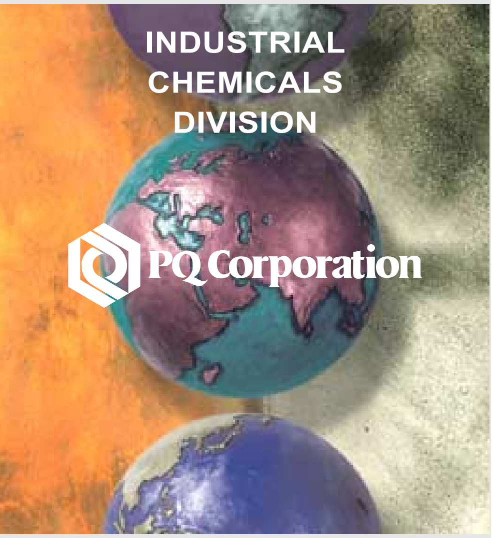

Bulletin 12-32/803

Using Kasil®6 Potassium Silicate and PM5108 Silica Hydrogel in Inorganic, Water-Based, Zinc-Rich Coatings

INTRODUCTION

In the 1970's, NASA initiated a research program to develop better coatings for use in space-related applications, such as gantries and other steel launch structures at the Kennedy Space Center in Florida. A successful coating would have to be able to withstand the corrosive effects of ocean spray and fog, as well as the extremely hot exhaust gases and thermal shock associated with the launching of space vehicles. NASA scientists discovered that such a coating could be formulated from a very high-ratio* potassium silicate binder incorporating a high loading of zinc dust. The addition of methyltrimethoxysilane was said to provide better adherence to steel structures through more uniform dehydration. A patent on this technology was issued in 1971 (U.S. 3,620,784).

*The mole ratio of a potassium silicate is defined as moles (SiO_2 / K_2O). The weight ratio is defined as weight (SiO_2 / K_2O). For potassium silicates, the mole ratio is 1.57 times the weight ratio.

This NASA patent specified that the mole ratio of the potassium silicate should be in the range of 4.8 to 5.3 and the solids* in the range 19-22%. However, commercially available potassium silicates only have mole ratios up to 3.9, and more commonly 3.3. These commercial potassium silicates were "totally ineffective... providing a coating subject to cracking and crazing upon heat application or air aging." So while a higher ratio potassium silicate was essential, it was not available commercially nor was the process for making one disclosed in the patent.

*The solids of a potassium silicate are defined as the sum of the weight percents SiO_2 and K_2O.

An additional NASA patent (U.S. 4,162,169) was issued in 1979 that embodied certain improvements to the prior art. The upper end of the claimed range of mole ratios was extended to 6.0, and the solids to 27%. Furthermore, the patent provided specific instructions for making a high-ratio potassium silicate. The process starts with a commercial potassium silicate, for example Kasil®6 from the PQ Corporation, which is a 3.3 mole ratio, 39% solids product. The ratio is raised to approximately 5.3 by dissolving a silica hydrogel powder into the commercial silicate. Such a silica hydrogel powder is available from PQ Corporation as PM5108 silica hydrogel.

Is a License Required to Practice the NASA Technology?

No. Both of the NASA patents have expired.

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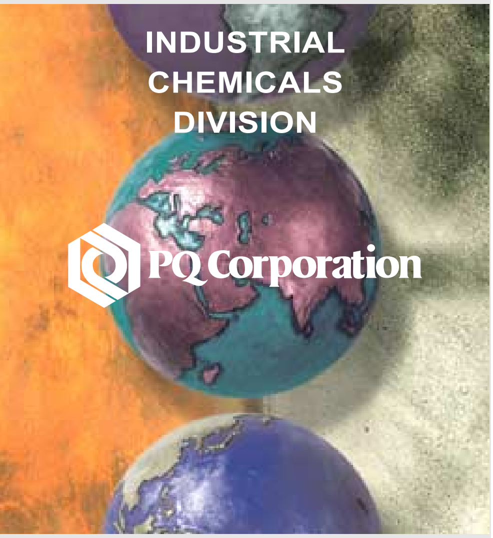

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PQ Corporation is a privately held global enterprise operating in 20 countries, with annual revenues in excess of $500 million. PQ is a leading producer of silicate, zeolite, and other performance materials serving the detergent, pulp and paper, chemical, petroleum, catalyst, water treatment, construction, and beverage markets.

Potters Industries, PQ's wholly owned subsidiary, is a leading producer of engineered glass materials serving the highway safety, polymer additive, fine abrasive, and conductive product markets.

Where Has the NASA Technology Been Applied?

In addition to structures at the Kennedy Space Center, NASA's inorganic zinc silicate coating technology has been applied on many important landmarks, particularly in coastal locations. The National Parks Service and Statue of Liberty Foundation chose inorganic zinc silicate paint for the iron skeleton of the Statue of Liberty during its renovation. Inorganic zinc silicates have also been applied to the Golden Gate Bridge, the Panama Canal, and numerous offshore drilling rigs, bridges, and antenna systems. They have also been used on the brake rotors for Jeep Cherokee and Chevrolet Corvette vehicles.

How Does it Work?

Zinc provides effective corrosion resistance through galvanic protection. Zinc is more electrochemically active than iron, so when the two metals are coupled through close contact and subjected to aqueous electrolytes, the zinc is preferentially oxidized and the iron is spared.

This is the principle at work in galvanized steel surfaces, in which steel is dipped into a bath of molten zinc metal. Inorganic zinc silicates provide the same sacrificial corrosion protection while being practical to apply (painting, not dipping) on large steel structures. Furthermore, the silicate binder reacts with the bare steel surface and the zinc filler to form strong chemical bonds that are very resistant to damage. Unlike organic binders, the inorganic silicate compositions are also extremely heat resistant up to 400ºC (750ºF).

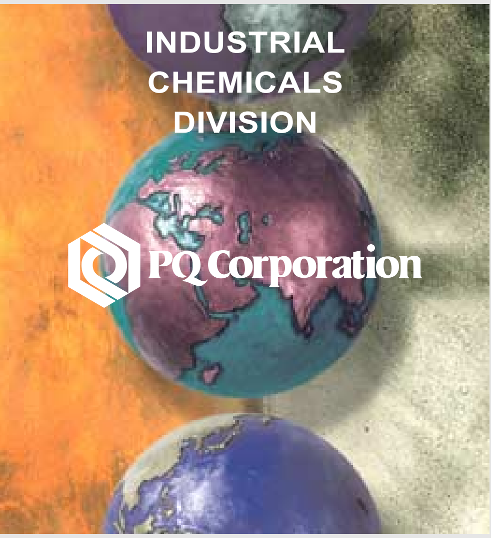
In zinc silicate primers, the zinc metal is incorporated at a very high loading-typically around 86% by weight. Such a high loading ensures that the zinc particles will be in close contact with each other and with the steel surface when the coating is dry, a requirement for galvanic protection.

What is a Typical Formulation?

The following formulation is taken from Example No. 1 of U.S. Patent 4,162,169, adapted to the typical properties of Kasil®6 and PM5108. This formulation will make somewhat less than a gallon of binder, but when the zinc powder is added before use, the final volume will be about one gallon.

COMPONENT	PROPERTY	VALUE
Kasil®6 potassium silicate	Wt. ratio SiO_2/K_2O	2.10
	Solids (%)	39.2
	Quantity as-is (kg)	1.79
	Quantity solids (kg)	0.70
PM5108 silica hydrogel	Solids (%)	37.0
	Water (%) [~LOD*]	63.0
	Quantity as-is (kg)	0.779
	Quantity solids (kg)	0.288
Water	To add (kg)	1.160
	From hydrogel (kg)	0.490
	From silicate (kg)	1.086
	Total (kg)	2.736
Methyltrimethoxysilane	To add (kg)	0.070

*LOD = loss on drying (2 hr @ 105^{o}C)



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This formulation should be adjusted for the specific properties of the raw materials being used. In particular, it is very important to adjust the formulation to compensate for even small variations in the moisture content of the silica hydrogel from batch to batch, because this will affect the solids level of the final binder-which influences the process time for complete dissolution of the silica as well as the water insolubility of the final dried paint.

How Is the Batch Prepared?

The steps to prepare the formulation are given in detail in the patent example; the following is a simplified summary:

1. The silicate is poured into a mixing vessel and stirred at 3000 rpm to generate a vortex.
2. The hydrogel is gradually added into the vortex.
3. The mixture will gradually thicken as the hydrogel dissolves, which will tend to collapse the vortex. Water is trickled in to expand the vortex back out. Eventually a clear, viscous solution is formed with a temperature between ~35-70ºC (owing partly to heat generated from the agitation), and all but 15-20% of the water will have been added.
4. The methyltrimethoxysilane is gradually added over ~ 5 min. The viscosity will drop and the solution will become essentially transparent.
5. Vortexing is continued for up to 1/2 hr, during which the impeller speed can be lowered and the remaining water added.
6. The final binder is immediately canned while still warm. During cooling, a light scum may form on the surface, but it will dissolve upon standing within a day or less. There should be no sludge on the bottom of the container.

How Is the Coating Prepared for Use?

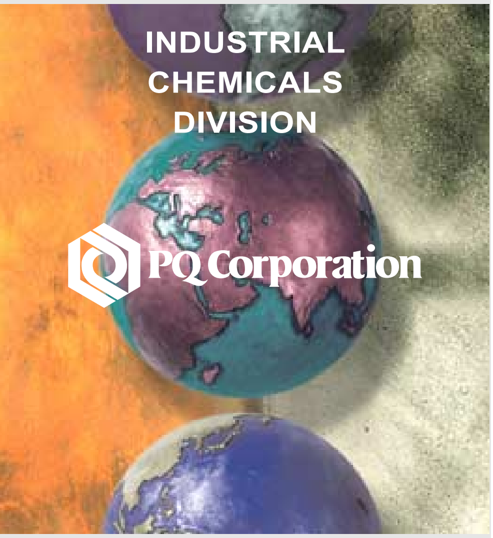
Inorganic zinc silicate coatings are typically self-curing, two-package compositions. The first package is the high-ratio potassium silicate binder, possibly with other additives such as pigments. The second package is zinc dust, which is added just before the paint is applied. The zinc cannot be incorporated into aqueous inorganic silicate paints because it will react slowly according to the equation:

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2\uparrow$$

This reaction not only passivates the zinc, but it also generates hydrogen gas that can blow the lid off of a paint can. Therefore, in practice the zinc is always added by the user. The zinc powder must be added to the liquid binder, not vice-versa. Once mixed, it should be constantly agitated, and the coating must be applied within a period of hours following this addition (pot life is shorter at higher temperatures).

How Is the Coating Applied?

Follow the specific recommendations of the coating manufacturer.



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12-32-9/03

What Are the Advantages of Inorganic Zinc Silicate Coatings?

- Unsurpassed corrosion resistance in severe environments, such as marine applications
- Significantly greater performance as single-coat systems than organic zinc epoxies
- High temperature resistance
- Good impact resistance
- Zero volatile organic content (VOC)
- Topcoating possible, but not generally required except when extremes of pH are likely to be encountered (e.g., a chemical plant with acid exposure)
- Good economics
- Cleanup requires no solvents, only water.

Why Use Potassium Silicate and Silica Hydrogel from PQ?

PQ is the world's leading supplier of soluble silicates. PQ has been a leader in potassium silicate since its introduction to the North American market in 1942, and currently supplies a wider variety than any other manufacturer. The company is also a world leader in the production of silica hydrogels, and has been serving this market continuously since 1979. Our technical service specialists stand ready to assist you in using our products in your application.

TYPICAL PROPERTIES OF KASIL®6

Property	Typical Value
Wt Ratio SiO_2/K_2O	2.1
Mole Ratio SiO_2/K_2O	3.3
K_2O (wt%)	12.65
SiO_2 (wt%)	26.5
Percent Solids	39.2
Density @ 20°C (°BÈ)	40.3
Density @ 20°C (lb/gal)	11.5
Viscosity (cp)	1050

TYPICAL PROPERTIES OF PM5108

Property	Typical Value
SiO_2 (%)	99.0
Loss on Drying 2 hr @ 105°C [LOD] (%)	63
Loss on Ignition @ 1000°C [LOI] (%)	2.8
BET Surface Area (m^2/g)	850
Water-Soluble Salts (%)	1
pH (12.5% w/v)	2.8
Particle Diameter, Microtrac Vol. 50%< (µm)	18