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OF

Alkyd Latex Polymers

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Alkyd polymers provided as a latex are a recent and commercially viable alternative to the more traditional solutions in organic solvents. Replacing the organic solvent with water provides coatings that have exceptionally low volatile organic compounds (VOCs) while maintaining the traditional benefits of alkyds including high gloss, adhesion, and—as is the subject of this paper—very high pigment loading capacity. Reichhold has previously presented research describing the polymer design and coating formulation of alkyd latex direct-to-metal primers. In a continuation of that research, we explore the pigment binding capacity of alkyd latex polymer performance as measured by both wet-cup and dry-cup permeability and with electrical conductance. These techniques clearly define the critical point for several extender pigment combinations and are used to maximize corrosion and humidity resistance in metal primer formulations with a reduced pigment volume concentration (PVC) approaching 82%. In highly filled traffic paint formulations where the reduced PVC may reach 90%, these techniques are used to compare alkyd and acrylic latex polymers, with the data further demonstrating the exceptional pigment binding capacity of the alkyd.

BACKGROUND

In a seminal paper, Asbeck and Van Loo[1] described the importance of pigment volume concentration (PVC) on many of the performance aspects of coatings. These include color, gloss, and as studied in this work, corrosion and humidity resistance. While PVC is of fundamental importance, it is the ratio of coating PVC to the critical pigment volume concentration, PVC/CPVC,

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referred to as the reduced pigment volume concentration and denoted as λ, that is the parameter of most interest in highly filled films.[2,3] CPVC is directly related to the oil absorption of the pigments utilized in the coating and this relationship may be used to calculate an empirical CPVC.[4] The calculation is simple and with today's coatings software the value of λ may be displayed among the coating physical properties on the computer screen as the formulator considers variations in composition.

This empirical value is subject to some inherent error. Oil absorption values are determined for pigments dispersed at closest (tetrahedral) packing, while in paint films, pigment is packed in a random configuration that includes the more widely spaced cubic packing. Further, oil absorption is derived for individual pigments; the calculation cannot allow for packing of pigments of dissimilar size. With sufficient knowledge of the pigment particle size distribution a pigment packing factor can be calculated. However, obtaining this information can be problematic and the associated mathematics become cumbersome.[5,6] Finally, a spatula rub-up oil absorption determination (itself subject to considerable error) wets the particles with a thin film of low molecular weight linseed oil. In formulated coatings the spacing between pigments is influenced by the considerably higher molecular weight of synthetic polymers and/or latex particles. It is this aspect of pigment packing and its influence on PVC/CPVC that is a key difference between solution and traditional latex polymers.

As a general rule, the T_g and particle size of a vinyl, (meth) acrylic, styrene, or other emulsion polymer are determining factors in the film former's ability to allow close pigment packing. High T_g particles cannot deform readily to allow close pigment packing. Similarly, large latex particles do not allow for the pigment packing density of smaller particles. That these polymers are essentially

solid at room temperature is a key consideration in this lack of deformability. A binder index or latex binder efficiency factor[4] describes this relationship as CPVC actual/CPVC calculated. This index is always less than 1.0; values in the range of 0.70 are common for architectural lattices.

Alkyd latex polymers have a T_g of 0–4°C and a minimum film forming temperature at or below 1°C. These polymers are liquid at room temperature and build T_g and molecular weight post-application through auto-oxidation reactions with molecular oxygen. This liquid state allows considerable deformation in response to the osmotic pressures associated with film formation.

The literature is rife with methods to determine the CPVC for a given coating composition. Measurement of pore volume via very low angle microtome sampling and fluorescence microscopy is described by Wang et al.[7] Tensile strength measured on free films as well as changes in color and gloss are also possibilities, but each of these determinations requires considerable time and effort. An expedient and practical method is described by Asbeck that takes advantage of the porosity of films above CPVC and is preferred for this work.[8] This film porosity method is referred to as a salt-water spot test in this article. The CPVC is a function of the property being measured and thus the critical point for corrosion resistance may not be the same as the CPVC for fracture strength, hiding power, permeability or other parameters.[9]

EXPERIMENTAL

Two alkyd latex polymers were used for the majority of this work. Polymer A was specifically designed for use in direct-to-metal primers. Development of this polymer and the associated paint formulations was described previously.[10] The key performance attributes for Polymer A were wet adhesion to metal and stability in the presence of anticorrosive pigments. Polymer B was specifically

FORMULATION 1—Model Direct-to-Metal Paint

RAW MATERIAL	WEIGHT PERCENT
WATER	16.75
28% AMMONIA	0.12
PIGMENT DISPERSANT	1.39
SURFACTANT	0.26
DEFOAMER	0.17
RED IRON OXIDE	4.31
ANTICORROSIVE PIGMENT	4.31
TALC	4.31
CALCIUM CARBONATE	27.8
THIXOTROPIC SILICA	0.43
POLYMER A (55% NV WEIGHT)	28.72
COBALT DRIER	0.14
ZIRCONIUM DRIER	0.23
WATER	9.21
FLASH RUST INHIBITOR	0.29
ASSOCIATIVE THICKENER	1.37
DEFOAMER	0.19
NON-VOLATILE BY WEIGHT	58.3%
PVC	50.4%
λ	0.82
VOC, G/L	16.8

designed for road markings; its development was detailed by Dziczkowski at the American Coatings CONFERENCE in 2014.[11] A key performance attribute of Polymer B was sufficient shear stability to tolerate addition into a pigment grind and subsequent processing in high-speed dispersion equipment.

Polymer A was formulated as a metal primer as shown in the generic *Formulation 1*. Pigment substitutions were made on an oil-absorption basis to arrive at the desired λ value for each experimental series. Dispersant/surfactant levels were adjusted for each

FORMULATION 2—Model White Road Marking Paint

RAW MATERIAL	WEIGHT PERCENT
POLYMER B (51% NV BY WEIGHT)	31.37
WATER	4.06
PIGMENT DISPERSANT	0.60
DEFOAMER	0.36
TITANIUM DIOXIDE	7.20
CALCIUM CARBONATE	52.60
ATTAPULGITE CLAY	0.21
IRON DRIER	0.16
METHANOL	2.99
DEFOAMER	0.07
ADHESION PROMOTER	0.11
20% CELLULOSIC THICKENER	0.27
28% AMMONIA	TRACE
NON-VOLATILE BY WEIGHT	76.8%
NON-VOLATILE BY VOLUME	60.0%
PVC	60.7%
VOC, G/L	75.0
λ	0.85

formulation based on the total pigment surface area. Each formulation was adjusted to ca. 41% volume solids. The use level of an associative thickener was varied as needed to produce finished coatings with a viscosity of approximately 90 KU. Where used, styrene-acrylic direct-to-metal latex polymers were substituted on a weight solids basis and the appropriate coalescing solvent(s) were added. Note that when using even the lower T_g styrene-acrylic latex, the coating VOC exceeded the 100 g/L limit for rust-preventative coatings set by the South Coast Air Quality Management District (SCAQMD).

Polymer B was formulated into white road marking paint per Federal

Specification TT-P-1952 E. This formulation, *Formulation 2,* used one pound of TiO_2 per gallon and the required loading of calcium carbonate to achieve the specified 60% pigment by weight. The coating was 60% volume solids and was formulated with a blend of methanol and water for a maximum VOC of 150 g/L. The specification allows for the coalescent required for pure acrylic latex polymers as part of the VOC, but this was replaced with water in the model formulation as alkyd latexes do not require film-forming aids. Note the formulated VOC of 75 g/L.

Metal primers were evaluated using films of nominal 37.5 μm thickness applied to cold-rolled steel panels. Films were air dried for seven days prior to testing. Exposure to salt fog was per ASTM B117 and exposure to humidity was per ASTM D 1735. The ratings for degree of blistering and scribe creep were per ASTM standards.

Permeability was carried out in triplicate with cups of 25 cm² using free films of nominal 87.5 μm (3.5 mils) thickness measured prior to testing. Per ASTM 1653 protocol, films were applied as two coats to release paper. Exposure was done in a walk-in chamber maintained at nominal 25°C and 50% RH. Most of this work utilized the wet-cup method with 10 ml of water placed in the cup below the film. Testing films at equilibrium against the 100% relative humidity environment afforded by the wet-cup method was considered more representative for evaluating films to be used in metal protection. Data reported in the tables was for this wet-cup method unless otherwise noted. For comparative purposes some films were tested using the dry-cup method; desiccant was placed in the cup below the film to allow equilibration at 50% relative humidity from the test chamber. Given the consistent dry film thickness utilized in these studies, the data was reported as mg of water lost/hour; this is denoted as "perms" for simplicity in the text.

As noted previously, the fast method of Asbeck was one method used to determine if a given pigmentation exceeded CPVC. In this test, the film was applied to the lower half of a steel panel and allowed to dry. A spot of 3% salt water was placed on the film and the electrical resistance was measured through the film. Films above CPVC will rapidly absorb salt water and the resistance will drop by several decades in a matter of minutes while films below CPVC will maintain much of their near-infinite resistance for extended periods of time. A standard volt-ohm meter with 1.5 VDC potential was used for resistance measurements between the film and the uncoated area of the panel.

RESULTS AND DISCUSSION

One part of this work involved a project to develop novel alkyd latex polymers for metal protection that offer very low VOC and contain bio-renewable resources. These polymers must produce coatings formulations below 100 g/L VOC to meet the requirements of the SCAQMD. Note that VOC is calculated differently in the United States than in the EU. The VOC reported as 16.8 g/L in the red oxide formula (*Formulation 1*) is per U.S. protocols where water is excluded in the volume of paint. The VOC of this coating is 9.0 g/L per the EU calculation where water is included in the volume of paint.

The coatings used to evaluate experimental polymers were formulated based on the industry's understanding, that metal primers exhibit the best performance when pigmented in the vicinity of the critical point.[4,9] An initial set of formulations was made to determine the relative pigment binding ability of the preferred experimental polymer. A formulation made with red iron oxide, anticorrosive pigment, and calcium carbonate as the extender was used to vary the PVC. Films were cast and tested via the method of Asbeck for pigment loading relative to the critical point. Films cast on metal were subjected to both salt

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fog and humidity exposure. Data are presented in *Table 1*.

The data show good correlation between λ and performance. Porosity as measured by permeability and the salt water spot test suggest that CPVC is around 0.95. The critical point for a film is a function of the property being tested. Blister resistance in humidity testing improves above the critical point as water is able to be transported through the film without building hydrostatic pressure. The converse is seen in corrosion resistance testing where films above the critical point allow the ingress of water leading to rapid failure. These tests suggest a critical point between 0.90 and 0.95, the same range as found by measures of permeability. Note that the failure mechanism in humidity testing of the film at λ=1.0 was corrosion, not blistering.

Blistering seen in the humidity resistance of the red oxide primer reported in *Table 1* was unacceptable. Subsequent formulation studies indicated that inclusion of platy talc provided the desired performance. The model direct-to-metal formulation (*Formulation* 1) was followed with respect to the loading of prime pigment, anticorrosive pigment and talc. The extender pigment loading was varied to achieve the desired PVC and λ value. Optimum performance was found at λ=0.80-0.85, sufficiently below critical to preclude loss of film integrity. Further, performance was acceptable through a range of PVCs and with multiple pigmentations. Representative data are provided in *Table 2*.

The data demonstrates the robustness of the polymer in its ability to bind pigment. Film permeability remained low across the tested range of pigmentation in red oxide primer formulations and indicates that, as was seen in the PVC ladder reported in *Table 1* and relative to the white enamel, decreases with increased PVC up to the critical point. Performance failure of the white enamel was due to the lack of proper pigmentation and is shown to further illustrate the PVC/permeability relationship. An

TABLE 1—Results from Alkyd Latex PVC Ladder

λ	0.80	0.85	0.90	0.95	1.00
PVC, %	51	53	57	60	63
P:B BY WEIGHT	2.7	3.0	3.4	3.8	4.3
EXTENDER PIGMENT	$CaCO_3$	$CaCO_3$	$CaCO_3$	$CaCO_3$	$CaCO_3$
SALT WATER SPOT TEST	PASS	PASS	PASS	PASS	FAIL
HOURS HUMIDITY TO FAILURE	96	96	96	336	96
HUMIDITY RESULT	VF #6 BLISTERS	VF #6 BLISTERS	VF #6 BLISTERS	SPOT RUST	SPOT RUST
HOURS SALT FOG TO FAILURE	336	336	336	96	96
PERMS	2.5	2.3	3.9	5.4	11.9

TABLE 2—Data for Several Pigmentations in an Alkyd Latex Primer

PAINT	WHITE ENAMEL	RED PRIMER	RED PRIMER	RED PRIMER	RED PRIMER
λ	.30	.50	.70	.82	.82
PVC, %	20	27.5	40	50	40
EXTENDER PIGMENTS	NONE	TALC, $CaCO_3$	TALC, $CaCO_3$	TALC, $CaCO_3$	TALC, $CaCO_3$ $CaSiCO_3$
HOURS SALT FOG TO FAILURE	48	336	336	336	336
HOURS HUMIDITY TO FAILURE	48	336+	336+	336+	500+
PERMS	7.4	3.3	3.5	2.4	2.7

improvement in corrosion resistance was noted for coatings containing calcium silicate in conjunction with calcium carbonate. Two mechanisms for this result are offered: improved pigment packing due to the small difference in particle size/shape and the more alkaline nature of calcium silicate relative to calcium carbonate. *Figure* 1 is a 336-h salt fog exposure for the red primer containing talc and $CaCO_3$.

The need to include talc for optimal humidity resistance was one in keeping with most of the supplier-published starting formulations for metal primers. Comparing perms at similar λ from *Tables 1 and 2* suggests a small, if any, change in permeability with the inclusion of talc.

Three formulations to evaluate the influence of talc on performance were made. The test data are summarized in *Table 3*.

Perms were consistent with the data collected in earlier experiments. Permeability testing for metal primer pigment combinations showed a small variation with changes to the pigmentation. This is consistent with the thermodynamics of water movement through a film. Films have an intrinsic porosity due to the random nature of polymers. Molecular vibrations create pores through which small molecules like water can move. The hydrophobicity of the polymer plays an important role in water uptake; the polymer's structure is largely responsible for the quantity of water a film will absorb. The relative humidity in the

TABLE 5—Performance of Alkyd Latex vs Styrene-Acrylic Latex

POLYMER	ALKYD LATEX	STYRENE ACRYLIC 1	STYRENE ACRYLIC 2
T_g, °C	3	23	67
PARTICLE SIZE, nm	250	87	82
EXTENDER PIGMENT	$CaCO_3$	$CaCO_3$	$CaCO_3$
COATING VOC, g/L[a]	18	147	208
λ	0.95	0.55	0.55
PVC, %	60	40	40
SALT WATER SPOT TEST	PASS	FAIL	FAIL

(a) VOC Limit is 100 g/L for this coating class per SCAQMD

FIGURE 1—336 hour salt fog exposure.

TABLE 3—Influence of Talc on Performance

EXTENDER PIGMENTS	CALCIUM CARBONATE	TALC/CaCO₃	TALC
λ	0.50	0.50	0.50
PVC, %	30	27	24
PERMS	3.4	3.5	3.0
HUMIDITY, 336 H	FEW #6 BLISTERS	VERY FEW #8 BLISTERS	NO BLISTERS

TABLE 4—Wet- and Dry-Cup Permeability

λ	0.80	1.00
EXTENDER PIGMENT	CALCIUM CARBONATE	CALCIUM CARBONATE
WET CUP PERMS	2.5	11.9
DRY CUP PERMS	1.8	6.9

TABLE 6—Performance of a 23°C T_g Styrene-Acrylic Latex

λ	0.40	0.50	0.60
PVC, %	25	33	48
SALT WATER SPOT TEST	PASS	PASS	FAIL
PERMS	2.4	2.8	4.8

permeability cup (100% for the wet cup method) in conjunction with the nature of the polymer determines the equilibrium water content at steady-state conditions. These factors result in the small variation in permeability versus pigmentation type at equal λ value.

This concept was demonstrated by using the dry-cup permeability method. In this method the cup was filled with desiccant and the film reached steady-state conditions at 50% relative humidity from the air space above the cup. Films from the PVC ladder presented in *Table 1* were used to compare these test methods; data are given in *Table 4*. This shows that polymer structure controls steady-state moisture content, PVC is a measure of polymer content in the film and controls transport.

The data in *Table 3* show that with calcium carbonate as the sole extender the film developed few blisters through 336 h of testing. The degree of blistering was rated as very few in 96 h, similar to the results reported in *Table 1*. Inclusion of talc reduced or prevented blistering, and this result cannot be solely attributed to the difference in permeability. The

harsh environments utilized in salt fog and humidity testing force much higher concentrations of water into the films. Under these conditions the pigments exhibit a very strong influence on water transport. Particles with a strong affinity for water will limit movement by creating an energy barrier. Talc binds strongly to water [9] and the platy nature of the particles creates a long and tortuous path for water movement. Thus, while the permeability of these films is similar at the lower equilibrium water concentration found in this test, performance under saturated conditions is not. Talc serves to limit the transport of water to the substrate, in turn preventing the buildup of hydrostatic pressure and the resultant blisters. Calcium carbonate is slightly soluble in water (0.0013 g/L) and its alkaline nature may aid in corrosion protection, but this was not sufficient to prevent the buildup of black corrosion products and/or blisters at the film/substrate interface.

Given the excellent pigment binding demonstrated for these alkyd latex formulations at high pigment loading, a comparison to styrene-acrylic latexes

that are traditionally formulated to much lower PVC was dictated. Two in-house styrene-acrylic lattices designed for metal protection were formulated using the same pigmentation as shown in *Table 1*. The formulations were as similar to the alkyd latex as practical; the key difference being the use of coalescing solvent required by the higher T_g latexes. Data are presented in *Table 5*.

Given the failure of the styrene-acrylic polymers in this experiment, the work was repeated through a narrow range of PVC/λ with the lower T_g styrene-acrylic latex. In addition to the salt-water spot test, the films were evaluated for wet-cup permeability. Data is presented in *Table 6*.

Perm values for the styrene-acrylic latex are similar to the alkyd latex for films near the critical point, in this case at λ=.40 to.50. As PVC increases above CPVC, film permeability increased as expected. The change from λ=0.50 to 0.60 suggests that the latter is above CPVC, and λ=0.55 from *Table 5* is most likely just above critical. The data for the styrene-acrylic latex indicates a reduced pigment binding efficiency relative to the

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TABLE 7—Performance of White Road Marking Paint

TEST	ALKYD LATEX POLYMER B	PURE ACRYLIC LATEX
λ	.84	.84
SALT WATER SPOT TEST	PASS	FAIL
PERMS	13.6	52.2
CONTRAST RATIO	.920	.935
WATER RESISTANCE	SLIGHT SOFTENING, NO BLISTERS	NO BLISTERS

alkyd latex and provides insight into the traditionally low PVC of formulations using this polymer chemistry. The much smaller particle size of the products was not sufficient to allow these hard, very high viscosity polymers to readily deform and allow for close pigment packing.

A second ongoing program was to develop alkyd latex polymers specific to road marking paints. A VOC under 100 g/L along with bio-renewable content was desired. Formulations for existing products based on pure acrylic latex per Federal Specification TT-P-1952-E were used to evaluate experimental alkyd latex products; in this article Polymer B was used. Control coatings were made with a commercially available acrylic latex meeting the requirements of the Type 2 paint, the so-called "quick dry" product. The formulation was presented as a Model White Road Marking Paint. Note that the pure acrylic latex formulation requires a coalescing solvent; this was eliminated in the alkyd latex formulation and replaced with water. Also note that methanol was used for fast evaporation and freeze–thaw stability, not film formation.

The Federal Specification required certain minimum performance standards in a battery of tests including dry opacity and water resistance. Dry opacity was measured from films of a specific thickness applied over black and white test charts. Reflectance was calculated as Y (black)/Y (white) with a minimum of 0.92 required. Water resistance was

tested on a film applied to concrete. These were air-dried for three days and then soaked in deionized water for 18 h. No blistering, adhesion loss, or excessive softening was allowed. The data from comparisons of alkyd latex Polymer B and the pure acrylic latex from this and other testing are given in *Table 7*.

The salt water spot test and permeability data show that the alkyd latex is below CPVC while the pure acrylic latex is above critical. The relationship of these two coatings relative to CPVC is also evidenced in the performance data. As a formulation exceeds CPVC air voids develop in the film; these are additional sites for light refraction and thus generate the increase in contrast ratio shown in the data for the acrylic latex. As noted previously, films above CPVC are not prone to blistering in humidity and water-soak tests; ready transport of water allowed blister-free performance for the pure acrylic. The alkyd latex relied on film integrity to prevent blisters. Retained water did cause some minimal softening, but this recovered in a matter of minutes after exposure, as is allowed in the test protocol.

Given two films below CPVC, the significant difference in perms for Polymer B in a white road marking paint versus that seen in *Table 1* for Polymer A in metal primer pigmentation may be attributed to two factors. Most importantly, the metal primer latex is considerably more hydrophobic,[10] so does not adsorb as much water. Also, the pigmentation is very different; the road marking paint uses a very high concentration of large particle size calcium carbonate. This does not allow for efficient pigment packing and the hydrophilic nature of calcium carbonate is considered influential. While pigmentation was not seen as the dominant factor in film permeability in red oxide primer formulations, the smaller particle size and lower concentration of the calcium carbonate in this formulation, in conjunction with the hydrophobic red iron oxide and anticorrosive pigment, produces a pigmentation that is tightly packed and inherently less permeable to water.[2,6]

CONCLUSION

The relationship between PVC and CPVC is dependent on both the binder and pigments. The fluidity of the binder is a key factor in discussions of influence on CPVC with viscosity and molecular weight being the critical parameters. The data presented demonstrate that the liquid, or fluid, nature of alkyd binders allows for higher pigment loading than their extremely high viscosity acrylic counterparts. This pigment binding ability is not compromised when the alkyd is supplied as a surfactant stabilized latex rather than as a solution in solvent. The critical point for alkyd latex polymers can be determined by any of the classic measures. ❈

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