Hydrolytic Stability of Silsoft® Dimethicone Copolyols

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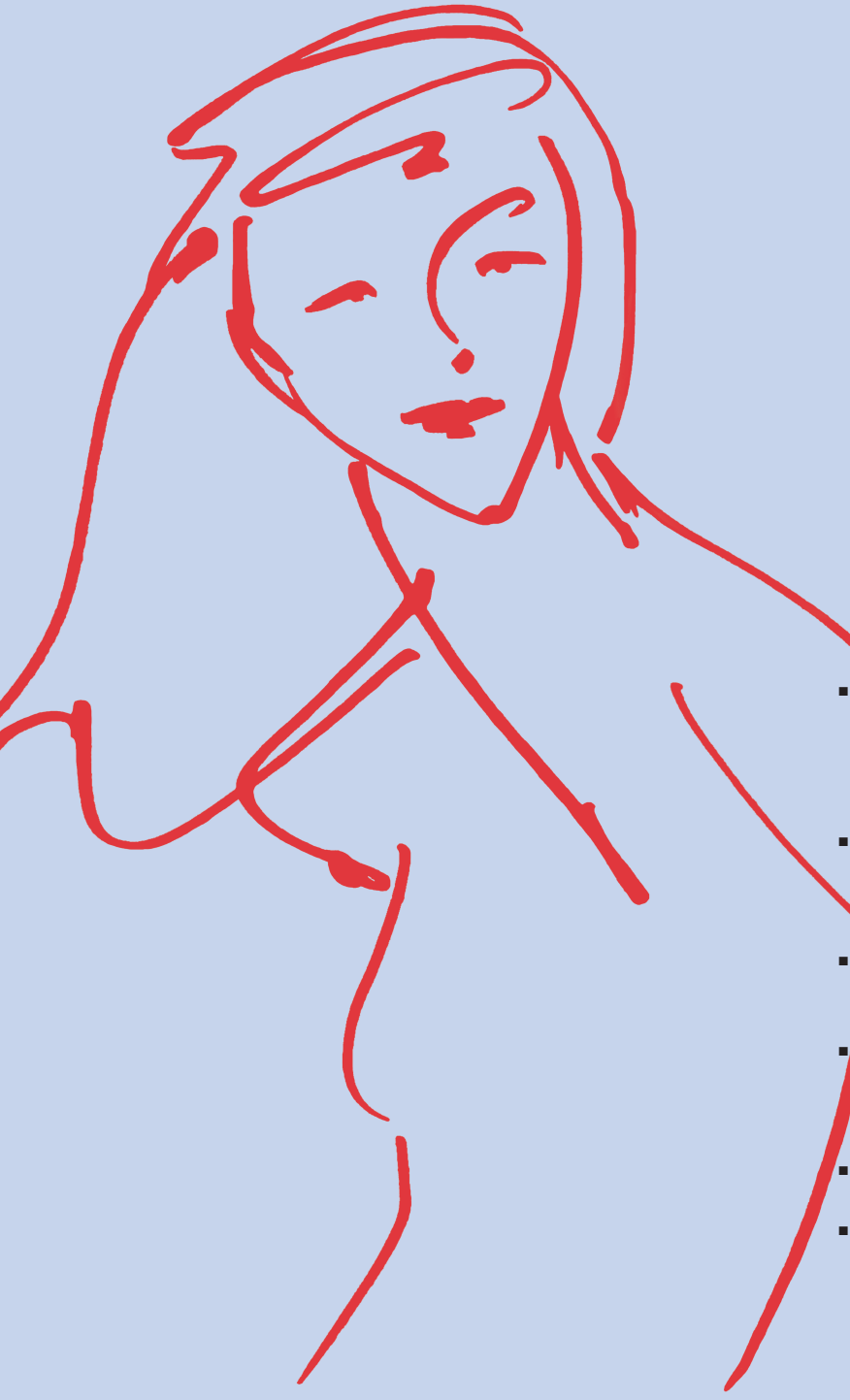
Crompton
OSi Specialties



Dimethicone copolyols are widely used in skin and hair formulations as aesthetic ingredients and as excellent dispersants, emulsifiers and foam modifiers. Unlike dimethicones, most dimethicone copolyols are compatible with aqueous systems. Since many formulations vary in pH, long-term hydrolytic stability of dimethicone copolyols is often questioned. We have attempted to define a "functional" pH range for dimethicone copolyols, to provide formulators with practical guidelines for working with these ingredients. We investigated the effects of varying structures and properties on the long-term stability of dimethicone copolyols in aqueous media. Selected copolyols were evaluated across wide pH and concentration ranges using reverse-phase HPLC.

CONCLUSIONS

- **Rate of hydrolysis of conventional dimethicone copolyols decreases as:**
  - solubility in water decreases
  - molecular weight increases (>10,000)
  - concentration of the copolyol increases (from 1% to 5%)
- **The recommended pH range for maintaining long term stability of conventional dimethicone copolyols is 5.5 - 8.5**

- **Hydrolyzable dimethicone copolyols are expected to have limited stability in aqueous media due to presence of Si-O-C linkage**
- **The recommended pH range for maintaining optimum stability of hydrolyzable dimethicone copolyols is 6 - 8**

- **Trisiloxane copolyols are susceptible to rapid hydrolysis under both acidic and basic conditions**
- **The recommended pH range for maintaining stability of trisiloxane copolyols is 6.5 - 7.5**
  - solutions maintained at these pH levels have been shown to be stable for 2+ years

Dimethicone Copolyol Type	pH Range for Optimum Stability
Conventional Dimethicone Copolyol	5.5 – 8.5
Hydrolyzable Dimethicone Copolyol	6.0 – 8.0
Trisiloxane Copolyol	6.5 – 7.5

EXPERIMENTAL / METHODOLOGY

Experimental

To determine the stability of Silsoft® dimethicone copolyols, solutions were prepared by dispersing the copolyols in standard buffer solutions at various pH levels and concentrations.

High Performance Liquid Chromatography (HPLC) was used to monitor the stability of the copolyols. Reverse-phase HPLC is an ideal method for separating dimethicone copolyols from the other components in the buffer solutions. A typical HPLC chromatogram of a dimethicone copolyol is shown in Plot 1.

To more conveniently classify the stability of a copolyol, the percent of unhydrolyzed material was plotted against time. Two points on the curves were used to characterize the stability of the copolyol:

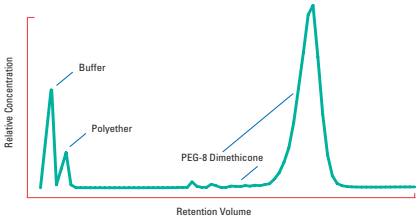
95% Unhydrolyzed – The amount of time over which there is no hydrolysis.
80% Unhydrolyzed – The amount of time at which a hydrolysis rate trend has been established.

Methodology

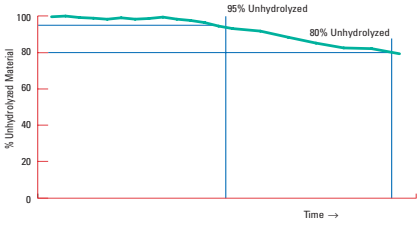
Waters Alliance 2960 HPLC Chromatograph
Alltech 500E Evaporative Laser Light Scattering Detector with Low Temperature Adapter (ELSD/LTA)
Conditions: 35°C 1.95 SLPM N_2 carrier
Column – Phenomenex LUNA C18 end cap, 5 micron, 75x4.6 mm.
Gradient – Water/Methanol/Isopropanol at 1.0 mL/min.

Solutions were injected without dilution. Injection volumes ranged from 5 mL for 5.0% solutions to 20 mL for 0.5% solutions.

PLOT 1
TYPICAL REVERSE-PHASE HPLC CHROMATOGRAM OF A DIMETHICONE COPOLYOL



PLOT 2
TYPICAL PERCENT OF UNHYDROLYZED MATERIAL VERSUS TIME FOR A DIMETHICONE COPOLYOL



SILSOFT CONVENTIONAL DIMETHICONE COPOLYOLS

Conventional dimethicone copolyols have excellent stability as the polyether groups are attached to the siloxane backbone through a series of hydrolytically stable Si-C bonds.

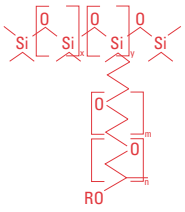
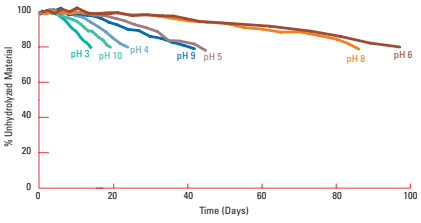


TABLE 1
TIME TO REACH 95% AND 80% UNHYDROLYZED MATERIAL FOR A PEG-8 DIMETHICONE* AT DIFFERENT pH LEVELS AND CONCENTRATIONS

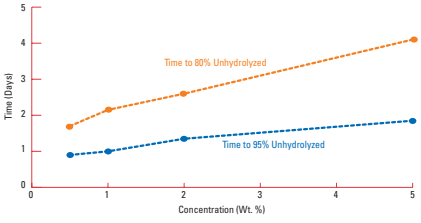
	1% Dimethicone Copolyol		*5% Dimethicone Copolyol*	
	80%	*95%*	*80%*	*95%*
	Unhydrolyzed	*Unhydrolyzed*	*Unhydrolyzed*	*Unhydrolyzed*
pH	**Time in Days**		**Time in Days**	
2	1.29	0.63	2.54	1.20
3	14.00	7.00	27.00	13.00
4	26.00	14.00	50.00	24.00
5	45.00	23.00	89.00	35.00
6	97.00	43.00	186.00	82.00
7		>> 2 years		
8	86.00	40.00	165.00	76.00
9	42.00	19.00	82.00	38.00
10	19.00	10.00	35.00	19.00
11	9.00	4.80	17.00	9.00
12	0.82	0.39	1.72	0.75

*Copolyol III

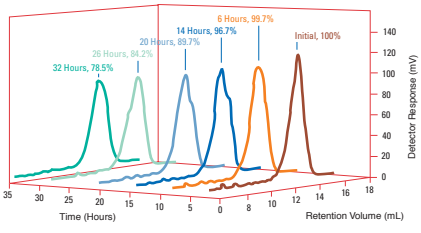
PLOT 3
PERCENT UNHYDROLYZED MATERIAL VERSUS TIME; A PEG-8 DIMETHICONE AT VARIOUS pH LEVELS (AT 1.0% CONCENTRATION)



PLOT 4
EFFECTS OF CONCENTRATION ON HYDROLYSIS RATES FOR A PEG-8 DIMETHICONE AT pH 2



PLOT 5
HPLC CHROMATOGRAMS OF A PEG-8 DIMETHICONE IN pH 2 BUFFER MONITORED OVER TIME



Hydrolysis does not affect performance properties of the copolyol!

SILSOFT HYDROLYZABLE DIMETHICONE COPOLYOLS

Hydrolyzable dimethicone copolyols are made by condensation chemistry and contain Si-O-C bonds between the silicone chain and polyether chains. This linkage offers limited resistance to hydrolysis under neutral and slightly alkaline conditions but breaks down quickly in acidic media.

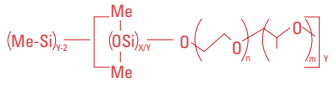
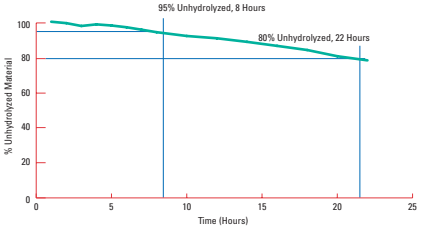


TABLE 2
TIME TO REACH 95% AND 80% UNHYDROLYZED MATERIAL FOR A PEG-20/ PPG-15 DIMETHICONE* AT DIFFERENT pH LEVELS AND CONCENTRATIONS

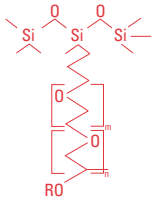
	1% Dimethicone Copolyol		*5% Dimethicone Copolyol*	
	80%	*95%*	*80%*	*95%*
	Unhydrolyzed	*Unhydrolyzed*	*Unhydrolyzed*	*Unhydrolyzed*
pH	**Time in Days**		**Time in Days**	
2	0.92	0.33	1.76	0.63
3	9.98	3.67	19.07	7.00
4	18.55	7.33	35.43	14.01
5	32.09	12.05	61.29	23.01
6	69.17	22.52	132.12	43.02
7		>180		
8	61.34	20.95	117.15	40.02
9	29.96	10.61	57.21	20.27
10	13.55	5.24	25.88	10.00
11	6.42	2.51	12.27	4.80
12	0.59	0.20	1.12	0.39

*Copolyol II

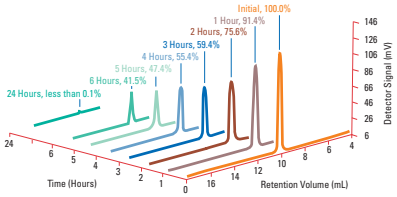
PLOT 6
PERCENT UNHYDROLYZED MATERIAL VERSUS TIME FOR A PEG-20/PPG-15 HYDROLYZABLE DIMETHICONE (pH 2, CONCENTRATION 1%)



Trisiloxanes represent a unique sub-set within conventional dimethicone copolyols. Their well-defined, compact siloxane backbone affords distinctive application benefits (e.g., spreading and wetting). However, they tend to be more prone to hydrolysis.



PLOT 7
HPLC CHROMATOGRAMS OF A PEG-8 TRISILOXANE IN pH 3 BUFFER MONITORED OVER TIME



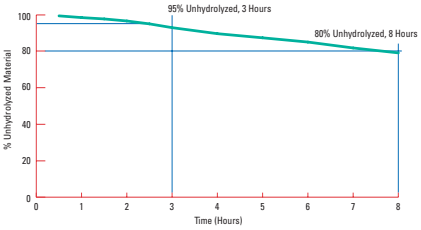
Unlike conventional dimethicone copolyols, the performance properties of trisiloxanes change rapidly due to hydrolysis!.

TABLE 3
TIME TO REACH 95% AND 80% UNHYDROLYZED MATERIAL FOR A PEG-5/PPG-3 DIMETHICONE* TRISILOXANE AT DIFFERENT pH LEVELS AND CONCENTRATIONS

	1% Dimethicone Copolyol		*5% Dimethicone Copolyol*	
	80% Unhydrolyzed	*95% Unhydrolyzed*	*80% Unhydrolyzed*	*95% Unhydrolyzed*
pH	**Time in Days**		**Time in Days**	
2	0.33	0.13	0.63	0.25
3	3.58	1.44	6.84	2.76
4	6.65	2.89	12.71	5.52
5	11.51	4.75	21.98	9.07
6	24.81	8.87	47.39	16.95
7	>> 2 years			
8	22.00	8.25	42.02	15.76
9	10.74	4.18	20.52	7.99
10	4.86	2.06	9.28	3.94
11	2.30	0.99	4.40	1.89
12	0.21	0.08	0.40	0.15

*Copolyol I

PLOT 8
PERCENT UNHYDROLYZED MATERIAL VERSUS TIME FOR A PEG-5/PPG-3 TRISILOXANE DIMETHICONE (pH 2, 1 % CONCENTRATION)



SUMMARY

TABLE 4
MOLECULAR WEIGHT, SOLUBILITY AND ARCHITECTURE OF DIMETHICONE COPOLYOLS INVESTIGATED

Designation	INCI Name / Polyether Type	Molecular Weight	Solubility in Water	Architecture
Copolyol I	PEG-5/PPG-3 Dimethicone	< 1000	Dispersible	Trisiloxane
Copolyol II	PEG-20/PPG-15 Dimethicone	> 10,000	Soluble	Branched / Hydrolyzable
Copolyol III	PEG-8 Dimethicone	< 5000	Soluble	Pendant
Copolyol IV	PEG-8 Dimethicone	< 5000	Dispersible	Linear
Copolyol V	PEG-8 Dimethicone	< 5000	Dispersible	Pendant
Copolyol VI	PEG-20/PPG-23 Dimethicone	> 10,000	Soluble	Pendant
Copolyol VII	PEG-8 Dimethicone	> 10,000	Insoluble*	Pendant
Copolyol VIII	PPG-12 Dimethicone	< 5000	Insoluble*	Linear
Copolyol IX	PPG-12 Dimethicone	< 5,000	Insoluble*	Pendant

*Hydrolysis experiments run in water-isopropanol solutions

PLOT 9
PERCENT UNHYDROLYZED MATERIAL VERSUS TIME; ALL COPOLYOLS INVESTIGATED, pH 2 (1.0% CONCENTRATION)

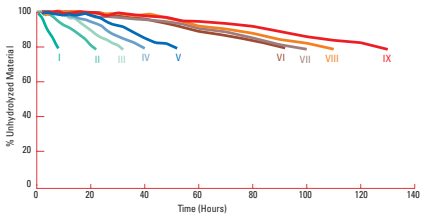


TABLE 5
TIME TO REACH 80% UNHYDROLYZED MATERIAL FOR ALL DIMETHICONES AT ALL pH LEVELS AND 1% CONCENTRATIONS

Dimethicone Copolyol									
pH	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
2	0.33	0.92	1.29	1.63	2.13	3.75	4.17	4.58	5.42
3	3.58	9.98	14.00	17.69	26.41	40.69	45.24	49.69	58.81
4	6.65	18.55	26.00	32.86	42.94	75.60	84.07	92.33	109.27
5	11.51	32.09	45.00	56.85	82.85	128.93	145.45	159.75	189.05
6	24.81	69.17	97.00	122.56	160.15	281.96	313.54	344.37	407.53
Dimethicone Copolyol									
pH	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
8	22.00	61.34	86.00	108.67	142.01	250.01	278.01	305.35	361.35
9	10.74	29.96	42.00	53.07	69.35	122.10	135.78	149.12	176.48
10	4.86	13.55	19.00	24.01	31.37	55.24	61.42	67.46	79.84
11	2.30	6.42	9.00	11.38	14.87	26.18	29.11	31.97	37.83
12	0.21	0.59	0.82	1.04	1.36	2.40	2.67	2.93	3.47

PLOT 10
TIME TO REACH 80% UNHYDROLYZED MATERIAL FOR ALL DIMETHICONES IN ACIDIC AND BASIC MEDIA, AT 1% CONCENTRATION