Reactive Silicones

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Editors Note: This edition of **The Silicone Spectator** will address silicone materials that can be used as reactants in the preparation of polymers in which silicone is merely one component. These hetro-polymers are of growing interest in many market segments, because the properties of common polymers can be altered by inclusion of small amounts of silicone if placed correctly in the polymer.

Reactivity

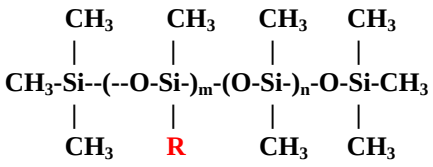
Contributed by: Tony O'Lenick of Siltech LLC

Silicone compounds that have been prepared to have reactive functional groups can be used as raw materials for the preparation of polymers in which they make up only one part[1,2]. The reason for the inclusion of the silicone portion in the new polymer is to obtain a new hetero-polymer possessing some of the properties of silicone.

This approach has been utilized in the preparation of many derivatives of dimethicone copolyol compounds[3].

There are two types of silicone compound that can contain reactive groups[4]:

Comb



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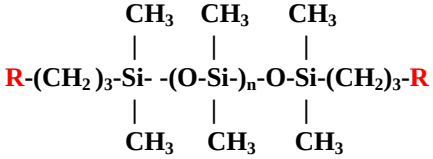

Clearly, the choice of the location of the reactive group (comb (internal) or terminal silicone), will have a dramatic impact on the properties of the hetero-polymer. Molecular weight, percentage silicone, and crosslink density are all affected by the choice.

Dimethicone Copolyol Derivaties

ANIONIC COMPOUNDS

Hydrocarbon Products	Silicone Products
Phosphate Esters	Silicone Phosphate Esters [5,6]
Sulfates	Silicone Sulfates [7]
Carboxylates	Silicone Carboxylates [8,9]
Sulfosuccinates	Silicone Sulfosuccinates [10,11]

CATIONIC COMPOUNDS

Hydrocarbon Products	Silicone Products
Alkyl Quats	Silicone Alkyl Quats [12]
Amido Quats	Silicone Amido Quats [13]
Imidazoline Quats	Silicone Imidazoline Quats[14]

AMPHOTERIC COMPOUNDS

Hydrocarbon Products	Silicone Products
Amino Proprionates	Silicone Amphoterics [15]
Betaines	Silicone Betaines [16]
Phosphobetaines	Silicone Phosphobetaines [17]

NONIONIC COMPOUNDS

Hydrocarbon Products	Silicone Products
Alcohol Alkoxylates	Dimethicone Copolyol
Alkanolamids	Silicone Alkanolamids[18]
Esters	Silicone Esters [19,20,21,22]
Taurine Derivatives	Silicone Taurine[23]
Isethionates	Silicone Isethionates[24]
Alkyl Glycosides	Silicone Glycosides[25]

References

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2. Siltech Brochure (http://www.siltechpersonalcare.com/pdfs/brochures/Siltech%20CorpBrochure%202007.pdf)
3. O'Lenick, Anthony, Silicones for Personal Care,
4. O'Lenick, Anthony, Silicones for Personal Care, 2nd edition
5. U.S. Patent 5,149,765, September 1992 to O'Lenick.
6. U.S. Patent 4,724,248, February 1988 to Dexter et al.
7. U.S. Patent 4,960,845, October 1990 to O'Lenick.

8. U.S. Patent 3,560,544, February 1971 to Haluska.
9. U.S. Patent 5,296,625, March 1994 to O'Lenick.
10. U.S. Patent 4,717,498, January 1988 to Maxon.
11. U.S. Patent 4,777,277, November 1998 to Colas.
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20. U.S. Patent 5,070,168, December 1994 to O'Lenick.
21. U.S. Patent 4,724,258, issued February 1988 to Dexter.
22. U.S. Patent 6,338,042, December 2002 to O'Lenick.
23. U.S. Patent 5,280,099, January 1994 to O'Lenick.
24. U.S. Patent 5,300,666, April 1994 to O'Lenick.
25. U.S. Patent 5,120,812, June 1992 to O'Lenick

These materials will be covered in detail in subsequent issues of Silicone Spectator.

In this edition, we will concentrate on silicone polymers that can be used as raw materials to make different polymers. The reactivity is based upon reactive groups attached to the silicone backbone through hydrosilylation.

Reactive Silicones

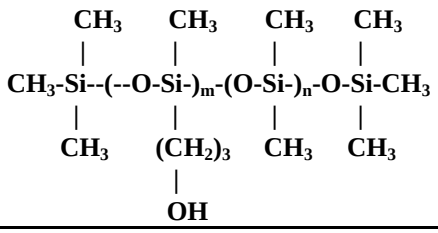
Contributed by: Rick Vrckovnik of Siltech Corporation

Reactive silicones consist of multifunctional or linear-difunctional silicone pre-polymers with reactive terminal end-groups. These silicones can be co-reacted into various polymers used in coatings, plastics, resins and other applications to increase flexibility, slip, mar resistance, high temperature stability and oxidative permeability. The inclusion of silicone pre-polymer can also help decrease the glass transition temperature of the polymer.

1. Silicone Compounds with Hydroxyl Groups

These can be used in esterfication, transesterfication and any other reaction where standard organic hydroxyl compounds are used.

Comb



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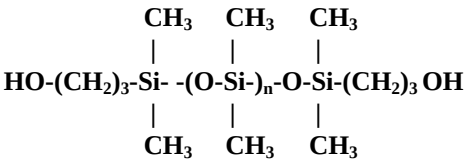
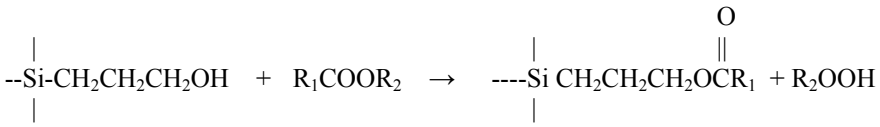


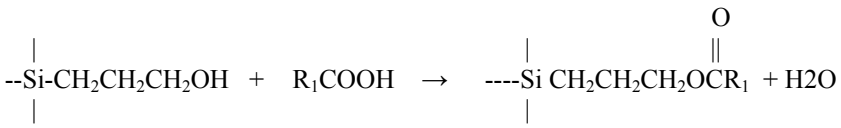
Examples

Typical Products	Properties & Applications	Appearance	Mol. Wt.	Equivalent Wt.
OH AO (Comb)	Low molecular weight reactive silicone. Contains one reactive group on a heptamethyltrisiloxane backbone. Used as a chain terminator and polymer modifier.	Clear Liquid	280	280
OH C50 (Comb)	High molecular weight trifunctional silicone pre-polymer.	Clear Liquid	11,600	3,800
OH J10 Comb	High molecular weight multifunctional silicone pre-polymer.	Clear Liquid	8,800	880
OH Di-50 Terminal	Linear difunctional hydroxyl-terminated silicone pre-polymer	Clear Liquid	4,000	1,980
OH Di-100 Terminal	Linear difunctional hydroxyl-terminated silicone pre-polymer. Twice the molecular weight of OH Di-50	Clear Liquid	7,700	3,800

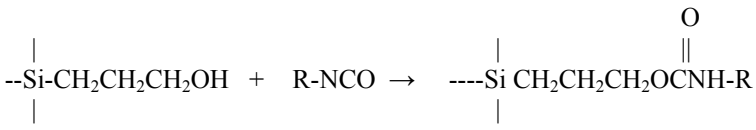
Reaction With Methyl esters



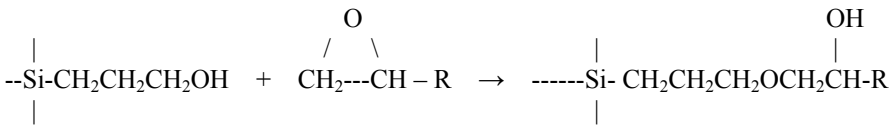
Reaction With Carboxylic Acids



Reaction With Isocyanates



Reaction With Epoxides



2. Silicones with acrylate functional groups.

These can be co-reacted with vinyl and other acrylate monomers in free radical polymerization reactions.

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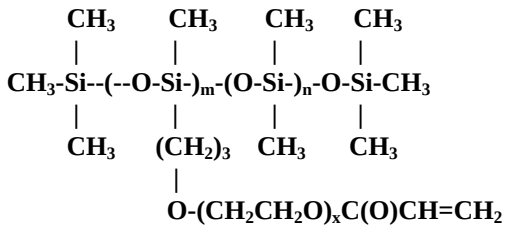

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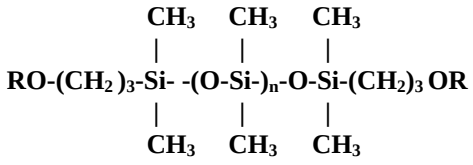
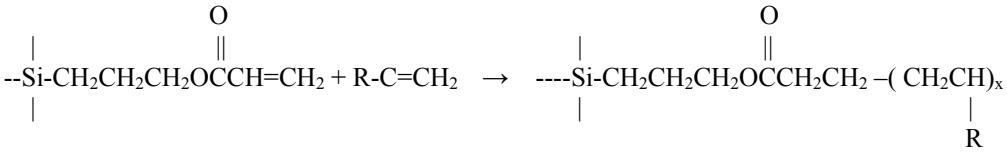


R is $-(CH_2CH_2O)_xC(O)CH=CH_2$

Typical Products	Properties & Applications	Appearance	Mol. Wt.	Equivalent Wt.
ACR D208	Water-soluble multi-functional acrylate silicone pre-polymer.	Clear Liquid	2,200	1,400
ACR D2	Multi-functional acrylate silicone pre-polymer.	Clear Liquid	1,790	700
ACR Di-50	Linear difunctional acrylate-terminated silicone pre-polymer.	Clear Liquid	4,100	2,050
ACR Di-100	Linear difunctional acrylate-terminated silicone pre-polymer. Twice the molecular weight of ACR Di-50	Clear Liquid	7,800	3,900
ACR Di-1508	Linear difunctional water dispersible acrylate Silicone pre-polymer	Clear Liquid	2,100	1,050

Reaction With Vinyl and other acrylate Monomers



3. Silicone compounds with amino functional groups.

These can be reacted with carboxylic acids, methyl esters and other reaction where standard organic amines are used.

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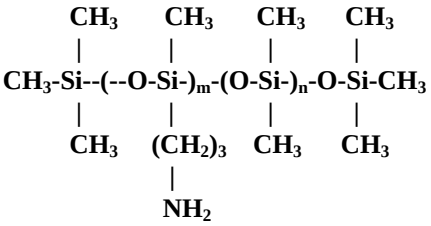

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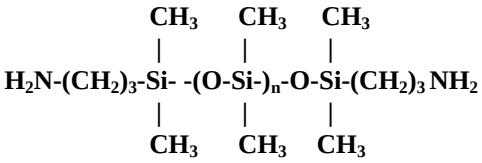
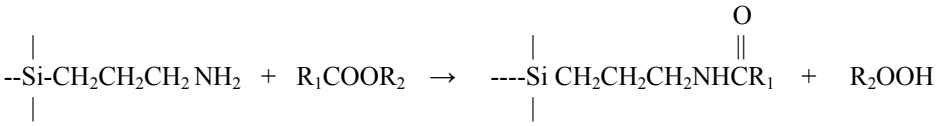
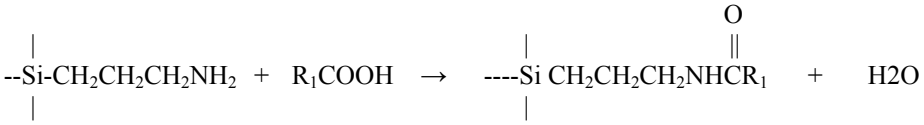


Products	Properties & Applications	Appearance	Mol. Wt.	Equivalent Wt.
NH Di-8	Linear difunctional amino-terminated silicone pre-polymer.	Clear Liquid	850	425
NH Di-50	Linear difunctional amino-terminated silicone pre-polymer.	Clear Liquid	3,600	1,800

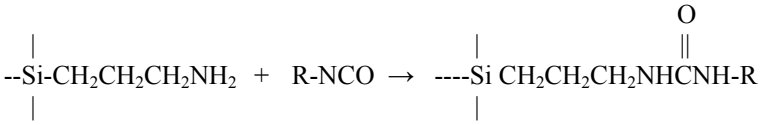
Reaction With Methyl Esters



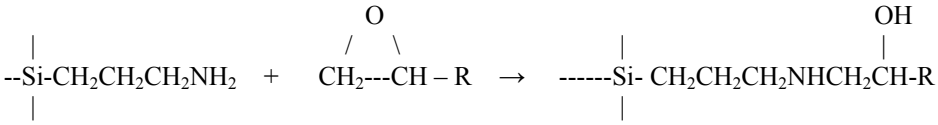
Reaction With Carboxylic Acids



Reaction With Isocyanates



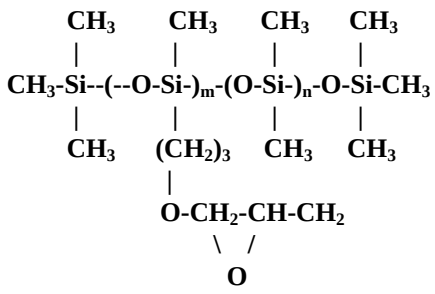
Reaction With Epoxides



4. Silicone with epoxy functional groups.

These can be reacted with alcohols, amines, epoxides and any other reaction where organic standard organic epoxides are used.

Comb



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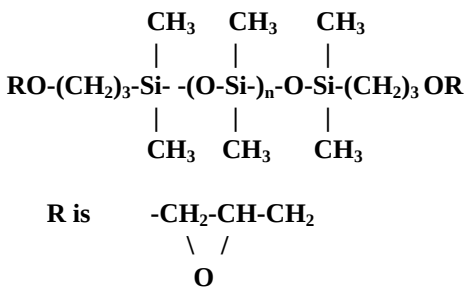

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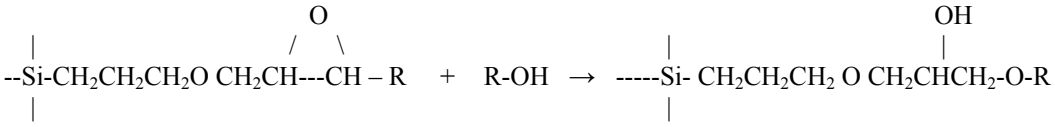
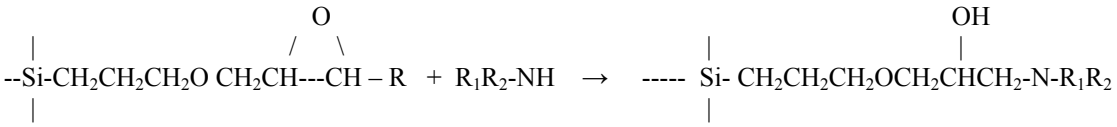
Products	Properties & Applications	Appearance	Mol. Wt.	Equivalent Wt.
EP C50	High-molecular-weight trifunc-tional silicone pre-polymer.	Clear Liquid	11,800	3,900
EP J10	High-molecular-weight multi-functional silicone pre-polymer.	Clear Liquid	9,300	930
EP Di-50	Linear difunctional epoxide-terminated pre-polymer.	Clear Liquid	4,100	2,050
EP Di-100	Linear difunctional epoxide-terminated silicone pre-polymer. Twice the molecular weight of EP Di-50	Clear Liquid	7,800	3,900

Reaction With Alcohols



Reaction With Amines



5. Silicone with vinyl functionality.

These can be reacted with other vinyl containing organic monomers in free radical polymerization reactions. They can also be reacted with silicone hydrides to make silicone elastomers.

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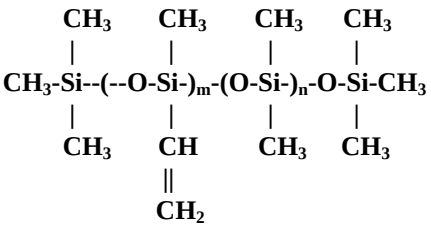

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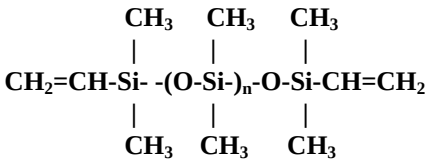
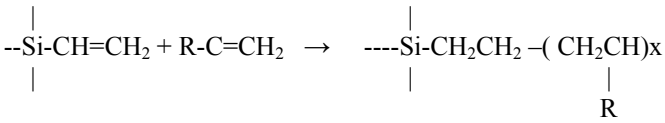
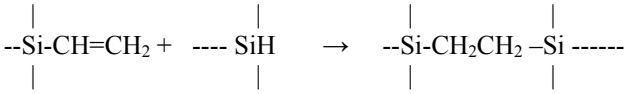


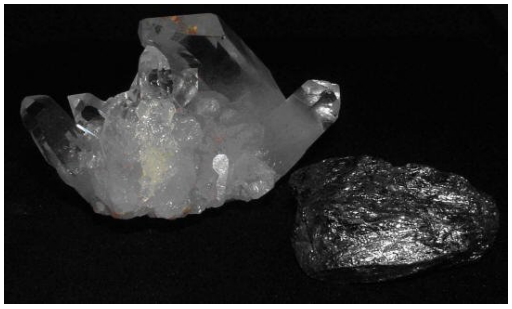
Products	Products & Applications	Appearance	% Vinyl	Vinyl mmoles/gm
VIN C50	High-molecular-weight trifunctional silicone pre-polymer.	Clear Liquid	0.701	0.260
VIN J10	High-molecular-weight multi-functional silicone pre-polymer.	Clear Liquid	3.190	1.182
VIN 70	70 cps linear vinyl terminated silicone pre-polymer.	Clear Liquid	1.390	0.514
VIN 100	100 cps linear vinyl terminated silicone pre-polymer.	Clear Liquid	0.882	0.327
VIN 200	200 cps linear vinyl terminated silicone pre-polymer.	Clear Liquid	0.500	0.185
VIN 1000	Linear 1000 cps vinyl-terminated silicone pre-polymers with viscosities ranging from 70-65,000 cps.	Clear Liquid	0.250	0.0925
VIN 5000	5,000 cps linear vinyl terminated silicone pre-polymer.	Clear Liquid	0.115	0.0426
VIN 10000	10,000 cps linear vinyl terminated silicone pre-polymer.	Clear Liquid	0.100	0.0370
VIN 20000	20,000 cps linear vinyl terminated silicone pre-polymer.	Clear Liquid	0.080	0.0296
VIN 65000	65,000 cps linear vinyl terminated silicone pre-polymer.	Clear Liquid	0.050	0.0185

Reaction With Vinyl Monomers



Reaction With SiH





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