Surfactant-Free, Aqueous, Acrylic Dispersions for Plastic Coatings

by Dirk Mestach and Eric Manning
Nuplex Resins b.v.*

Special demands apply to the paints designed for plastic coatings. The requirements of adhesion; fast drying; and resistance to solvents, chemicals, and light call for a thorough understanding of binder technologies. Given this background, a new waterborne surfactant-free acrylic binder has been developed that meets these requirements and allows environmentally compliant plastic coatings to be formulated. Experimental results are presented that underline the high performance characteristics of this new material.

INTRODUCTION

Industrial Plastic Coatings

Plastics are used in virtually all sectors of industry, from the manufacture of mobile phones to automotive engineering. Most plastics are now coated for protection against weathering, attack by solvents and scratching, as well as for decorative reasons.

Coating systems commonly used in this industry fall into three categories: three-coat, two-coat, and single-coat systems. The three-coat system is the most common —a primer, a basecoat, and a clearcoat. After each layer the paint is allowed to dry for a short period (flash-off for 5–15 min at 60°C). Once the complete system is applied, the coating is force dried at temperatures of 60 to 80° for 15–30 min. Typical dry film thickness for the three-coat system ranges from 25–75 µ for the primer, 25–50 µ for the basecoat, and 25–125 µ for the clearcoat. A two-coat system is only a basecoat applied straight to the substrate, then a clearcoat. Typical dry film thickness for the two-coat system is 50 µ for the basecoat, and 50–125 µ for the clearcoat.

Presented at European Coatings Conference "Modern Coatings for Plastics Substrates," Berlin, Germany, November 24–25, 2003.

*P.O. Box 79, 4600 AB, Bergen OpZoom, The Netherlands.

Single-coat systems apply only a thin coat, either to protect the plastic substrate or to improve color matching between parts whose color and texture are molded in. They can take the form of a pigmented, matte, or gloss coating. A specialty single-coat is a soft feel coating which endows the plastic with a leather-like surface. Less coating solids are applied with the single-coat system than with the other systems. The dry film thickness applied for the single-coat system depends on the function of the coating. If protective properties are desired, the dry film thickness must be at least 25 µ. Whatever the coating system is, the ability to turn out high quality products quickly and economically is essential in the competitive world of plastics manufacturing and finishing. Waterborne plastic coatings can significantly contribute to this requirement.

WATERBORNE COATINGS FOR PLASTIC SUBSTRATES

As in all industrial coating areas, the implementation of legislation to reduce the emission of volatile organic compounds (VOC) is the main driver of the switch to waterborne plastic coatings. Waterborne coating systems have already been used for some time on non-polyolefin plastic substrates, including polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS), polyamide (nylon), polystyrene (PS), and polyvinyl chloride (PVC).

Because of the vulnerability of plastics to certain solvents, inducing solvent stress cracking, waterborne coating systems can offer an advantage over solventborne systems since they do not contain any aggressive solvents. Waterborne primers, basecoats, and single-coats therefore have already gained some acceptance in the marketplace. The binders most commonly used in these applications are thermoplastic acrylic or styrene-acrylic dispersions. To reach the required end-properties such as scratch and chemical resistance, generally polymers with a high glass transition temperature (T_g) and corresponding high minimum film formation temperature (MFFT) are used.

Waterborne clearcoats for plastics have to satisfy requirements similar to those for most other clearcoats. They must protect the plastic substrate against solvents, weathering, and soiling. Also, protection against scratching is a prerequisite. Finally, the clearcoat has to deliver the required optical (high gloss, wet-look effect, matte-look) and tactile effects. Waterborne two-component urethane coatings are being used for this application. However, paint users that are accustomed to one-component thermoset acrylics often do not want to change to two-component systems with a defined pot life. Therefore, there is a need for high quality waterborne one-component coating systems.

REQUIREMENTS FOR WATERBORNE PLASTIC COATINGS

Ensuring strong adhesion of waterborne coatings to plastic substrates can be a challenge, as plastics are typically non-porous substrates and adhesion to these surfaces is often difficult to achieve. Unlike metal substrates, where a chemical as well as a physical bond can occur, plastic substrates have only a physical bond present. Good adhesion is not only very important for primers but also for basecoats that are applied directly to a non-primed substrate. Adhesion on plastics can be improved if the substrate can be swollen to some extent so interpenetration of the binder in the substrate can take place. Many factors affect the ability of a coating to swell a substrate, including viscosity, molecular weight, the size of the molecules, temperature, time of exposure, and compatibility with the substrate or solubility parameters. The most common examples of swellable substrates are polycarbonate, polyvinyl chloride, and polystyrene.

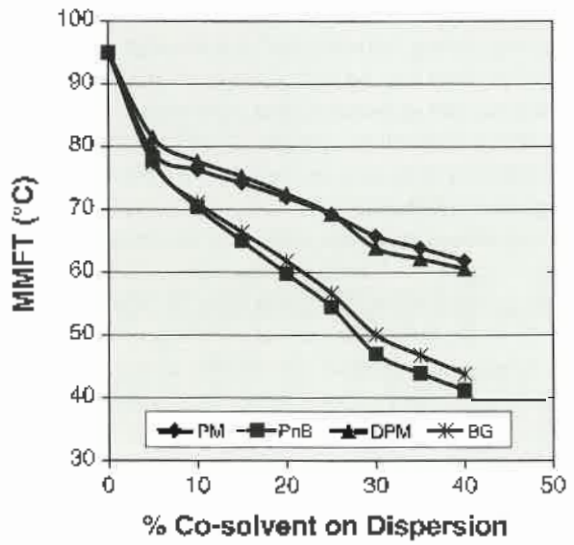
Solubility parameters are a variable that can be used in estimating the ability of a coating to adhere to a particular substrate. The concept of solubility parameters has been described by, among others, van Krevelen and Hoftyzer[1] and Hoy.[2] Determining the solubility parameter of a substrate provides a good idea of which monomer-compositions will act as "adhesion promoters" in a polymeric binder. Polymers become more compatible the closer their solubility parameters are to each other. The solubility parameters can be determined theoretically using calculations, or experimentally by measuring the swelling of a polymer in different solvents with known solubility parameters.

Coating lines for plastic components run at high speed. Fast drying is therefore required. Because the plastic part needs to be handled as soon as possible, the coatings should be tack-free after short periods of drying. Resistance to solvents, chemicals, and light are other requirements. Furthermore, a coating's flexibility must be matched to that of the substrate to prevent splintering on mechanical impact.

BINDERS FOR ONE-COMPONENT PLASTIC COATINGS

Currently, the binders used in one-component plastic coatings are either acrylic or styrene acrylic dispersions or polyurethane dispersions. However, these existing waterborne binders have some disadvantages. Developments in acrylic dispersion technology in the early 1980s led to the use of a new generation of polymers based on monomers such as butyl acrylate, butyl methacrylate, methyl methacrylate, styrene, methacrylic acid, and acrylonitrile. Better gloss, hardness, and dura

Figure 1—MFFT as a function of the weight of co-solvent added to a conventional acrylic dispersion (at 40% solids and T_g of 95°C).



bility were exhibited, making these binders suitable for industrial applications. As a consequence, however, the MFFT increased in many cases from a value below 20°C (typical for dispersions used in architectural coatings) to above 20°C, thereby necessitating the use of co-solvents. For good film formation of a water based paint at ambient temperature, an MFFT below 5°C is necessary. This provides good film forming even under adverse conditions. When high T_g acrylic dispersions are being used, as is generally the case for plastic coatings, this means that rather high levels of co-solvents are required. Additions of up to 20% co-solvent on dispersion solids are frequently reported.

We investigated the film-forming behavior of a commercially available acrylic dispersion recommended for one-coat applications on electronic housings. This dispersion has a T_g of 95°C at 40% solids. In *Figure* 1, the MFFT for this dispersion is given as a function of the amount of different co-solvents added (PM = methoxy propanol, PnB = propylene glycol n-butyl ether, DPM = dipropyleneglycol methylether, and BG = butyl glycol). From this figure it is clear that if we want to have an acceptable film formation under forced drying conditions (approximately 60°C), the VOC levels of the coating will be unacceptably high.

If we want to obtain coating compositions containing levels of VOCs and plasticizers that are in line with future European legislation, we obviously have to select other types of binders. Furthermore, the high T_g of the acrylic polymer often causes the coating to have poor flexibility.

Polyurethane dispersions are a second class of binders used in one-component plastic coatings. However, polyurethane dispersions that are based on polyesters show a tendency to hydrolyze, resulting in a decline of the chemical resistance properties caused by humidity over time. Polyurethane dispersions based on polyethers do not have the tendency to hydrolyze, but lack the light and heat stability required for these applications.

NOVEL SURFACTANT-FREE SELF-CROSSLINKING DISPERSION FOR PLASTIC COATINGS

An acrylic dispersion was developed for use in waterborne plastic coatings (dispersion A). The composition of the polymeric surfactant was tuned in such a way that adhesion was improved on a series of plastics except for polyolefines. To get sufficient adhesion on polyethylene, or polypropylene, additional adhesion promoters, such as dispersions of chlorinated polyolefines should be added to the binder.

The properties of the new acrylic dispersion are given in *Table* 1.

The drying of dispersion A at ambient temperature was investigated using the Rhopoint Thin Film Analyzer (TFA). The TFA is an instrument which can continually measure the relative viscosity or visco-elastic properties of a film of paint or dispersion during the drying or curing process. A sample of dispersion A was drawn down on a glass slide using a 200 µm wet film applicator. The TFA was set up to perform test scratches through the film at predefined times (during which time, the film cured). The probe was drawn through the film and the forces acting on it were measured and plotted graphically (*Figure* 2). As the film cured, the forces increased on the probe until such time that the probe failed to draw through the coating and skipped over the surface. At this point the probe measured the resulting reduction in restore force through the final tack phase and subsequently, if tested, through to full cure. For

Table 1—Typical Properties of Dispersion A

Property	Value	Units	Method
Nonvolatile content	39–41	%	ISO 3251
pH	7.0–9.0		
MFFT	7	°C	ASTM D 2354
Particle size (average)	60–100	nm	Photon Correlation Spectroscopy
Density	Approx. 1.04	kg/dm³	DIN 53213

Figure 2—Thin Film Analyzer plot for dispersion A drying at ambient temperature (23°C).

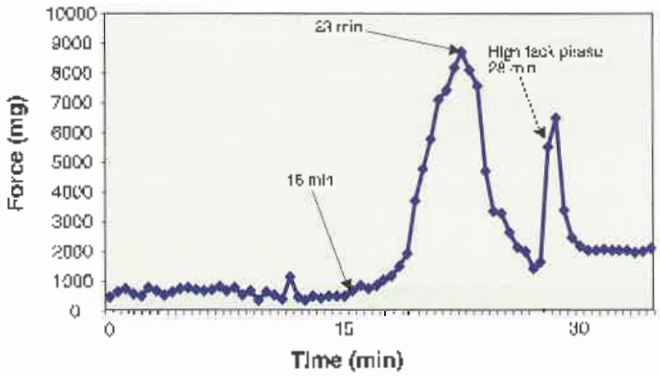
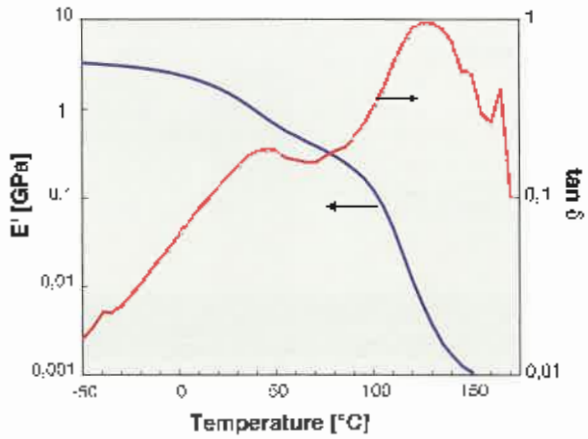


Figure 3—DMTA for dispersion A after aging at room temperature for one week.



the purpose of this study, the point at which the probe skipped over the surface was deemed to be the cure point.

In *Figure* 2 we can observe a period of approximately 16 min before a steady increase in restoring forces of approximately 4 min occurs. At around 20 min, a rapid increase in force is measured and the film becomes quite hard at 23 min. A rapid reduction in restoring forces can clearly be seen prior to the subsequent high tack phase, which started at approximately 29 min. This rapid increase in force is followed by a rapid decrease onto the final drying phase. After the film is physically dry, the covalent crosslinking begins, which continues for about one week at ambient temperature before reaching full conversion.

MECHANICAL PROPERTIES

We used dynamical mechanical analysis (DMTA) to study the glass transition temperature of a cured film cast from dispersion A. DMTA is carried out by subjecting the sample to an oscillating deformation and measuring the resulting oscillating stress. In tensile mode, this results in a tensile storage modulus (E') and a tensile loss modulus (E"). The peak in stress lags behind the peak in strain by an amount that is given by the loss angle delta that reflects the viscous character of the sample. For a sample with no viscous character, delta is equal to zero degrees. Usually, the value of delta is given in the form of its tangent because tan d = E"/E'. The experiment is usually performed while the temperature of the sample is changed from –150°C to about 150°C. The values of E' and tan delta are plotted as a function of temperature.

Figure 3 shows the DMTA plot for the novel dispersion.

From looking at *Figure* 3 it becomes clear that the polymer film exhibits two transitions, a minor one at about 40°C and a major transition between 130 and 140°C. This is quite extraordinary in view of a MFFT of only 7°C. Hydroplastization effect, caused by the polymeric surfactant, may explain this feature.

PAINT APPLICATIONS

We formulated three different plastic coatings based on dispersion A: a clearcoat, a primer, and a pigmented coating that may either serve as a basecoat or a one layer coating. For comparison's sake, a conventional commercially available self-crosslinking dispersion with a similar MFFT that is advertised as being suitable for plastic coatings was used as a reference.

Clearcoat

Some of the basic properties of dispersion A were tested in a simple clearcoat formulation with a VOC of about 116 g/L. The clearcoat formulation consists of the ingredients listed in *Table* 2.

The clearcoat made from dispersion A had good gloss (78 GU at 20°/90 GU at 60°). Dust-free time was 15 min and the film was tack-free after 25 min. This can be correlated very well with the TTA experiment. The clearcoat based on the comparative dispersion was tack-free after 30 min. The König hardness was deter-

Table 2—Clearcoat formulation

Dispersion	87.1
Butyl glycol	5.8
Biocide	0.3
Wetting agent (polyether modified poly-dimethyl-siluxane)	0.3
Defoamer (polysiloxane copolymer)	0.3
HEUR thickener solution	0.6
Demineralized water	5.6

Table 3—Mill Base for Primer

Water	14.6
Dispersing agents	8.0
Surfactant	0.5
Defoamer	0.5
Biocide	0.5
Zinc oxide	2.7
Calcium carbonate	19.9
Titanium dioxide	53.2

Table 4—Primer Formulation

	Disp. A	Comp.
Surfactant-free acrylic dispersion	48	—
Conventional acrylic dispersion	—	46
Mill base	48	51
Defoamer	0.2	0.2
Wetting agent (polyether-modified dimethylpolysiloxane copolymer)	0.2	0.2
Coalescing agents	3	3

Table 5—Mechanical Properties of Primers

	Disp. A	Comp.	Units
Hardness	—	—	—
Persoz	117	120	S
König	51	58	S
Erichsen indentation	5.75	2.35	Mm
Impact			
Face	35	30	Kg.cm
Reverse	<5	<5	Kg.cm

Table 6—Adhesion of Primers onto Various Substrates

	Ambient Cure		80°C Cure	
	A	Comp	A	Comp
PC	5	5	0	4
ABS	0.5	0.5	0	0
PS	5	5	0	4
PA	2	3.5	0	3
PVC	0.5	4	0	3

0 = Excellent; 5 = total loss of adhesion.

Table 7—Mill Base for a Pigmented Coating

Demineralized water	15.8
Dispersing agent	7.6
Titanium dioxide	76.6

Table 8—Additives Premix for a Pigmented Coating

Butyl glycol	53.3
Polysiloxane copolymer defoamer	20.5
Wetting agent 1 (solution of a polyether-modified dimethylpolysiloxane-copolymer 52% in butyl glycol)	13.1
Wetting agent 2 (polyether-modified dimethylpolysiloxane)	13.1

Table 9—Pigmented Coating for Plastics

	Disp. A	Comp.
Acrylic dispersion	134.0	121.8
Mill base	54.2	54.8
Premix additives	3.0	3.0
Butyl glycol	4.0	2.0
Demineralized water	5.5	15.2
HEUR thickener (25% in butyl glycol)	1.3	1.3

Table 10—Adhesion of a Pigmented Coating onto Different Substrates

	Ambient Cure		80°C Cure	
	Disp. A	Comp	Disp.	Comp
PC	5	5	0.5	1
ABS	0.5	5	0	0.5
PS	5	5	0	3
PVC	1	4	0	0
PA 6	0.5	0.5	0	0.5

0 = Excellent; 5 = total loss of adhesion.

mined after one and seven days of drying at 23°C. From *Figure* 4 it can be seen that the hardness of the clearcoat based on dispersion A increases with time. The comparative dispersion shows no increase in hardness.

Block resistance of both coatings was determined using the BYK blocking tester. It was found that both clearcoats had excellent blocking resistance at ambient temperature. However, when the block-resistance was determined at 50°C, the coating based on dispersion A was far better (force needed to separate coated objects: 0.26 N/cm² for dispersion A and 2.27 N/cm² for the comparative dispersion). Both clearcoats were tested for chemical resistance properties. The clearcoat based on dispersion A could withstand over 50 double rubs with ethanol (50%), whereas the clearcoat based on the comparative dispersion already was attacked after 20

double rubs. Also, the resistance against ammonia, soap solution, and hand cream was found to be very good.

Primer

The new dispersion was also tested in a plastic primer. First, a mill-base primer was prepared using the ingredients listed in *Table* 3.

Mill-base primers based on both dispersions were formulated as indicated in *Table* 4.

Nonionic associative thickeners and water was used to adjust the viscosity to 25 s DIN 4. Solids content of primer A was 39%; the comparative primer had a solids content of 30%.

The calculated VOC of the primer was 54 g/L.

The mechanical properties of both primers were determined via application on Bonder panels. The results are given in *Table* 5.

The primers were then applied on a number of plastic substrates. Prior to application the surface was cleaned in order to remove all dirt, oil, grease, mold release, and other surface contaminates. After application the primers were either force dried at 80°C for 20 min after a 15-min flash-off or at ambient temperature. After seven days the adhesion was tested (cross-hatch adhesion according to ASTM D 3359-B). The results are given in *Table* 6.

Surprisingly, the adhesion of the primers dried at ambient temperature is very mediocre, contrary to the comparative dispersion. However, the adhesion becomes excellent when the primer is dried at 80°C. As this temperature is above the T_g of the polymeric surfactant, this may be an indication that some interpenetration of oligomer into the substrate is taking place.

Pigmented Coating

Next we developed a pigmented coating that may be applied either onto the primer or directly onto the substrate. The compositions of the mill base and the additives premix are given in *Tables* 7 and 8.

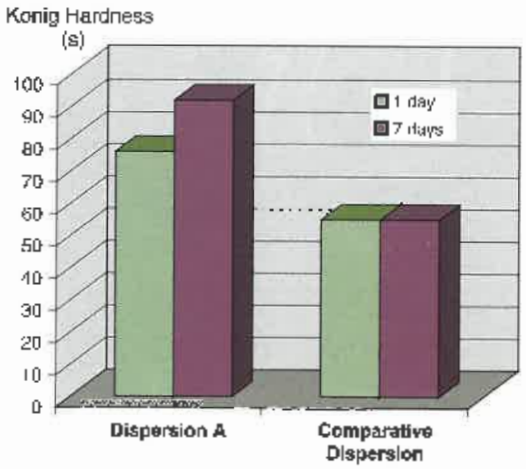
The pigmented coating was prepared by adding the mill base, the additives premix, a polyurethane thickener, and some butyl glycol to the acrylic dispersions under stirring. The ingredients are given in *Table* 9.

The viscosity was adjusted to 19–20 s DIN 4 with demineralized water.

The VOC of the pigmented coating is 104 g/L.

In order to check adhesion of the pigmented coating straight onto a plastic substrate, as would be the case in a one- or two-layer coating system, the pigmented coating was applied on a number of substrates. Again, the adhesion was determined after seven days of drying after an ambient or forced dry cycle. The results are given in *Table* 10.

Figure 4—Hardness build-up for clearcoats.



For the pigmented coating the same effects as for the primer were observed. Once again this may be attributed to interpenetration of the polymeric stabilizer into the substrate.

The properties of the different systems (one-coat, basecoat-clearcoat, and primer-basecoat-clearcoat) are currently being investigated in more detail.

CONCLUSIONS

Modern techniques for the control of dispersion particle morphology, combined with self-crosslinking chemistry, allow for the development of binders where T_g and MFFT are separated over a wide temperature range. Using polymeric surfactants can overcome some basic problems associated with the use of conventional surfactants in emulsion polymerization. These binders have the required surface hardness to be suited for use in industrial applications. As shown in this article, a binder aimed especially at coatings for plastic was developed and it was demonstrated that excellent adhesion can be obtained provided the right curing conditions are being used.

ACKNOWLEDGMENTS

We would like to thank Jolanda Ligtenberg-Vriens for the paint evaluation work and Tony Burrows of Rhopoint Instrumentation Ltd. for the Thin Film Analyzer measurements.

References

(1) van Krevelen, D.W. and Hoftyzen, P.J., *Properties of Polymers*, Elsevier Science Publishing Co., New York, 1990.
(2) Hoy, K.L., ACS, Div. of ORPL, Papers (now Div. Polym. Mat. Sci. Eng.), Vol. 51, 566-77, 1984.