kosmetikos*

By Steve Herman

NOT EXACTLY CARBON

"Grain of sand in eye may hide mountain."
— Charlie Chan in Paris (1935)

Try as we may to see the world through informed eyes, few of us take a lively scientific interest in dirt—oops, I mean soil—or in the slightly more elegant qualities of sand. But, naturally enough, soil and sand are made up of atoms and molecules, just like the Sistine Chapel. Unlike the Sistine Chapel, a big pile of sand can be heated up in just the right way to yield a substantial quantity of silicone. Silicone can then be cajoled into a variety of forms useful to personal care products. Sand to silicone to cosmetics through the magic of chemistry!

The unique properties of silicon center on the similarities and differences vis-à-vis carbon. Carbon is the center of a pivotal science, organic chemistry, primarily due to its ability to bond to itself, forming an infinite variety of rings and chains. Carbon chemistry makes life on earth possible. By contrast, silicon plays no role in the human body or most life forms. Diatoms are a rare exception, making their skeletons from SiO_2.

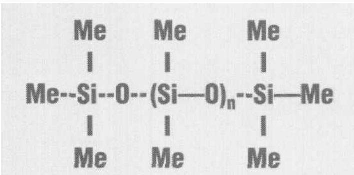
The silicon atom is a wee bit larger than a carbon atom, accounting for many of the significant differences between their compounds. Since the atoms are held less tightly together, many silicon compounds are more reactive than their carbon analogs. The silicon hydrides, called silanes (Si_nH_{2n+2}), offer an example. Methane (CH_4) is stable in air, while monosilane ignites spontaneously:

$$SiH_4(g) + 2O_2(g) \longrightarrow SiO_2(s) + 2H_2O(l)$$

There are no silicon analogs of ethylene or acetylene, and compounds containing Si=Si or Si=C are rare.

Two reasons favor carbon over silicon as the basis of life. Carbon dioxide is a monomer, readily soluble in water. By contrast, silicon dioxide forms a macromolecule, not soluble in water, and incapable of taking part in acid-base reactions. Secondly, regarding catenation (the linking of like atoms), carbon forms long chains and stable rings consisting of five or six members, while silicon can form only short chains.

Losing the "Basis-of-Life Sweepstakes" does not make silicon an also-ran among element—just add oxygen and we are off to the races. The most common silicone is officially named polydimethysiloxane trimethylsilyloxy terminated:



The INCI name of our new friend is dimethicone, a common cosmetic ingredient and official skin protectant.

Another common form of silicone is a small ring of five to six silicon atoms separated by oxgen, with methyl groups off to the side. Its INCI name is cyclomethicone.

One important application of cyclomethicone is as the primary carrier in suspensoid antiperspirant sticks. One frequently encounters these materials characterized as D4 or D5, D being the unit -($SiMe_2O$)-,which is capable of propagating in two directions. M, D, T, and Q describe silicon structures which can connect in one, two, three or four directions respectively.

Wonderful as dimethicone and cyclomethicone are, their use was somewhat limited in cosmetics because of limited solubility in many common systems. This situation is changing with mind-boggling rapidity. Taking silicone structure as a starting point, a near infinite number of derivatives can be created by grafting on a variety of side groups.

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***Greek kosmEtikos, skilled in adornment or decorating.**

kosmetikos

Figure 1 SAND TO SILICONE

Quartz (SiO_2) + C + energy → Si metal + CO

Si + 2 MeCl → Chlorosilane Mix (Me_2SiCl_2)

Me_2SiCl_2 + H_2O → Hydrolyzate

Hydrolyzate → Cyclics / Linears

Basic Molecular Units:

Monofunctional Unit	R-Si(R)(R)-
Difunctional Unit	-Si(R)(R)-
Trifunctional Unit	R-Si(-)(-)-
Tetrafunctional Unit	-Si(-)(-)-

Figure 2 CYCLOMETHICONE (D4)

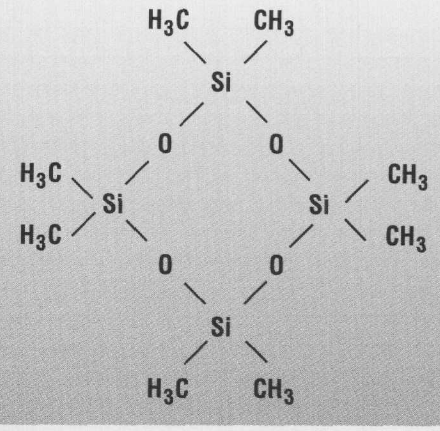

Figure 3 SILLY PUTTY

65%	Dimethyl Siloxane, hydroxy-terminated polymers with boric acid
17%	Silica
9%	Thixotrol ST
4%	Polydimethylsiloxane
1%	Decamethyl cyclopentasiloxane
1%	Glycerin
1%	Titanium Dioxide

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One example, polysiloxane copolymers

$$Me_3SiO(Me_2SiO)x(MeSiRO)ySiMe_3$$

can have R=Phenyl, Alkyl or $-CH_2CH_2CF_3$. With variations in the value of x and y, the possibilities are endless.

Grafting ethoxy groups can provide surface activity, creating silicone emulsifiers. The further addition of fatty groups provides a strange animal indeed, a union of silicone properties with traditional nonionics such as HLB theory deals with. O'Lenick developed an interesting approach to these molecules with his 3D HLB system.

We cannot begin to examine all the currently available silicone products, their properties and applications. But it would be unconscionable to end without considering the last material, a marvel of dilatant rheology, dimethyl siloxane hydroxy-terminated polymers—Silly Putty.

In 1943, while working on an inexpensive substitute for synthetic rubber for the war effort, James Wright of GE in New Haven accidentally dropped boric acid into silicone oil. No one was interested in this "nutty putty" until 1949, when Peter Hodgsen purchased the rights. Hodgsen, an out of work ad man, renamed the material "Silly Putty®" and it has been available ever since.

This brief romp through silicone from sand to Silly Putty couldn't do justice to the vast number of compounds useful in personal care, but hopefully we have enjoyed an introduction to the marvelous qualities of this unique element. ■

Digging Deeper

Two books cover the basic chemistry of silicones:

Rochow, Eugene G. An Introduction to the Chemistry of Silicones, *2nd Edition, John Wiley, New York, 1951.*

Fordham, S., ed. Silicones, *George Newnes Ltd., London, 1960.*

Dow Corning has some interesting resources for novices:

Discover Dow Corning Personal Care CD ROM, 1998.

Silicone Chemistry Overview, 1997.

Two sites with interesting references to Silly Putty® are:

http://www.geol.binghamton.edu/faculty/barker/demo1.txt

http://www.sirds.com/sillyputty/creations/ingredients.html

The second site was the source of the Silly Putty formula.

For an extension of the HLB Theory to silicones, consult O'Lenick, A.J. and Parkinson, J.K. Three-Dimensional HLB, *C&T, Oct.1996.*