Hydrophobic Coatings from Emulsion Polymers

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One of the chief requirements of protective coatings is the ability to confer water resistance to painted substrates. To accomplish this task, the coating itself must be water resistant but should also possess the additional performance properties expected of modern coatings. Branched vinyl esters provide the building blocks for preparing very hydrophobic binders by emulsion polymerization. Not only do these monomers have favorable reactivity with vinyl acetate but they also react effectively with acrylates and can be formulated into a wide range of performance coatings. Hydrophobic polymers find use in a wide range of applications including architectural paints, building products and corrosion resistant coatings. In addition to the design of reliable measurements of water resistance, it would be beneficial to be able to predict the water sensitivity of materials based on composition. Calculations of oxygen contents and solubility parameters of polymers are proposed as useful approaches to estimating the hydrophilicity of coatings in order to define the hydrophilic limit imposed on coatings by various water resistance tests.

INTRODUCTION

One important feature of protective coatings which determines utility is the resistance to water in the form of liquid and vapor. Since water is present in most applications, a task of the formulator is to choose the most water resistant components available consistent with cost and processing requirements. The functions of a polymeric binder are to encapsulate and localize pigment particles, to provide an adhering interface at the substrate to be coated, and to form a coherent film which will resist water penetration. In this way structural and adhesive strength can be maintained while the substrate is protected. Since the binder is a major part of most coatings, current research in emulsion polymer design is aimed at providing more effective barrier properties by minimizing hydrophilic components and increasing the hydrophobic nature of the polymers produced. The availability of long-chain branched vinyl esters provides the polymer designer with new choices of raw materials with which to accomplish this task. Not only do these monomers react favorably with vinyl acetate (VAc) but they also react with acrylic monomers. This versatility provides the means of tailoring polymer properties to fit a variety of applications including interior and exterior paints, clear and pigmented wood coatings, corrosion resistant metal coatings, and stable coatings and additives for cement and concrete.

Emulsion Polymerization

Emulsion polymers continue to grow in popularity with coatings formulators and end-users because of their well-known features including safe handling, low toxicity, low odor, and easy clean-up. The emulsion polymerization process produces polymer particles of sub-micron size, and the resulting latex is properly called a polymer colloid. The complexity of the process arises because of the interplay of chemical reactions and colloidal factors, chiefly those involving particle generation and stabilization. The essential characteristic which dif-

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Table 1—Glass Transition Temperatures of Vinyl Ester Monomers

Monomer	Total Carbons	T_g, °C
Vinyl Acetate	(VAc) 4	+30
Vinyl Neo-pentanoate	(neo-5) 7	+65
Vinyl 2-Ethylhexanoate	(V2EH) 10	–36
Vinyl Neo-nonanoate	(neo-9) 11	+60
Vinyl Neo-decanoate	(neo-10) 12	–3
Vinyl Neo-undecanoate	(neo-11) 13	–40
Vinyl Neo-dodecanoate	(neo-12) 14	–3

ferentiates emulsion polymerization from other polymerization processes is the compartmentalization of the reaction, i.e., each particle acts as an isolated reaction zone. This isolation leads to restricted chain termination and results in much higher molecular weights, which generally yield superior polymer performance than in the case of solution polymerizations. Contrary to the case of solution polymers, dispersion viscosities depend on volume solids and particle packing, not molecular weight. Consequently, dispersions of high molecular weight particles can be prepared at relatively high solids and low viscosity. This fact, combined with the good heat removal capacity of water, results in attractive process characteristics and accounts for the great economic value of emulsion polymerization in providing useful polymers for a wide variety of coatings.

One disadvantage of emulsion polymers is the need for stabilization of the dispersed particles. In addition, the high molecular weight particles often require assistance in the coalescence process to form tough films over a wide temperature range. Unfortunately, the additives employed to rectify these deficiencies are generally hydrophilic in nature and tend to decrease the water resistance of latex films. While the choices of additives, such as surfactants, initiators, buffers, co-solvents, defoamers, and other common latex components, are important in addressing particular end-uses, the choice of the monomer building blocks is crucial in determining the ultimate properties of the coating.

Monomers used in emulsion polymerization encompass a wide range of chemical structures. VAc homopolymer was one of the first commercially produced emulsion polymers in the 1930s, and is still widely used.

Table 2—Monomer Solubilities in Water

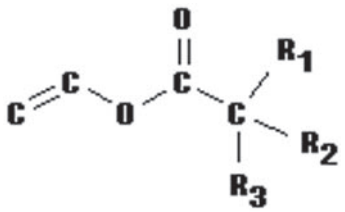
Monomer	Solubility at 20°C (wt%)
Acrylonitrile	7.1
Methyl acrylate	5.2
Vinyl acetate	2.5
Ethyl acrylate	1.8
Methyl methacrylate	1.5
Ethylene	1.1
Vinyl chloride	0.60
Butyl acrylate	0.16
Styrene	0.03
2-Ethylhexyl acrylate	0.01
Vinyl neo-pentanoate	0.08
Vinyl 2-ethylhexanoate	< 0.01
Vinyl neo-nonanoate	< 0.001
Vinyl neo-decanoate	< 0.001
Vinyl neo-undecanoate	< 0.001
Vinyl neo-dodecanoate	< 0.001

Generally co-polymerized with an acrylate (butyl or 2-ethylhexyl), vinyl-acrylics are favored for their cost-performance in many coatings applications. All-acrylics are generally copolymers of methyl methacrylate (MMA) and butyl acrylate (BA) and comprise a second polymer family. Styrene-acrylics (styrene/butyl acrylate) and the pressure polymers (vinyl acetate/ethylene) complete the grouping of copolymers commonly made by emulsion polymerization. Functional (acrylic acid and methacrylic acid) monomers, along with specialty (wet adhesion, crosslinking) monomers are also used successfully to add specific properties to coatings. Each of these polymer families has a role to play in the various coatings end-uses; but, as always, relentless competitive forces in the market place provide strong incentives to maximize cost-performance for a given application.

In North America, vinyl-acrylic latexes dominate the interior architectural market because of their low cost and good pigment binding characteristics. Exterior applications have long been the domain of all-acrylics due to their durability over many different substrates. However, pressure polymers (VAEs) are gaining a foothold in interior markets because of their good filming properties at low temperatures. Styrene-acrylics are mainly used in industrial coatings and some specialty applications, such as high gloss enamels. In Europe, the situation is quite different. Vinyl-acrylics and all-acrylics are minor participants in the architectural market, whereas styrene-acrylics enjoy wide popularity. The other major polymer type consists of copolymers of vinyl acetate and branched vinyl esters (BVE) valued for their stability over concrete and their excellent exterior durability.

BRANCHED VINYL ESTERS

Shell Chemical Company developed a manufacturing process for making highly branched tertiary monocarboxylic acids (actually a mixture of isomeric acids) over 30 years ago. The C9-C11 acid mixture (versatic acid) is prepared via the Koch process which involves oligomerizing propylene in the presence of water and carbon monoxide to produce branched acids containing a neo structure on the carbon adjacent to the carbonyl carbon. The acid can then be converted into its vinyl ester by reaction with acetylene. The generic structure of branched vinyl esters is shown in the following:



Where R_1, R_2, and R_3 are alkyl groups. The neo-esters are named according to the average number of carbons in the neo acid precursor.

Today, the most commonly used branched vinyl ester is the neo-10 monomer, although several other producers have started to make various neo-esters under differ-

ent trademarks. Union Carbide recently developed a transvinylation process for preparing a variety of vinyl esters, including vinyl 2-ethylhexanoate (V2EH) and vinyl pivalate (neo-5), from vinyl acetate.[1] Although versatile, this process has proven to be less economical than the traditional acetylene process. Shell has introduced neo-9 and neo-11 under the tradenames VeoVa 9 and VeoVa 11, while Exxon has recently started to market neo-12 (Exxar 12) as well as neo-10 (Exxar 10). Consequently, latex producers are beginning to have a number of choices to suit particular coatings applications. Although available for experimental purposes, not all these monomers are free of regulation barriers in the U.S.

A list of glass transition temperatures (T_g) for vinyl ester homopolymers is given in *Table* 1. The range of T_gs is surprising considering the narrow range of molecular weights involved. Scholten and van Westrenen[2] illustrated the effect of chain branching by measuring the glass transition temperatures of a series of polymers prepared from neo-9 isomers. The T_gs were found to range from 10 to 119°C. The conclusion from this study was that the T_gs of neo-ester homopolymers are a consequence of the chain lengths and degree of branching within the various isomer mixtures. The broad range of T_gs available within the class of neo-monomers becomes very important in addressing the requirements of disparate coatings applications with a common need for water resistance.

WATER RESISTANCE

As noted in the introduction, one of the chief requirements of protective coatings is their ability to confer water resistance to painted surfaces. The concept of hydrophobicity is easily understood but not so easily measured reliably, and numerous tests have been devised to estimate the water sensitivity/water resistance of materials. Hydrolytic stability measurements, as discussed in the last section, are related to water resistance because the process begins with water swelling which permits the entry of hydroxyl ions to attack the carbonyl group. Water absorption and permeability tests, as well as blush tests, are also indications of water sensitivity. Likewise, efflorescence resistance and scrub resistance must be related to water uptake, among other factors. Finally, corrosion tests indicate the resistance of a coating to permeation of water and/or oxygen to form rust at a steel surface.

In addition to reliable experimental measurement of water sensitivity, it would be beneficial to be able to predict the water sensitivity of polymeric materials based on composition. A logical idea would be to assume that the water solubility of monomer segments might also serve to indicate the relative contribution of each component to water sensitivity. *Table* 2 lists the solubilities of selected monomers in water. As expected, most of the neo-monomers exhibit much lower solubilities than the other monomers, an exception being the low solubility of 2-ethylhexyl acrylate. Another approach to quantifying water sensitivity involves the use of solubility parameters to characterize the hydrophilic/hydrophobic

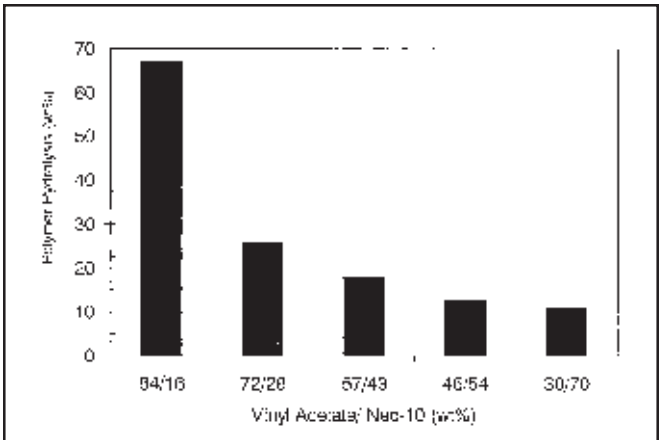


Figure 1—Hydrolysis of VAc/neo-10 latexes after 24 hr in 1.0 N KOH.

balance of copolymers based on contributions of the individual components. A further approach attempts to relate the oxygen content of materials to their hydrophilic/hydrophobic nature assuming oxygen to be the dominant polar component. Finally, the surface properties of polymer films, as measured for example by contact angles, give an indication of their surface energy and, therefore, information regarding the hydrophilic/hydrophobic nature of the material. The next step is to relate these approaches to experimental results using some of the tests mentioned previously.

NEO-VINYL COPOLYMERS

With the exception of the U.S., concrete has taken the place of wood as the prime building material in most of the world so that coatings for cementitious substrates are in great demand. One of the most useful features of branched vinyl esters is their resistance to hydrolysis, a valuable property for coatings on high pH substrates such as cement and new cement composites which are beginning to replace wood and hardboard house siding. Alkaline hydrolysis of a vinyl-acrylic latex can be measured by exposing the latex to 1N KOH for one or two days and then determining the amount of acetic acid produced.[3] The results in *Figure* 1 show that hydrolysis is greatly reduced by the introduction of neo-10 into the copolymer. The latexes employed in this series were prepared at 65°C using a redox couple as described previously.[4] Colloid stabilization was provided by a mixed protective colloid, anionic/nonionic surfactant combination, and hydrolysis determined by conductometric titration. Hydrolytic stability can be explained by a neighboring group steric effect. It has long been known that in the case of simple esters, such as ethyl acetate, substitution of methyl groups on the carbon adjacent to the acid carbonyl results in a dramatic reduction in the relative hydrolysis rate.[5] Similarly, the branched structure next to the carbonyl carbon provides strong resistance to alkali attack of branched esters themselves. In addition, the bulky nature of the branches apparently serves to protect the neighboring vinyl acetate segments.

Oxygen Content

Assuming oxygen to be the most polar constituent of most polymer compositions, oxygen content has been used with some success to predict the hydrolytic stability of vinyl copolymers.[6] The oxygen content is simply the weight fraction of oxygen based on the formula weight of the composition. *Table* 3 lists oxygen contents for a selected group of monomers. The branched esters have noticeably lower values compared with those for other monomer types. Of course, this approach does not apply to materials which contain no oxygen, for which we must rely on other indicators. Note that several monomers containing no oxygen (acrylonitrile, ethylene, and vinyl chloride) possess appreciable water solubility. In *Table* 4, the hydrolysis results shown in *Figure* 1 are listed with the oxygen content of each composition. Hydrolysis decreases with oxygen content but not as abruptly as in *Figure* 1. It appears that the VAc is adequately protected at a mole ratio of 2/1 VAc/neo-10.

Not all branched esters afford equal protection, however. The relative effectiveness of different branched esters in retarding hydrolysis is shown in *Table* 5. Each polymer was prepared at a constant 2:1 molar ratio of VAc to branched ester: neo-5, neo-9, neo-10, and V2EH. These results show that the length of the branches on the neo carbon of the ester is important in providing protection to the neighboring vinyl acetate units. Apparently, neo-5 is too small, whereas the longer chains of the other three monomers provide adequate shielding of the adjacent carbonyls from hydrolytic attack.[6] It is this "umbrella" effect which makes the branched ester monomers so attractive in the preparation of vinyl copolymers with excellent hydrolytic stability. *Table* 6 shows the alkaline stability of copolymers containing 70 wt% VAc reacted with various flexibilizing monomers: BA, 2-EHA,V2EH and neo-10. The BA provides poor protection for VAc and 2-EHA provides even worse protection even though the oxygen content of 2-EHA is less than that of V2EH. The answer to this puzzle is related to monomer sequence distribution.

Besides being itself resistant to hydrolytic attack and having sufficiently hydrophobic side chains to provide an effective protection for adjacent vinyl acetate moieties, a successful stabilizing co-monomer must also be positioned along the polymer chain in a relatively uniform manner in order to maximize its effect. Reactivity ratios can be used to estimate the tendency of two monomers to react in a random or blocky manner. Randomness is predicted when the reactivity ratios are close to unity, i.e., both monomers will have equal reactivity to a growing chain end regardless of its identity. *Table* 7 lists the reactivity ratios for vinyl acetate with a variety of comonomers. Since all the vinyl monomers have the same reactive group, it should not be surprising that their reactivity ratios predict random copolymerization with each other. The large differences in reactivity ratios of the acrylate monomers with vinyl acetate predict a high tendency to form blocky runs. Butyl acrylate, for instance, is effective in providing flexibility to VAc but contributes little to the alkaline stability of vinyl-acrylic copolymers.

Acrylic monomers, however, can be used along with BVEs to prepare a variety of vinyl-based binders for exterior, as well as interior, applications having excellent cost/performance.[4]

Conclusions from alkaline hydrolysis studies indicate that an effective co-monomer for VAc must:

(1) itself be resistant to alkali attack (branched structure);

(2) react with VAc randomly to interrupt the VAc sequences (reactivity ratios close to unity); and

(3) possess hydrophobic branches long enough to provide protection to neighboring VAc segments (umbrella effect).

The inherent hydrophobicity of long-chain branched vinyl esters turns out to be one of their most important

Table 3—Oxygen Content of Selected Monomers

Monomer	Formula	Total Mass	Oxygen Content, wt%
VAc	$C_4H_6O_2$	86.1	37.2
MMA	$C_5H_8O_2$	100.1	32.0
BA	$C_7H_{12}O_2$	128.2	25.0
Neo-5	$C_7H_{12}O_2$	128.2	25.0
V2EH	$C_{10}H_{18}O_2$	170.3	18.8
Neo-9	$C_{11}H_{20}O_2$	184.3	17.4
2-EHA	$C_{11}H_{20}O_2$	184.3	17.4
Neo-10	$C_{12}H_{22}O_2$	198.3	16.1
Neo-11	$C_{13}H_{24}O_2$	212.3	15.1
Neo-12	$C_{14}H_{26}O_2$	226.4	14.1

Table 4—Hydrolysis and Oxygen Content for VAc/Neo-10 Copolymers Following Exposure to High pH

VAc/neo-10 (Mole Ratio)	VAc/neo-10 (wt%)	Hydrolysis* (wt%)	Oxygen Content (wt%)
12/ 1	84 / 16	67	34
6 / 1	72 / 28	26	31
3 / 1	57 / 43	18	28
2 / 1	46 / 54	13	26
1 / 1	30 / 70	11	23

*Exposure to 1N KOH for 24 hr at RT.

Table 5—Hydrolysis of Vinyl Acetate Copolymers with Vinyl Acetate/Comonomer Molar Ratio = 2 / 1

Co-monomer	Polymer Oxygen, wt%	Polymer Hydrolysis,* wt%
Neo-5	32.0	26
Neo-10	25.9	15
Neo-9	27.0	14
V2EH	28.0	13

* Latexes exposed to 1N KOH for 24 hr at RT.

Table 6—Hydrolysis of Copolymers Containing 70 wt% Vinyl Acetate

Comonomer (30%)	Polymer Oxygen, wt%	Polymer Hydrolysis,* wt%
BA	33.5	80
2-EHA	31.3	94
V2EH	31.7	23
Neo-10	30.8	24

* Latexes exposed to 1N KOH for 24 hr at RT.

properties, but all three factors appear to be operating in conjunction to enhance the hydrolytic stability of VAc copolymers.

In order to determine the ease with which water swells neo-vinyl films, a series of VAc/neo-10 copolymers were prepared with neo-10 concentrations from 10 to 60% by weight. Free films were prepared by putting the test latexes in a Teflon mold and drying for five days at 120°C to get a film about 5 mils thick. Weighed strips of the films were immersed in water at room temperature for varying lengths of time, removed from the water bath, blotted dry, and then weighed again. The gain in weight is shown in *Figure* 2 as a function of immersion time for the different compositions denoted by their oxygen contents. The correlation with oxygen content is clear: water uptake is accelerated with increased oxygen content.

Blush resistance is another test of water sensitivity and happens to be more sensitive than the water absorption test. In this method, loss of film clarity is determined by measuring the color change in films on a black background after immersion in water at room temperature. Films at 20 mil thickness were prepared on clear glass plates, dried for five days at 120°C and then immersed in water for one hour. After removal from the water bath, the films were blotted dry and the glass plates were placed on a black background. Color changes were measured using a BYK Gardner colorimeter with illumination set at D65/10. The color difference index (delta E) between the black area and the film was taken as a measure of the blush. The larger the delta E, the greater the loss of film clarity. Blushing (water whitening) is illustrated in *Figure* 3 for the same series of films used in *Figure* 2. These results show that hydrophobicity can have a positive effect on blush resistance. The tolerance for a given blush level comes from the intended application.

Scrub resistance is a common test method used to evaluate the performance of coatings for interior applications. A series of paints was made from 19 latexes prepared within a statistical design involving combinations of four monomers, butyl acrylate, 2-ethylhexyl acrylate and neo-10, with the VAc concentration set at 70 wt%.[8] Scrub resistance was measured according to ASTM D 2486 and is expressed as scrub cycles to failure. In *Figure* 4, the results are presented in decreasing order of scrub resistance for a 50% PVC paint formulation. The correlation with oxygen content is clear although not dominant. No cor-

Table 7—Calculated Monomer Reactivity Ratios for Copolymerization with Vinyl Acetate (m_1)

Monomer 2 (m_2)	r_1	r_2
Acrylic acid	0.02	20.64
Butyl acrylate	0.05	5.89
2-Ethylhexyl acrylate	0.04	7.5
Ethylene	1.00	1.00
Methyl methacrylate	0.03	22.21
Styrene	0.03	24.18
Vinyl chloride	0.60	1.40
Vinyl neo-decanoate	0.99	0.92
Vinyl neo-nonanoate	0.93	0.90
Vinyl neo-pentanoate	0.79	0.96
Vinyl propionate	1.06	0.76
Vinyl 2-Ethylhexanoate*	1.20	1.90

* Measured value.[7]

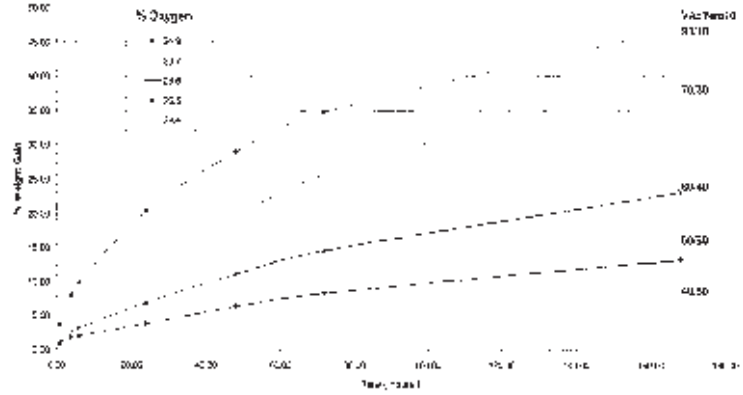


Figure 2—Water absorption of VAc/neo-10 latexes with varying oxygen contents.

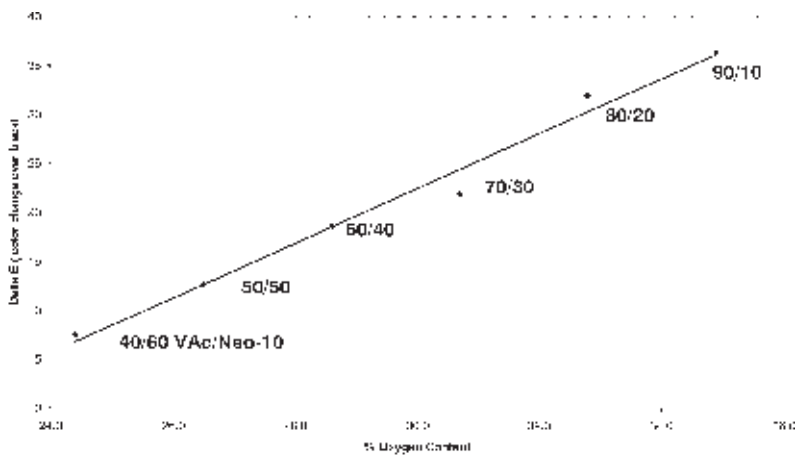


Figure 3—Blush resistance of neo-vinyl latexes with varying oxygen contents.

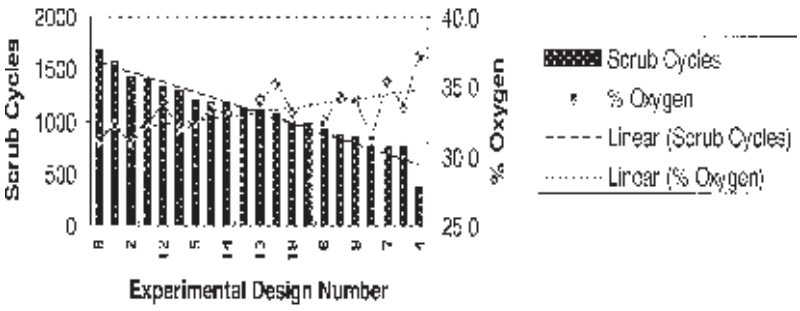


Figure 4—Scrub resistance of neo-vinyl latexes in statistical design with varying oxygen contents.

relation, positive or negative, was observed at 75% PVC (above critical). Many factors contribute to scrub resistance. Effective film formation is probably the most important,[9] and polymer molecular weight also contributes to toughness. Surface active components and particle stabilizers are also important and will be discussed later. The particular scrub test used here included an abrasive soap so that the test can be considered a test of film toughness as well as water resistance, but a minimization of swelling should promote better film integrity in water.

In the limited examples described, the oxygen content of polymeric films offers a way to estimate trends in water resistance based on composition. The results presented here show that, compared to traditional vinyl-acrylics, neo-vinyl latexes have significantly improved properties related to water resistance and alkali stability. These copolymers also exhibit excellent exterior durability due to their toughness and transparency to ultraviolet radiation. With more than five years of exterior exposure history, paints based on neo-vinyl binders have been rated for chalking, color fade, and erosion and compare quite favorably with other polymer types.[10]

Solubility Parameters

As developed by Hildebrand, the concept of solubility parameters is based on estimating the internal energy of solvents and solutes and comparing the values to predict solvation.[11,12] This approach assumes that molecules with similar internal energy (cohesive energy density) will have the greatest interactions for each other. For this reason, solubility parameters can also be called "interaction parameters." Hildebrand developed equation (1) for the heat of mixing of two materials, where ϕ is the volume fraction, χ is the mole fraction, V the molar volume, and δ the solubility parameter of a polymer, p, and solvent, s:

$$\Delta H \cong \phi_p\phi_s(\chi_p V_p + \chi_s V_s)(\delta_p - \delta_s)^2 \quad (1)$$

Dissolution is facilitated when the heat of mixing is minimized, and this situation occurs when the two interaction parameters are similar. The old expression "like dissolves like" is vindicated as well. On the other hand, when immiscibility is the desired result, as with increasing the hydrophobicity of a polymer film to promote water resistance, the aim must be to maximize the difference in the interaction parameters.

The cohesive energy density postulated by Hildebrand is now generally regarded as emanating from the aggregate effect of three component quantities: (a) nonpolar interactions (dispersion forces) ΔE_d, (b) polar interactions ΔE_p, and (c) hydrogen bonding forces ΔE_h. These constituent quantities are related to the total solubility parameter as follows:

$$\Delta E_{total}/V = \delta_{total}^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2)$$

where δ_d (dispersion component) $= (\Delta E_d/V)^{1/2}$
δ_p (polar component) $= (\Delta E_p/V)^{1/2}$
δ_h (hydrogen-bonding component) $= (\Delta E_h/V)^{1/2}$

The need for a refinement of Hildebrand's general theory is evident from the widely differing solvency characteristics exhibited by solvents with similar total solubility parameters as illustrated with the solvents listed in *Table* 8. The true nature of solvency is thus established by matching the component or partial solubility parameters of the solvent and the solute.

The solubility parameters of numerous solvents can be found in the literature.[14] Except for those materials for which solubility parameters are not readily available, there are at least three routes for obtaining the total solubility parameter. It can be determined (1) from physical properties such as boiling point,[12] vapor pressure,[14] or surface tension,[12,15] which can be related to the energy of vaporization, (2) from the chemical structure utilizing Small's Molar Attraction Constants,[14,16] or (3) from experiment by matching the solubility nature of the material against the solubilities of other materials of known solubility parameter.

The δ_{total} values calculated for the monomers listed in *Table* 9, were derived from boiling point data utilizing the empirical relationship given in the following[12]:

$$\delta_{total} = [(23.7T_{boiling} + 0.020T^2_{boiling} - 3542)/V]^{1/2} \quad (3)$$

The partial solubility parameters were calculated utilizing chemical group contribution constants.[16]

Table 8—Component Solubility Parameters (δ_d, δ_p, δ_h) for Three Solvents with Similar Total Solubility Parameters (δ_{total})[13]

Solvent	δ_{total}	Solubility Parameter $(cal/cm^3)^{1/2}$ δ_d	δ_p	δ_h
Carbon disulfide	10.0	10.0	0.0	0.0
Nitrobenzene	10.7	9.0	5.0	3.0
2-Ethylhexanol	9.9	7.8	1.0	6.0

An improvement on this approach would be to calculate the partial solubility parameters for polymers instead of the constituent monomers, but that requires reliable values for the polymer densities.

The relative solubility of a given monomer (polymer) in water can now be calculated utilizing vector algebra, with the length of the vector ($\Delta\delta_{water}$) connecting the partial solubility parameters of the solvent (water), and the solute (polymer) being an absolute measurement of solubility.[17] The greater the separation of the polymer from water, the more hydrophobic is the polymer, so that $\Delta\delta_{water}$ may be taken as an indication of water resistance. The utility of the interaction/solubility parameter approach to predicting water sensitivity is demonstrated in *Figure* 5, in which hydrolytic stability is shown for the series of VAc/neo-10 copolymers illustrated previously in *Figure* 1 (and *Table* 4). The same trend is observed, i.e., alkaline hydrolysis decreases as the hydrophobic character of the polymer increases (larger $\Delta\delta_{water}$). Given the harsh nature of the alkaline hydrolysis test, these results suggest that a value of $\Delta\delta_{water}$ above about 18.25 $(cal/cm^3)^{1/2}$ and an oxygen content of about 28% should yield adequate stability in neo-vinyl coatings on alkaline surfaces.[10,18] The relationship between oxygen content and $\Delta\delta_{water}$ will be discussed later.

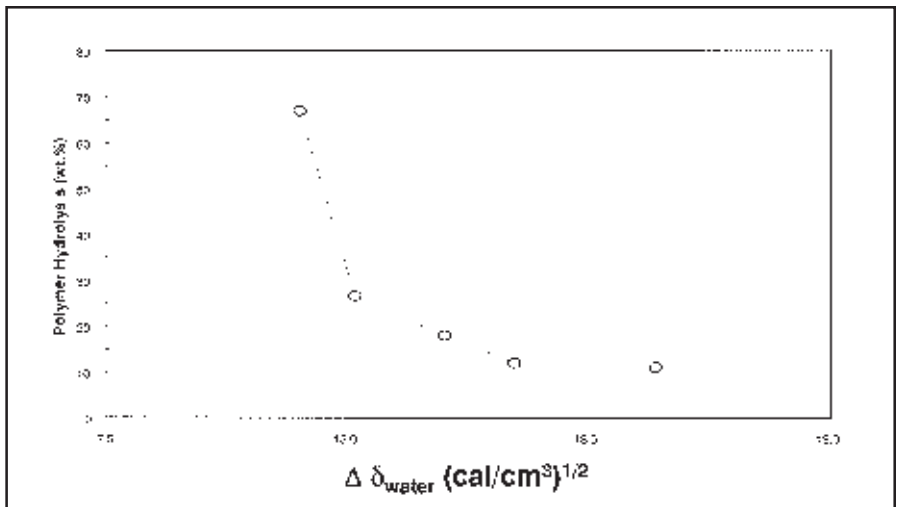


Figure 5—Hydrolytic stability of neo-vinyl latexes from Figure 1 and the effect of polymer hydrophobicity expressed as $\Delta\delta_{water}$.

NEO-ACRYLIC COPOLYMERS

One step toward reducing the hydrophilicity in vinyl copolymers is the elimination of VAc itself. Although vinyl-acrylic copolymers possess excellent resistance to discoloration in sunlight, and neo-vinyls possess sufficient water resistance for most exterior as well as interior applications, replacement of the VAc with acrylic monomers does lead to increased hydrophobicity. This change moves away from the great economic incentive for using VAc, but it also offers the possibility of designing polymers with exceptional water resistance for more demanding applications.

The term neo-acrylic describes a copolymer of vinyl neo esters with acrylate and methacrylate monomers. Given the relatively low T_g of neo-10 (–3°C), a combination with MMA serves to adjust the T_g and the minimum filming temperature, to yield copolymers with useful properties for a variety of coatings applications. Butyl acrylate and/or 2-ethylhexyl acrylate (2EHA) can also be used to vary the T_g while maintaining reasonable hydrophobicity. Since methyl methacrylate is now the most hydrophilic part of the terpolymer, there is an incentive to reduce its concentration if possible. Neo-9, with a T_g of 60°C becomes the monomer of choice, although cost is still an issue at present.

The reactivities of acrylic monomers, as indicated by the values in *Table* 7, are not very favorable for the

Table 9—Solubility Parameters for Selected Monomers

Monomer	FW ($gmol^{-1}$)	Density ($g\ cm^{-3}$)	V ($cm^3\ mol^{-1}$)	Solubility Parameter $(cal/cm^3)^{1/2}$				$\Delta\delta_{water}$
				δ_{total}*	δ_d	δ_p	δ_h	$(cal/cm^3)^{1/2}$
Water	18.10	1.000	18.1	23.40	7.60	7.80	20.70	0.00
Styrene	104.15	0.909	114.6	9.28	9.14	0.50	1.50	20.61
Vinyl chloride	62.50	0.911	68.6	7.60	6.10	4.37	1.21	19.85
Neo-11	212.31	0.870	244.0	7.48	7.06	1.02	2.26	19.65
Neo-10	198.31	0.882	224.8	7.56	7.09	1.11	2.36	19.53
Neo-9	184.31	0.887	207.8	7.55	7.04	1.20	2.45	19.41
2-Ethylhexyl acrylate	170.25	0.885	192.4	8.18	7.67	1.30	2.55	19.28
Neo-5	128.17	0.873	146.8	7.63	6.84	1.70	2.92	18.81
Butyl acrylate	128.17	0.894	143.4	8.30	7.55	1.74	2.95	18.75
Ethyl acrylate	100.12	0.924	108.4	8.62	7.58	2.31	3.40	18.15
Methyl methacrylate	100.12	0.936	107.0	8.69	7.65	2.34	3.42	18.12
Vinyl acetate	86.09	0.934	92.2	8.74	7.45	2.71	3.68	17.76
Methyl acrylate	86.09	0.956	90.1	9.02	7.73	2.78	3.73	17.70
Acrylonitrile	53.06	0.806	65.8	10.46	5.20	8.50	3.20	17.68
Methacrylic acid	86.09	1.015	84.8	11.18	9.26	2.59	5.69	15.97
Acrylic acid	72.06	1.051	68.6	11.85	9.48	3.21	6.33	15.20

*Calculated from boiling points.

Table 10—Critical Surface Tension and Contact Angles of Different Polymer Types

Polymer	Water Contact Angle (degrees)	Critical Surface Tension, γ_c (dynes / cm)
Vinyl-acrylic	15	—
Neo-vinyl	41	31
Acrylic	69	28
Neo-acrylic	80	25
Neo-10	80	24
Styrene-acrylic	82	25

production of random copolymers with the neo esters, and various monomer addition profiles can also be used to counteract compositional drift.[19] However, the effect of inhomogeneity is much less of a problem compared with preparation of neo-vinyls since the major monomer is now hydrophobic, and acrylic-rich domains would be expected to be dispersed in the neo-matrix. Another advantage of replacing VAc with acrylic co-monomers is that particle stabilization can be achieved with conventional surfactants rather than protective colloids so that total hydrophilicity can be further reduced. In general, a small amount of a functional monomer, such as acrylic or methacrylic acid, is used to improve stability and adhesion to various substrates. One consequence of these approaches to particle stabilization is that small particle sizes are easily obtained compared to the case of the neo-vinyls which are usually stabilized with protective colloids. Smaller particle size generally leads to higher pigment binding power and also improves penetration of latex particles into porous substrates. The resulting neo-acrylic copolymers represent a significant improvement in water resistance, when compared with all-acrylic and vinyl-acrylic types, and show excellent performance as vehicles for industrial coatings, clear and pigmented stains for wood, and in coatings for corrosion control.[20]

Contact Angles

There is no direct method for measuring the surface energy of solids because of elastic and viscous constraints. However, wettability measurements employing liquids of different polarity can serve as a convenient indirect method to estimate the surface energy of a solid as well as the nature of the interactions between two materials. In the method of Zisman,[21, 22] contact angles are measured for liquid drops applied to the surface of interest for a series of selected liquids. The cosine of the contact angle (θ) is plotted against the liquid surface tension, and the intersection of the resulting curve with the coordinate, where $\theta = 0$ (complete wetting) and cosine $\theta = 1$, gives the critical surface tension (γc) for wetting the surface. The critical surface tension is not the total surface energy of the solid but is related to it, and various approaches have been proposed to quantify the relationship. For the purpose of ranking the relative hydrophobicity of different coatings, test liquids should contain both polar and non-polar components.

Table 10 presents a listing of critical surface tensions for various polymer types of interest in coatings applications. Test liquids used in these experiments (with their respective surface tensions in dynes/cm at room temperature) were: water (γ = 72.5); formamide (γ = 58.3); ethylene glycol (γ=48.3); and tricresyl phosphate (γ = 40.8). The observed critical surface tensions decrease with the expected hydrophobicity of the films, as indicated also by the oxygen content and by $\Delta\delta_{water}$. This agreement may be surprising given the non-trivial problems of film preparation, the presence of surface active ingredients, and the probable variations in latex particle morphologies. While contact angles are easy to measure and provide useful information regarding surface polarity, they do not necessarily reflect the properties of the bulk material which are more important in preventing water absorption and permeation.

WATER RESISTANCE OF NEO-ACRYLIC COPOLYMERS

Studies carried out by Shell researchers serve to illustrate the effect of hydrophobicity on the water resistance of neo-acrylic copolymers.[20,23] Two sets of polymers were prepared with constant T_g of 20°C using a colloid-free recipe and including one percent acrylic acid as a stabilizing monomer. Water resistance was monitored by measuring water absorption by weight after immersion of clear films in water for 14 days at room temperature. One series used neo-10 and the second used neo-9, in increments of 10% from 0 to 70% by weight. BA and MMA were employed as co-monomers to keep the T_g of the terpolymers constant at 20°C. The results, recast to show the effect of oxygen content, are shown in *Figure* 6. In both cases, water absorption increased with increasing oxygen content (decreasing neo-monomer concentration). Moreover, neo-9 was somewhat more effective in providing resistance to swelling, especially above 26% oxygen (30 wt% VAc). These results indicate that incremental replacement of MMA was effective in improving water resistance, and that the best water resistance was

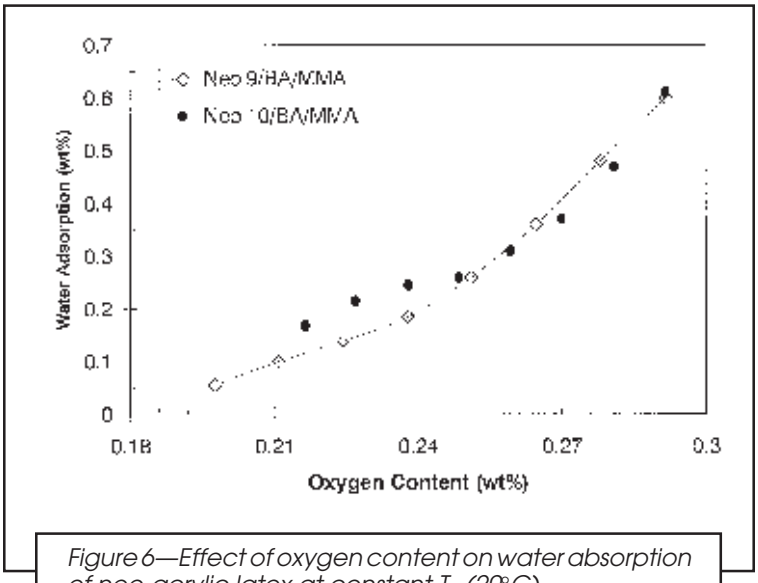


Figure 6—Effect of oxygen content on water absorption of neo-acrylic latex at constant T_g (20°C).

obtained by increasing film hydrophobicity as measured by oxygen content.

An analysis of these results was also carried out using the solubility parameter approach. In *Figure* 7, water absorption values for the two series of eight terpolymers are plotted against $\Delta\delta_{water}$. Assuming the differences in water absorption between the two series to be significant, the same conclusions can be drawn as in the oxygen content analysis: as $\Delta\delta_{water}$ increases (polymers richer in the neo-monomers) the water absorption decreases. *Figure* 8 illustrates an example of how hydrophobicity differences, as measured by $\Delta\delta_{water}$ at equal T_g, can be represented for two copolymers of BA, one with neo-9 and the other with MMA. In this exercise a desired T_g can be obtained in two ways with BA as the starting monomer. It is clear that the copolymer containing neo-9 will have the greater value of $\Delta\delta_{water}$ and should have the better water resistance. One advantage of using interaction parameters for assessing water resistance, compared to the oxygen content approach, is the ability to characterize materials containing no oxygen.

The relationship between $\Delta\delta_{water}$ and oxygen content is shown in *Figure* 9 for four series of neo copolymers, the first for neo-9 and neo-10 combinations with VAc, and the second for neo-acrylic combinations of neo-9 and neo-10 with MMA/BA. In this plot there is excellent agreement between the two approaches for estimating polymer hydrophilicity. The close agreement came as a surprise since the calculation of oxygen content does not differentiate among various oxygen types, whereas solubility parameters include structural differences, and these differences were thought to play a role in the water sensitivity of polymer films.

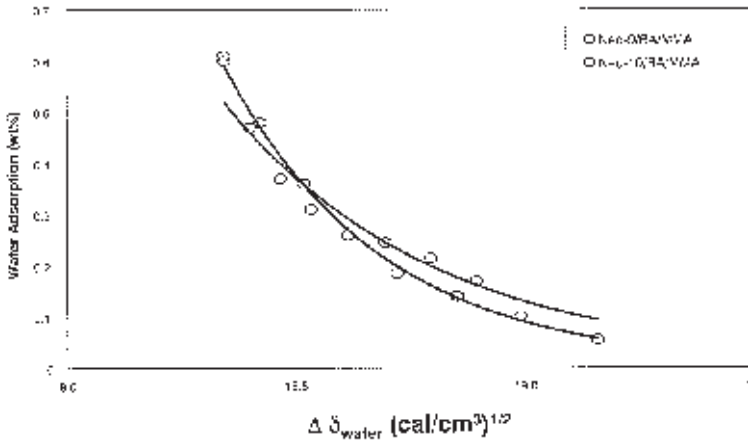


Figure 7—Effect of polymer hydrophobicity on water absorption of neo-acrylic latexes at constant T_g (20°C).

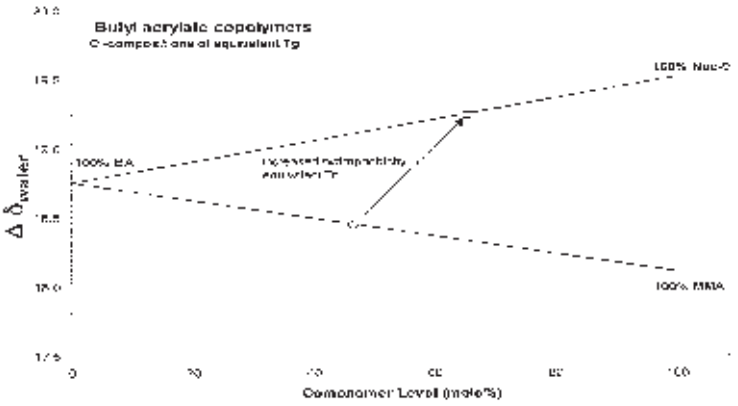


Figure 8—Effect of copolymer composition on hydrophobicity at equivalent T_g.

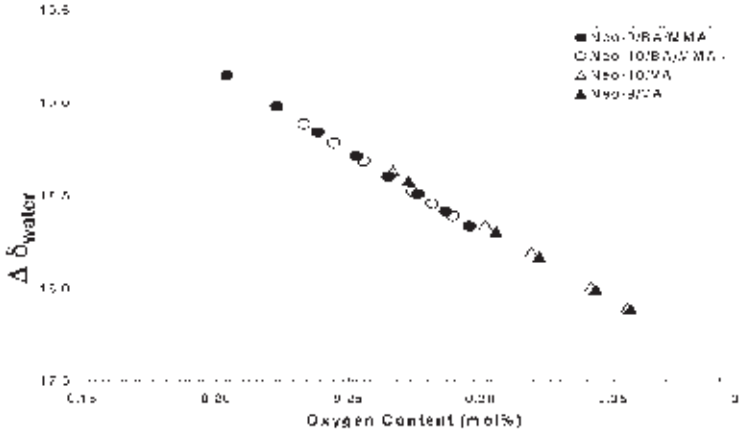


Figure 9—Relationship of $\Delta\delta_{water}$ and oxygen content of neo-vinyl and neo-acrylic copolymers.

APPLICATIONS

Architectural Latexes

The water resistance of developmental latexes featuring five different polymer types have been examined for water absorption and blushing

after immersion in water. The test methods used were the same as those described earlier. The polymers included all-acrylic, styrene-acrylic, vinyl-acrylic, neo-vinyl and neo-acrylic latexes. The water absorption results in *Figure* 10 show that the neo-acrylic (containing neo-10 monomer) and the styrene-acrylic had the best water resistance by this test, followed by the all-acrylic, neo-vinyl, and the vinyl-acrylic. While styrene-acrylic copolymers perform well in many water resistance tests, they suffer from poor exterior durability related to UV degradation and color changes.[24]

The blush results in *Figure* 11 show that most film whitening occurred within the first few minutes of immersion for the vinyl-acrylic, the neo-vinyl and the all-acrylic. Moreover, a somewhat different trend in blush resistance was observed, with the neo-acrylic and styrene-acrylic exhibiting very good blush resistance and the acrylic, neo-vinyl and vinyl-acrylic giving significantly poorer performance. It must be remembered that a blush or water spot test is a measure of refractive index variations and may be more related to the hydrophilic uniformity of a sample than the total water sensitivity. While quite useful in developing blush-resistant coatings, the blush test may not probe the bulk properties of the film. Consequently, blush results must be interpreted carefully with respect to the physical processes taking place in the test. Nevertheless, neo-acrylic copolymers have achieved excellent results in clear and pigmented exterior coatings for wood[25] where water and blush resistances are of prime importance.

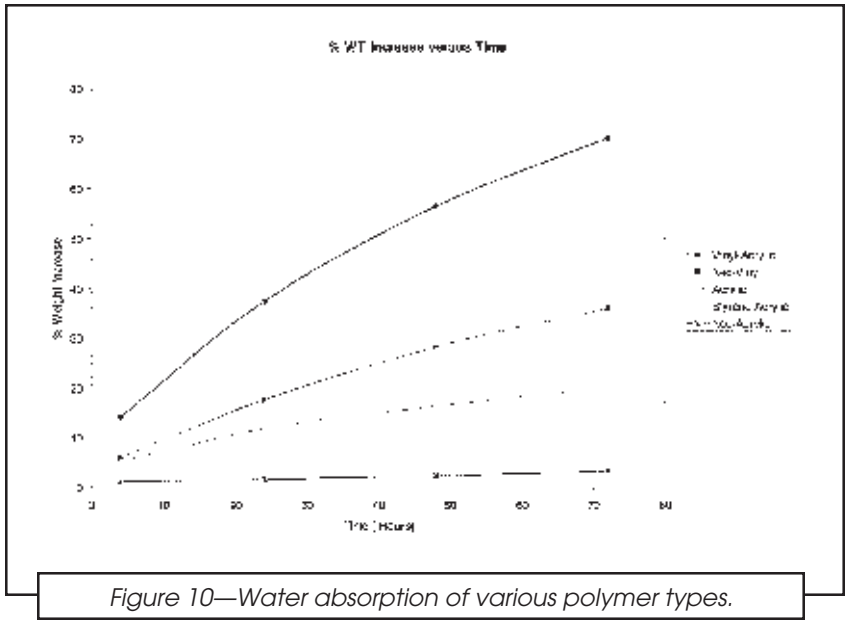


Figure 10—Water absorption of various polymer types.

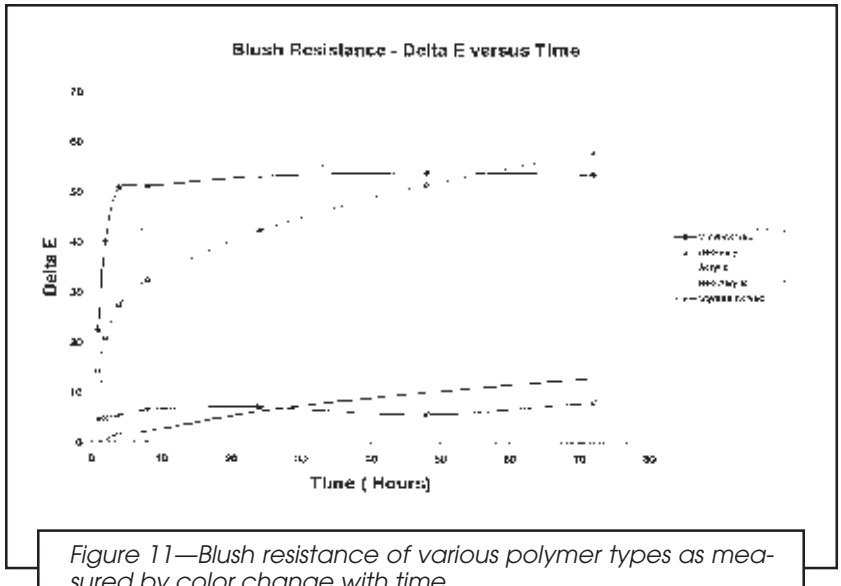


Figure 11—Blush resistance of various polymer types as measured by color change with time.

Corrosion Control

A particularly difficult test of water resistance is the protection of bare steel from corrosive environments. The essential requirements for an effective coating include the suppression of oxygen and/or water permeation through the film to the steel surface. The absence of water serves to restrict the migration of ions so that a high resistance is imposed on the circuit of the corrosion cell. Failure can occur when water enters the coating by absorption or by migration through capillaries or micropores, aided by osmotic diffusion in response to strong localized interactions at hydrophilic sites. Along with water resistance, film formation again plays an important role in the success of the protective coating.

The water resistance of neo-acrylic latexes designed for corrosion resistant primers has been determined and compared with a leading commercial styrene-acrylic latex advertised for this purpose. Absorption of water by free films was measured gravimetrically at room temperature after a filming time of seven days and exposed to water vapor or liquid water for 500 hr. Both latexes contained sodium nitrite to inhibit flash rusting. The results of these measurements are presented in *Table* 11. In both modes of contact with water, the neo-acrylic exhibited better water resistance than the styrene-acrylic, with a very large margin observed in the case of contact with liquid water. Contact angles of water droplets were also measured at several locations on the dried films. The results averaged 84° for the neo-acrylic and 61° for the styrene-acrylic, clear evidence that the surface of the neo-acrylic film was more hydrophobic.

The simplest of the various corrosion tests is a salt spray procedure using a 5% NaCl solution and carried out at 35°C (ASTM B 117-57T). The coating to be tested is applied to obtain a final dry thickness of 2.5 mils (clear) or 3.5 mils (pigmented) on cold-rolled steel, dried for seven days, scribed through the film into the steel substrate, and exposed in the spray chamber for varying lengths of time. Three aspects

Table 11—Absorption of Water by Copolymer Films

	Water Absorption (% by weight)	
Exposed to*	Neo-Vinyl	Styrene-Acrylic
Vapor	2.3	6.9
Liquid	10	80

* 500 hr at RT.

of failure can be measured: (1) the extent of rusting along the scribe line (scribe), (2) the extent of rust formation on the face of the panel away from the scribe (field), and (3) the extent of film delamination and discoloration in a direction normal to the scribe line (blush). Results of these measurements are given in *Table* 12 for clear and pigmented coatings after exposure times of 1000 hr and 456 hr, respectively. In the case of the clear films, the scribe and blush results were similar, but the neo-acrylic polymer performed much better than the styrene-acrylic in the field area. With careful selection of surfactants, and the use of inhibitive pigments, the performance gap narrowed for the pigmented coatings. In a more practical test of corrosion protection, three commercial latexes designed for primer applications were tested in a marine environment. The three paints were formulated with inhibitive pigments (Halox SZP391) at 24% PVC and applied on cold-rolled steel at a thickness of 2.5 mils. The relative corrosion resistance after two years is illustrated in *Figure* 12. The most obvious advantage of the neo-acrylic formulation is the much better field protection in agreement with the laboratory salt spray results. These results also correlate with the water absorption results in *Table* 11 and serve to illustrate the advantages of hydrophobicity in reducing the permeation of water through protective coatings.

THE HYDROPHILIC BUDGET

It is important to remember that the water resistance of a coating is a function not only of the nature of the polymeric binder but of the other components of the formulation as well. Rarely is the polymer the sole component. In emulsion polymerization, recipes may call for surfactants for emulsification, stabilization and particle generation, protective colloids for stabilization and rheology control, initiators for radical production, defoamers for foam control, and buffers for pH control. Add to these items the numerous components in pigmented systems and the list of materials becomes long indeed. The concept of the "hydrophilic budget" arises from the fact that all the components of a formulation contribute in some degree to the hydrophilicity of the coating. The "hydrophilic budget" is defined as the total hydrophilicity of a film or coating above which the coating will fail a specific water resistance test. While this concept may promote a mental tally of factors to consider when putting together a formulation for a given end use, the challenge is to devise ways of measuring or estimating the hydrophilic contribution of individual components.

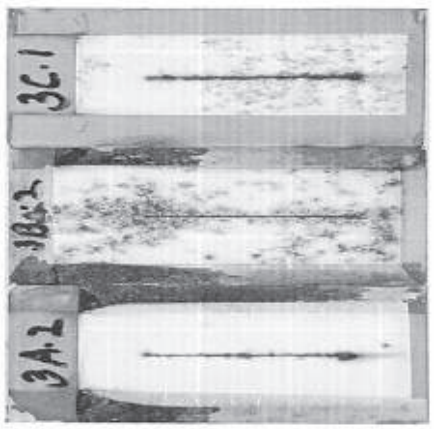


Figure 12—Corrosion resistant primers based on commercial latex formulation, after two years' exposure at the Kure Beach Marine Exposure Site, North Carolina.

Several attempts to quantify material properties (water solubility, oxygen content, interaction parameters and contact angles) have been discussed here and related to common water resistance tests used in our industry; but not all tests measure the same aspect of water sensitivity. Nevertheless, a systematic attempt to rate, or index, all the components of coatings formulations according to hydrophilicity, and perhaps compatibility, would be a valuable addition to formulation technology.

One problem inherent in the hydrophilic budget approach is that the important contribution of film formation is not included. The subject of particle coalescence and film formation in waterborne coatings is a subject of much current interest and investigation.[26] Since the structural integrity, as well as the compositional nature, of a coating has a major influence on the permeation and swelling by liquid water and vapor, the factors affecting film formation will play a role in determining the level of water resistance to be expected. These factors, such as particle size, T_g, ambient temperature, nature of the substrate, presence of filming aids and other additives, coating solids and PVC, and numerous others, are beyond the scope of this argument. As far as water resistance is concerned, the assumption is that the binder, being a major part of the formulation and a critical part of the continuous barrier, should be as hydrophobic as possible in order to accommodate the more hydrophilic

Table 12—Corrosion Resistance of Clear and Pigmented Coatings on Cold-Rolled Steel

	Corrosion Resistance			
	Clear (2.5 mil), 1000 hr		Pigmented (3.5 mil), 456 hr	
Test	Neo-Acrylic	Styrene-Acrylic	Neo-Acrylic	Styrene-Acrylic
Scribe	8.0	7.5	9.5	8.5
Field	7.5	2	9.5	8.5
Blush	6.5	5.5	10	10

Salt Spray Test (ASTM B117-57T at 35°C); 10 Rating = no change.

components while still meeting the hydrophilic limit set by the intended application. The beneficial use of hydroplasticization, and other hydrophilic techniques employed to enhance stabilization and film formation, must be included in the budget.

CONCLUSIONS

Branched vinyl esters with long hydrophobic chains attached to the neo-carbon, adjacent to the carbonyl group, can be used to significantly improve the water resistance, hydrolytic stability, and coating performance of vinyl-acrylic and acrylic latexes in exterior and interior applications. In order to promote alkaline stability of VAc, an effective co-monomer must be resistant to alkaline attack and possess a hydrocarbon chain large enough to protect adjacent VAc moieties. In addition, the monomer must be able to interrupt VAc sequences along the copolymer chain. The neo 9-12 monomers fit these requirements very well. It appears that one such monomer unit can protect 2-3 VAc units. Branched vinyl esters can also be reacted with acrylic monomers to prepare high performance emulsion polymers for industrial and corrosion resistant applications. The benefits of hydrophobicity have been demonstrated in several common tests including alkaline hydrolysis, film swelling in water, scrub resistance, and corrosion protection on steel.

Three approaches have been explored in an effort to predict the water resistance of films. These include calculations of the oxygen content and the solubility parameter of the films given their compositions, and measurements of the critical surface tension of the films using contact angles. Contact angles represent a easy way to qualitatively assess the relative hydrophobicity of polymeric films, but calculations of oxygen content and $\Delta\delta_{water}$ offer a more quantitative estimate of hydrophilic/hydrophobic balance. These studies have led to a concept called "the hydrophilic budget" which has been proposed as a way of relating the hydrophobicity of coatings to their success in passing common coatings evaluations related to water resistance. The current challenge is to make the concept more practical.

Clearly, copolymers which have very low oxygen content over a wide T_g range would be of interest in developing new latexes for coatings having improved water resistance. The disadvantage of using very hydrophobic monomers in emulsion polymerization is the very low water solubility of the monomers themselves which results in slow monomer transport and low reactivity. There is also evidence of a curious inhibition in the preparation of neo homopolymers which is not well understood.[27] On the other hand, a process like miniemulsion polymerization, pioneered at Lehigh University,[28] does not require monomer transport. Sub-micron-size emulsion droplets are generated which permit polymerization within the droplets to produce polymer particles directly. In fact, low monomer solubility in water may facilitate the stabilization of the miniemulsion droplets to assist in polymerization. Advances in process chemistry and engineering are expected to aid in the further adoption of new monomer systems for the production of high performance polymers.

ACKNOWLEDGMENTS

Joseph J. Mattiello was a remarkable man whose impact on the coatings industry, and the Federation of Societies for Coatings Technology in particular, is felt even today. His life and contributions were reviewed by Robert F. Brady, Jr., in his 1999 Mattiello Memorial Lecture presented at the International Coatings Expo in Dallas.[29] One lasting contribution is the five-volume series, *Protective and Decorative Coatings,* which was edited by Mattiello and which became a standard reference on coatings for many years following its publication in the 1940s. In the preface to the third volume,[30] Mattiello wrote: "It is safe to say that few discoveries are the result of chance or shear inspiration. More often they are the result of chance plus a long course of study, training, and work. Each new discovery builds on the past, and new basic principles are developed from old ones, produced by the same labor which produced the old ones. The main stream of discovery has a perceptible continuity." It is this continuity which is promoted by technical sessions and education programs supported and organized by the FSCT and other scientific societies concerned with coatings and films.

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