

Cationic silicone polymers

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Tony O'Lenick is President of Siltech LLC. Tony has published six books, numerous articles and has over 300 patents. He received the 1996 Samuel Rosen Award, the 1997 Innovative Use of Fatty Acids Award and the 1996 Partnership to The Personal Care. Tony was President of the U.S. SCC in 2015 and is currently Education Chair of IFSCC.



ABSTRACT

Traditional (fatty) cationic compounds, referred to as quats, are used very commonly in the personal care industry as conditioners and softeners on the hair and skin. This is due to the fact that hair and skin have a net negative charge and as a result of ionic interactions, the positively charged quats become substantive to the hair and skin (1).

It is therefore not surprising that the silicone analogues of traditional quats are likewise important compounds in personal care vis-à-vis conditioning and softening. The structure of the compound and the balance of silicone, fatty and water-soluble groups determine the properties of silicone quats, as is the case with all other silicone compounds. In the instance of these compounds the cationic group is a water-soluble group. Numerous silicone quats have been produced over the years (2-4). They differ in structure and properties. This article will look at a structure function relationship between the polymeric structure and their performance.

FORMULATOR TIP

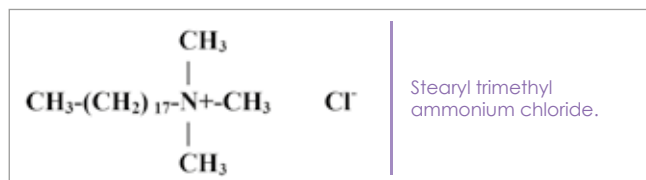
The creation of new, cost effective formulations for hair care require the product to provide many attributes. These include consumer perceptible wet and dry comb attributes, softness, and antistatic properties. Because these properties are determined by the exact structure of the cationic silicone chosen and how it interacts in the formulations, formulators need to carefully and thoughtfully screen materials. This requires an understanding of the product under evaluation and specifically the understanding of how the structure affects the performance in a specific formulation.

Cationic Compounds (5)

The most common class of cationic is the quaternary compound, Commonly, called a "quat" in surfactant jargon for a quaternary ammonium compound. This class of compounds includes nitrogen-containing materials in which the nitrogen has four non-hydrogen atoms surrounding them. Quats by virtue of their hydrophobic group and their cationic charge are substantive to hair, skin and cell walls of bacteria. These substrates are fatty in nature and generally have a negative charge, the result of oxidation of sulfur-bearing amino acids.

The nature of the interaction between hair, skin and bacteria cell walls is critical to the function of the quat at the surface. If the quat coats the hair and skin with minimal penetration, it is mild and conditioning. If the quat is made to maximize the disruption of the bacteria cell wall, it will be antimicrobial.

Stearyl trimethyl ammonium compound is an example of a fatty quat.



Fatty quats can be either conditioning or germicidal depending upon their exact structure. Not surprisingly so can the silicone analogue. This article will concentrate on cationic silicone polymers for conditioning.

Silicone Chemistry

There are three types of reactions to make cationic silicone polymers. They are (1) construction, (2) functionalization and (3) derivatization.

Construction

Silicone polymers are made in several steps, depending upon the specific polymer chosen. Most of the silicone polymers are have as a first step the so called "construction step". In this step a ring opening reaction is conducted to make an intermediate that has a silanic hydrogen (Si-H) present. The reaction is shown in Table 1. This reactive group is subsequently reacted with a vinyl compound to make an organo-functional product.

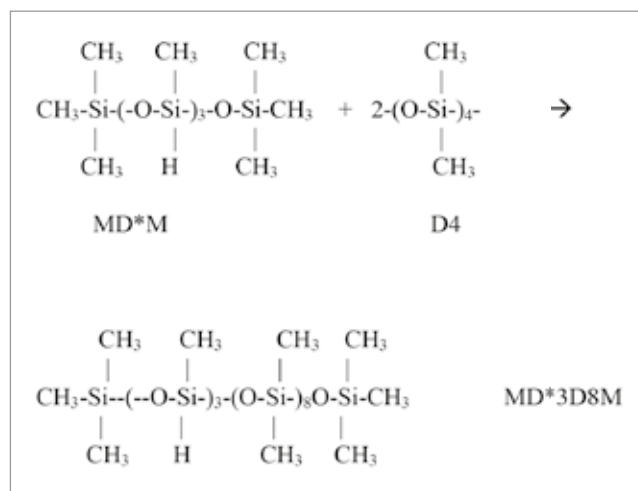


Table 1. Cationic Silicone Polymers Construction (6).

FORMULATOR TIP

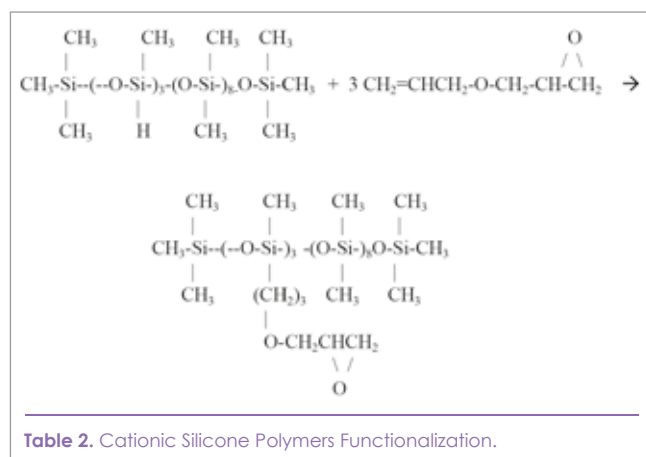
All silicone compounds find their way back to silicon dioxide. Silicon dioxide, also known as silica (from the Latin silix), is an oxide of silicon with the chemical formula SiO_2 , most commonly found in nature as quartz (7).

The silanic hydrogen (-Si-H) is used to coat pigment (8). In order to get chemically reacted coating on pigment, one must choose a silicone that is reactive with the pigments. One choice is to use a silanic hydrogen (-Si-H) reactive silicone, like the one shown in Table 1.

Silicone fluids are the result of the above reaction in which there is no silanic hydrogen (-Si-H) present in the molecule (9).

Functionalization

The next reaction is functionalization. It is a reaction in which the reactive silanic hydrogen product made in the construction step is reacted with a vinyl containing group to make an organo-functional polymer. Table 2 shows the reaction.

**Derivatization**

The next step (or steps) is to react the group added in the functionalization process to make a final product. This step is shown in table 3.

Structure

The following compounds were chosen to illustrate the structure of silicone quats.

Class 1 - Dialkyl Cationic Silicone Polymers

The silicone dialkyl quats have the structure shown in Figure 1.

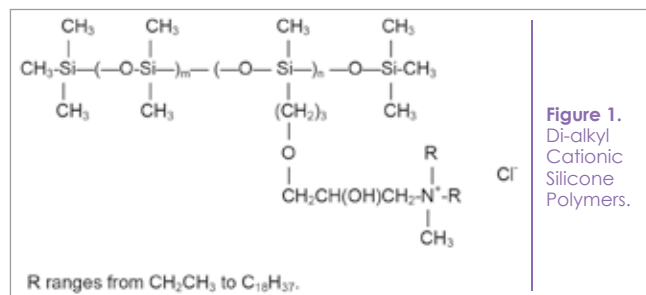
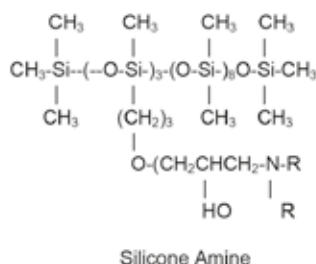
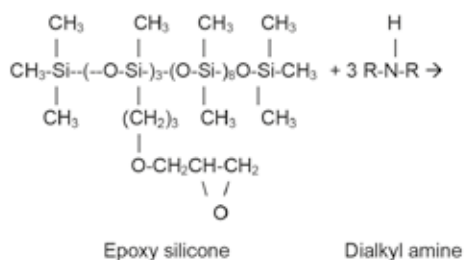
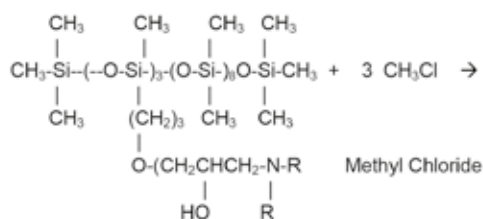
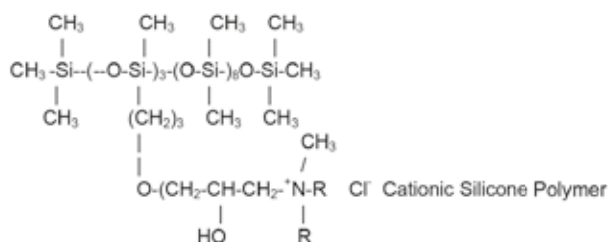
**Step 1****Step 2****Silicone Amine**

Table 3. Cationic Silicone Polymer Derivatization Steps.

There are two different types of compounds within this group. The first class of compounds has methyl or ethyl "R" groups. The second class of compounds has higher alkyl C12 or C19.

The lower alkyl products have the following properties;

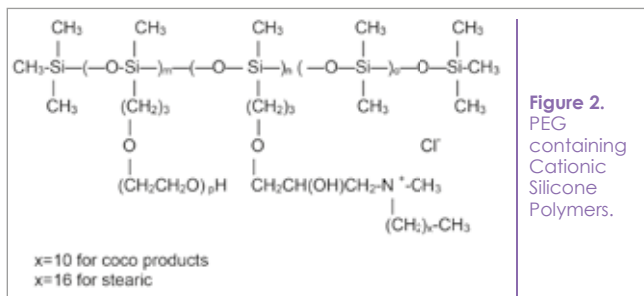
- Less oleophilic than the higher alkyl products.
- Better antistatic properties than the higher alkyl products.
- More water compatible than the higher alkyl.
- Less build up on hair than the higher alkyl.

The higher alkyl products have the following properties:

- More buttery (fatty) feel on hair.
- More oleophobic than the lower alkyl products.
- More intensively conditioning.

Class 2 - Cationic silicone polymers containing PEG groups

This class of compounds contains not only cationic groups but also added PEG groups. The structure of this class of compounds is shown in Figure 2.



Compound	Class	Name
1.	1	Silquat D2
2.	1	Silquat J2
3.	1	Silquat J15AO
4.	2	Silquat D208-B
5.	2	Silquat J208-2B
6.	2	Silquat Di 008 – 2B

Table 4. Designation of Cationic Silicone Polymers.

Evaluation

The properties of silicone quats are determined by the amount of silicone present, the number of cationic groups present in the molecule, the carbon number of the alkyl groups around nitrogen, the molecular weight of the compound and the class of compound (i.e. structure). The critical functional attributes that allow for the utilization of these compounds in personal care products include water solubility of the compound, hydrophobicity of the compound when applied to the substrate, and hydrophobicity of the compound on the hair or skin.

Softness - Protocol for measuring softness

The similarity of cotton fabric to hair makes cotton a good model for predicting the performance of silicone evaluated on cotton fabric. It represents one of the most thorough evaluations of silicone quats carried out to date. The cotton was cut into 4 x 4 inch squares and weighed. Originally, the amount of water used for the test was 10 times the weight of the cotton, however it was found that this would not be enough to fully cover the surface area of the cloth. Hence, the value was increased to 40 times the weight of the cloth.

The ratio of grams of quat to grams of water is 0.06:100. The desired amount of quat was added to the water and the pH of the mixture was adjusted to 5-6. The mixture was heated to 55-60°C and the cotton was added. After stirring the cotton in the mixture for 10 minutes, the cotton was squeezed dry and then air-dried.

After completion of all the samples, 10 people were asked to test the softness of each cotton piece against a control on a scale from 1 (the control) to 5 (most soft).

RESULTS

Table 5 shows compositional information on the cationic silicone polymers studies.

Group	Silicone	Degree of Softness	% Silicone	% Cationic	Alkyl groups	Mol. Wt.
1	Silquat D2	2.6	53	6.0	Ethyl	1,960
1	Silquat J2	2.6	49	6.5	Ethyl	4,400
1	Silquat J15AO	4.8	75	3.0	Ethyl	11,000
2	Silquat D208-B	3.3	36	1.0	Stearyl	2,900
2	Silquat J208-2B	3.8	33	0.84	Stearyl	6,900
2	Silquat Di 008 – 2B	3.8	11	1.7	Stearyl	1,700

Table 5. Physical properties and Softness Results for Selected Cationic Silicone Polymers.

Solubility

Table 6 shows the solubility of the cationic silicone polymers in several solvents.

	Water		IPA		Mineral Spirits		Mineral Oil		Aromatics		Cyclo Methicone		350 Visc. Silicone Fluid
	1%	10%	1%	10%	1%	10%	1%	10%	1%	10%	1%	10%	1%
1. Silquat D2	S	S	S	S	I	I	S	S	I	I	I	I	I
2. Silquat J2	S	S	S	S	I	I	I	I	I	I	I	I	I
3. Silquat J15AO	D	D	S	S	D	I	I	I	I	I	I	I	D
4. Silquat D208-B	D	D	S	S	I	I	I	I	S	S	I	I	D
5. Silquat J208-2B	S	S	S	S	I	I	I	I	S	S	I	I	D
6. Silquat Di 008 – 2B	D	D	S	S	S	I	I	I	S	S	I	I	D

Table 6. Solubility of Cationic Silicone Polymers.

FORMULATOR TIP

The selection of the “proper” cationic silicone polymer for a particular formulation is not a simple task. The conditioning includes aspects of wet comb properties, dry comb attributes, build up and how they affect the LGN (laminar gel network). All of these parameters are driven by the consumer and marketing.

George Deckner teaches (10)

Lamellar gel networks (LGNs) are combinations of low- and high-HLB (hydrophilic-lipophilic balance) crystalline surfactants that form colloidal structures that can swell and thicken water. The gel network is stabilized by lamellar bilayers of surfactant, which bind water. A lamellar gel network can be defined as a network formed by bilayer sheets where the alkyl chains in the bilayers are essentially in a frozen, non-melted state. This type of lamellar phase is also called alpha phase or alpha gel. These systems have viscoelastic properties and shear thin when applied to skin. LGNs are important because most oil-in-water skin-care emulsions sold globally are based on LGNs stabilized with polymers. Most hair conditioners sold globally are also based on LGNs.

Table 7 shows the cationic silicone polymers in each of these groups and the softness results for each.

In the Group 1 the J15AO has by far the highest degree of softness. The molecular weight is very large and so is the percent silicone, whereas the percent cationic charge is smaller than the cationic silicone polymers designated D2 and J2. The cationic silicone polymers designated as J2 and D2, although differing in molecular weight, have relatively the same percentages of silicone and cationic charge. This suggests that, all things being equal, molecular weight may not be a factor in determining softness. The higher percent cationic charge also is a factor since the higher the cationic charge, the more water-soluble the silicone becomes and, therefore, may be easier to wash off.

Product	Degree of Softness
3	4.8
5	3.8
6	3.8
4	3.3
1	2.6
2	2.6

Table 7. Softness of cationic silicone polymers.

The Group 2 products show great promising results for softness. The cationic silicone polymers designated as J208 and D208 were fairly similar, with the J208 having a higher degree of softness. Although the products in Group 1 show no difference in softness with increasing molecular weight, there does seem to be a correlation between degree of softness and molecular weight with the distearyl content in the product. This could be due to the high degree of branching that may make the cationic silicone polymers more substantive.

Surface Tension Silicone Quats

The ability to lower a surface tension is critical to the utilization of silicone quats. The polymers need to lower surface tension to (a) wet, (b) spread out, and (c) condition the hair. Recalling that water has a surface tension of 72 dynes/cm², fatty surfactants 32 dynes/cm² and silicone surfactants 22 dynes/cm², the value obtained for the silicone quat will allow for the determination in the product orients itself with the fatty or silicone portion at the surface. Table 8 shows the methodology used for surface tension analysis.

All the surface tension measurements were done with 0.1% solution of the cationic silicone polymer in de-ionized water at room temperature. Sigma 70 with software version 2.52 was used for the measurements. The 0.1% solution was made by mixing 0.6 gram of silicone polyether with 600 ml of de-ionized water. The solution was then divided into three parts in 4 oz bottles. The first part was used "as is" without any pH adjustment. The second part was adjusted to pH value of 10 with diluted ammonium hydroxide. And the third part was adjusted to pH value of 4 with diluted acetic acid. The pH of the solution was re-adjusted to the desired value after the first week, if needed.

Table 8. Surface Tension Test Methodology.

Silicone Fluids have Methyl Groups (Grey and white below)

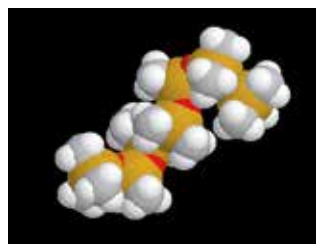


Image 1. The presence of this group provides the low surface tension values observed in silicone fluids.

Fatty Surfactants have an abundance of methylene groups, which account for their higher surface tension. When both groups are present in a single organo-functional cationic silicone polymer, the lowest free energy of the system will determine the group found at the interface and consequently the surface tension.

Table 9 shows the surface tension of the polymers tested.

Day	Silquat D-2 #1	Silquat J2 #2	Silquat J-208-2B #5
0	30.2	30.1	29.0
7	29.5	29.0	29.0

Table 9. Surface tension of Cationic Silicone Polymers.

CONCLUSION

It can be seen from the above analysis that incorporating cationic silicone polymer onto fiber will increase the degree of softness. The higher the percent of silicone and the higher percent of fatty amine in the molecule, the greater the degree of softness. It can also be seen that the larger the alkyl groups, the better the increase in softness as well. The cationic silicone polymer designated J15AO gave the highest degree of softness, mainly due to the high percent of silicone in the molecule. The cationic silicone polymer designated J208-2B (distearyl) also gave higher degrees of softness due to the larger amount of fatty alkyl groups in the molecule. Solubility also plays an important factor in determining the substantivity and degree of softness. If the quat is too soluble, it can be easily washed off. The quats need to have a degree of dispersibility in water so they can better deposit onto the substrate. In the Group 1, the solubility is provided by the diethylamine in the cationic group. Therefore, the higher the cationic charge, the more water-soluble the product.

FORMULATION TIP: SILICONE BASIC RAW MATERIALS

The basic raw materials used to make silicone polymers is quartz. (SiO₂). The Photo below shows the quartz (left and silicon metal of the right). The earth's crust is made up of around 25% SiO₂.



Image 2. Quartz and Silicon metal (11). The transformation of quartz to silicon metal is the first step in making silicone compounds. Quartz is in the upper left, silicon metal in the lower right. Photo by Dr. Thomas O'Lenick - Copyright 2005 used with permission

REFERENCES

- O'Lenick, Anthony, Surfactants Chemistry and Properties, Allured Publishing, 2002, p. 592.
- U.S. Patent 4,891,166 to Schaeffer et al, 1990, assigned to Goldschmidt.
- U.S. Patent 5,098,979 to O'Lenick, Anthony, 1992, assigned to Siltech.
- U.S. Patent 5,602,224 to Vrckovnik et al, 1992, assigned to Siltech.
- <http://www.cosmeticsandtoiletries.com/formulating/function/antimicrobial/8055977.html?page=2>
- https://en.wikipedia.org/wiki/Silicon_dioxide
- <https://www.sciencedirect.com/science/article/pii/S0022328X00908994>
- US Patent 5143722, Revlon, 1992
- <https://www.siltech.com/products/silicone-fluids/>
- <https://knowledge.ulprospector.com/4712/pcc-lamellar-gel-network-technology-a-primer/>
- <https://www.scribd.com/document/363504812/Anthony-O-Lenick-Silicones-for-Personal-Care> ■

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