Formulation and Production Forum

A Challenge: Aluminum Pigments in Aqueous Coatings

David P. Chapman—Silberline Manufacturing Co., Inc.*

The coatings industry has been in an evolutionary process of formulating to reduce the levels of volatile organic compounds in coatings. The process has been driven by regulatory considerations.

The aluminum pigment manufacturer has been in lock step with this process to develop user-friendly treated aluminum pigments for aqueous coatings. The focus of this paper is to present a historical overview of the progress, to date, and review two new surface treatment technologies recently introduced to the industry. These new chemistries give the coatings formulator more options in the process of creating aqueous aluminized coatings.

Formulating techniques are presented utilizing treated aluminum pigment technologies, along with formulations, where appropriate, representing commercially available resin systems.

These technologies can be and are used in general industrial coatings, industrial maintenance formulations, high performance maintenance systems, roof coatings, as well as automotive OEM and refinish coatings.

When was the last time you gave any thought to the significance of 174°F in your daily life? Life has many simple pleasures which are taken for granted—like waking up to the scent of coffee brewing or bacon sizzling on the stove. What about the warm, comfortable, pleasant scent that harks our memory back to Grandma's kitchen, where freshly baked bread is prepared? Actually, this wonderful aroma, from baking bread, occurs at 174°F when ethanol is emitted as a gas. This industry, too, as the coatings industry, is being regulated by the 1990 Clean Air Act. Many large bakeries are now required to submit plans to eliminate the pollution of ethanol in the atmosphere during the baking process.[1] The coatings industry is just one facet of our busy lives impacted by the Clean Air Act of 1990.[2]

The coatings industry has been in an evolutionary process of formulating to reduce the levels of volatile organic compounds in coatings. The process has been driven by regulatory considerations, not only at the national level, but at the state and local levels as well. State and local laws limiting VOCs in industrial coatings have been in place for a number of years, creating a need for alternatives to the traditional high VOC solvent-based coatings. At the Federal level, in 1990 Congress enacted the Clean Air Act amendments which broadened the mandate for volatile organic compound reduction over the next 10 years.

The extent of the regulatory process in future years is shown in *Table* 1. This table shows maximum VOC contents of coatings—extracts from the table of standards as shown in Appendix II EPA final framework from the AM coatings rule, July 14, 1994.[3]

Additionally, the ACT targeted many commonly used coatings solvents as hazardous air pollutants: toluene, xylene, methyl ethyl ketone, methyl isobutyl ketone, methanol, and ethylene glycol monyl butyl ether.[4]

With this double-edge regulatory sword, the aluminum pigment manufacturer and the coatings formulator must keep both eyes open—one on VOCs and the other on solvent choice. An additional challenge for the aluminum pigment manufacturer is to provide aluminum pigments which will function well in aqueous coatings, providing good gas stability, aesthetics, and application characteristics.

With the shift to lower VOCs in general industrial coatings, industrial maintenance formulations, high performance maintenance systems, roof coatings, automotive refinish, and OEM coatings, the choice of resin system is gravitating toward water-reducible and waterborne coatings.

As defined in ASTM D 3960, a volatile organic compound, VOC, is any organic compound that participates in atmospheric photochemical reactions.

To calculate determined VOC, the following formulas are used by the American Society for Testing and Materials under Method D 3960.

(1) Determine the non-volatile content of the coating—ASTM Method D 2369.

(2) Determine the density of the materials—ASTM D 1475.

(3) Determine the water content—ASTM D 4017.

Table 1—Maximum VOC Contents of Coatings

Category	1996 (g/L)	2000 (g/L)	2004 (g/L)
Industrial maintenance coatings	350	350	300
High performance coatings			
Floor coatings	400	350	300
Rust-preventive coatings	400	350	300
Concrete protective coatings	400	350	300
Metallic-pigmented coatings	500	450	400
Traffic marking paints	150	150	100
Low volume coatings			
Anti-fouling coatings	450	450	450
Extreme high durability coatings	800	800	800
High temperature coatings	650	650	650
Impacted immersion coatings	780	780	780
Nuclear power plant coatings	450	450	450
Pre-treatment wash primers	780	780	780
Repair/maintenance thermoplastic coatings	650	650	650

Presented at the 23rd International Waterborne, High-Solids,and Powder Coatings Symposium, February 14-16, 1996, New Orleans, LA.

*Lincoln Dr., P.O. Box B, Tamaqua, PA 18252-0420.

(4) VOC (Grams/Liter* $-H_2O$) =

$$1000 \times \frac{[(100-\%NV)(DM)-(\%H_2O)(Dm)]}{100-\frac{[(\%H_2O)(Dm)]}{.997}}$$

% NV = % non-volatile
Dm = density of paint in gm/ml
% H_2O = % of water by weight
0.997 = density of water at 25°C

OR

$$(5)\quad \frac{\text{Total Pounds of Solvent}}{\text{Total Gallonage} - \text{Gallonage of Water}} = \text{Pounds/Gallon} = \text{VOC}$$

*To convert grams per liter to pounds per gallon VOC, multiply VOC g/L by 8.345×10^{-3} or divide by 119.8.

Looking back in time, Silberline offered aluminum pigments which were treated with surfactant to make them water miscible in aqueous systems. These were marketed under the treatment of "WD" (water-dispersible) aluminum pigments. While they, as a family, offered water dispersibility, they were not passivated to offer long-term package stability. These grades were, and are, used typically in two-pack systems in general industrial and maintenance types of systems.

Not too long after the introduction of water dispersible grades, a newer technology was offered in the marketplace, consisting also of the utilization of surfactants for water miscibility, but in addition a volatile corrosion inhibitor was incorporated into the paste, providing a synergistic effect, which offered improved resistance to gassing over time. The volatile corrosion inhibitor used comes from the class of nitroparaffin solvents. These grades were marketed to the general industrial and maintenance markets under the trade name of Hydro Paste™ grades. Not too long after the introduction of Hydro Paste grades, further technological improvements were made in the passivation of aluminum pigments. Utilizing phosphate chemistry, the surface of the flake was treated to provide much longer-term package stability in terms of hydrogen gas evolution. This family of pigments, Aqua Paste™ inhibited aluminum pigments finds uses also in the general industrial and maintenance markets, as well as the roof coating market. This passivated aluminum pigment technology, offering greatly reduced potential to hydrogen gas evolution while at the same time retaining maximum brilliant metallic effects, was widely accepted in these markets. However, the need for a more universal passivated aluminum pigment continued to be requested from the marketplace.

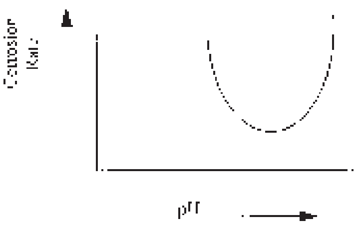

Figure 1—pH effects; aluminum.

Table 2—Waterborne Starting Point Formulations Based on Joncryl 537[a]

	Gallons	Pounds
Aluminum premix		
Silberline Aquasil BP 3500	3.98	49.43
Butyl cellosolve (Ethylene glycol monobutyl ether)	6.87	51.59
Texanol	0.32	2.50
Main batch vehicle		
Joncryl 537	66.68	583.48
DPM (Diproplyene glycol methyl ether)	3.28	26.00
Add premix, then add		
Deionized water	16.42	136.78
Patcote 519	0.28	1.91
DC 14	0.17	1.15
	98.00	852.84

Theoretical weight/gallon	8.70
Theoretical non-volatile/weight	35.14
Pigment/binder ratio	0.1/1.0
pH	8.67
VOC	2.32 lb/gal (277 g/L)
Viscosity	21 sec #4 Ford cup @ 73°F

(a) Joncryl is a registered tradename of Johnson Wax.

To better understand the passivation process, one needs to understand the basic properties pertaining to aluminum metal itself. Aluminum metal found naturally will have an aluminum oxide layer chemically bonded to the surface of the metal several angstroms thick. Aluminum metal has a tremendous affinity for oxygen and only will be found in nature in this state. Looking at the surface of an aluminum flake, this is the first layer that we find on the flake. After the manufacturing or milling process, we find a second layer consisting of a fatty acid used in the milling process. This can be either oleic acid, in the case of non-leafing aluminum pigments, or stearic acid, if leafing type pigments are manufactured. Surrounding the aluminum metal, aluminum oxide, and fatty acid layers is the solvent carrier or solvent phase—typically mineral spirits or other aliphatic solvent. It is this combination that needs to be fully passivated or protected from attack, not only by water, but acids and alkali materials as well. In addition to the reaction of aluminum with water, as shown in the following, which can generate a substantial amount of hydrogen gas in a relatively short period of time, one has to deal with the amphoteric nature of the metal itself.

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2\uparrow$$

In a strongly acidic media, the aluminum corrosion process will involve proton reduction at cathodic sites on the aluminum surface and liberate hydrogen gas. Under alkaline conditions, the cathodic reaction site will liberate hydrogen and the aluminum ion complexes

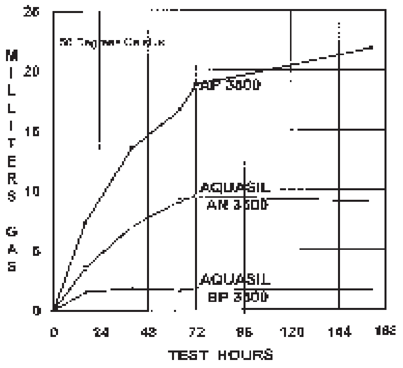

Figure 2—Aquasil/Aqua Paste technologies; gassing—Joncryl 537.

with the hydroxyl ion to produce a water-soluble aluminum species. Thus, it can be seen that the pH of the paint or coating ideally should be held as closely to neutral as possible. In actuality, there are two ways to chemically control corrosion, including maintaining the pH at the appropriate level or adding inhibitors. Control of pH can be very effective, but it is not uncommon that the pH required for corrosion control results in poor product performance. Typically, most of today's waterborne systems are formulated for performance within a range of pH between 8 to 9. Levels much lower or higher than these can cause stability and performance problems.

Aluminum metal is known to resist corrosion in some cases, because of its ability to form an aluminum oxide layer on the surface of the metal. This layer can be an effective barrier between the metal surface and the aqueous environment. However, aluminum oxide is soluble in both acidic and alkaline systems. When exposed to either environment the layer can dissolve and the metal will typically react; hence, the control of pH in the formulation is of importance. The relationship between corrosion rate and pH in the formation of this aluminum oxide layer is parabolic in nature, as illustrated in *Figure* 1. There is a range in which the aluminum oxide layer does contribute to the protection of the aluminum metal itself from reaction.

Further enhancing this natural ability of aluminum metal to form an oxide layer is the incorporation of several types of passivation chemistries, such as the previously discussed phosphate chemistry.

Many other manufacturers have been conducting extensive research, looking for improved methods of passivation of the aluminum flake. Surprisingly, there are several different types of corrosion inhibitors, two of which are passivating and film-forming inhibitors. Film forming inhibitors form barriers between the metal surface and the aqueous environment, and can be organic or inorganic. Organic film-forming inhibitors are long chain molecules with a polar end that adsorbs on the metal surface and an organic end which is present in the aqueous environment to repel it. Examples of such inhibitors would be phosphates. Inorganic film forming inhibitors precipitate an insoluble layer on the surface of the metal and include compounds such as silicates.[5]

Recently introduced into the marketplace is the Aquasil™ family of passivated aluminum pigments. At the present time, two new distinct passivation chemistries have been utilized in the development of Aquasil AN type pigments, as well as Aquasil BP type pigments. The Aquasil AN technology uses phosphate chemistry, as referenced in U.S. Patent No. 5,215,579.[6] The Aquasil BP technology uses unique passivation chemistry, as referenced in U.S. Patent No. 5,348,579.[7] Both of these chemistries offer substantially reduced tendencies for the evolution of hydrogen gas in many different types of resin systems.

The two new patented Aquasil technologies provide additional passivated chemistries for the formulator involved with aqueous aluminized coatings formulations. The following four starting point formulations illustrate the use of these technologies in general industrial and maintenance coatings.

The formulation illustrated in *Table* 2 shows a starting point formulation based on Johnson Wax's Joncryl 537 (a waterborne general industrial acrylic). Viewing this formulation, we see that a premix is prepared utilizing the Aquasil BP 3500 which is slurried with butyl cellosolve. This, in turn, is added to the main batch portion of the formulation which contains Joncryl 537 and dipropylene glycol methyl ether. A small adjustment is made after the pre-mix, utilizing deionized water, Patcote 519 and DC14. The additives provide flow and leveling characteristics to the formulation. It is important to realize that the creation of this formulation is done under low speed agitation, preferably with paddle-type mixing apparatus. High-speed dispersing equipment causes flake damage and loss of aesthetics.

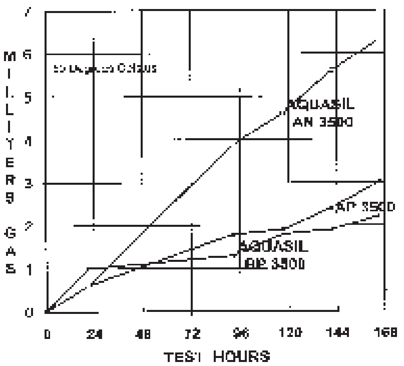

Figure 3—Aquasil/Aqua Paste technologies; gassing—Rhoplex WL-51.

Figure 2 shows the results of the 168 hr, 50°C, hot oil bath testing, with Aqua Paste 3500, Aquasil AN 3500, and Aquasil BP 3500. It can be seen from this table that the Aquasil BP 3500 offers the lowest tendency toward gassing, at approximately 2 ml. The Aquasil AN 3500 shows 8 ml of gas produced, while the older Aqua Paste technology is approximately 22 ml.

This particular formulation has a VOC of 2.32 lb/gal with a package vis-

Table 3—Waterborne Starting Point Formulations Based on Rhoplex WL-51[a]

	Gallons	Pounds
Aluminum premix		
Silberline Aquasil BP 3500	3.84	47.66
Butyl cellosolve (Ethylene glycol monobutyl ether)	2.37	17.80
Butyl carbitol (Diethylene glycol monobutyl ether)	3.18	25.30
Main batch vehicle		
Rhoplex WL-51	71.27	612.90
Water	8.40	70.00
Butyl cellosolve (Ethylene glycol monobutyl ether)	10.23	76.80
Dibutyl phthalate	1.45	12.70
Add premix, then add		
Patcote 519	0.06	0.40
BYK 301	0.31	2.50
	101.11	866.06

Theoretical weight/gallon	8.57
Theoretical non-volatile/weight	34.44
Pigment/binder ratio	0.1/1.0
pH	7.44
VOC	2.80 lb/gal (366 g/l)
Viscosity	31sec #4 Ford cup @ 74°F

(a) Rhoplex is a registered tradename of Rohm and Haas.

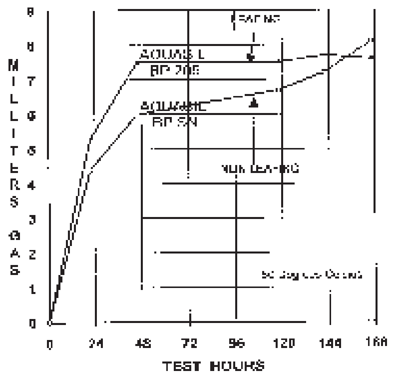

Figure 4—Aquasil technology; gassing—Maincote HG56.

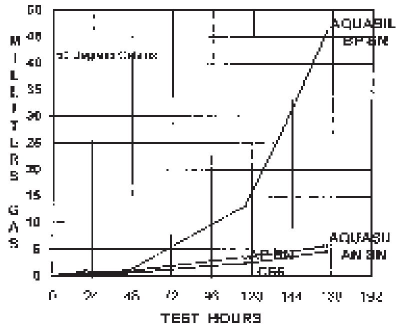

Figure 5—Aquasil/Aqua Paste technologies; gassing—Kelsol 3960.

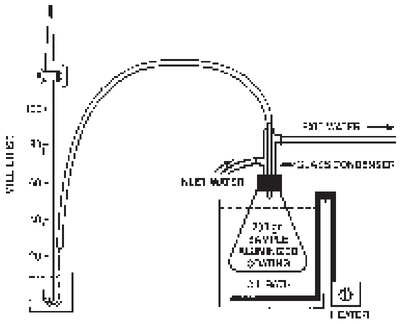

Figure 6—Accelerated stability test.

cosity of 21 sec, No. 4 Ford Cup.

In reviewing the second starting point formulation, using Rohm and Haas' Rhoplex WL51, which is a waterborne acrylic designed for industrial coatings on both metal and plastic substrates, it can be seen that the incorporation methods are similar to that of the previous formulation. A simple pre-mix is prepared utilizing Aquasil BP 3500 with butyl cellosolve and butyl carbitol as co-solvents. This, in turn, is then added to the main batch under low agitation, followed by the addition of two flow and leveling additives—Patcote 519 and BYK 301. This formulation is shown in *Table* 3. The gassing results utilizing the Aquasil AN and BP technologies, as well as the older Aqua Paste technology are shown in *Figure* 3. It can be seen that the Aquasil BP 3500 offers the lowest gassing at approximately 2.2 ml, whereas here it can be seen that the older technology performs very well, offering gassing results at 3 ml, while in turn the Aquasil AN 3500 is a little higher at slightly over 6 ml. This particular formulation has a VOC of 2.8 lb/gal with a package viscosity of 31 sec, No. 4 Ford cup.

Another starting point formulation based on Rohm and Haas' Maincote HG56, a waterborne acrylic designed for industrial maintenance coatings, is prepared in a slightly different manner than the previous two formulations. Here, it is interesting to note that the Aquasil BP 205 which is an ASTM Class B leafing aluminum, is simply slurried in water during the pre-mix process. In the premix the Maincote HG56 acrylic resin is added until a pourable consistency is obtained, which can be transferred to the main batch. The resin is then added to the formulation. Additional Texanol is added, followed by some ammonia, a foam control agent (Tego Foamex 825), along with some additional co-solvent, methyl carbitol, and finally QR708, which is used to control viscosity. The resulting pH of this formulation is 8.4 with a VOC of 2.01 lb/gal. The package viscosity is 21 sec, #4 Ford cup. This is a single package maintenance type formulation. This particular formulation offers excellent appearance, and can be made *in situ*. The formulation is referenced in *Table* 4.

Table 4—Waterborne Starting Point Formulations Based on Maincote HG 56[a]

	Gallons	Pounds
Aluminum premix		
Silberline Aquasil BP 205	11.13	144.53
Deionized water	11.84	98.63
Maincote HG 56	73.76	624.75
Texanol	4.74	37.56
Ammonia 28	.59	4.50
Tego Foamex 825	.36	3.00
Methyl carbitol	5.80	49.36
QR708 (10%)	.24	2.00
	108.46	964.33
Theoretical weight/gallon	8.89	
Theoretical non-volatile/weight	43.73	
Pigment/binder ratio	0.26/1.0	
pH	8.43	
VOC	2.01 lb/gal (241 g/L)	
Viscosity	21 sec #4 Ford cup @ 73°F	

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[a] Maincote is a registered tradename of Rohm and Haas.

The accelerated gassing test is shown in *Figure* 4. It can be seen that the relative gassing obtained is low at slightly below 8 ml. Also shown in this table is a non-leafing general industrial type aluminum pigment, Aquasil BP SN. The gas results for this particular formulation are approximately 8 ml.

The last formulation shown in *Table* 5 is based on Reichhold Chemical's Kelsol 3960, which is a chain-stopped water-reducible alkyd. This alkyd can be used in the general industrial as well as the maintenance coating market. This particular formulation shows the use of Aquasil AN SN, which is a general industrial, non-leafing type of aluminum pigment. As in the first two formulations, the aluminum pigment is first prepared as a pre-mix utilizing butyl cellosolve as the co-solvent. The main batch containing the Kelsol 3960 resin, the manganese and cobalt driers, along with Active 8, and finally water is adjusted to a pH of 8.3 with ammonium hydroxide. The pre-mix is then added to the homogeneous mixture. The VOC of this air-dry coatings system is 3.34 lb/gal. The resulting viscosity is 61 krebs units.

Figure 5 shows the relative gassing utilizing Aqua Paste SN, as well as Aquasil BP SN and the Aquasil AN SN as illustrated in the Kelsol 3960 formulation. Here it can be seen that the Aquasil BP SN type technology is at a relatively high amount of gas—approximately 45 ml, whereas the Aquasil AN SN type technology is relatively low—around 5

Table 5—Waterborne Starting Point Formulations Based on Kelsol 3960[a]

	Gallons	Pounds
Aluminum premix		
Butyl cellosolve	7.117	53.45
Silberline Aquasil AN SN	7.007	92.21
Main batch vehicle		
Kelsol 3960	27.607	234.11
Mang. hydrocure II 8%	.387	3.27
Cobalt hydrocure II 5%	.715	5.47
Active 8	.271	2.14
Water	54.220	451.65
Adjust main batch vehcile pH		
Ammonium hydrocide 28	1.467	11.00
	98.791	853.30

Theoretical weight/gallon	8.64
Theoretical non-volatile/weight	29.07
Pigment/binder ratio	.326/1.0
pH	7.2
VOC	3.34 lb/gal (400 g/L)
Viscosity	61 KU

(a) Kelsol is a registered tradename of Reichhold Chemicals.

ml. It is also interesting to note that the older Aqua Paste SN type technology offers low gassing at approximately 5 ml, as well. After over one year, the package stability of this particular formulation is very good.

This formulation, serving as a light duty maintenance coating, was applied approximately 18 months ago to solvent storage tanks at the Silberline facility located in Lansford, PA. The system using the Aqua Paste technology continues to perform very well, providing corrosion resistance to the tanks.

In conclusion, it can be seen that the newly introduced Aquasil type technologies offer the formulator additional choices in the coatings development process. A challenge remains for the formulator in that the Aquasil technologies are system-dependent, as shown in earlier results. A wide range of aluminum pigment grades is available in these technologies (see *Table* 6).

The hydrogen gas accelerated stability test was designed to study the gas generation potential and stability characteristics of any water-based aluminized coating system.[8] The equipment used for a single set-up is shown in *Figure* 6. The equipment consists of the following components:

- Wide-mouth, glass Erlenmeyer flask—250 ml capacity.
- Beaker—glass, 250 ml
- Burette—standard glass 100-ml graduated with glass stop cock and 0.2 ml divisions.
- Condenser—glass jacketed, special order.
- Glass tubing—standard glass 1/4-in. (6.35 mm) inside diameter, 5/16-in. (7.94 mm) outside diameter. and 5-in. (127 mm) length for forming the "J" tube.
- Tubing—pure latex amber rubber tubing, 1/4-in. (6.35 mm) I.D., 1/2-in. (12.7 mm) O.D. for hydrogen.
- Neoprene rubber stopper—preferred connection for glass condenser to 250-ml Erlenmeyer flask No. 8 with one hole.
- Oil bath—constant temperature immersion circulating bath capable of temperature control.
- Oil—commercially available mineral oil or suitable heat transfer fluid.
- Thermometer—ASTM thermometer having a range from 30° to 180°F (–2 to +80°C) and conforming to the requirements for thermometer 15°F or 15°C as prescribed in Specification E1.

The procedure for conducting the hydrogen gas stability test is as follows:

—Weigh 200 g of the sample directly into the 250-ml Erlenmeyer flask, assuring that none coats the neck where the stopper is placed.

—Insert the filled flask into the oil bath (temperature controlled to 125°F (51.7°C)) and connect the glass condenser-stopper into the neck of the flask. Flask should be supported internally via flask holder or externally with vinyl-coated, three-pong clamps.

—Fill the 250-ml beaker with water and insert the 100-ml burette and J-tube into the water.

—Draw the water level to the 100-ml mark on the burette and close the stopcock.

—Record the time at the start of the induction period.

—After a one-hour induction period, record the time and the water level point on the burette. The latter figure is the zero point.

—Unless otherwise specified, conduct the test continuously for one week, 168 hr, with a reading taken every 24 hr, at the corresponding time that the zero point was taken.

—If the water level exceeds the confines of the burette, the test should immediately be terminated.

Table 6—Aquasil Aluminum Pigment Grades

Silberline Grade	Non-Volatile % by Weight (±2.0%)	Max. % Retained 325 Mesh	D(50%) Microns
Aquasil AN 205	69.6	1.0	—
Aquasil AN SN	72.7	1.0	19.0
Aquasil AN SQ	72.7	2.0	28.0
Aquasil AN 2750	72.7	1.0**	55.2
Aquasil AN 3500	72.7	2.0	31.0
Aquasil AN 3622	81.3	1.0	39.5
Aquasil AN 3641	72.7	1.0	34.2
Aquasil AN 5500	75.0	0.1	18.8
Aquasil AN 5745	72.7	0.1	22.0
Aquasil BP 205	68.0	1.0	—
Aquasil BP SN	63.0	1.0	19.0
Aquasil BP SQ	63.0	2.0	28.0
Aquasil BP 2750	68.0	1.0**	55.2
Aquasil BP 3500	63.0	2.0	31.0
Aquasil BP 3622	76.0	1.0	39.5
Aquasil BP 3641	68.0	1.0	34.2
Aquasil BP 5500	62.0	0.1	18.8
Aquasil BP 5745	62.0	0.1	22.0

The calculation of the total milliliters of hydrogen gas evolved to the nearest 0.1 ml follows:

$$H = V - Z$$

where:

H = hydrogen gas evolved in milliliter
V = volume of water in burette at 168 hr
Z = zero point volume of water in burette

The search continues in an effort to find additional chemistries which will offer even better stability in aqueous types of formulations, whether they are for the general industrial, industrial maintenance, or OEM automotive and refinish automotive markets.

Acknowledgments

This paper represents the cumulative efforts of members of the Silberline Manufacturing Co., Inc., Research and Development, and Technical Service Departments. Their support and guidance in writing this paper was essential to its creation.

The following people are acknowledged: William G. Jenkins, Director of Research and Development; Craig B. Keemer, Research Associate; H. Taylor Lamborn, Research Associate; Michael A. Curcio, Technical Service Representative; and Richard A. Johnsen, Technical Service Representative.

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