# REGULATORY DRIVEN INNOVATION

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**Summary**

In this article we would like to review some of the innovation examples that we at Siltech have developed in response to relevant regulatory changes and trends in the silicone and paints and coatings industries. These examples demonstrate how research and development efforts have provided improvements and solutions that positively impact human and environmental health and safety. Regulatory mandates and consumer trends will undoubtedly continue to influence R&D and innovation into the future.

**Keywords**

Regulation, innovation, silicone, green, sustainable

## Introduction

Regulation and Regulatory Agency are words that often cause angst among chemists and formulators. Our first thought is that these rules will be barriers to our efforts. However, with hindsight and reason one sees there have been many times when regulation caused innovation to occur rather than blocking it's path.

There is always vigorous debate about whether agencies are regulating too much or too little.[i] However, it is difficult to argue that regulatory changes and trends do not significantly influence both the products developed and much of the innovation in paint and coating formulations. When confronted with the challenges of regulatory changes, the English proverb "necessity is the mother of invention" certainly seems appropriate.[ii]

In this article we would like to review some of the innovation examples that we at Siltech have developed in response to relevant regulatory changes and trends in the silicone industry. These examples demonstrate how research and development efforts have provided Improvements and solutions that positively impact human and environmental health and safety. Regulatory mandates and consumer trends will undoubtedly continue to influence R&D and innovation into the future.

## "Green" Chemistry, Labeling and Technology Transparency

"Green" or "sustainable" chemistry are terms that have been used for a long time.[iii] At first these terms were not well defined, but today "green" has come to be associated with non-petroleum, naturally derived materials. While there is clearly consumer and market interest in these types of products, successful chemistries are still expected to do the job and commanding any premium pricing for these greener products is challenging.

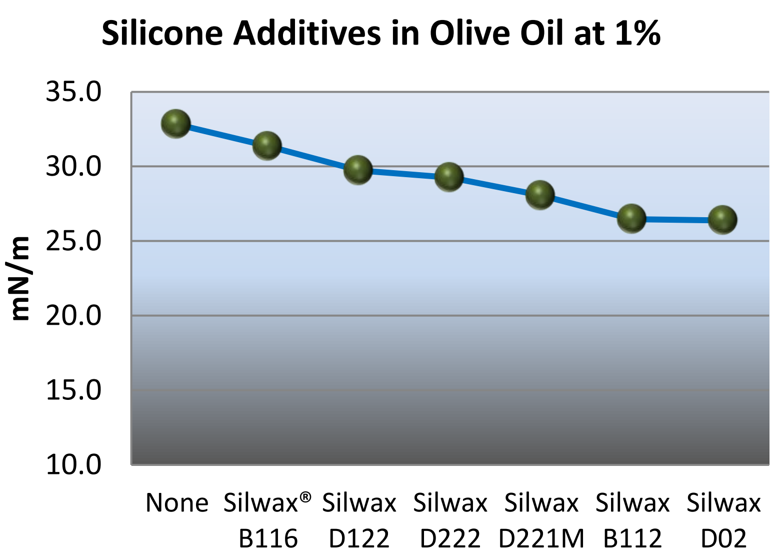
The "green" trend has led to the creation of a number of voluntary eco-labeling initiatives typically driven by NGOs (non-governmental organizations), Industry Trade Groups and other third party agencies. Some of these include Nordic Ecolabel[iv] (Swan), EPA Design for Environment (DfE)[v] and Energy Star[vi], as well as Green Seal[vii]. Other end-use driven labeling requirements and specifications, such as those set forth by Nestle, further push the inks and coatings industry to provide transparency about the chemistry used in additive technologies. While these do not always carry the force of law, they are often encouraged by regulatory agencies as early progenitors of regulations. There has been much "green washing", which is the tendency for companies to exaggerate and "spin" environmental claims beyond their true benefits. Nonetheless, these eco-labeling initiatives labels do afford the end-user with transparency and consistent information regarding compliance to labeling guidelines.viii

Many coatings innovations have created products which utilize natural feed stocks. There are a myriad of examples of solvents and resins based on plant derivatives. However, additives have provided a greater challenge. Coatings additives are historically petroleum-, fluorocarbon- or silicone-based.

**Silicone polymers and natural oils**

In order to reduce the dependency on petroleum-based additives, Siltech Corporation has produced silicone copolymers based on castor oil, essential oils and alpha olefins. This enables the increased use of botanically derived materials in formulations. An example is shown in Chart 1. In this case, alpha-olefin modified silicones have been utilised to reduce the surface tension of olive oil from 33 to 26 mN/m. The lower surface tension of the natural oil imparts a soft feel and improved wetting properties, while involving a high percentage of natural components. The same approach works with nut, safflower, sunflower, and Crambe oils.[ix]

**Chart 1**



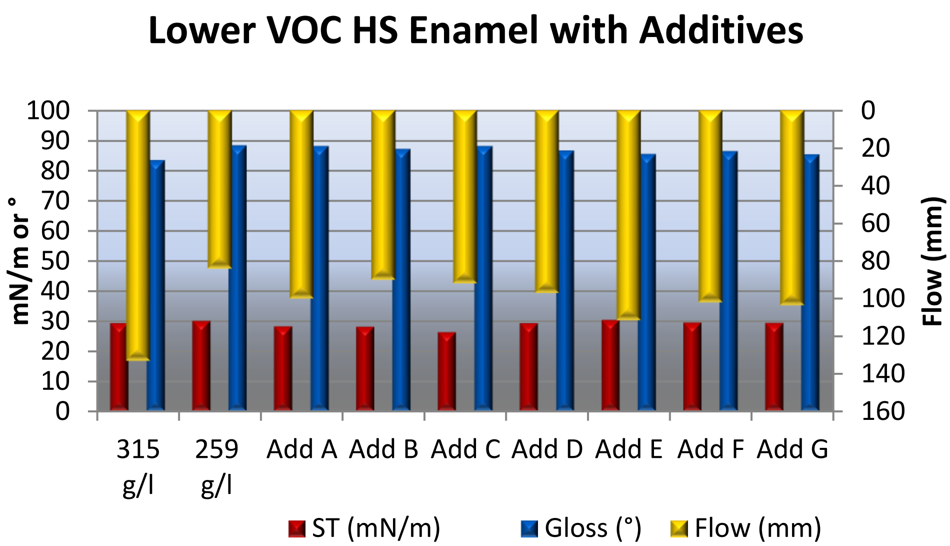

**VOCs (volatile organic compounds) and Emissions**

Perhaps the best example of regulations which affected innovation in coatings are those related to reducing VOCs and emissions. These regulations are directed at improving air quality, and are not only complex but also differ from region to region. [x] VOC reducing laws have been particularly impactful to the paint and coatings industry which was largely solventborne four decades ago.

The changes required to develop compliant paints and coatings have required a myriad of innovations that address the inherent challenges of creating paints and coatings that are water-based or contain very low or no solvent. For example, silicones and other types of polymeric additives have been successfully used to overcome wetting and rheological hurdles.[xi]

From reference xi, Chart 2 shows an example where the amount of solvent in a high-solids (HS) alkyd enamel is reduced from 315 g/l to 259 g/l, a decrease of about 20%. This causes flow to decrease as expected, although gloss increases somewhat (defects as well). Then, as various alpha-olefin-modified silicones are introduced, it can be observed that the properties gradually return. For example, with Additive E, similar levels of gloss, flow and surface tension are obtained as with the original 315 g/l enamel.

**Chart 2**




Volatile cyclic silicones and other exempt solvents have also found utility in formulating VOC and emission-compliant paints and coatings.[xii] A range of additives and new formulations have improved pot-life and open time, which has been another challenge of low VOC and high solid coatings.

While silicones such as cyclomethyltetrasiloxane ($D_4$) and cyclomethylpentasiloxane ($D_5$) are classified as exempt or non-HAP (non-hazardous air polluting) solvents by the California Air Resource Board, there have been concerns in Canada and some Eurozone countries about the environmental fate and/or toxicity of some of these types of materials. This has caused some to consider limitations in the $D_4$ and $D_5$ content within their formulations. Although few current regulations require these limitations, and despite the fact that the scientific evidence exonerates the chemicals[xiii], some companies have responded by providing technical capabilities that enable ultra-low volatile silicone content to address market needs. For example, Siltech has installed a state of the art Wiped Film Evaporator to drive the content of these volatile silicones to fractions of a percent. The benefit is that customers who utilise these building blocks with ultra-low volatile silicone content can benefit from the advantage in their end user formulations. This is a case where public perception, driven by regulatory actions and debate, has driven innovation.

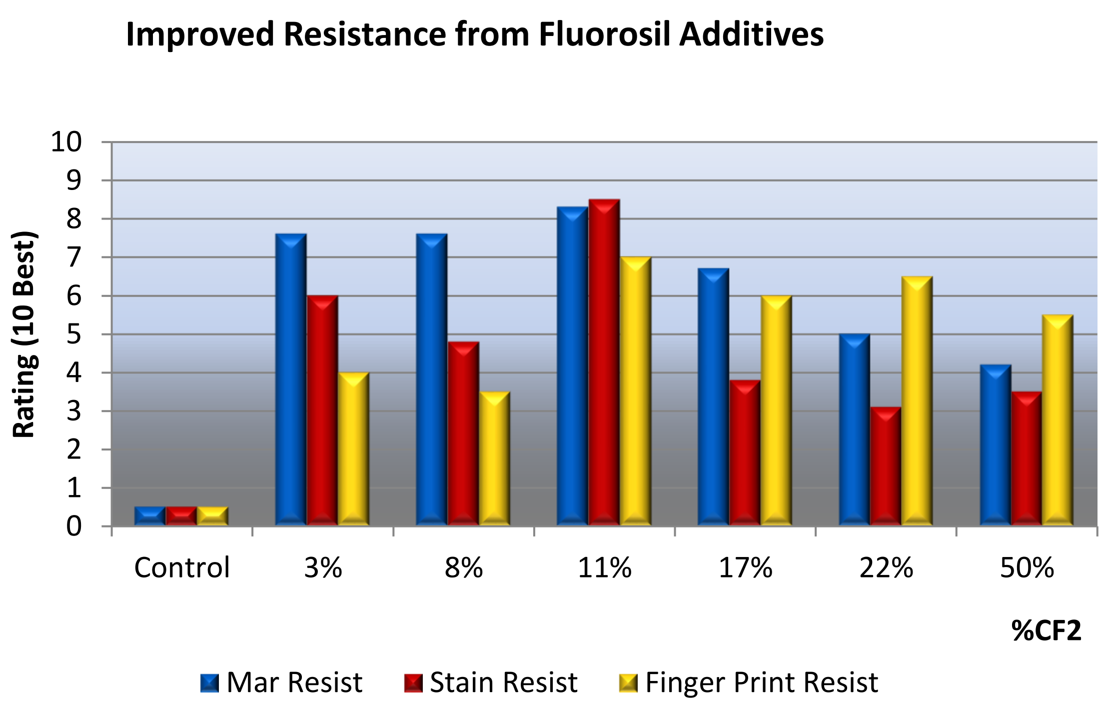
**Polymers containing Fluorine**

PFOA is an acronym for perfluorooctanoic acid, a chemical that is used to make fluoropolymers, substances with low surface energy properties used especially in paint and coating applications to impart soil, stain, chemical, and water resistance. However, this material and the related intermediate PFOS (sulphonic acid derivative) have been under scrutiny due to concerns about persistency in the environment. Both are the subject of an EPA Enforceable Consent Agreement (ECA).[xiv]

Efforts to replace the $C_8F_{17}$-containing PFOA and PFOS have encouraged the development of polymers based on $C_6F_{13}$ and lower. For example, Siltech has utilized the more favourable lower chain length fluoroalkyls in the synthesis of a new class of fluorosilicone copolymers. Indeed, our Fluorosil® products are made from 99% pure $C_3F_5$ fluoroalkyl chains.

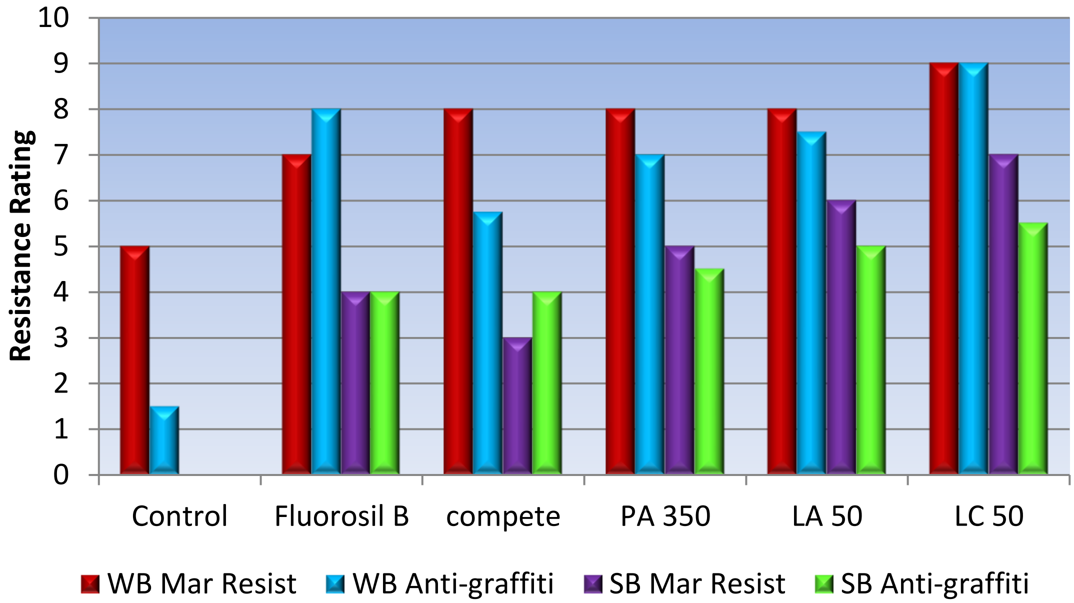
Furthermore, synergies with the silicone polymer have been observed that enable an even lower level of fluorine in many applications.[xv] In the results shown in Chart 3, 1% of various fluorosilicone additives in a UV cured epoxy resin formula show that, for stain, fingerprint and mar resistances, performance ratings are not a simple function of $CF_2$ content in the additive. This indicates that there is a favourable interaction between the silicone and fluoroalkyl polymers. This synergy allows for the environmentally troubling (and expensive) fluoroalkyl component to be minimized in the molecular design with maximum properties at 11% fluoroalkyl in this case.

**Chart 3**




In our most recent innovation, our Silmer® OHT products provide stain resistance and release properties without any $CF_2$ content at all. In Chart 4 one sees the material labeled LC50 has higher mar resistance and stain resistance relative to both a competitive control and $CF_2$ containing Fluorosil B.

**Chart 4**




**Metals and Catalysts**

The coatings industry has been challenged by the need to replace cobalt and chromates.[xvi] Furthermore, tri-substituted organo stannic compounds such as tributyltin and triphenyltin compounds have been outlawed since July, 2010 where the concentration in the article, or part thereof, is greater than the equivalent of 0.1% by weight of tin, according to a European Commission Decision.[xvii]

In order to comply with these rulings, Siltech is actively developing systems cured with titanium, zirconium or other catalysts. Siltech has also developed systems which don't need to be catalyzed at all.

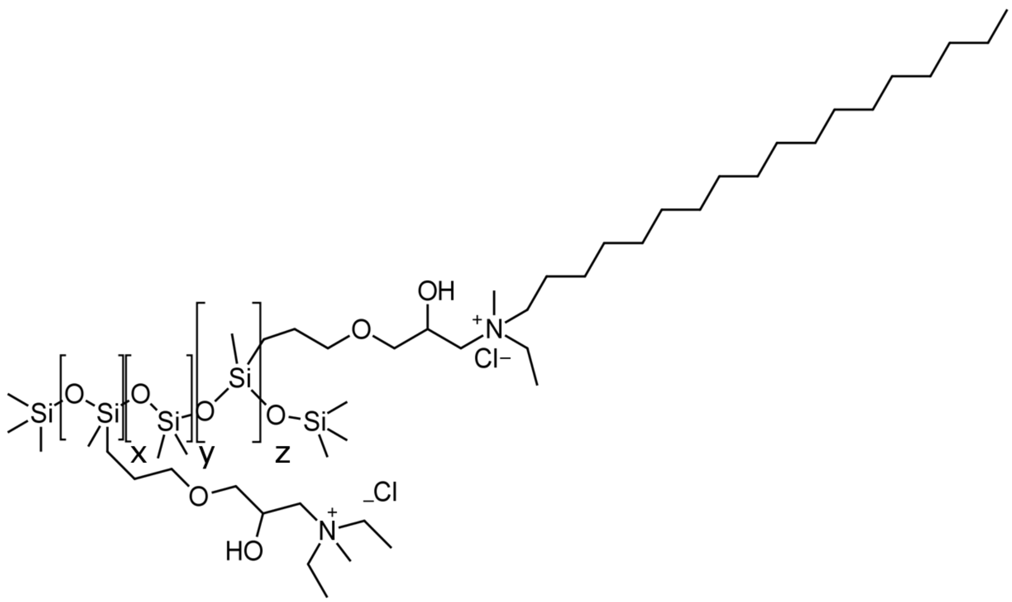
**Water-based Formulations and Emulsifiers**

EU and Canadian regulations have driven NPE(nonylphenol ethoxylate) -free emulsions, this is now becoming law in the US as well.[xviii]. Being a Canadian manufacturer, Siltech has never used NPE emulsifiers and relies upon linear alcohol ethoxylates and silicone emulsifiers to stabilize our emulsions.

There is also a market driver for allyl-ethoxylate-free surfactants, due to the alleged toxicity of these materials. Siltech has developed polymeric surfactants and emulsifiers which are silicone-based and use non-ethoxylated hydrophiles. These quaternary ammonium silicone surfactants and emulsifiers have no EO groups at all.

These Silquat® materials are excellent emulsifiers, EO/APEO free and multi-functional. The generic structure is shown in Chart 6, which derives its requisite ambiphilic nature from hydrophilic diethyl methyl quaternary amine groups juxtaposed with lipophilic hydrocarbon quaternary amine groups. Many variants with differing hydrophilic-lipophilic balances (HLBs) are possible by varying “x”, ”y” and “z” values.

**Chart 6**




**Biocides**

Biocides are implicated in a variety of human maladies and some have been limited or ruled out, particularly in the EU.[xix,xx] Therefore, regulation is driving the replacement of chemicals such as parabens and formaldehyde donor based preservatives.

This has encouraged the use of pH control and alternative bio-stats whenever possible. For example we are exploring the possibility that the quaternary emulsifiers above control bacterial growth as well. The inherent biological activity of materials used to control and inhibit microbial growth offers some unique challenges in innovating new options for protecting emulsion products.

**Conclusion**

History has demonstrated that the paints and coatings industry can effectively rise to the challenges of regulatory change. While there may be a tendency to bemoan increased regulations, one can also reflect on the innovation that has been achieved as a result of these perceived and actual constraints. Consumers and governmental agencies will undoubtedly continue to demand products and technology that further reduce risk, and improve health and safety. Increasing transparency, partnerships and collaboration between companies, industry and regulatory agencies can help the chemical industry to rise to the challenges, while simultaneously leading to continued innovation.

## References


[i] James E. McCarthy and Claudia Copeland, *EPA Regulations: Too Much, Too Little or On Track?* Congressional Research Service, **July 2014.**

[ii] English proverb traced to a quote from Ancient Philosopher Plato

[iii] Anastas, P.T., and Zimmerman, J.B., *Design through the Twelve Principles of Green Engineering*, *Env. Sci. Tech.* ***2003****, 37(5), 94A-101A*

[iv] http://www.nordic-ecolabel.org/

[v] http://www.epa.gov/sustainability/analytics/epa-design.html

[vi] https://www.energystar.gov/

[vii] http://www.greenseal.org/

[viii] Greg Zimmerman*, Don't Get Overwhelmed by Eco-Labels, Facilities.net,* **June 2011.**

ix Tom Seung-Tong Cheung, Robert Ruckle; *Silicone additives to Increase Solids and Lower VOC's in Solvent Borne Systems*; Proceedings of the Waterborne Symposium, **2012**

[x] Jennifer Cogar, *Puzzled by Global VOC and Emission Standards in Architectural Paints?* Paint & Coatings Industry, **January 2015.**

[xi] Tom Seung-Tong Cheung, Rick Vrckovnik and Robert Ruckle, *Silicone Additives for High Solids and Low VOC Coatings,* Paint & Coatings Industry, **September 2012.**

[xii] Formulation Strategies using Exempt Solvents: Latest Developments, Paint & Coatings Industry, **July 2000.**

[xiii] http://sehsc.americanchemistry.com/Research-Science-Health-and-Safety

[xiv] http://www.epa.gov/oppt/pfoa/

[xv] Tom Seung-Tong Cheung, Robert Ruckle, Rick Vrckovnik and Steve Wilkowski, *Incorporation of Reactive and Non-Reactive Fluoro-Silicones into Various Coatings Films and the Resulting Properties,* PCI Webinar, **January 2015**.

[xvi] Rick Holland and Tom Alderson, *Cobalt Free Technology for Trivalent Chromates on Zinc Plating*, **SUR/FIN 2010.**

[xvii] http://ec.europa.eu/health/scientific_committees/environmental_risks/opinions/sctee/sct_out26_en.htm

[xviii] http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/np-npe.html

[xix] Commission Regulation (EU) No 358/2014

[xx] http://ec.europa.eu/consumers/consumers_safety/cosmetics/index_en.htm