SOLVENTLESS AND LOW-VOC ARCHITECTURAL COATINGS FORMULATED FROM NOVEL LATEXES WITH LOW MFT AND HIGH TG

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INTRODUCTION

In order to meet requirements of the Clean Air Act Amendments of 1990 and subsequent government legislation, coatings manufacturers must develop technologies allowing the formulation of low volatile organic compounds (VOCs)/low odor products that possess desirable end-use properties. The demands for change are both a challenge, and an opportunity for coating industries[1-7].

A common ideology of the coatings industry is that performance of solventless architectural coatings must be poor since they lack conventional coalescing agents. Indeed, it is well established that useful protective coatings must possess below ambient minimum film formation temperatures (MFT or MFFT) for flow, leveling, and substrate adhesion, **and** reach a glass transition temperature (T_g) well above ambient for a useful lifetime. While the synthesis of low MFT polymers alone is a relatively simple matter, the combination of low MFT and high T_g has been elusive for some time. The common problem associated with low MFT latexes is low film T_g and therefore poor performance properties. To overcome this dilemma, most contemporary water-based coatings are formulated from latexes with high MFT, and consequently require co-solvents and coalescing agents to facilitate film formation such that significant VOCs are present.

The focus of this work has concentrated on the design, synthesis, characterization, and formulation of novel low temperature MFT latexes that cured to above ambient T_g polymers. Consequently, emulsion polymers with T_g-MFT differentials approaching 20 ± 3°C have been synthesized and coating film properties formulated from the novel latexes are compared with those derived from a well-known commercial latex requiring coalescing agents.

EXPERIMENTAL DETAILS

Chemicals

Butyl carbitol (99+%) and propylene glycol (99%) were purchased from Aldrich, sodium bicarbonate (A.C.S. grade) from Fisher Scientific, potassium tripolyphosphate (KTPP, 94%) from

Pfaltz & Bauer, and Tronox CR-800 (rutile titanium dioxide pigment) from Kerr-McGee. Ti-Pure R900 (rutile titanium dioxide pigment) was obtained from DuPont, Huber 70C (Kaolin clay) from JM Huber, Beavewhite 325 (TALC) and Duramite (calcium carbonate) from ECC, Natrosol Plus (grade 330, an associative cellulosic thickener) from Aqualon, Kathon LX (1.5%, solventless microbicide), Tamol 731 (25%, polyacrylic acid dispersant), Ropaque OP-62 LO (36.5%, polymeric pigment), and QR-708 (35%, rheology modifier) from Rohm & Haas, UCAR Polyphobe 102 and 107 (25%, associative thickeners), and commercial latex (CL, 55% vinyl acrylic latex), Surfynol 465 (65%, nonionic surfactant, VOC content < 0.01%) from Air Products, and Byk 034 (defoamer, VOC content <2%) and Byk 035 (defoamer, VOC content <3%) from Byk. All ingredients were used as received.

Emulsion Polymerization

Starve-fed emulsion copolymerizations were used to synthesize solventless latexes of 40-50% solids content. The latexes have remained stable at room temperature for 10 months from this writing.

Emulsion Polymer Characterization

Latex properties have been determined and are listed in Table 1, together with those of a well-known vinyl acrylic latex. The solids contents were determined gravimetrically, while particle sizes were measured by a Coulter N4 MD Sub-micron Particle Analyzer. A Mettler DSC-30 measuring cell was used to determine T_g of the latex films (mid-point value). In a typical measurement, the temperature range for DSC analysis was from -50°C to 250°C at a heating rate of 10°C/min. Minimum film forming temperature of latexes was determined by a MFFT Bar 90.

Table 1. General Properties of Latex Paint Formulations

Latex Code	USM Latex A	USM Latex B	Commercial Latex (CL)[a]
Solids content (%)	45	42.5	55
pH	4.9	5.1	5.0
Dn (nm)	180	190	330
T_g (°C)	16.9	21.8	12
MFT (°C)	-1	2	8

[a] Technical data obtained from manufacturing specifications.

Latex Paint Formulations

A mill base for each latex of Table 1 was prepared according to the formulations in Table 2. The formulation recipes for vinyl-acrylic paints at 55% PVC derived from the mill base **a** are listed in Table 3, while the formulation recipes for 20% PVC acrylic paints from mill base **b** are itemized in Table 4. Table 5 contains formulations from mill base **c** and QR-708 or Natrosol Plus thickeners formulated to 55% PVC.

Coating Film Characterization

Tensile strength and percent elongation of films were determined with an 810 Material Test System. The coatings were cast onto polyethylene sheets which allowed easy film removal. The test specimen were approximately 13 mm wide, 0.06-0.12 mm thick with a gauge length of 15 mm. Film dry times were determined from a 7-mil wet film on standard Leneta charts via a Gardner Circular Dry Time Recorder. Pencil hardness was measured according to American Society of Testing and Materials method (ASTM) standard D-3363, while the conical mandrel flexibility was determined via ASTM method D-522. Crosshatch adhesion tests were performed according to ASTM standard D-3359 on chromate pretreated aluminum plates and phosphatized steel plates. Scrub resistance was conducted on coated panels (PC-P121-10N, black plastic) after one and four weeks dry time, respectively, to obtain the number of cycles to initial break or to film failure with a 10-mil brass shim, according to ASTM standard D-2486. Specular gloss at 20°, 60°, and 85° was determined with a Byk-Gardner Micro Triglossmeter, while contrast ratios were measured with a Chroma-QC quality control system. Film thickness was determined by a Gardner Minitest 4000 Coating Thickness Gauge.

Table 2. Formulations for Mill Bases **a**, **b** and **c**[a]

Ingredients	Base **a**	Base **b**	base **c**	Suppliers
Tronox CR-800 (g)	455	1200	0	Kerr-McGee
Ti-Pure R900 (g)	0	0	1200	DuPont
Huber 70C (g)	292.5	0	0	JM Huber
Beavewhite 325 (g)	260	0	0	ECC
Duramite (g)	325	0	0	ECC
Natrosol Plus (g)	12	5	0	Aqualon
Kathon LX 1.5% (g)	5	4	4	Rohm & Haas
KTPP (g)	6.5	5	5	Pfaltz & Bauer
Byk 034 (g)	12	9	9	Byk
Tamol 731 25% (g)	39	30	30	Rohm & Haas
Surfynol 465 (g)	0	4	4	Air Products
Deionized Water (g)	715	500	498	
Total	2122	1757	1750	

[a] Ingredients were added at 800 rpm and mixed at 3500 rpm for 20 min.

RESULTS AND DISCUSSION

While the synthesis and composition of the solventless vinyl acrylic latexes cannot be disclosed at this time, it is instructive to examine the properties of formulated coatings. The T_g-MFT differential (Table 1) of the commercial latex is 4°C, while the differential for USM latex A and USM latex B is 18°C, and 20°C, respectively. T_g values were determined from clear films that had air-dried for two weeks. These data are suggestive of ambient temperature crosslinking. For instance, the films were immersed in THF and have remained intact, clear, and non-cloudy after 3 months as of this writing.

Table 3. Formulations of Vinyl Acrylic Paints of 55% PVC from Mill Base **a**

Paint Code[a]	USM A-**a**	USM B-**a**	Commercial CL-**a**	Suppliers
Mill Base **a** (g)	180	180	180	This work
Deionized Water (g)	29.5	22	36	
Na2CO3 (20%) (g)	6.0	7.0	6.0	Fisher
Byk 035 (g)	0.4	0.4	0.4	Byk
Surfynol 465 (g)	1.0	1.0	1.0	Air Products
USM Latex A (45%) (g)	86.7	0	0	This Work
USM Latex B (42.5%) (g)	0	91.8	0	This work
Commercial Latex (55%) (g)	0	0	71.0	
Ropaque OP-62 LO (36.5%) (g)	20	20	20	Rohm & Haas
Polyphobe 107 (25%) (g)	0.8	1.2	1.3	Union Carbide
Polyphobe 102 (25%) (g)	5.0	6.0	6.4	Union Carbide
Butyl Carbitol (g)	0	0	3.0	Aldrich
Propylene Glycol (g)	0	0	7.0	Aldrich
Total	329.4	329.4	332.1	
<u>Paint Properties</u>				
PVC (%)	55	55	55	
Volume Solids (%)	33.6	33.0	33.5	
Weight Solids (%)	49.9	50.0	49.6	
Stormer Viscosity (KU)	99	100	105	
ICI (poise)	1.6	2.0	2.0	
pH, Initial	9.1	9.4	8.6	
VOC (g/L)	<0.4	<0.4	122	

[a] Latex name - mill base code.

Table 4. Formulations of Vinyl Acrylic Paints of 20% PVC from Mill Base **b**

Paint Code[a]	USM A-**b**	USM B-**b**	Commercial CL-**b**	Suppliers
Mill Base **b** (g)	100	100	100	This work
Deionized Water (g)	35.3	25.3	58.0	
Na2CO3 (20%) (g)	8.4	8.0	8.0	Fisher
Byk 035 (g)	0.4	0.4	0.4	Byk
Surfynol 465 (g)	1.6	1.6	1.6	Air Products
USM Latex A (45%) (g)	170	0	0	This work
USM Latex B (42.5%) (g)	0	179	0	This work
Commercial Latex (55%) (g)	0	0	138	
Polyphobe 107 (25%) (g)	1.0	1.0	1.3	Union Carbide
Polyphobe 102 (25%) (g)	7.0	7.0	11.0	Union Carbide
Butyl Carbitol (g)	0	0	3.0	Aldrich
Propylene Glycol (g)	0	0	7.0	Aldrich
Total	323.7	322.3	328.3	
<u>Paint Properties</u>				
PVC (%)	20	20	20	
Volume Solids (%)	33.0	33.0	32.6	
Weight Solids (%)	46.3	46.4	45.6	
Stormer Viscosity (KU)	83	78	81	
ICI (poise)	1.3	1.0	1.3	
pH, Initial	8.8	9.3	8.1	
VOC (g/L)	<0.3	<0.3	118	

[a] Latex name-mill base code.

Table 5. Formulations of Vinyl Acrylic Paints
of 55% PVC from Mill Base **c**

Paint Code[a]	USM A-c-1	USM A-c-2	USM B-c	Suppliers
Mill Base **c** (g)	200	200	200	This work
Natrosol Plus[b] (3.5%) (g)	30.1	0	0	Aqualon
QR-708[c] (7%) (g)	0	17.8	17.6	Rohm & Haas
Na2CO3 (20 %) (g)	4.2	3.8	3.8	Fisher
Surfynol 465 (g)	0.9	0.9	0.9	Air Products
Byk 035 (g)	0.4	0.4	0.4	Byk
USM Latex A (45%) (g)	72.3	72.5	0	This work
USM Latex B (42.5%) (g)	0	0	76.6	This work
Total	307.9	295.4	299.3	
<u>Paint Properties</u>				
PVC (%)	55	55	55	
Volume Solids (%)	33	34.0	33.3	
Weight Solids (%)	56.0	58.3	57.6	
Stormer Viscosity (KU)	76	83	80	
ICI (poise)	0.8	1.1	1.0	
pH, Initial	8.4	8.6	8.8	
VOC (g/L)	<0.51	22.5	22.3	

[a] Latex name-mill base code - numerical number if applicable.

[b] Pre-mixed at 500 rpm to obtain 3.5% Natrosol Plus (grade 330) water solution.

[c] 140 g of QR-708 (35%) was diluted in 560 g of water and pre-mixed, containing 7.8% of propylene glycol.

USM vinyl acrylic latexes and the commercial latex were formulated into paints at 55 and 20% PVC according to the formulations of Table 3 (mill base **a**) and Table 4 (mill base **b**), respectively. A formulation above the critical pigment volume concentration (CPVC) was chosen, even though some suggest formulating below CPVC for solventless coatings[8]. The CPVC was approximated by determining an oil absorption of 24.3 g/L for mill base **a** according to ASTM D-281. Although an approximate CPVC of 54.8 was calculated, the true CPVC is less since the oil absorption technique gives values greater than those for latex paints, a result of lower binder efficiencies of the lattices[9,10].

USM vinyl acrylic lattices were formulated at 55% PVC using Natrosol Plus or QR-708 as thickener rather than UCAR Polyphobes as noted in Table 5. This approach was undertaken since the rheology modifier QR-708 contains 7.8% propylene glycol and contributes to VOC. Small amounts of propylene glycol were added to the formulation to study, and thus better appreciate, the performance of solventless USM latexes in low VOC coatings as well as solventless coatings.

Paints produced according to Tables 3, 4, and 5 formulations were made into films for film property determinations. All film properties of Tables 6-8 were determined after 7 days air dry. Films used for tensile and elongation tests were of 16-mil wet film thickness, while the remaining films were of a 7-wet mil thickness.

Paint film coalescence is crucial to developing film properties, and the efficacy of film formation was estimated from tensile property measurements. As shown in Tables 6 and 7, all films prepared from solventless paints were much stronger than their counterparts, the films derived from paints of CL.

Table 6. Film Properties Vinyl Acrylic Paints Formulated from Mill Base **a**

Paint Code	USM A-**a**	USM B-**a**	Commercial CL-**a**	ASTM Method #
Tensile Strength (psi)	853	884	596	D-2370
Elongation at Break (%)	8.4	8.6	26.1	D-2370
Wet Thickness (mil)	7	7	7	
Volume Solids (%)	33.6	33.0	33.5	
Dry Time (min)	50	40	55	D-1640
MFT (°C)	0	0.5	1	D-2354
Pencil Hardness	4H	4H	2H	D-3363
Conical Mandrel (1/8")	pass	pass	pass	D-522
Adhesion on Aluminum	5B	5B	4B	D-3359
Adhesion on Steel	5B	5B	4B	D-3359
Scrub				
Initial Break	170	160	170	D-2486
Film Failure	240	230	250	D-2486
Sheen, 85°	1.9	1.9	1.7	D-523
Contrast Ratio	94.8	94.9	94.1	D-3022

The dry time for solventless paints was consistently shorter than for conventional paints. Also, films from the solventless coatings were typically harder after 7 days dry (Tables 6, 7 and 8). All paint films changed little after the 7 days air dry period as noted by pencil hardness determinations (Table 9).

A determination of MFTs for all paints, solventless and low-VOC systems were similar and in the 0-2°C range.

Table 7. Film Properties Vinyl Acrylics Coatings Formulated from Mill Base **b**

Paint Code	USM A-**b**	USM B-**b**	Commercial CL-**b**	ASTM Method #
Tensile Strength (psi)	468	821	245	D-2370
Elongation at Break (%)	717	403	1130	D-2370
Wet Thickness (mil)	7	7	7	
Volume Solids (%)	33.0	33.0	32.6	
Dry Time (min)	45	55	60	D-1640
MFT (°C)	2	2	2	D-2354
Pencil Hardness	F	H	HB	D-3363
Conical Mandrel (1/8")	pass	pass	pass	D-522
Adhesion on Aluminum	5B	5B	4B	D-3359
Adhesion on Steel	5B	5B	4B	D-3359
Scrub				
Initial Break	700	600	400	D-2486
Film Failure	860	720	530	D-2486
85° Gloss	82.8	79.5	85.3	D-523
60° Gloss	70.4	66.6	73.0	D-523
20° Gloss	31.9	22.9	28.8	D-523
Contrast Ratio	97.2	97.2	95.7	D-3022

Wet and dry adhesion values for USM lattices derived coatings applied to aluminum and steel panels were superior to coatings formulated with commercial lattices. Conventional latex paints have long suffered from wet adhesion limitations by virtue of being stabilized in, and delivered from water[11]. Thus, techniques to evaluate the hydrophobicity of paint films are significant to paint performance, and scrub resistance tests are therefore a common practice. In the present circumstance, scrub resistance values (Tables 6, 7, and 8) of the solventless, coalescent-free, paints are comparable with conventional formulations.

Table 8. Film Properties Vinyl Acrylic Coatings Formulated from Mill Base c

Paint Code	USM A-c-1	USM A-c-2	USM B-c	ASTM Method #
Wet Thickness (mil)	7	7	7	
Volume Solids (%)	33.0	34.0	33.3	
Dry Time (min)	30	35	40	D-1640
MFT (°C)	2	2	2	D-2354
Pencil Hardness	F	F	F	D-3363
Conical Mandrel (1/8")	pass	pass	pass	D-522
Adhesion on Aluminum	4B	4B	4B	D-3359
Adhesion on Steel	4B	4B	4B	D-3359
Scrub				
Initial Break	200	240	190	D-2486
Film Failure	280	300	260	D-2486
85° Gloss	58.2	57.1	48.4	D-523
60° Gloss	13.5	13.3	14.3	D-523
20° Gloss	1.9	1.9	1.9	D-523
Contrast Ratio	98.5	98.6	98.0	D-3022

It has been suggested that the analytical methods for evaluating solventless coatings should be reviewed since no- and low-VOC coatings are new technology[2,3]. For instance, while conventional latex coating formulations possess added coalescing agents, it is reasonable to conclude that full coalescence, and thus film properties, would occur quickly. However, solventless latex coatings contain no added coalescing agents, and it is likewise reasonable that film property development would be delayed to some extent. Thus, scrub resistance of the lattices were evaluated at 7 and 28 day dry times, the latter being consistent with the DIN 53.778 standard scrub test used in Germany[3]. The results are plotted in Figures 1 and 2.

Flat paints (55% PVC) (Figure 1) are heavily pigmented and are not expected to equal the performance of the less pigmented semi-gloss coatings (20% PVC) (Figure 2). Indeed, this is confirmed for all coatings of Figures 1 and 2, i.e., all 20% PVC coatings are superior in scrub resistance to the best 55% PVC formulation whether dried 7 or 28 days. The addition of small amounts of coalescing aids in formulas USM A-c-2 and USM B-c provide slight improvement in coalescence as reflected in improved scrub resistance after 7 days dry time. However, greatest improvement in scrub resistance was developed in the solventless coatings USM A-a, USM B-a and USM A-c-1 by simply extending the drying period from 7 to 28 days. This latter effect is clearly a result of the unique coalescence and curing mechanism of the USM lattices.

Table 9. Pencil Hardness as a Function of Dry Time

Paint Code	MFT °C	Thickness mils	Pencil Hardness (Scratch) 1 day	7 days	17 days
USM A-**a**	0	1.37	HB	4H	4H
USM B-**a**	0.5	1.51	F	4H	4H
CL-**a**	1	1.22	H	2H	2H
USM A-**b**	2	1.05	B	F	F
USM B-**b**	2	1.16	B	H	H
CL-**b**	2	1.13	B	HB	HB
USM A-**c**-1	2	1.28	HB	F	F
USM A-**c**-2	2	1.28	HB	F	F
USM B-**c**	2	1.39	HB	F	F

Gloss values demonstrate that the solventless coatings of Table 7 are effectively coalesced and are gloss competitive with the conventionally formulated coating. The lower gloss values are noted when Ti-Pure R900 is the lone pigment (Table 8).

CONCLUSIONS

Vinyl acrylic lattices have been synthesized that require no coalescing aids, and possess T_g-MFT differentials of 20 ± 3°C. The low MFT allows formulation of waterborne coatings that will film form near 0°C. Film properties have been evaluated and found to be equal or better than coatings formulated with VOC contributing coalescing aids.

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Figure 1. Scrub Resistance For Flat Wall Paints

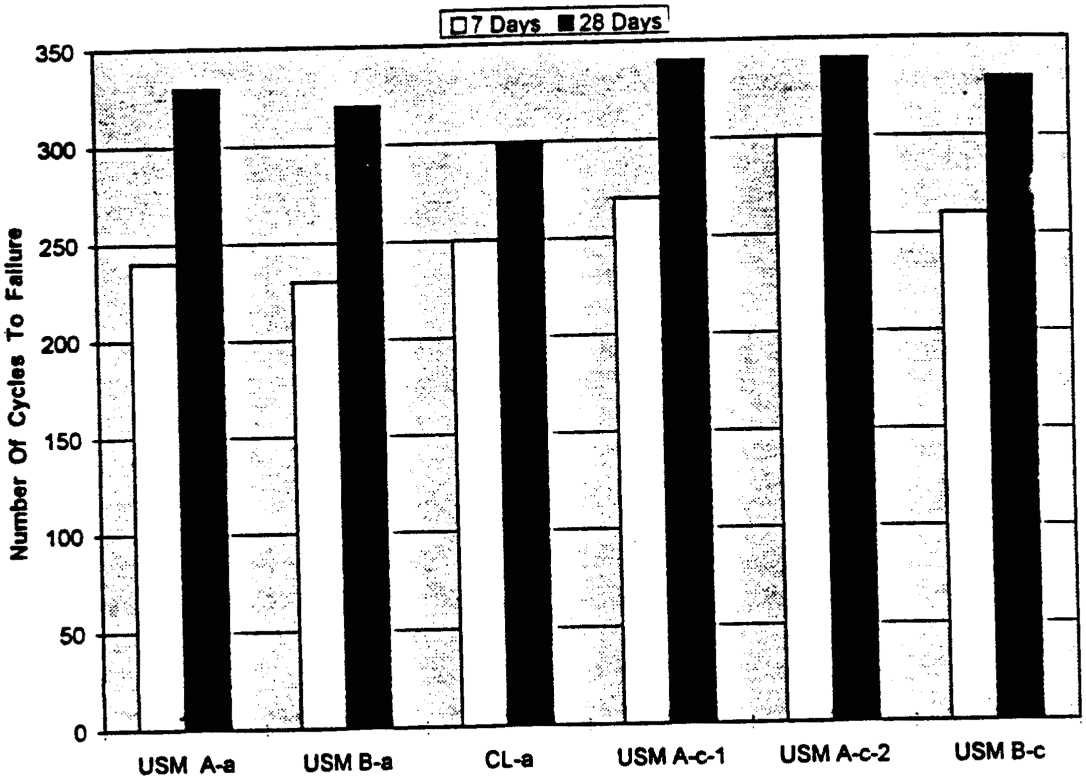

Figure 2. Scrub Resistance For Semigloss Paints