

**THE EVOLUTION OF SILICON-BASED TECHNOLOGY IN  
COATINGS**

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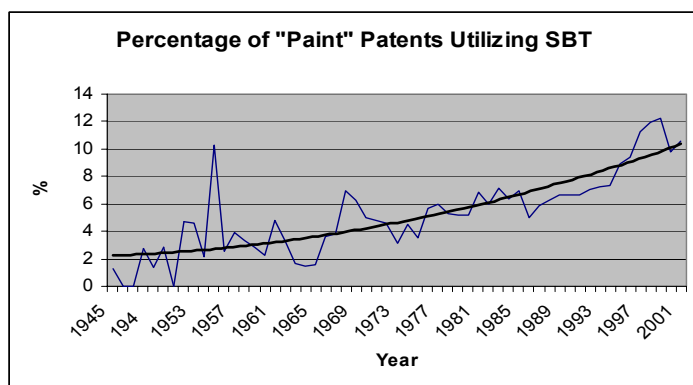
## ABSTRACT

The utility of silicon-based technologies in coatings has evolved from specialty, high-performance applications into broad usage throughout the coatings industry. Tailored chemistries and cost-effective performance provide an increasing number of formulators with solutions to demanding application requirements. This paper looks at the scope of silicon-based technologies and the new wave of applications benefiting from these materials. Significant emphasis is placed on the blurring of the boundaries between silicon-based and organic chemistries. Extensive patent references provide the reader with an overview of the state of the art.

## INTRODUCTION

It was not until 1935 that the first practical use for silicon-based technology (SBT) was created: Glass tapes impregnated with the resin provided excellent insulation and protection for electrical wiring on U.S. Navy submarines. During the last few decades, the utility of SBT has expanded beyond traditional applications to include a majority of coatings markets. In the last five years, at least 3,000 patents have been issued that discuss its use to improve the performance of protective paints, coatings and finishes. A search of chemical abstracts for paint patents issued between the years 1945 and 2001 reveals a steady increase (See Chart One) in the percentage of issued patents citing the utility of silicon-based technologies. Interest continues to focus on the traditional benefits of SBT materials, including weathering and heat resistance. Patent filing, however, has increased in new areas of SBT utilization.

Chart One



This paper will review the utility of reactive silicone fluids, silanes and siloxanes. These are available as 100% active monomers, emulsions, polymer/solvent solutions, 100% liquid polymers, or flakes. These materials are used as adjunct and modifiers of organic resins, or as the primary binder in protective coatings formulations. These include coatings, which possess heat, weather corrosion, biofouling, abrasion resistance, and other performance properties enhanced by SBTs.

## PRIMERS

Silicates and alkoxy silanes have broad utility in formulating primers for a variety of metal and siliceous substrates. Widely known as adhesion promoters, alkoxy silane-based primers also offer controlled hydrophobicity, excellent UV and thermal stability, surface activity, chemical resistance and corrosion protection. Two areas of interest include zinc-rich primers and chromium replacement.

As early as 1962, partial hydrolyzates of alkoxy silanes (e.g., tetra-ethoxysilane) or alkali silicates, combined with zinc metal powder, were found to provide galvanic protection of ferrous substrates above that imparted by organic resin-based zinc primers.<sup>i</sup> A limitation of this technology was the inherently short pot and shelf life. Twelve years later, it was found that by transesterifying the silicate with organic polyols (e.g., ethylene glycol or glycerol), the stability and overall performance of the primer were greatly improved.<sup>ii</sup> This innovation is one of the most widely cited silicon-based inventions (34 citations) in the 1964-1985 time period.

Many metal surface preparations contain hexavalent chromium. As a result of the new regulations, alternatives to chromium are being sought. In 1983, it was found that a primer composed of an acrylic copolymer, an epoxy resin, a silica sol and a trialkoxysilane compound provides superior paintability, degrease resistance and corrosion resistance after paint coating.<sup>iii</sup> Twelve years later, it was found that a wash primer, without the acrylic copolymer or the epoxy resin, could provide similar benefits.<sup>iv</sup>

## HEAT-RESISTANT COATINGS

Utilizing SBT resins as the primary binder in high-temperature coatings began in the late 1940's for a few demanding applications. Now, silicone-organic copolymer and cold-blend coatings provide a balance of high performance properties for a spectrum of applications (See Table One). Key to the success of the coating is the correct selection of the SBT resin and pigmentation.

**TABLE ONE  
HIGH TEMPERATURE COATINGS  
END APPLICATIONS**

Exhaust stacks	Wood-burning stoves
Automotive mufflers and manifolds	Fireplace inserts and doors
Boilers, ovens and furnaces	Space heaters
Steam lines	Lighting fixtures and bulbs
Heat exchangers	Camp stoves
Barbeque grills and smokers	Kitchen stoves
Cookware	Laundry driers
Incinerators	

If we look at Table Two, we can surmise that at 250°C, phenyl groups, as compared to methyl, attached to silicon, have greater thermal stability. At extended or elevated (>400°C) temperatures, all organic substituents will eventually oxidize. In those cases, a resin containing a high level of phenyl will exhibit a greater weight loss than a methyl resin (See Table Two). Additionally, the reactive silanols sharing a silicon atom with a phenyl group are sterically hindered. This can result in poor cure and subsequently reduced physical properties. Phenyl content, on the other hand, improves the compatibility of the SBT resin with organic resins (e.g., acrylics). Without mutual miscibility, the resins can establish distinct domains, the boundary layers of which are weak links in the resin matrix and detract from the film's physical properties. Additionally, while a particular formulation may be comprised of only one resin, the processing and application equipment will invariably handle other formulations. Cross-contamination is inevitable. It is therefore necessary to balance the needs of thermal stability, physical properties, cure rate, and compatibility when selecting a suitable resin.

**TABLE TWO  
THERMAL HALF-LIFE OF ORGANIC  
SUBSTITUENTS ON SILICON**

Group Covalently Bonded to Si	Approximate Half-life (hours) at 250°C in Air
Phenyl	>100,000
Methyl	>10,000
Vinyl	101
Ethyl	6
Propyl	2

The selection of pigmentation is also critical to achieving maximum temperature resistance. Coatings with short-term exposures (< 1,000 hours) at temperatures up to 350°C or long-term exposure (> 1000 hours) up to 225°C can be produced with titanium dioxide and mica. Applications with short-term exposures at temperatures up to 525°C or long-term exposure up to 250°C often include black iron oxide. Aluminum, zinc and stainless steel are utilized in high-temperature applications (short term 650°C, long term 350°C). The high thermal conductivity of these metals transfers heat away from the coated substrate. In addition, as the resin oxidizes, the metal particles will fuse with the resin to form a ceramic coating with stable metalo-siloxane bonds. Further enhancements to the thermal stability of the coating can be achieved by increasing the loading of reinforcing fillers such as mica or Wolastonite.

## INDUSTRIAL MAINTENANCE

Cold-blends and copolymers of SBT and organic resins allow formulators to create coatings benefiting from the UV and chemical resistances of SBT and physical properties and cure mechanisms of organic resins. Emerging research in silicon-based technologies is focused on overcoming the limitations inherent to silicone and organic homopolymers. One of the most widely cited patents related to SBT materials in protective coatings (sixty-three citations) documents the benefits of silicone-organic copolymers in a wide array of systems including epoxies, urethanes, amide-imides, sulfones, polyesters, polyphenylene sulfide and polycarbonates.<sup>v</sup>

The drive to improve the physical properties of UV- and heat-resistant coatings has resulted in a variety of approaches, such as acid equilibration of siloxane precursors with organic polyols before

hydrolysis to produce resins with a unique combination of hardness, flexibility and solvent resistance.<sup>vi</sup> Investigators have also studied copolymers of epoxy-functional materials with siloxanes for improved flexibility,<sup>vii</sup> butanolized polyphenyl siloxane for improved adhesion,<sup>viii</sup> polyperfluoroalkylene siloxane resins for resistance to oxygen etching<sup>ix</sup> and silane hydrolyzates combined with polyester resins for reduced discoloration after exposure.<sup>x</sup> Patented blends of silicones and acrylic resins evidence the renewed interest in SBT for the powder coating industry<sup>xi</sup> and for electrical insulation.<sup>xii</sup> The primary focus of these patents was to use a small modification level of organic crosslinking to provide improved physical properties to what is primarily a siloxane resin. Other systems employ organic resins as the primary binder and SBT as the modifier.

### **SILICONE ALKYDS**

During the 1950's, low molecular weight silicone resin intermediates were developed for copolymerization with carbinol-functional resins, such as alkyds and polyesters. By pre-reacting the silicone and organic resins prior to paint formulation, the formulation gains improved miscibility (less discrete silicone-organic domains) and increased molecular weight, contributing to better physical properties and overall performance. Improvement of a bulk property such as weatherability requires a significant level of silicone modification: The minimal effective level is 15% of the resin weight, typical is 30% and 50% silicone alkyd copolymers are also employed.

In the early 1960's, the U.S. Navy began painting the superstructures of ships with silicone alkyd paint and the use has expanded to commercial ships. While the "haze gray" exterior paint for the U.S. Navy continues to be the single largest application for silicone alkyds; other applications such as communication towers, storage tanks, chemical processing equipment, locomotives, rail cars, bridge structures and metal building exteriors employ silicone-modified alkyd-based coatings.

### **SILICONE EPOXIES**

Relying on the rapid cure, excellent barrier properties of epoxy resins and the stability of siloxane resins, formulators created high performance coatings with

excellent resistance to corrosion and chemical attack as well as thermal and UV degradation as early as 1959.<sup>xiii</sup> These innovations rely on a broad spectrum of SBT. Monomeric alkoxy silanes, silicone resins and fluids of various molecular weights and chain lengths, all with a variety of functional groups, provide options to tailor the resin system to meet specific performance requirements for such far-ranging applications as electronic conformal coatings and automotive finishes. In some uses, the polymeric materials are exposed to high temperatures that result in a lowering of the film integrity. A blend of an epoxy resin, a curing agent for epoxy resins, an organofunctional alkoxy silane and a catalyst for condensation polymerization of a silane compound was found to provide high heat resistance and excellent mechanical strength.<sup>xiv</sup> Similarly, complete or partial hydrolysis of alkyl/phenyl alkoxy silanes to form silanol or alkoxy-functional siloxane resins and the subsequent reaction with epoxy resins have been shown to produce copolymers with improved water and moisture resistance.<sup>xv,xvi</sup>

Utilizing the functional groups available from silane monomers, resin formulators have created organofunctional (e.g., epoxy and amine) silicone resins for epoxy resin modification.<sup>xvii, xviii</sup> The chain length of linear siloxanes possessing terminal reactive groups impacts the function of the SBT in the epoxy matrix. Silicone fluids with shorter chain lengths are inherently more reactive and miscible with the epoxy resin. This allows for modification of the bulk properties of the epoxy matrix such as toughness<sup>xix</sup> and impact resistance.<sup>xx,xxi</sup> Formulating with siloxanes with longer chain lengths decreases the miscibility with the epoxy and the properties of the SBT are governed less by the terminal organo-functional groups than the polydimethylsiloxane portion of the molecule. In those cases, the SBT becomes more of a surface modifier, contributing lubricity and water repellency.<sup>xxii</sup>

### **HYGIENIC COATINGS**

Recent concerns surrounding hygienic conditions in health care and food processing facilities drive the need to provide coatings, that either allow easy and recurring cleaning or active sterilization of the surface. While the demand for cleanliness grows, the list of potential solutions to the problem may be growing shorter. Biocides are coming under increased scrutiny. Commercialization of new biocidal-active

materials will require costly testing and documentation. In contrast, passive bio-contamination control, achieved via easy-clean coatings, provides a less cumbersome route to hygienic surfaces. One of the most common methods employed to sterilize surfaces is ultra-violet (UV) light exposure. Unfortunately, UV light exposure also degrades organic resin paint binders; combined with normal wear, abrasive cleansers and chemical disinfectants, this can quickly destroy the protective properties of a coating. Inclusion of SBT materials allows application-tailored performance with excellent UV resistance, hydrophobicity, low surface energy (20-22 dynes/cm<sup>2</sup>), non-stick properties and resistance to chemical cleansers.

### **MARINE BIO-FOULING CONTROL**

Ship bottoms, buoys, fish farming and stationary fishing nets and other structures submerged in both fresh and seawater such as water intake pipes and oil platforms foul with organisms such as zebra mussels, barnacles, tube worms and algae. This biofouling creates problems ranging from reduced fuel efficiency to structural instability. It is routine practice to prevent the attachment of these marine fouling organisms by coating the surfaces with antifouling paints that are roughly divided into the following two-classes: biocidal and fouling release.

#### **BIOCIDAL**

Antifouling paint that employs antifoulants such as organotin copolymers and cuprous oxide, which are toxic to marine organisms, prevent the attachment via chemical activity. Global restrictions on the use of tributyltin antifouling coatings forced the development of alternative coatings technologies for protecting ship hulls and underwater structures. Hydrolyzable, organosilyl acrylate copolymers<sup>xxiii</sup> allow formulators to produce antifouling coatings, that are much less dependent on the water-solubility of the pigments. Instead, superior control of the erosion rate is provided by chemically tailoring the binder polymer with selectively weakened sites pendant to the polymer chain at the paint/water interface. Incorporating C-O-Si bonds into the polymer allows seawater to slowly attack the binder, generating carbinol (COH) sites, which gradually solubilize the polymer. The rate of hydrolysis can be controlled by attaching larger, more hydrophobic silyl groups,

including pendant siloxane chains.<sup>xxiv</sup> This greater control of binder hydrolysis allows the coating formulator to utilize less toxic antifouling agents and provide longer life coatings. The fouling resistance of this technology is further enhanced with the inclusion of a polysiloxane fluid.<sup>xxv</sup> The silicone oil serves as a slip agent and provides the added benefit of a weak boundary layer decreasing bio-adhesion to the surface. This innovation overlaps with the second class of bio-fouling control technology, which relies primarily on the mobility, low surface tension and inertness of siloxanes to provide fouling release.

#### **FOULING RELEASE**

A new approach toward maintaining clean underwater hull surfaces is to use a non-toxic coating that allows easy mechanical removal of fouling, ideally by water movement as a vessel moves through the water. Known as “fouling release” or “non-fouling” coatings, this silicon-based technology relies on the unique surface chemistry of siloxanes to which fouling can not easily adhere.<sup>xxvi</sup> These formulations are typically comprised of a silanol (SiOH) functional polydimethylsiloxane, silica, catalysts and an alkoxy functional silane or silicate crosslinker. Physical smoothness and low surface energy are characteristics that contribute to producing a “non-stick” surface. Because they employ a physical rather than a chemical means to reduce fouling, these silicone coatings have been ruled exempt from reporting under FIFRA (Public Law 95-396).

#### **ABRASION-RESISTANT COATINGS**

While nearly all coatings are formulated to possess at least some level of abrasion resistance, one technology segment, based on Sol gel chemistry, focuses primarily on that one performance attribute. In 1977, a patent<sup>xxvii</sup> was issued for an acidic dispersion of colloidal silica and hydroxylated silsesquioxane in an alcohol-water medium for coating onto solid substrates, such as acrylic lenses, to provide an abrasion-resistant coating. Since that time, abrasion-resistant coating (ARC) systems have been created that provide alternative cure mechanisms, antifogging and excellent stability.<sup>xxviii</sup> Organic/inorganic hybrids, where a gel (usually silica) is dispersed into an organic polymer to provide specific performance properties, are widely utilized. One highly cited patent<sup>xxix</sup> (60

citations) demonstrates a UV-curable coating composition based on the use of a photoinitiator with the hydrolysis product of silylacrylate and aqueous colloidal silica. The addition of a small amount of polysiloxane polyether copolymer to an aqueous ARC formulation provides improved flow and reduces defects.<sup>xxx</sup>

Today, ARC thin film coatings are used extensively for such diverse applications as protective and optical coatings, passivation and planarization layers, sensors, high or low dielectric films, inorganic membranes, electro-optic and nonlinear optical films, electrochromics, semiconducting anti-static coatings, superconducting films, strengthening layers and ferroelectrics. Although substrates of soft plastic sheet material show the greatest improvement upon application of the coating, the composition can be applied to other substrates, such as wood, metal, printed surfaces, glass and ceramics. One particular application, automotive clearcoat formulations, is the center of much attention.

### **AUTOMOTIVE CLEARCOATS**

Color-plus-clear coating systems involving the application of a colored or pigmented base coat to a substrate followed by application of a clear top coat have become increasingly popular as OEM finishes for automobiles. These clear coatings are, however, subject to damage from environmental elements such as acid rain, UV degradation, high relative humidity and temperatures, stone chipping and abrasive scratching of the coating surface. Typically, a harder, more highly crosslinked film may exhibit improved scratch resistance, but it is much more susceptible to chipping and/or thermal cracking due to embrittlement of the film resulting from a high crosslink density. A softer, less crosslinked film, while not prone to chipping or thermal cracking, is susceptible to scratching, water spotting and acid etch. One patent discloses clear coats in color-plus-clear systems that have improved scratch resistance with the inclusion of surface reactive inorganic microparticles such as colloidal silica that have been modified with a silane coupling agent.<sup>xxxii</sup> Post-weathering of these coatings can cause "cure drift" during which residual inorganic reactivity (i.e., silanol or alkoxy) slowly crosslinks, resulting in embrittlement and potential film crazing. By incorporating siloxanes that possess minimal inorganic functionality and linear structure,<sup>xxxii</sup>

<sup>xxxiii</sup> rather than silica, the benefit of silicon dioxide is gained without the associated risk of embrittlement.

### **ARCHITECTURAL COATINGS**

Changes in building practices, including concrete facades on multi-floor buildings and shifts in the economics of material and labor costs, have contributed to the trend toward SBT performance-differentiated architectural paints. Along with the noted benefit of improved UV resistance, SBT materials possess two seemingly contradictory attributes beneficial to the performance of paints applied to building materials: water repellency and water vapor permeability.

Acrylic latex binders perform reasonably well in architectural coatings, providing an acceptable sealer of wood and masonry surfaces. Porous substrates, however, require not only protection from exterior attack from chemicals, rain and sun, but also protection from attack from within the substrate itself. Moisture wicks through concrete walls and wooden boards destroying the adhesion of the coating. Ideally, therefore, architectural coatings need UV, chemical and water resistance, but also moisture vapor permeability to reduce hydrostatic pressure beneath the coating. Silicone elastomeric emulsions can be blended with acrylic latex binders to provide the required performance. Addition levels as low as 5% are sufficient to demonstrate benefit. The low inherent Tg of silicones provides excellent coalescence with minimal solvent addition and film integrity when cracks in the substrate expand or contract with temperature fluctuations.

### **SILICON-BASED ADDITIVES**

The wide variety of technologies and delivery options of SBT (See Table Three) not only solve coating problems, but also provide enabling performance for functional, high performance coatings (See Table Four). The performance requirements of an application dictate consideration of the organic substituents attached along the siloxane chain to deliver the desired level of performance for the coating. Inorganic alkoxy functionality, such as methoxy and ethoxy attached to silane monomers, provides SBT materials with moisture-activated, room-temperature curing. This chemistry is utilized in protective coatings, allowing ambient curing,

reductions in energy requirements and expanding applications.<sup>xxxiv</sup> Energy-cured systems benefit from SBT reactivity, providing additional cure on complicated parts with shaded areas.<sup>xxxv</sup> When used at additive levels (0.2- 0.5% on resin solids), organofunctional alkoxy silanes act as crosslinkers, pigment dispersing aids and adhesion promoters.

**TABLE THREE**  
**SBT ADDITIVE MATERIALS**

Polydimethylsiloxane (PDMS, Silicone Oil, Polydimethicone)
PDMS Emulsion and Dispersions
Organoreactive Alkoxy Silanes (Coupling Agents)
Alkyl Alkoxy Silanes
Aryl Alkoxy Silanes
Fluorosilicones
Silicone Polyethers (Silicone Surfactants)
Silicone Latex Elastomers
Silicone Resins
Silicone Polyesters
Silicone Acrylates
Silicone Rubber Particles

**TABLE FOUR**  
**SBT ADDITIVE BENEFITS**

Adhesion	Leveling
Antiblocking	Mar Resistance
Antifoam	Pigment Dispersion
Deaeration	Release
Defoam	Slip
Flow	Texturizing
Gloss	Water Resistance
	Wetting

Silicone polyether (SPE) copolymers comprise a large portion of the SBT additive market. Tailoring the ratio of Si to PE, the molecular weight of the copolymer, the polarity of the PE groups, end-capping or attaching reactive groups creates additives that often provide multiple benefits. Slip, mar resistance, flow, leveling, wetting, antiblocking, and gloss are all common benefits to coatings derived from this technology. Water resistance, repellency and permeability are central to several recent patents.<sup>xxxvi</sup> Polyethylene oxide (EO) is very polar and hydrophilic, while polypropylene oxide (PO) is relatively nonpolar and hydrophobic. Higher EO levels increase the water solubility and compatibility with polar organic resins, but tend to stabilize foam. PO content reduces water solubility and reduces the tendency to foam. In this way, the structure of the polyether plays an important

role in a recent trend toward shear and shelf-stable defoamers.

SBT defoamers are based on a range of compositions. Polydimethylsiloxane (PDMS) fluids have long been used as defoamers in solvent-based coatings. Their utility is, however, limited due to a lack of compatibility with organic resins, and poor aqueous dispersibility tends to create phase separation that could lead to surface defects in the film. Both fluorinated and alkyl/aryl siloxanes provide the needed level of miscibility to provide defect-free defoaming of solvent-based coatings. For decades, formulators of aqueous coatings utilized compounds of PDMS fluid emulsions containing hydrophobic silica. While effective defoamers, these defoamers are not without limitations, potentially leading to film defects.

Several newly developed defoamers are based on silicone polyether copolymers. Controlling the hydrophobicity by varying the EO/PO ratio provides material with utility as surfactants, emulsifiers or wetting agents. Used alone, or compounded with PDMS or glycols, these copolymer dispersions are designed to be effective defoamers with advantages over traditional silicone defoamers such as being 100% active for lower use levels, self-emulsifying for easy incorporation into aqueous or polar coatings, and shear stable, and containing no hydrophobic particle separation to cause surface defects. The elimination of the solid particle component in the defoamer makes this SBT attractive for applications such as inkjet printers that must avoid blockage of the cartridge aperture.

Another property associated with SBT is the toughness of silicone rubber. Elastomeric emulsion coatings with improved impact properties embody this characteristic.<sup>xxxvii</sup> Additives based on this branch of silicon-based technology are available in three forms: silicone latex emulsions, elastomeric dispersions and elastomeric powders. Applications for these materials include masonry coatings, furniture varnishes, printing inks, electronic cabinets and automotive interior coatings. Use levels range from additive (0.5%) levels to formulations using the silicone elastomer as the primary binder. Benefits include improved water resistance, flexibility, antiblocking, matting and soft-feel texturizing.

## CONCLUSIONS

Resins and coatings systems using silicon-based technologies have historically operated in a distinct portion of the market for high-temperature and weatherable maintenance coatings. The traditional benefits of SBT – thermal and UV resistance from resins, slip and leveling additives, defoamers and adhesion promoters – continue to be widely utilized by coating formulators. In recent years, however, newly discovered synergies between SBT materials and organic polymers have led to improvements in both traditional silicones and what were once solely organic coatings. Moisture cure systems, ablative polymers, improved chemical, corrosion and abrasion resistant coatings and ease of cleaning for bio-contamination control highlight the long list of benefits attributed to SBT usage in paints and coatings. The distinction between silicon-based and organic systems will continue to blur as more formulators discover the versatility and durability of silicon-based technologies.

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