Phosphate Polymerizable Adhesion Promoters

by **Hui Shirley Yang, Herve Adam, and Jon Kiplinger**
Rhodia, Inc.*

We describe novel applications of phosphate functional monomers in polymers obtained by radical polymerization. These polymers are designed to improve the dry/wet adhesion of coatings and adhesives on metal surfaces. Two phosphate monomers were incorporated smoothly into the polymer resins without major formulation or procedure change. These monomers have been used in a wide range of applications to improve the properties on a variety of substrates. They dramatically improved adhesion as well as other related properties, such as wet scrub resistance and corrosion resistance, for the formulated coatings.

INTRODUCTION

The ability of a coating to adhere onto different substrates under both dry and wet conditions is critical for many applications. One method of improving adhesion is to incorporate functional groups that promote adhesion into the resins. These functional groups engage in specific interactions with the substrates, and, thus, improve the adhesion.

There have been many publications reporting adhesion promotion to metal substrates by phosphorus-containing functional groups.[1-6] The phosphorus-containing functional groups can be incorporated into the polymers during the polymerization or through post-modification of the resins. When these resins are used in coatings or adhesives, the adhesion and anticorrosion performance of the final products are significantly improved. DelDonno[7] discussed the adhesion promotion to metal using polymers with pendant phosphorus groups.

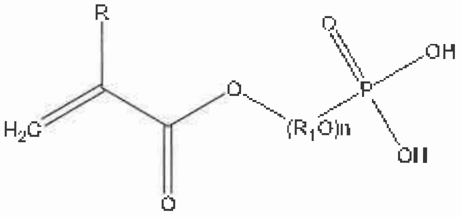
Obviously, incorporating a phosphorus-containing monomer during the radical polymerization is a more direct approach than the post-modification of the resins. However, commercially available phosphonate monomers are generally very expensive and have poor reactivity (for example, vinyl phosphonic acid). On the other hand, there are very few

---

*259 Prospect Plains Rd., Cranbury, NJ 08512.

phosphated monomers available on the market. Of these existing monomers, some are not compatible with other common monomer compositions, the polymer formed, and solvents. Moreover, they generally contain a substantial amount of residual phosphoric acid that can be detrimental to the end use properties. This, combined with the usual high dialkyl phosphate content [low ratio of monoalkyl phosphate (MAP) to dialkyl phosphate (DAP)] of these monomers, makes them difficult to use, especially in a solution polymerization process, because dialkyl phosphate has two double bonds and is a crosslinker for polymerization.

Rhodia has developed a proprietary technology that makes it possible to produce phosphate monomers with high MAP/DAP ratio, low acid content, and good compatibility with commonly used monomer compositions or solvents. Three monomers (two methacrylates– Sipomer® PAM-100 and Sipomer® PAM-200; and one acrylate—Sipomer PAM-300), all made by this technology, are commercially available. All the monomers have the following general structure:



where R = CH_3 or H, and R_1 = alkyl.

The monomers were incorporated into resins by radical polymerization and subsequently formulated into paints. These paint formulations have shown a significant improvement in both wet and dry adhesion as well as other coating properties.

MATERIALS

The phosphate monomers were prepared using Rhodia's proprietary technology. No further purification was performed. They are yellow to brown viscous liquids. Typically the monomers have a MAP/DAP ratio higher than 80:20, and the weight percentage of the residual nonionic compound and phosphoric acid are typically less than 6%.

All other materials were purchased from Aldrich or obtained from other suppliers directly. They were used without further treatment.

RESIN SYNTHESIS

Acrylic latexes were polymerized thermally at 80°C in a 1.2 liter resin kettle with mechanical agitation using a seeded procedure (*Table* 1). The phosphate monomers were incorporated at a level of 0–4% based on total monomer (BOTM). While PAM-200 had no impact on the monomer pre-emulsion stability or polymerization, PAM-100 did de-stabilize the monomer emulsion at >2% BOTM level. A separate monomer feed is needed in this case.

Table 1—Latex Formulation for Coatings

Ingredients	Weight (g)	% BOTM
Kettle Charge		
Deionized water	200.6	—
Anionic surfactant	5.0	0.3
Monomer Emulsion		
Deionized water	181.3	
Anionic surfactant	20.0	1.2
Methyl methacrylate	260.0	52.0
Butyl acrylate[a]	235.0	47.0
Methacrylic acid	5.0	1.0
Initiator Solution		
Deionized water	98.0	—
Ammonium persulfate	2.0	0.4
Total	1006.9	—

[a] PAM-100 or 200 at 1–6% were used to replace BA in evaluating phosphate monomers.

A similar latex polymerization procedure was used to make the thermosetting coil coating latex with a different monomer composition (*Table* 2). To provide the hydroxyl functionality which would later allow crosslinking by melamine, 2-hydroxyethyl methacrylate (HEMA) was used. In addition, isobonyl methacrylate (IBOMA) was used to adjust the mechanical properties

Table 2—Coil Coating Latex Synthesis

Ingredient	Weight (g)	BOTM (%)
Kettle Charge		
Deionized water	140.00	—
Abex 2005 @ 30%	1.33	0.1
Na Bicarbonate @ 100%	0.40	0.1
Monomer Emulsion		
Deionized water	159.33	—
ABEX 2005 @ 30%	17.33	1.3
Hydroxyethyl methacrylate	20.00	5
Styrene	80.00	20
Butyl acrylate[a]	160.00	40
MMA	84.00	21
IBOMA	48.00	12
Initiator Solution		
Deionized water	96.00	—
Ammonia persulfate	2.40	0.6
PAM-100	8.00	2
Total	816.80	

[a] PAM-100 or 200 at 1–6% were used to replace BA in evaluating phosphate monomers.

Table 3—Polyol Synthesis

Ingredient	Weight (g)	% BOTM
Kettle Charge		
n-Butyl acetate	79.6	—
Monomer Mixture		
IBOMA	63.0	20.7
Methyl methacrylate	45.0	14.7
2-Hydroxyethyl methacrylate	75.8	24.8
Butyl acrylate	58.4–x	19.1–Y
Styrene	63.0	20.7
PAM-200 or 100	x	Y=x/305.2
n-Dodecyl mercaptane	24.7	8.1
Initiator Solution		
Vazo 67	2.4	0.8
n-Butyl acetate	30.0	—
Chaser Solution		
Vazo 67	1.2	0.4
n-Butyl acetate	5.0	—

Theoretical values: % solids: 75%; MW 2500; Equivalent weight: 524; Glass transition temperature: 56°C.

of the film. Phosphate monomers were used at a level of 1, 2, and 4% BOTM, respectively, to compare with the control that did not contain any phosphate monomer.

The solventborne acrylic polyol was made by solution polymerization with a monomer composition of MMA/2-hydroxyethyl methacrylate (HEM)/BA/Styrene/Sipomer® IBOMA with PAM-200 (*Table* 3). At 0–10%, PAM 200 was used in the same formulation without change of the procedure. IBOMA was used to reduce the viscosity of the resins while improving the mechanical properties of the film. The polymerization was carried out at 122°C in butyl acetate, and n-dodecyl mercaptan was used to control the molecular weight.

Table 4—White Pigmented Gloss Paint Formulation

Materials	Lb	Gal
Grind to Hegman 6.5–7.0		
Water	38.5	4.6
Rhodaline 111 (Rhodia)	7.6	0.8
Triton CF-10 (Rohm and Haas)	2.3	0.3
TiPure R900 (DuPont)	151.2	4.5
NH_4OH 28%	1.0	0.1
Letdown		
Water	49.7	6.0
Acrylic latex (41.5%)	625.2	71.8
Dowanol EB	41.6	5.6
Dowanol DB	22.8	2.9
BYK 080	2.0	0.2
Irgacor 252FC (30% in water)	14.0	1.7
NH_4OH (28%)	1.0	0.1
Total	956.9	98.6

PAINT FORMULATION

The latexes were formulated into an industrial white paint (*Table* 4) or clearcoat in order to evaluate the performance. Rhodoline® 1560 (from Rhodia) at a level of 0.7–0.8% of the total formula weight was used to adjust the rheology of the formulation. Irgacor® 252FC (from Ciba) was necessary to keep the flash rusting from occurring in some situations such as cold rolled steel substrate.

The solution polyols were formulated with Tolonate® HDT-LV, which is an isocyanate crosslinker, and other additives/solvents into a polyurethane clearcoat (*Table* 5). For further salt spray tests, anticorrosion pigments, titanium dioxide, and fillers were used to formulate into a polyurethane primer. The polyurethane primers were applied to proper substrates with dry film thickness of 25 µm and cured at room conditions for five days before the tests.

TEST METHODS

The following test methods and instruments were used to characterize the latexes: viscosity measurement by Brookfield Model DV-III Programmable Rheometer; mechanical stability by Waring Blender 22,000 RPM; freeze/thaw cycles, accelerated aging tests at 60°C for 30 days; and particle size analysis by Nicomp Submicron Particle Sizer Auto Dilute model A370. Wet gum was determined by weighing the amount, in grams, of the coagulum on the blade and thermocouple. The collected grit was filtered, rinsed, and dried by paper towel. The total dry gum is the sum of the grit and coagulum after drying overnight. Grit is used to describe the amount of filtered particles only.

Aluminum, cold rolled steel, galvanized steel, iron phosphate treated steel (Bonderite® 1000), and zinc phosphate treated steel (Bonderite® 952) were used to conduct the paint property studies. In the case of coil coatings, chromated aluminum and steel were used for

Table 5—Polyurethane Formulation and Evaluation

	Weight (g)	% Solids	Notes
Part I			
Polyol	51.4	70.0	eq. wt. 524.0
BYK-361 (1%)	3.0	1.0	
T-12 (0.5% in butyl acetate)	5.0	0.5	
Butyl acetate	9.0		
Xylene	17.9		
Part II			
Tolonate HDT	13.8		eq. wt. 191.0

(a) Weight % solids 50.0%, NCO/OH ratio 1.05, xylene/butyl acetate ratio 2.0

Table 6—Latex Properties of Phosphate Monomer Modified Latexes

	Reference #					
	M1	M3	M4	M5	M6	M7
PAM-100 % BOTM	0	0.25	0.5	1.0	2.0	—
PAM-200 % BOTM	—	—	—	—	—	2.0
% Wet gum (BOTL)	.02	.06	.04	.02	0.08	0.02
% Solids/% conversion	50.4/99.8	50.4/99.8	50.5/99.9	50.6/100	50.4/100	50.4/100
Mean diameter (nm)/std dev	119/8	117/18	120/15	115/17	111/17	124/19
Viscosity (cP)	263	371	392	382	720	237
F/T stability (# cycles)	0	0	0	>5	>5	>5
60°C oven stability (days)	>30	>30	>30	>30	>30	>30

(a) Monomer composition: 52 MMA/47BA/1 MAA/0–2% BOTM phosphate monomer.

comparison. All panels were cleaned with acetone before the application. The test paints were applied with either S28 or S36 wet film applicator rods, depending on the individual tests. The targeted wet film thickness was 2.8 mils × S28 or 3.6 mils × S36. The coatings were allowed to dry for seven days at ambient conditions prior to testing. Wet and dry adhesion over the metal substrates was determined by X-hatch tape test, ASTM D 3359. Gloss measurements were performed at 20° and 60° using a BYK Gardner Micro Tri Gloss meter. The wet scrub resistance was measured according to ASTM D 2486 with slight modifications. The control paint and the experimental paint were applied on the same test panel side by side, and allowed to dry at ambient conditions. Scrub test, using a Gardco scrub testing apparatus with Leneta Standard Scrub Media Abrasive Type SC-2, was performed. Scrubbing was stopped as soon as one of the paints failed, and the numbers of cycles were recorded.

RESULTS AND DISCUSSION

Phosphate Monomers in Thermoplastic Latex and Latex Coatings

Phosphate monomers were incorporated into thermoplastic latex at a level of 0–4% based on total monomers, even though they can be incorporated into the latexes up to 10% without problems.

Table 6 shows the latex performance data when PAM-100 was used in the latex synthesis. There is a clear trend of improved latex stability and increased viscosity when the PAM-100 usage level increases. It has been found that PAM-100 could destabilize emulsions in some monomer compositions at >2% level and a separate monomer feed is needed in this case. It was observed that PAM-200 gave similar performance improvement without increasing the viscosity significantly.

After formulating the latexes into white pigmented light industrial paints or clearcoats, the film properties were examined with the methods described previously. The data in *Table* 7 indicates that the phosphate monomer improves the wet adhesion on both aluminum and zinc phosphate-treated steel substrates. A wet adhesion improvement from 0B to 5B was obtained in the paint with 3% BOTM phosphate

Figure 1—Hiding power of PAM-100 depicted by contrast ratio vs. concentration.

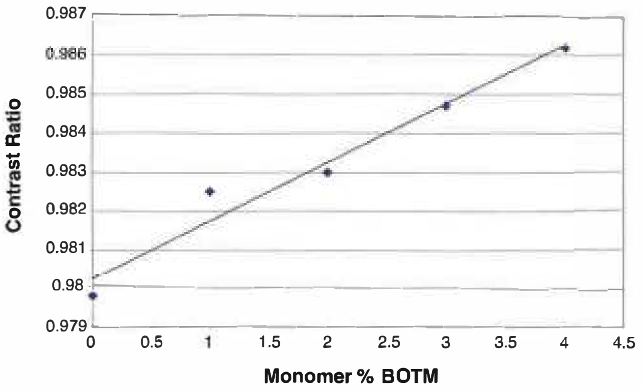


Table 7—Coating Properties of Acrylic Latex Paint Made with PAM-100 over Untreated Aluminum and Zinc Phosphate Steel Panels.

Monomer: 51 MMA/47 BA/1 MAA/X PAM-100

Paint ID	PAM-100 (% BOTM)	Dry Adhesion	Wet Adhesion
Coatings over Al:			
153A	0	4B	0B
153B	1	4B	3B
153C	2	5B	3B
153D	3	5B	5B
153E	4	5B	4B
Coatings over Zinc Phosphate Steel:			
153A	0	5B	1B
153B	1	5B	5B
153C	2	5B	5B
153D	3	5B	5B
153E	4	5B	5B

Table 8—Substrates for Coil Coating Evaluation

Reference	Description of the Substrates
CRS	Cold roll steel
B1000P95	Phosphated non-chromated steel, DI water rinsed
B1000P60	Phosphated chromate sealed steel, DI water rinsed
Al	Aluminum 3105 mill finished
Al-36	Aluminum 3105 mill finished with chromate treatement
HDG	Hot dipped galvanized steel

monomer on the aluminum substrate and with only 1% BOTM of the same monomer on the zinc phosphate-treated steel substrate. The dry adhesion also showed significant improvement using latex with only 1% BOTM of the phosphate monomer.

Phosphate monomers can also improve the appearance of the film surface. With 3–4% dosage of PAM-100, the film gloss was superior to the control. On zinc phosphated panels, the resin made with different dosages of PAM-100 gave equivalent or higher gloss compared to the control. In addition, the hiding power of the paints was investigated by measuring the contrast ratio and comparing to the control. The results are shown in *Figure* 1. The hiding power of the paint improved and the improvement was proportional to the amount of PAM-100 in the latex.

Wet scrub resistance of the latex paints was significantly improved by PAM-100. *Figure* 2 shows the scrub resistance of two phosphate-monomer modified paints on aluminum substrate. Two percent of PAM-100 was used in the latex synthesis. Scrub resistance was increased from ~300 cycles to over 4000 cycles in one system and from ~600 cycles to over 2700 cycles in another system. It is also noted that the failure mode in the test had changed. The control failed by adhesion loss, while the experimental paint films containing phosphate monomers failed by wearing (*Figure* 3). This test further confirms that the adhesion under wet conditions was improved significantly by the use of phosphate monomers in the latex.

Figure 2—Scrub resistance of latex paint. A and B are different paint formulations.

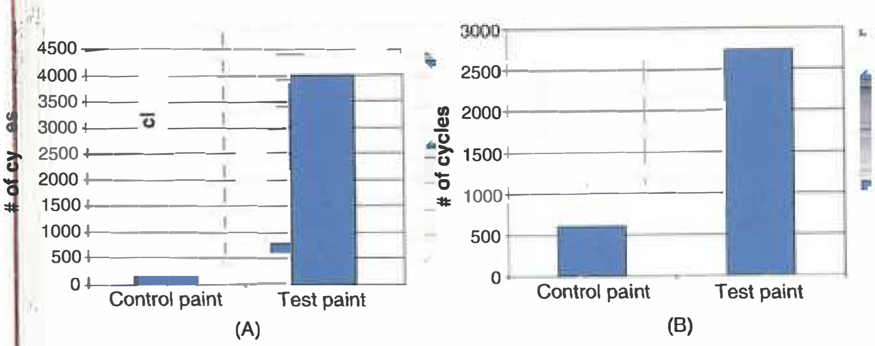
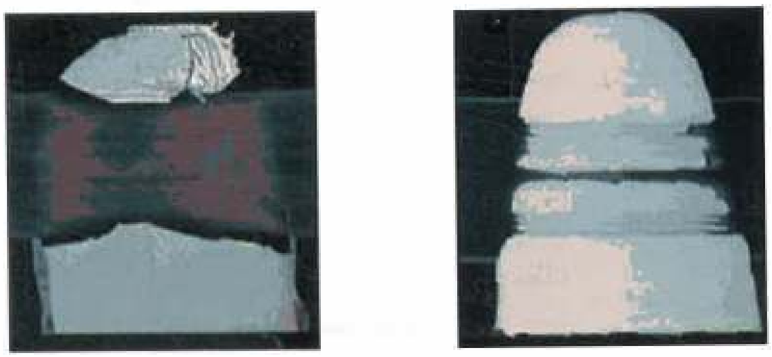


Figure 3—Fail mode of film after wet scrub resistance test.



A—Control paint without monomer

B—Test paint with phosphate monomer

Phosphate Monomer in Thermosetting Acrylic Coil Latex Coatings

The thermosetting latexes were synthesized by incorporating both PAM-100 and PAM-200, respectively, and formulated into clearcoats crosslinked by Cymel® 303 (Cytec). The paints were applied onto either steel or aluminum substrates and cured in an oven at 180–190°C for two minutes. A comparison of the impacts of phosphate monomers on coatings with phosphate or chromate pretreated panels was also conducted (*Table* 8). The dry/wet adhesion properties were examined upon cooling. The results are summarized in *Figure* 4 and *Table* 9. It is clear that 2% PAM-100 or PAM-200 not only improves the adhesion on these substrates significantly, but also performed better than the control latexes without phosphate monomers coated on phosphate (CRS vs B1000P95) or chromate (Al vs Al-36; CRS vs B1000 P60) treated substrates.

Phosphate Monomers in Polyol Resin and Polyurethane Coatings

Polyols were synthesized using the standard recipe and procedures indicated in the previous section. Up to 4% BOTM of PAM-100 and 10% of PAM-200 were successfully incorpo-

Table 9—Phosphate Monomers to Improve Dry/Wet Adhesion of Coil Coatings

	0% PAM	1% PAM-100	2% PAM-100	2% PAM-200
CRS				
Dry	5B (100%)	5B (100%)	5B (100%)	5B (100%)
24 hr wet	0B (0%)	0B (0%)	5B (100%)	5B (100%)
B1000P60				
Dry	5B (100%)	5B (100%)	5B (100%)	5B (100%)
24 hr wet	0B (0%)	5B (100%)	5B (100%)	5B (100%)
B1000P95				
Dry	5B (100%)	5B (100%)	5B (100%)	5B (100%)
24 hr wet	1B (65%)	5B (100%)	5B (100%)	5B (100%)
Al				
Dry	3B (94%)	5B (100%)	5B (100%)	4B (99%)
24 hr wet	0B (0%)	4B (98%)	5B (100%)	5B (100%)
Al-36				
Dry	5B (100%)	5B (100%)	5B (100%)	5B (100%)
24 hr wet	0B (0%)	5B (100%)	5B (100%)	5B (100%)
HDG				
Dry	0B (0%)	5B (100%)	5B (100%)	5B (100%)
24 hr wet	0B (0%)	2B (70%)	5B (100%)	4B (97%)

rated into the polyol systems without difficulty. PAM-100 generated turbidity even at low usage level (1% BOTM), while PAM-200 gave a clear solution even up to 4% BTOM. Nevertheless, the final polyols were clear with almost no turbidity or precipitation and were light yellow to light brown in color. Although both monomers were successfully used in polyol synthesis, most application test data reported here is for PAM-200 due to its better compatibility with the organic system.

No significant differences in the process or final products were observed during the polymerization with phosphate monomers compared to the control polymerization without the phosphate monomers. *Table* 10 summarizes the GPC analysis data for polyols with both phosphate monomers. The molecular weight did increase slightly when the phosphate monomers were used but it was not significant, even at 4% BOTM level. The relatively high MAP/DAP ratio dramatically minimized the degree of crosslinking and allowed the system to maintain a proper molecular weight/viscosity.

To understand the benefits of high MAP/DAP ratio, four phosphate monomers with different MAP/DAP ratios were synthesized. The monomer types and their MAP/DAP mole ratios are shown in *Table* 11, and the MAP/DAP ratio difference in each monomer set was designed to be about 10%. These monomers were incorporated into polymer backbones by using a model polymer system with ~2% of phosphate monomer and ~98% of MMA. In the ex-

Table 10—Effect of Phosphate Monomer on Molecular Weight of Polyol in Solution Polymerization

Sample	Peak MW M_p	Wt Avg. M_w	No. Avg. M_n	Polydispersity M_w/M_n
Polyol control—no phosphate monomer	4,660	3,730	2,070	1.80
1% PAM-200	5,040	4,290	2,140	2.01
1% PAM-100	4,760	4,170	2,100	1.98
2% PAM-200	5,170	4,800	2,180	2.20
4% PAM-200	5,730	5,480	2,280	2.41

Figure 4—Adhesion improvement by 2% of PAM-100 in clear coil coating application. (The coating is a melamine crosslinked system and was cured at 180–190°C for 2 min.)

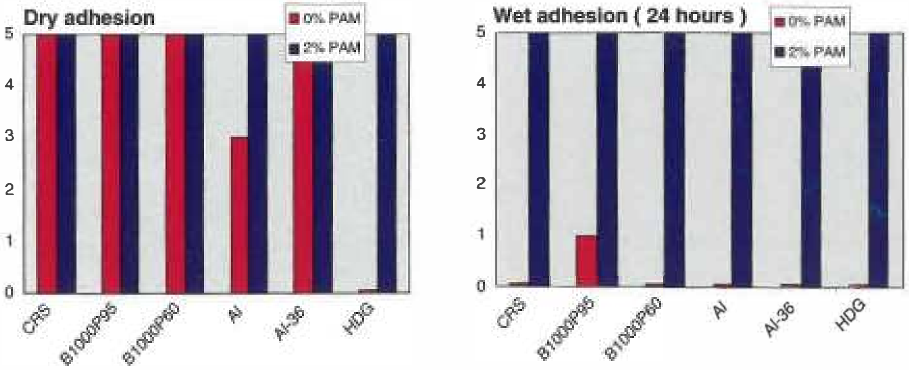


Figure 5—Compare the viscosity of copolymer solution with phosphate ester of pentapropylene glycol monomethacrylate at different MAP/DAP ratio.

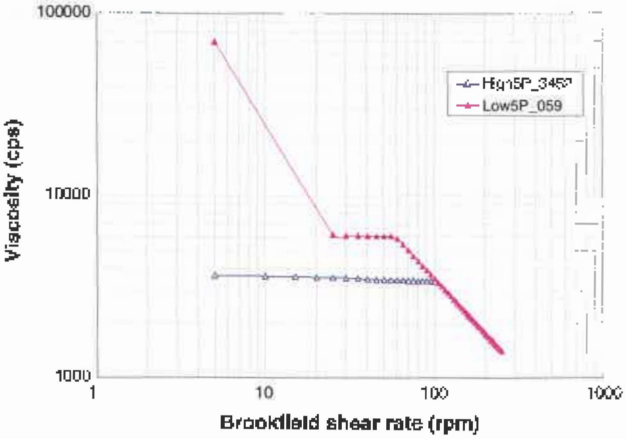


Figure 6—Compare the viscosity of copolymer solution with phosphate ester of hexaethylene glycol monomethacrylate at different MAP/DAP ratio.

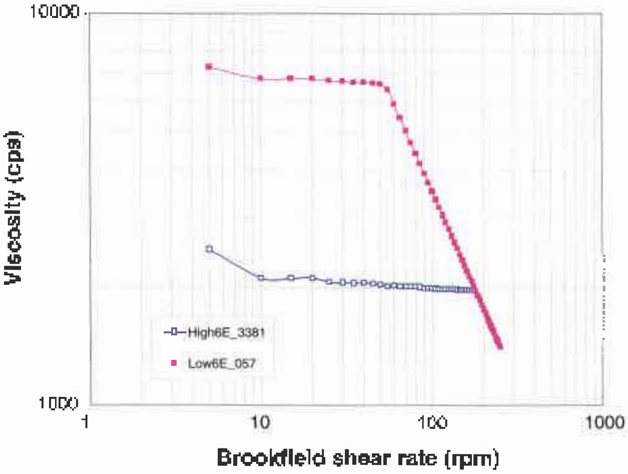


Figure 7—Relationship of G', G" vs. frequency for copolymer solution with PAM-200 at different MAP/DAP ratio.

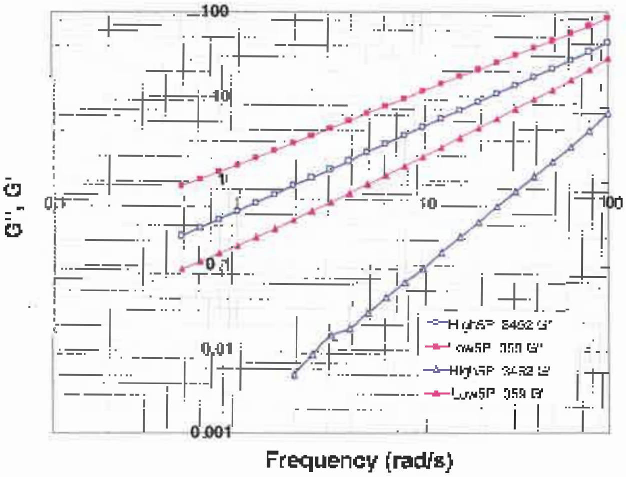


Table 11—Phosphate Monomers at Different MAP/DAP Mole Ratio

Sample Code	MAP/DAP Ratio (Molar)
LowP_059	85/15
HighP_3452	93/7
LowE_057	72/28
HighE 3381	86/14

periments, 1.0 g of phosphate monomer, 50.0 g of methyl methacrylate monomer, 0.2 g of azobisisobutyronitrile (AIBN) as the initiator, and 119.1 g of THF solvent were placed in a closed pressure reaction vessel equipped with a magnetic stir bar. After bubbling nitrogen through the reaction bottle, it was placed in a water bath for about 24 hr with magnetic stirring. At the end of the reaction, it was observed that the products with lower MAP/DAP ratio phosphate monomers had obviously higher viscosity and the solution was more elastic (the liquid drop can be elongated which indicates that the solution is closer to a gel state).

The polymer solution viscosities were measured using a Brookfield Rheometer and the G'/G" with an ARES strain-controlled Rheometer. The data are summarized in *Figures* 5–7. All the data clearly showed that the polymers with high MAP/DAP ratio phosphate monomer had lower molecular weight and had less gel-like properties, and the differences were significant enough to be observed even when the MAP/DAP ratio decreased from 93/7 to 85/15 or from 86/14 to 72/28. A high MAP/DAP ratio phosphate monomer is critical in the synthesis of polyols to prevent gelation and allow a useful phosphate level to be introduced in the polyols.

In a polyurethane clearcoat formulation, the polyols were tested for their dry/wet adhesion. The results again showed significant improvement in adhesion when phosphate monomers were used (*Table* 12). In addition, a white pigmented polyurethane primer with anticorrosion pigment was also examined. Slight viscosity reduction was observed with the phosphated polyols. Salt spray performance was tested by an independent lab. Significantly better corrosion resistance was observed (*Figures* 8 and 9). For the coatings on cold rolled steel substrate in *Figure* 8, the control panels without the phosphate monomer failed after only 100 hr and were full of blisters and rust, while the testing panels with PAM-200 remained clean until 500 hr.

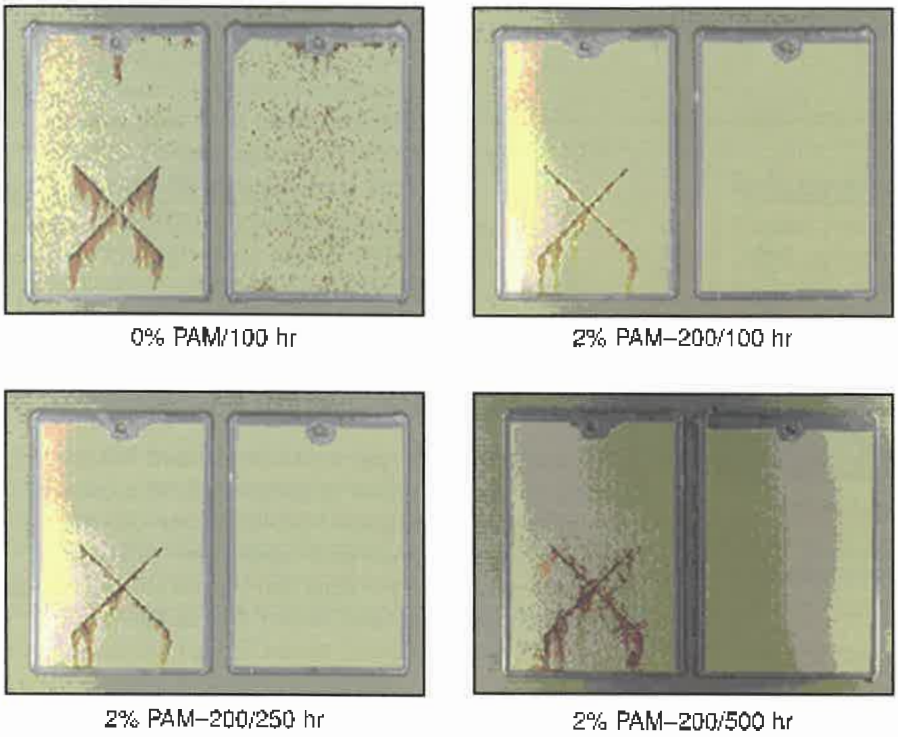
Similar results were also found on phosphate-treated steel substrates (*Figure* 9). The polyurethane film with 2% of PAM-200 passed 1000-hr salt spray tests, and outperformed the controls with 0% PAM, which rusted by 750 hr.

It is to be noted that both the polyol synthesis and polyurethane formulation were not optimized for the test. The tests were also in very tough conditions, i.e., dry film thickness of 25 µm and five days' curing before the tests. Better results could be obtained with careful optimization and formulation when phosphate monomers are used. The results indicate that it may be possible to formulate the real direct-to-metal polyurethane coatings, or to reduce or eliminate the coating steps in high performance situations such as automotive applications.

Phosphate Monomers in UV-Curable Coatings

Limited work was done on UV-curable coatings. However, significant adhesion improvement was observed as well. As a monomer in UV-curable formulations, PAM-100 was examined as an adhesion promoter. IBOA was used in the formulation to adjust the hardness of the film. The adhesion was tested immediately after curing by UV light at 50 ft/min for two passes. With 2% of PAM-100, the adhesion improved from 0B

Figure 8—Salt spray tests on cold rolled steel surface.



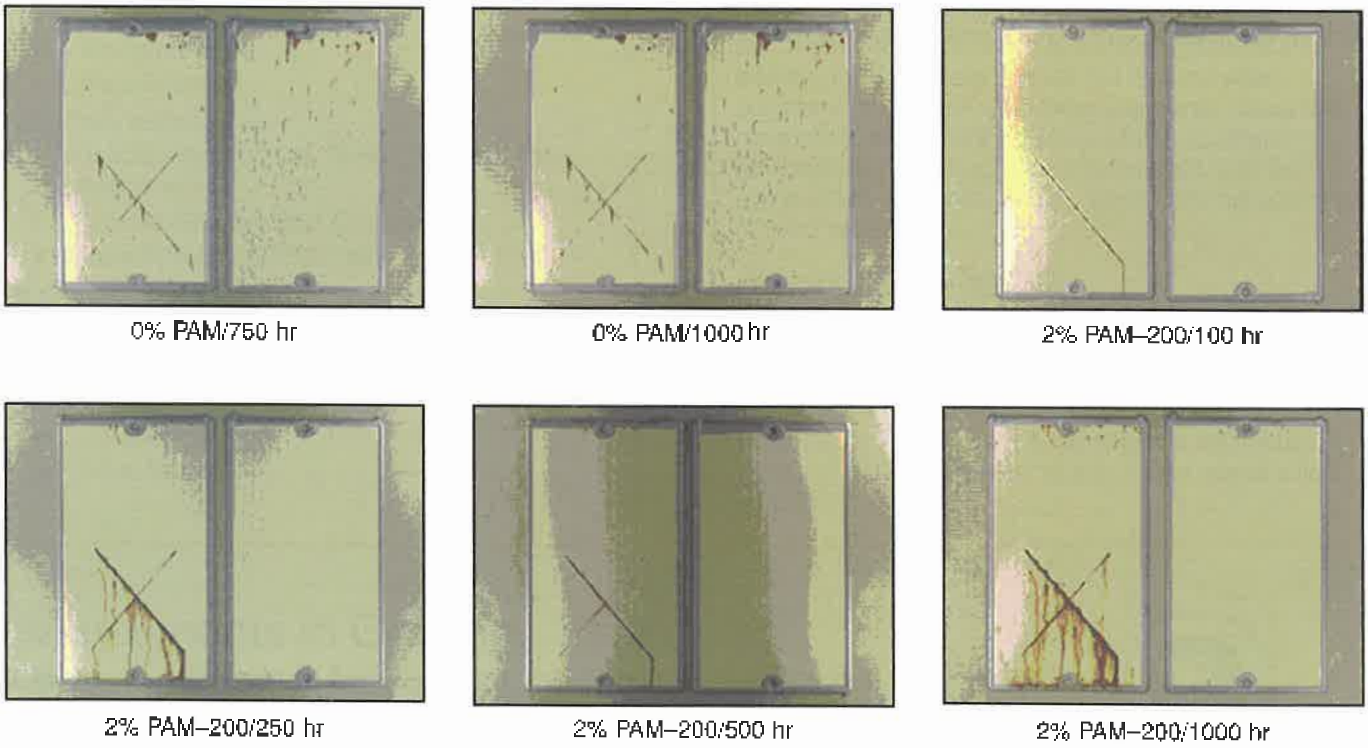
0% PAM/100 hr

2% PAM–200/100 hr

2% PAM–200/250 hr

2% PAM–200/500 hr

Figure 9—Salt spray tests on phosphate steel surface.



0% PAM/750 hr

0% PAM/1000 hr

2% PAM–200/100 hr

2% PAM–200/250 hr

2% PAM–200/500 hr

2% PAM–200/1000 hr

Table 12—Dry/Wet Adhesion Improvement of PAM-200 in Polyurethane Clear Coatings

Aluminum						
Immersion hours	Dry	2	4			
Control	3B	0B	0B			
1% PAM	3-4B	0B	0B			
4% PAM	5B	2-3B	0B			
Cold Rolled Steel						
Immersion hours	Dry	2	4	8	24	48
Control	5B	4-5B	2B	0B	0B	0B
1% PAM	5B	3B	2B	1B	0B	0B
4% PAM	5B	5B	5B	5B	4-5B	4-5B

Table 13—Adhesion Improvement in UV-Curable Coatings

	Control—no PAMs	2% PAM-100
Untreated Al	0B (0%)	5B (100%)
CRS	0B (0%)	3-4B (95-92%)

to 5B on aluminum and from 0B to 3-4B on cold rolled steel substrates (*Table* 13). This again proves the effectiveness of phosphate monomers for adhesion promotion on metal surfaces.

CONCLUSIONS

PAM-100, PAM-200, and PAM-300—a novel class of phosphate monomers—have been shown to have some unique characteristics compared to other similar products in the market. These characteristics include better compatibility with common organic systems, higher MAP/DAP ratio, and lower phosphoric acid content. Coatings with resins made with these monomers, including thermoplastic latex, thermosetting latex coil, solvent-borne polyurethane, and UV-curable coatings, have shown significant adhesion improvement on various metal substrates. Other adhesion-related properties, such as scrub resistance and corrosion resistance, are also improved.

ACKNOWLEDGMENTS

The authors thank Eugene Anderson and Robert Reierson for the syntheses of the phosphate monomer samples used in these experiments. We are also indebted to the NMR analytical support by Heiko Mauermann, and the polyurethane application test support by Richard Rosen and Satyen Trivedi. ■

References

(1) Bressy-Brondino, C., Boutevin, B., Hervaud, Y., and Gaboyard, M., *J. Appl. Polym. Sci.*, 83 (11), 2277-2287 (2002).
(2) Wang, C. S. and Shieh, J.-Y., *Eur. Polym. J.*, 36 (3), 443-452 (2000).
(3) Abd El Salam Shakal, M. and Pfeiffer, P., *J. Adh. Sci. Technol.*, 12 (3), 349-361 (1998).
(4) Matsumura, H., Tanaka, T., and Atsuta, M., *J. Dentistry*, 25 (3-4), 285-290 (1997).
(5) Lin, Y.-L., Hsiue, G. H., and Chiu, Y.-S., *J. Polym. Sci., Part A: Polym. Chem.*, 35 (3), 565-574 (1997).
(6) Clark, P.J., Loctite Corp. Newington, CT, U.S. Patent 4,990 (1991).
(7) DelDonno, T.A. U.S. Patent 5,191,029 (1993).