface tension of substrate to liquid coating):

$$\text{Surface Energy (total, lodged bubble)} = 2\pi r^2 \gamma_{SA} + \pi r^2 \gamma_{LA}$$

The total surface energy of the dislodged bubble is:

$$\text{Surface Energy (total, dislodged bubble)} = 4\pi R^2 \gamma_{LA} + 2\pi r^2 \gamma_{LS} \\ = 4\pi (1/2)^{2/3} r^2 \gamma_{LA} + 2\pi r^2 \gamma_{LS}$$

The total gravitational potential of the dislodged bubble will be approximately equal to the volume of the air bubble formed times the density difference between the coating and the air bubble times the acceleration of gravity times the thickness of the coating (ρ_L = density of liquid coating, ρ_A = density of air):

$$\text{Gravitational Potential Energy (dislodged bubble)} \approx (\rho_L - \rho_A) \\ gh(2/3)\pi r^3 = (2/3)(\Delta\rho)gh\pi r^3$$

One need not consider expansion of the bubble as it rises through the coating. The total thickness of the coating is assumed to be 1 mm or less, and the maximum density of the coating is assumed to be around 10 g/cm³. Thus, the maximum pressure the coating could exert would be 1 g/cm². Atmospheric pressure is about 1 Kg/cm². We assume that air is trapped in the pore at ambient pressure, and the maximum expansion the bubble will undergo upon rising from the pore to the surface of the coating will be approximately 0.1% in total volume.

Summing terms for surface tension and gravitational potential, we can now calculate the energy change that will occur upon expulsion of the bubble (negative energy equates with a spontaneous process):

$$\Delta E (\text{bubble expulsion}) = 4\pi (1/2)^{2/3} r^2 \gamma_{LA} + 2\pi r^2 \gamma_{LS} - 2\pi r^2 \gamma_{SA} - \pi r^2 \gamma_{LA} \\ - (\Delta\rho)gh(2/3)\pi r^3$$

Recall that Young's equation relates the three interfacial tensions γ_{LA} , γ_{SA} and γ_{LS} .⁵

Young's Equation: $\gamma_{SA} = \gamma_{LS} + \gamma_{LA} \cos\theta$, where θ = contact angle between liquid and solid

The contact angle can be measured by taking a photograph of a drop of liquid on a flat solid surface under controlled conditions. Rearranging terms and using Young's equation, we get:

$$\Delta E (\text{bubble expulsion}) = 2\pi r^2 (1.26) \gamma_{LA} - \pi r^2 \gamma_{LA} - 2\pi r^2 (\gamma_{LA} \cos\theta) - \\ (2/3)\pi r^3 (\Delta\rho)gh$$

Further rearrangement yields the simplified bubble expulsion equation below:

$$\Delta E (\text{bubble expulsion, simplified}) = \pi r^2 \gamma_{LA} (1.52 - 2\cos\theta) - (2/3) \\ \pi r^3 (\Delta\rho)gh$$

The gravitational potential will, assuming the density of the liquid coating is greater than that of air, always be favorable for bubble expulsion. Assuming that the difference in density between the coating and the air bubble is 1 g/cm³ and that the coating is 100 microns thick with acceleration due to gravity of 9.8 m/sec², a pore radius of 1 micron and a liquid-air surface tension of 0.030 N/m, then we have for ΔE

FIGURE 4 | Contact angles of 0.5% aqueous solutions of some commercially important alkanolamines on seven different plastics. Contact angle data was taken from Table 1.

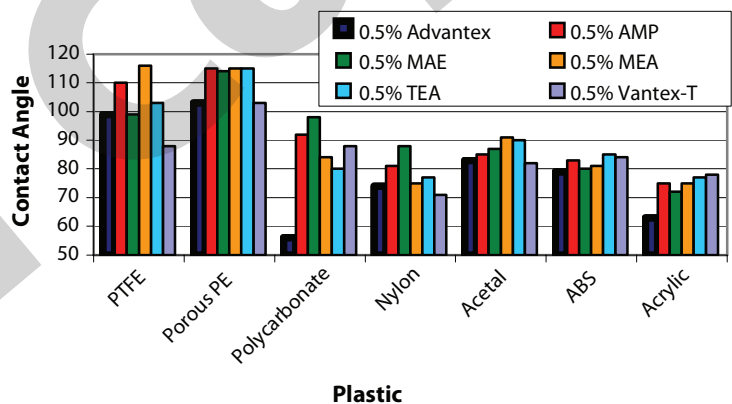
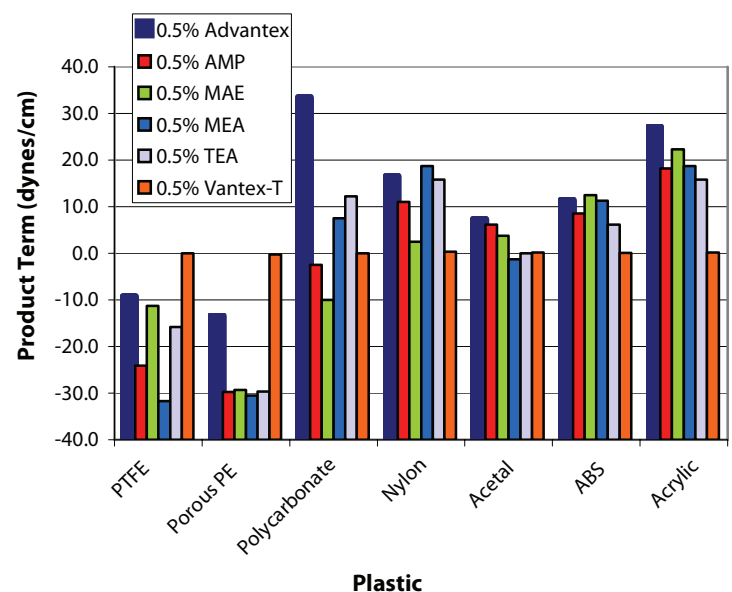


FIGURE 5 | Cosine contact angle x air/liquid surface tension product terms for 0.5% aqueous solutions of alkanolamines used in coatings. The $\gamma_{LA} \cos\theta$ product term data was taken from Table 4.



(bubble expulsion, $\Delta\rho = 1 \text{ g/cm}^3$, $g = 9.8 \text{ m/sec}^2$, $h = 100 \text{ microns}$, $r = 1 \text{ micron}$, $\gamma_{LA} = 0.030 \text{ N/m}$) = ΔE (bubble expulsion, assumptions):

$$\Delta E (\text{bubble expulsion, assumptions}) = 9.425 \times 10^{-14} \text{ joule} \{1.52 - 2\cos\theta\} - 2.0525 \times 10^{-18} \text{ joule}$$

TABLE 1 | Contact angle measurements for six different aqueous alkanolamine solutions on six different substrates at 22 °C. Contact angles measured in degrees by the tangent method.

Plastic	DI Water	50% Advantex*	50% Vantex-T*	50% AMP	50% MAE	50% DGA	50% MEA	50% TEA
PTFE	102	56	63	66	71	117	83	85
Porous PE	119	0	0	53	56	97	93	90
Polycarbonate	104	27	7	50	66	33	63	82
Nylon	67	5	19	31	35	49	44	59
Acetal	86	33	31	56	61	73	63	69
ABS	78	13	6	37	50	51	51	67
Acrylic	74	21	21	30	38	53	52	52

Plastic	DI Water	5% Advantex	5% Vantex-T	5% AMP	5% MAE	5% DGA	5% MEA	5% TEA
PTFE	102	54	60	88	90	89	92	84
Porous PE	119	87	81	108	104	123	115	111
Polycarbonate	104	64	54	94	71	93	86	80
Nylon	67	36	31	48	52	62	64	67
Acetal	86	58	56	79	80	76	77	74
ABS	78	36	44	85	67	70	56	62
Acrylic	74	30	39	57	59	87	65	86

Plastic	DI Water	0.5% Advantex	0.5% Vantex-T	0.5% AMP	0.5% MAE	0.5% DGA	0.5% MEA	0.5% TEA
PTFE	102	99	88	110	99	99	116	103
Porous PE	119	103	103	115	114	116	115	115
Polycarbonate	104	56	88	92	98	90	84	80
Nylon	67	74	71	81	88	96	75	77
Acetal	86	83	82	85	87	81	91	90
ABS	78	79	84	83	80	80	81	85
Acrylic	74	63	78	75	72	77	75	77

*Advantex and Vantex are products of TAMINCO, Allentown, PA.

Thus, the predominant energy component for liquid wetting in a small pore is dependent on the surface tension and the contact angle, and this relative importance of interfacial tension increases as the pores get smaller. If we now assume that only small pores are important and ignore the favorable gravitational component of the equation ($\Delta\rho = 1 \text{ g/cm}^3$, $g = 9.8 \text{ m/sec}^2$, $h = 100 \text{ microns}$, $\gamma_{LA} = 0.030 \text{ N/m}$, $r = 1 \text{ micron}$):

$$\Delta E (\text{bubble expulsion, interfacial tension}) = 9.425 \times 10^{-14} \text{ joule} \{1.52 - 2\cos\theta\}$$

This energy must be negative for the coating to wet the substrate and spontaneously flow into the pore. Thus:

$$1.52 - 2\cos\theta < 0 \quad 1.52 < 2\cos\theta \quad \cos\theta > 0.76 \quad \theta < 41^\circ$$

Based on this model, for a coating to adhere to a substrate with microscopically dimensioned pores, the contact angle between the liquid and the substrate must be less than 41°. In general, the lesser the contact angle of the liquid on the solid, the more effective the permeation of the liquid into the solid. Further, the better the permeation of a liquid coating into pores on a solid surface, the better anchored the dried/cured coating will be.

Contact Angle and Surface Tension Results

The contact angles made by 50%, 5% and 0.5% aqueous solutions of seven different alkanolamines on seven different plastics at 22 °C are given in Table 1. The contact angle measurements were made with a Kruss Contact Angle Measuring System G10 (contact angles rounded to the nearest integer). The plastic panels were prepared by washing with dilute Liqui-Nox (Alconox) followed by rinsing with DI water. The panels were allowed to air dry on paper towels for 24 hours prior to testing. The contact angles were calculated via the tangent

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method using Drop Shape Analysis software (Version 1.0, Kruss Corporation). All measurements were rounded to the nearest integer value.

The plastic pieces used were analyzed by scanning electron microscopy (SEM). A small piece of each sample was coated with a gold/palladium alloy using an ion-beam coater from South Bay Technologies (model IBS/e). SEM images were obtained using the In-Lens detector of a LEO 1530 field emission electron microscope. The accelerating voltage was 4 kV, the working distance was varied

TABLE 2 | SEM characterization at various magnifications of plastics used for contact angle measurements.

Plastic	Morphology from SEM Images
PTFE	Smooth but scratched up to 1KX; smooth with 30% plateau irregularities up to 5KX; smooth, craters < 1 nm deep, no pores, 20% plateau irregularities at 25KX.
Porous PE	Deep pores of at least 100 µm depth, spherical cell structure polished flat up to 1KX; semi-smooth with over 50% crystalline surface irregularities up to 5KX; semi-smooth, craters < 1 nm deep, no pores, 50% plateau irregularities at 25KX.
Polycarbonate	Very smooth up to 5KX; very smooth, craters < 1 nm deep, 1 surface imperfection per 10 square µm at 25KX.
Nylon	Smooth but scratched up to 1KX; smooth with 50% plateau irregularities up to 5KX; semi-smooth, craters < 1 nm deep, 50% covered with plateau irregularities at 25KX.
Acetal	Smooth up to 100X; completely porous surface with tiny pores apparent at 1KX; completely cracked surface apparent at 5KX; covered with deep cracks of typical dimension 30 nm by 200 nm at 25KX.
ABS	Very smooth at 100X; approximately 10% crystalline/plateau irregularities at 1KX; completely covered with rough scalloping at 5KX; smooth, craters < 1 nm deep, 1 surface imperfection per square µm at 25KX.
Acrylic	Smooth with occasional spot irregularities up to 5KX; smooth, craters 10 nm deep, 1 surface imperfection per square µm at 25KX.



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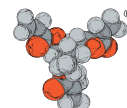
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TABLE 3 | Room temperature liquid/air surface tensions in milliNewtons/m.

Concentration (% wt/wt)	Advantex	Vantex-T	AMP	DGA	MAE	MEA	TEA
0.5%	59.8	60.1	70.4	72.1	70.7	72.3	70.2
1.0%	52.8	54.8	68.8	70.9	69.7	72.3	70.1
5.0%	37.9	41.0	60.6	68.0	64.6	70.6	66.6
50.0%	29.8	33.4	41.3	55.6	46.0	60.7	54.8

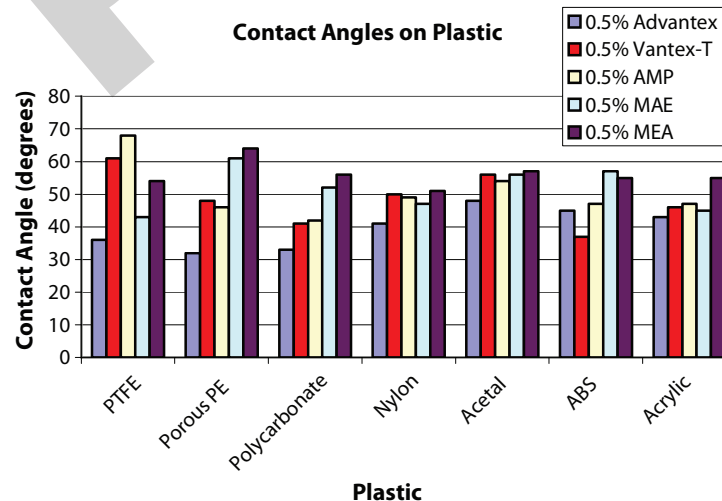
Note: Samples were measured by the maximum bubble pressure method on a Sita t60 maximum bubble pressure tensiometer with a bubble lifetime of 1 second. Sample size was less than 4 ml, and a slow bubble rate was used to keep the liquid level constant. Ten bubbles were averaged per reading with five readings per sample for a total of 50 reading per sample.

TABLE 4 | Product term ($\gamma_{LA}\cos\theta$) for 0.5% aqueous alkanolamine solutions on different types of plastic. Contact angle data was taken from Table 1; liquid/air surface tension data was taken from Table 3.

Plastic	DI Water	0.5% Advantex	0.5% Vantex-T	0.5% AMP	0.5% MAE	0.5% DGA	0.5% MEA	0.5% TEA
PTFE	-15.0	-9.4	2.1	-24.1	-11.3	-11.1	-31.7	-15.8
Porous PE	-34.9	-13.5	-13.5	-29.8	-29.3	-31.0	-30.6	-29.7
Polycarbonate	-17.4	33.4	2.1	-2.5	-10.0	0.0	7.6	12.2
Nylon	28.1	16.5	19.6	11.0	2.5	-7.4	18.7	15.8
Acetal	5.0	7.3	8.4	6.1	3.8	11.1	-1.3	0.0
ABS	15.0	11.4	6.3	8.6	12.5	12.3	11.3	6.1
Acrylic	19.8	27.1	12.5	18.2	22.3	15.9	18.7	15.8

TABLE 5/FIGURE 6 | Contact angles for 50% aqueous resin emulsion with 0.5% added alkanolamines on various plastics. Designations for alkanolamines and plastics are identical to that used in Table 1.

Plastic	0.5% Advantex	0.5% Vantex-T	0.5% AMP	0.5% MAE	0.5% MEA
PTFE	36	61	68	43	54
Porous PE	32	48	46	61	64
Polycarbonate	33	41	42	52	56
Nylon	41	50	49	47	51
Acetal	48	56	54	56	57
ABS	45	37	47	57	55
Acrylic	43	46	47	45	55



between 4 mm and 9 mm and the samples were imaged at various magnifications. The surface features of the plastics used are given in Table 2.

The room temperature liquid/air surface tensions (millinewtons/m; equivalent to dynes/cm) of the aqueous alkylalkanolamine solutions used for contact angle measurements are given in Table 3 (liquid/air surface tension of DI water @ 22 °C = 72.8 dynes/cm).

Surface Affinity

The affinity of a liquid for a solid can be assessed with Young’s equation: $\gamma_{SA} = \gamma_{LS} + \gamma_{LA}\cos\theta$ (θ = contact angle between liquid and solid). The rearrangement of Young’s equation yields: $\gamma_{LS} = \gamma_{SA} - \gamma_{LA}\cos\theta$. The solid/air surface tension term (γ_{SA}) is a constant. Thus, the larger the $\gamma_{LA}\cos\theta$ term (cosine term), the smaller will be the liquid/solid surface tension (γ_{LS}). We can assume that the affinity of one phase for another is in some way inversely proportional to the interfacial tension between the two phases, as the interfacial tension is a macroscopic indicator of the microscopic incompatibility of the two phases with each other.⁶ Thus, the cosine term is directly proportional to the affinity of the liquid for the solid. Table 4 gives cosine term values ($\gamma_{LA}\cos\theta$) for 0.5% aqueous alkanolamine solutions on a number of plastics.

Figure 4 tabulates contact angle values on seven different plastics for 0.5% aqueous solutions of some commercially important alkanolamines used in coatings. Examination of the data reveals that the contact angles for 0.5% aqueous solutions of Advantex® and Vantex®-T vary from somewhat to significantly lower on all substrates tested. Figure 5 tabulates $\gamma_{LA}\cos\theta$ (theta is the contact angle) product terms on seven different plastics for 0.5% aqueous solutions of some commercially important alkanolamines used in coatings. The 0.5% concentration is typical for use in coatings.

A quick examination of the data in Figure 5 reveals that the contact angle multiplied by the air/liquid surface tension (we designate this the product term) for 0.5% aqueous solutions of Advantex and Vantex-T are anywhere from somewhat to significantly higher on all the substrates tested. Combined, the data in Figures 4 and 5 indicate that coatings containing Advantex and Vantex-T should exhibit better anchor type adhesion (based on the expulsion of bubbles from microscopic pores on the plastic surface) and better chemical adhesion (based on surface affinity) than coatings containing alternative alkanolamines.

A similar variation in liquid/solid contact angles is observed for prototype coating emulsions. Table 5 and Figure 6 give the contact angles for 50% resin emulsions (Acronal Optive 130, 100% acrylic resin in water, product of BASF Corporation) with 0.5% added

alkanolamine on the plastics listed above. Again, the contact angles for 0.5% aqueous emulsions with Advantex and Vantex-T are anywhere from somewhat to significantly lower on all the hydrophobic plastic substrates tested.

Adhesion Testing

The hypothesis that contact angles can be used to predict adhesion on plastic, as presented herein, was tested by the cross-hatch adhesion method (ASTM D 3359). A prototype waterborne coating was made from a 50% solids resin emulsion of Acronal Optive 130 with 0.5% wt/wt alkanolamine and 5% wt/wt Dupont R960 TiO₂. A 10 mil coating was applied to Leneta paper and dried for 120 hours. Adhesion testing results are given in Table 6.

TABLE 6 | The amount of coating (%) removed by Permacel tape after 30 seconds brushing and 30 seconds of set time.

Alkanolamine	% Coating Removed
Advantex	40%
Vantex-T	60%
AMP	85%

TABLE 7 | Cross-hatch adhesion results for a dried (120 hours) coating on three different plastics.

Plastic	0.5% Advantex	0.5% Vantex-T	0.5% AMP	0.5% MAE	0.5% MEA
PTFE	-	-	-	-	-
Porous PE	0%	5%	10%	20%	20%
Polycarbonate	-	-	-	-	-
Nylon	-	-	-	-	-
Acetal	-	-	-	-	-
ABS	70%	80%	70%	80%	80%
Acrylic	60%	40%	100%	100%	100%

TABLE 8 | Torsion pull adhesion results for a dried (72 hours) coating on four different plastics. Torsion pull force was measured with a modified top loading balance.

Plastic	0.5% Advantex	0.5% Vantex-T	0.5% AMP	0.5% MAE	0.5% MEA
PTFE	18 g	17 g	16 g	12 g	17 g
Porous PE	-	-	-	-	-
Polycarbonate	58 g	60 g	58 g	42 g	42 g
Nylon	45 g	48 g	44 g	38 g	32 g
Acetal	109 g	104 g	75 g	96 g	99 g
ABS	-	-	-	-	-
Acrylic	-	-	-	-	-



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The coating used in Table 6 was tested for adhesion to the different plastics discussed above. The data is given in Tables 7 and 8. For coatings that adhered to the plastic more strongly than they cohered together, we used a cross-hatch adhesion test (ASTM D 3359) to assess adhesion (Table 7). For coatings that cohered together more strongly than they adhered to the surface we used a torsion pull test (maximum pulling force in grams necessary to peel the coating).

The results in Tables 7 and 8 clearly support the contention that an improvement in adhesion, particularly on hydrophobic surfaces like plastic, can be a significant benefit of the particular alkanolamine used in a waterborne coating formulation.

Summary

Coating adhesion is an important part of the coating's overall performance. Optimal adhesion can be obtained through both chemical and physical means. In the case of chemical adhesion, the general affinity of the coating for the solid substrate is most important. In the case of physical adhesion, anchor type attachment of the cured coating to the substrate is most important. The improvement of the permeation of a liquid coating into a solid surface allows for better anchor type attachment of the cured/dried coating to the surface. In this paper we have shown that contact angles between uncured/undried liquid coatings and solid substrate surfaces can be used to predict the ease of ejection of trapped air bubbles from micropores on the solid surface, and this tendency for bubble ejection can, in turn, be related to the degree of anchor type adhesion that develops. In addition, we have shown that the product of the liquid/solid contact angle with the air/liquid surface tension (cosine term of Young's Equation) can be used as a good assessment of the general surface affinity of a liquid coating for a solid surface. We have found that better surface affinity of a liquid coating for a solid equates

to better overall chemical adhesion of the coating to the solid. Thus, lower contact angles between a liquid coating and a solid substrate equate to better adhesion by both physical and chemical mechanisms. Some alkanolamines, despite their typically low

percent composition in coatings, can have a significant impact on the interfacial properties of the coating, and we have observed that certain alkanolamines have a significant effect on the adhesion of dried waterborne coatings on plastics. Specifically, alkanol-

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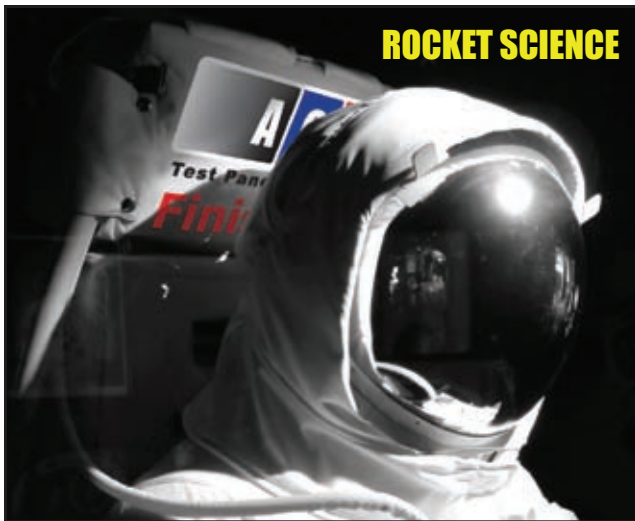
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Alkanolamine Influence on Adhesion of Waterborne Coatings to Plastics

lamines with mid-range calculated HLB values (hydrophilic to lipophile balance – calculated as 20 times the hydrophilic GMW divided by the total molecular weight), like Advantex and Vantex-T, yield coatings with lower solid/liquid contact angles and measurably better adhesion. ■

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2. Myers, D.; *Surfactant Science and Technology*, Third Edition 2006, pages 349–352, Wiley-Interscience.
3. D. E. Packham; “Surface energy, surface topography and adhesion” *International Journal of Adhesion and Adhesives*, 2003, 23(6), 437-448.
4. The approximate nature of the gravitational potential equation need not be considered for coatings that are at least 20 times as thick as the radius of the ejected bubble. For thinner coatings, one might consider that different parts of the bubble travel different distances before finally emerging from the top of the coating. A more exact equation for the gravitational potential of the collapse of a thin coating into a large pore would be $(\rho = \text{density of coating, } g = \text{acceleration of gravity, } h = \text{thickness of coating, } r = \text{radius of pore}): \text{Gravitational Potential Energy (collapse thin coating)} = (2\pi/4)(\rho)gh\pi r^3 = 1.5708(\rho)gh\pi r^3$ This equation is derived by considering the gravitational potential of the coating falling into the pore. We assume a thin film coating of thickness h and area πr^2 ($r = \text{radius of pore}$) stretched over the surface of a pore. The mass of coating covering the pore is $\rho\pi r^2 h$ where ρ is the density of the coating. Because in this case we assume the coating breaks apart upon collapse, we don't need to consider the density and/or pressure (via compression) of air within the pore ($\Delta\rho \rightarrow \rho$). The gravitational force is $\rho\pi r^2 hg$ where g is the acceleration of gravity. All we need to calculate is the average distance that each infinitesimal chunk of coating falls before hitting the bottom of 2 the pore. This average distance can be calculated from the following integral

$$\frac{2}{r} \int_0^r \sqrt{r^2 - x^2} dx$$

The integral

$$\int_0^r \sqrt{r^2 - x^2} dx$$

represents the summation from 0 to r of the distance that an infinitesimal slice of coating falls multiplied by the infinitesimal thickness dx of the slice. This summed value is then divided by the total distance $x = r$ from the center of the pore to the edge in order to convert the x weighted average of the distance y into the actual average distance y that the slice of coating falls. This value is multiplied by 2 because the pore is an assumed hemisphere that radiates out from the center to both the left and the right. The indefinite solution of the integral is

$$\frac{1}{r} \left[\frac{x\sqrt{r^2 - x^2}}{2} + \frac{r^2}{2} \sin^{-1} \left[\frac{x}{r} \right] + c \right]. \text{ The exact solution is}$$

$$\frac{1}{r} \left[\frac{r^2}{2} \sin^{-1} \left[\frac{r}{r} \right] - \frac{r^2}{2} \sin^{-1} \left[\frac{0}{r} \right] \right] = \frac{r\pi}{4}$$

Because a hemisphere is perfectly symmetrical around the sin central axis, we need only solve this problem in two dimensions.

5. Roura, P.; Fort, J.; “Local Thermodynamic Derivation of Young's Equation” *J. Colloid Interface Sci.* 2004, 272, 420 – 429.
6. As a point of interest, a negative surface tension between two phases implies that an increased surface area of contact between the two phases is favored. Maximizing the surface area between two phases is equivalent to the formation of a single phase. Thus, a negative surface tension implies miscibility between the phases.
7. Gernon, M. D.; Dowling, C. M.; Carlozzo, B. Alford, D.; “The Influence of Anchor Type Adhesion of Coatings to Hydrophobic Surfaces” *Future Coat Proceedings, New Orleans, LA 2006*, published by: Federation of Societies for Coatings Technology, Blue Bell, PA [CAS Accession # 2007: 1428596]. For more information, visit <http://www.taminco.com> or email Michael.Gernon@Taminco.com (technical information) or conor.dowling@taminco.com (sales/market information).

This work was initially presented at the 2006 ICE Show in New Orleans.⁷

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