Structure Function Relationships of Dimethicone Copolyol

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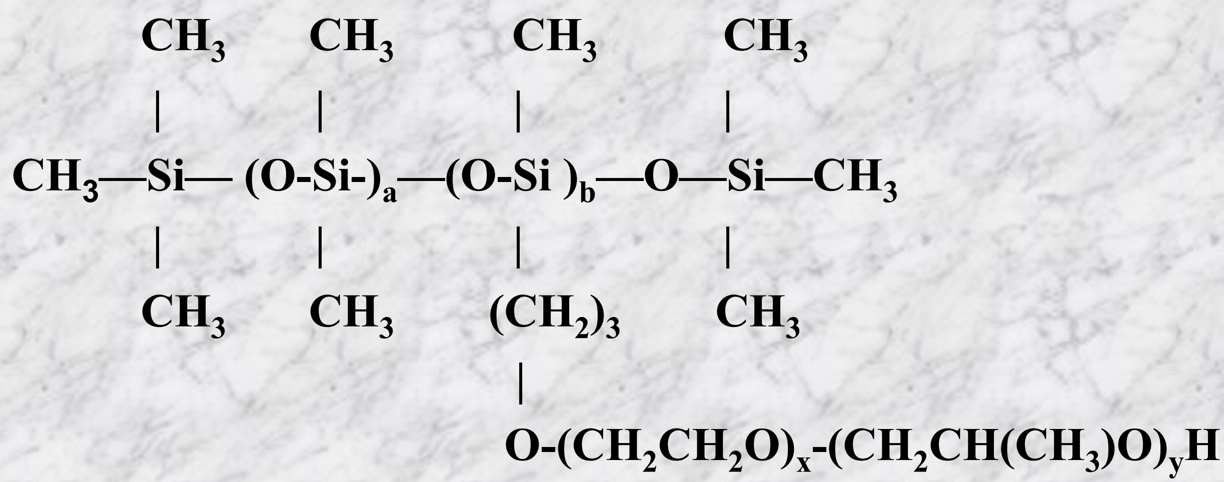
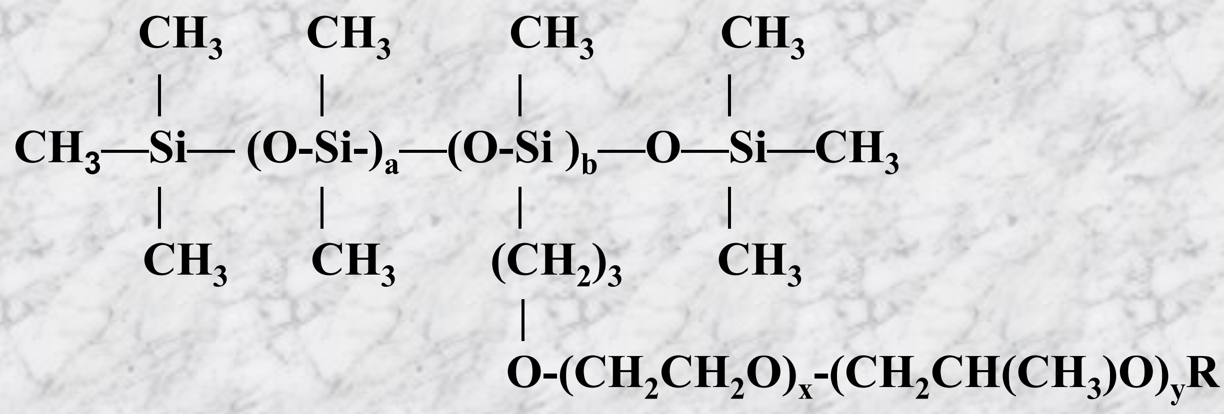
Dimethicone Copolyol, DMC

- DMC surfactants and their derivatives are an important and growing class of surfactants.
- They are used in a diverse area of applications due to their ability to provide maximum surface active properties in a cost-effective manner.
- Despite their growing use, studies regarding the basic understanding of the chemistry and the effect of structure on surfactant properties remain limited.

DMC Surfactants General Structure

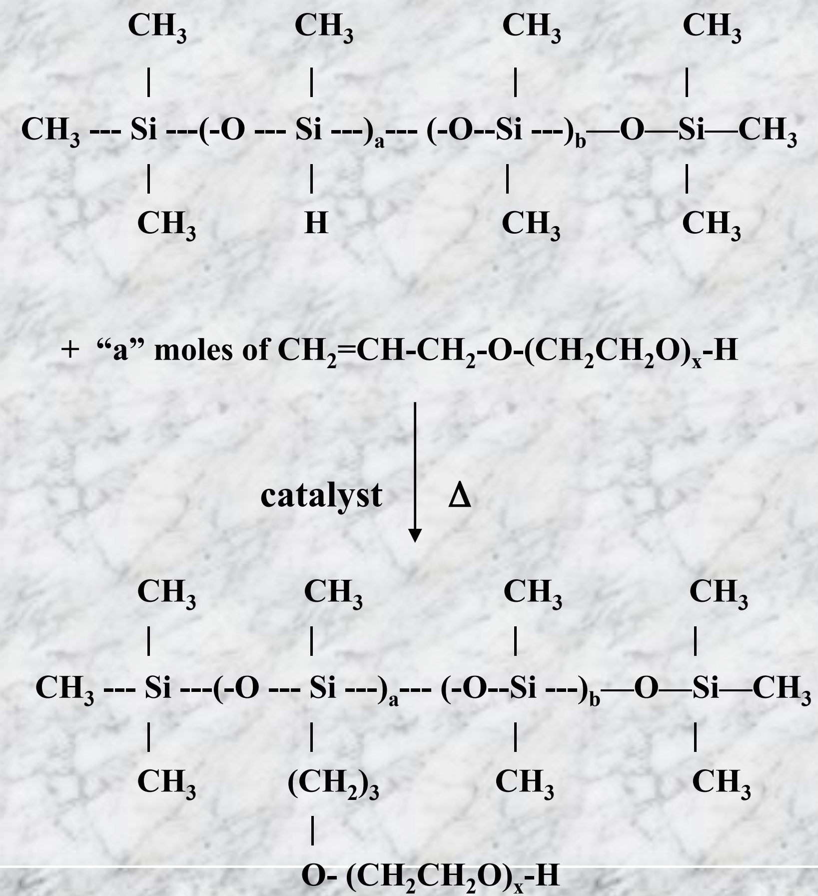


DMC Surfactant Derivatives
General Structure

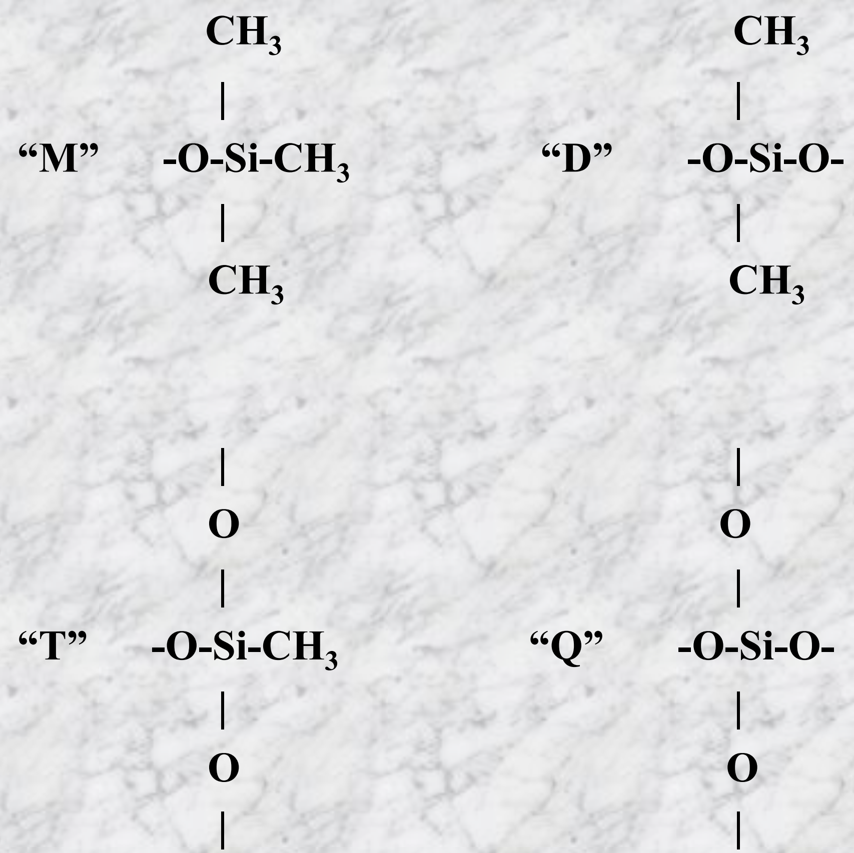


where R = alkyl,amino, etc.

General Reaction Scheme for the Synthesis of DMC



DMC Nomenclature - “shorthand”



DMC Nomenclature - Organofunctional

CH_3

|

"M*" -O-Si- CH_3

|

R where R = functional group

For example, the structure for MD_2D_3*M is:

CH_3 CH_3 CH_3 CH_3

| | | |

CH_3-Si-$(O\text{-}Si)_2$-$(O\text{-}Si)_3$-O-Si-CH_3

| | | |

CH_3 CH_3 R CH_3

Properties Evaluated

- Solubility
- Cloud point
- Surface tension/cmc
- Spreading (in a polyester surface)
- Foaming (ASTM D 1173)
- Emulsification
- Draves wetting (ASTM D 2281)
- Draize primary ocular irritation (via independent lab)

DMC Structures Synthesized

Designation[a]	Molecular Weight	Equivalent MW[b]
MD*M	607	607
MD*DM	808	612
MD_2*D_2M	1108	619
MD_3*D_5M	1610	630
MD_3*D_7M	2111	642
MD_4*D_8M	2412	648

a) where D* is $–(CH_2)_3$-O-$(CH_2CH_2O)_7$-H

b) EMW = Molecular weight / number of D* units

Solubility at 1%w (24^{o}C)

Designation	DI Water	Methanol	Mineral Oil	Silicone Oil
MD*M	Soluble	Soluble	Insoluble	Insoluble
MD_2*D_2M	Soluble	Soluble	Dispersible	Insoluble
MD_3*D_7M	Soluble	Soluble	Dispersible	Dispersible

Products with higher molecular weight showed better dispersibility in nonpolar media.

Cloud Point

Designation	**% EO**	**Cloud Point, °C (1 % w)**
MD*M	74.4	58
MD*DM	67.0	57
MD_2*D_2M	75.8	58
MD_3*D_5M	73.5	58
MD_3*D_7M	74.5	58
MD_4*D_8M	74.7	57

Surface Tension and CMC
(24°C, DI water)

Designation	Surface Tension at CMC, $dynes/cm^2$	CMC, mg/L
MD*DM	20	3
MD_2*D_2M	19	4
MD_3*D_5M	23	6
MD_3*D_7M	21	5

Compares with typical values.

Spreading

Designation	Relative Spreading Area
MD*M	4
MD*DM	6
MD_2*D_2M	8
MD_3*D_5M	2
MD_3*D_7M	4
MD_4*D_8M	2

Conditions: Polyester surface (3M overhead slide film), 10 μL sample, (DI water), diameter measured after 45 seconds using a Vernier caliper at 23±1°C (65% RH).

Relative area = area of sample / area of distilled water.

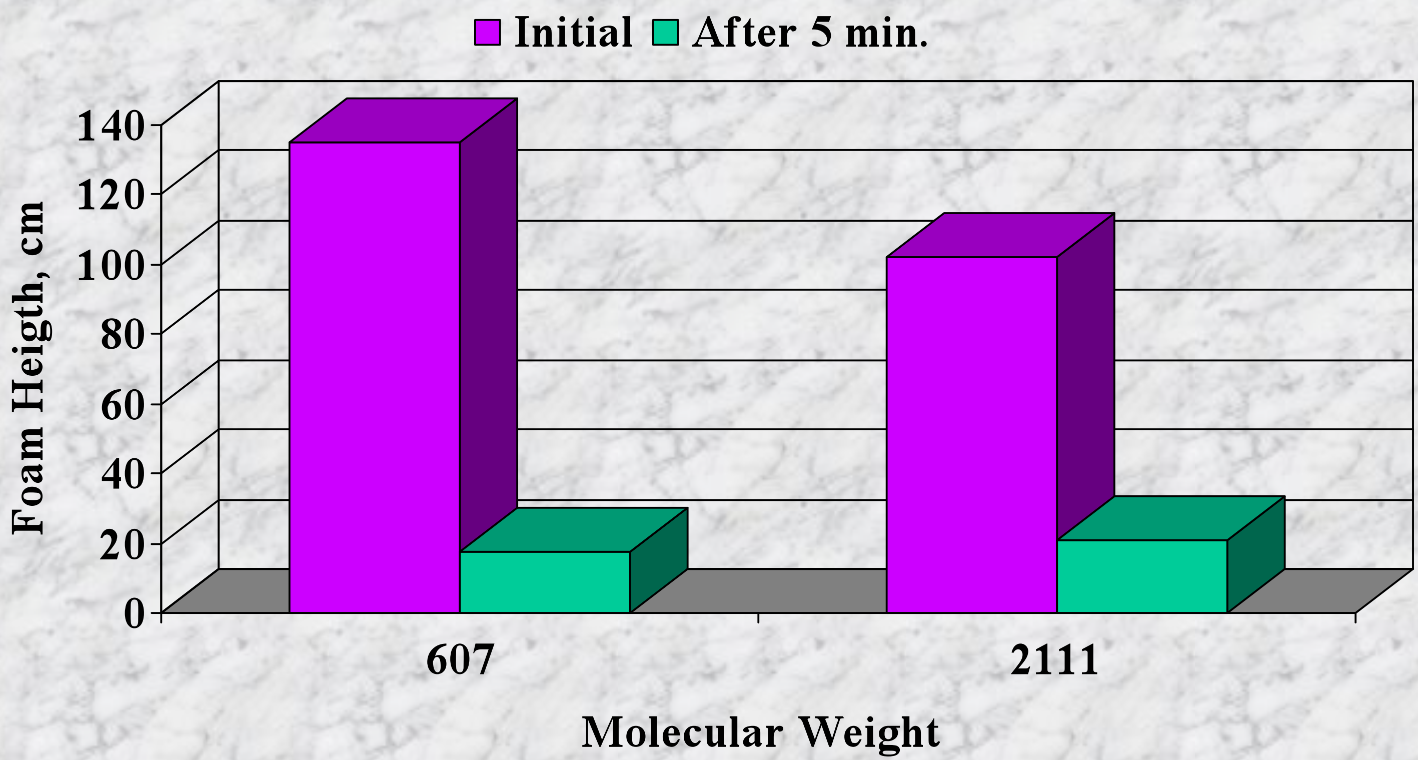
Spreading

- The isomers studied spread slightly better than water but cannot be considered superspreaders.

- These materials are too hydrophilic and thus do not contain the needed subphases present that provide the necessary surfactant concentration gradient in the droplet spreading front that drives the spreading.

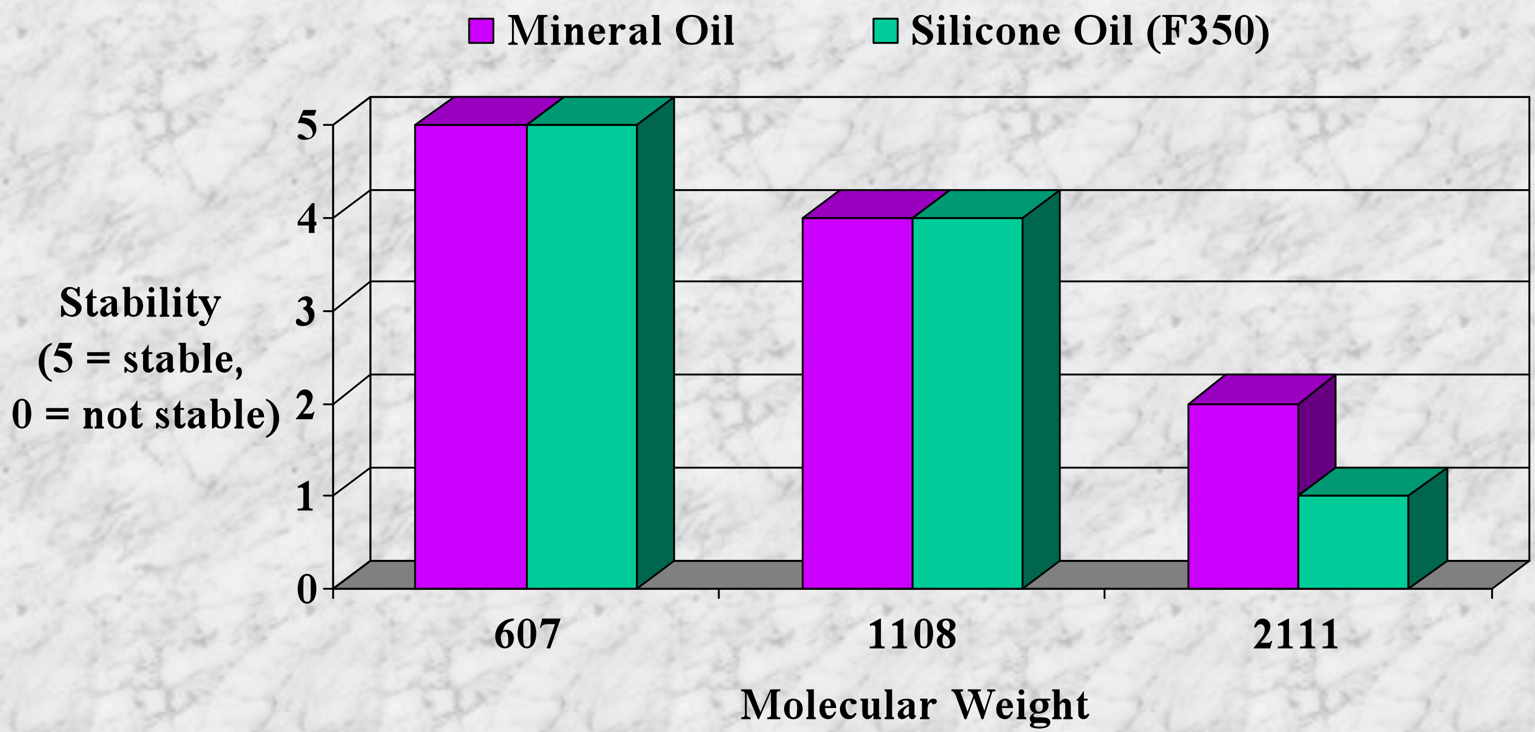
- $S_{L/S} = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA})$ where A=air, L=liquid, S=substrate

DMC Foaming at 1% w (ASTM D1173)

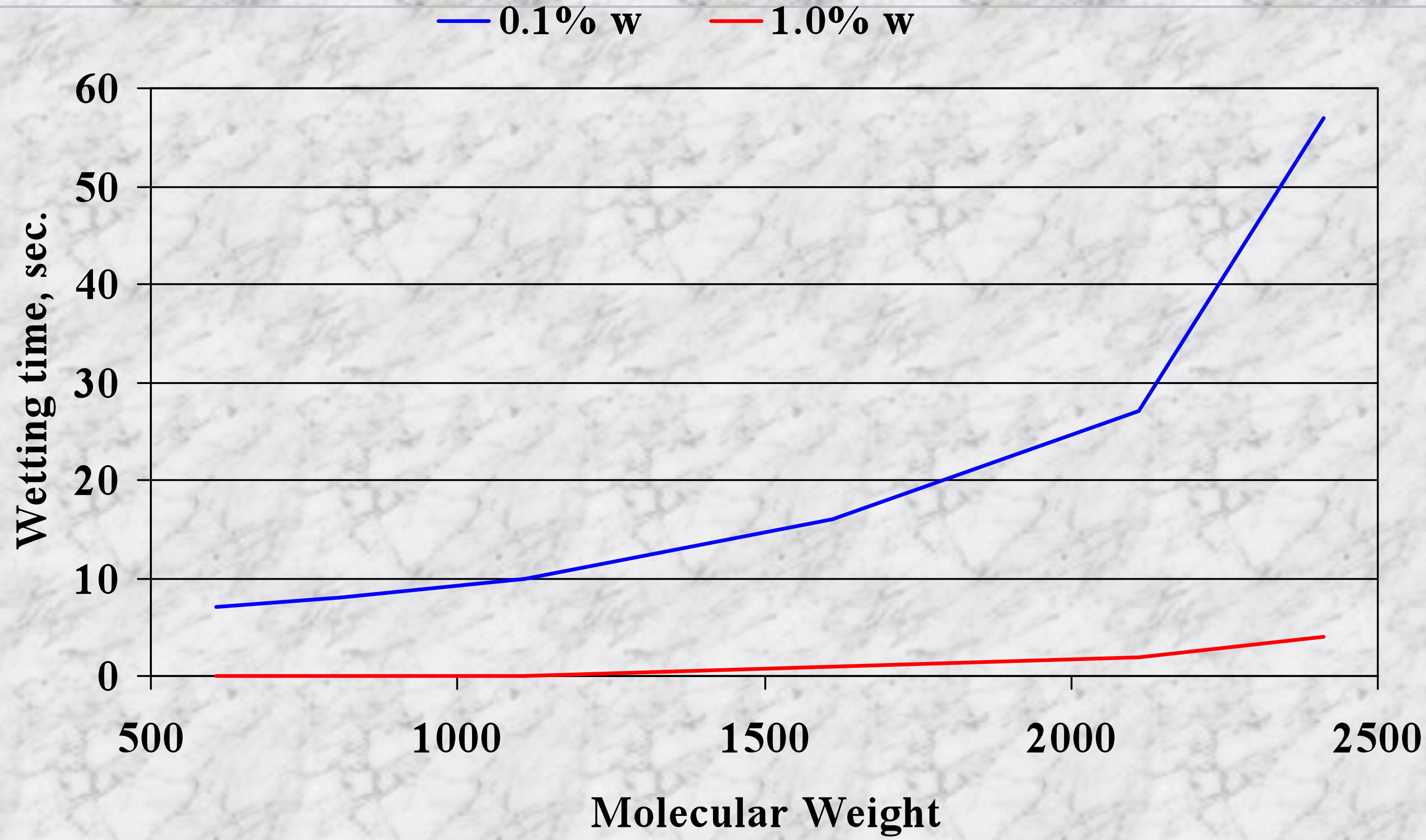


DMC Emulsification Ability

(5% DMC/47.5% Water/47.5% Oil, mixed 5 min. at high shear)



Draves Wetting of DMC's (24 C, DI water)

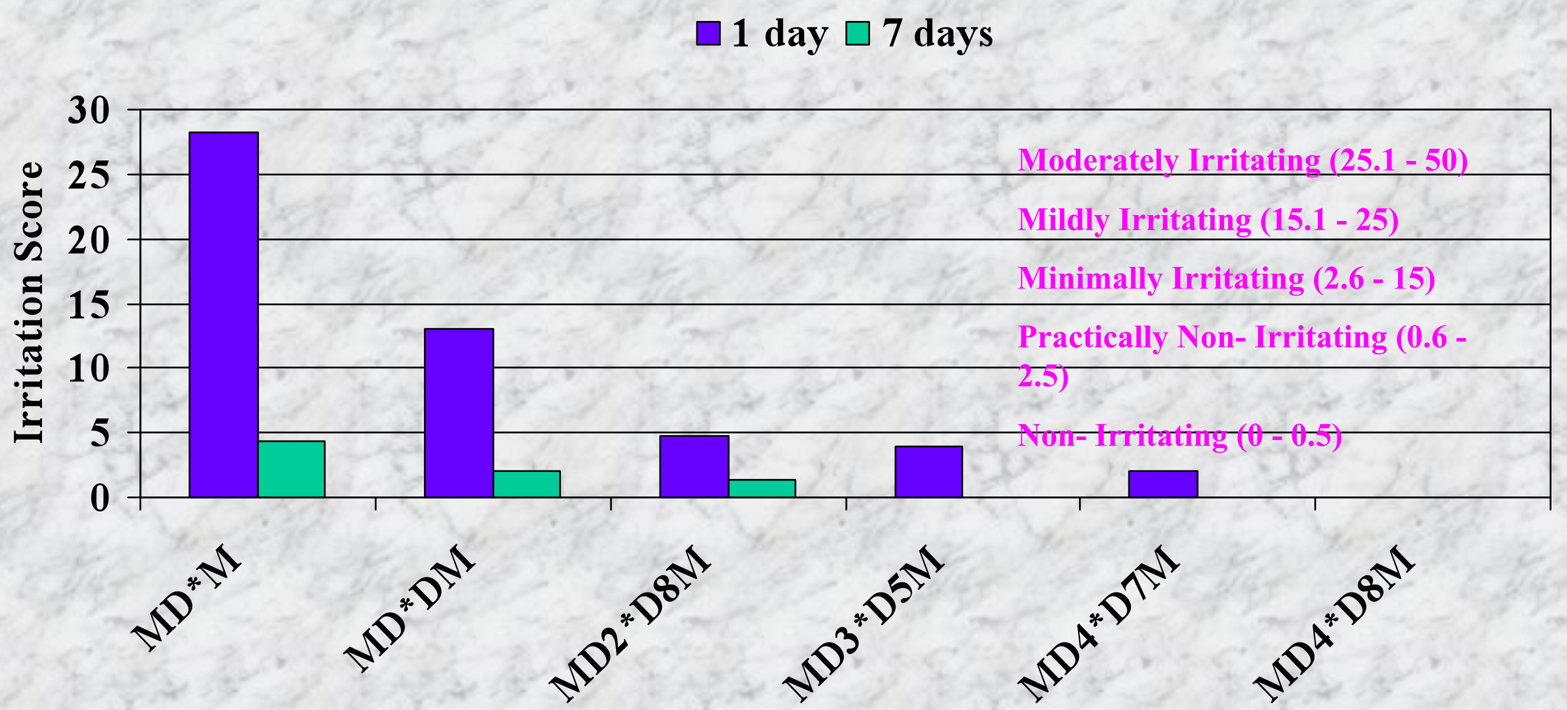


Wetting of DMC's

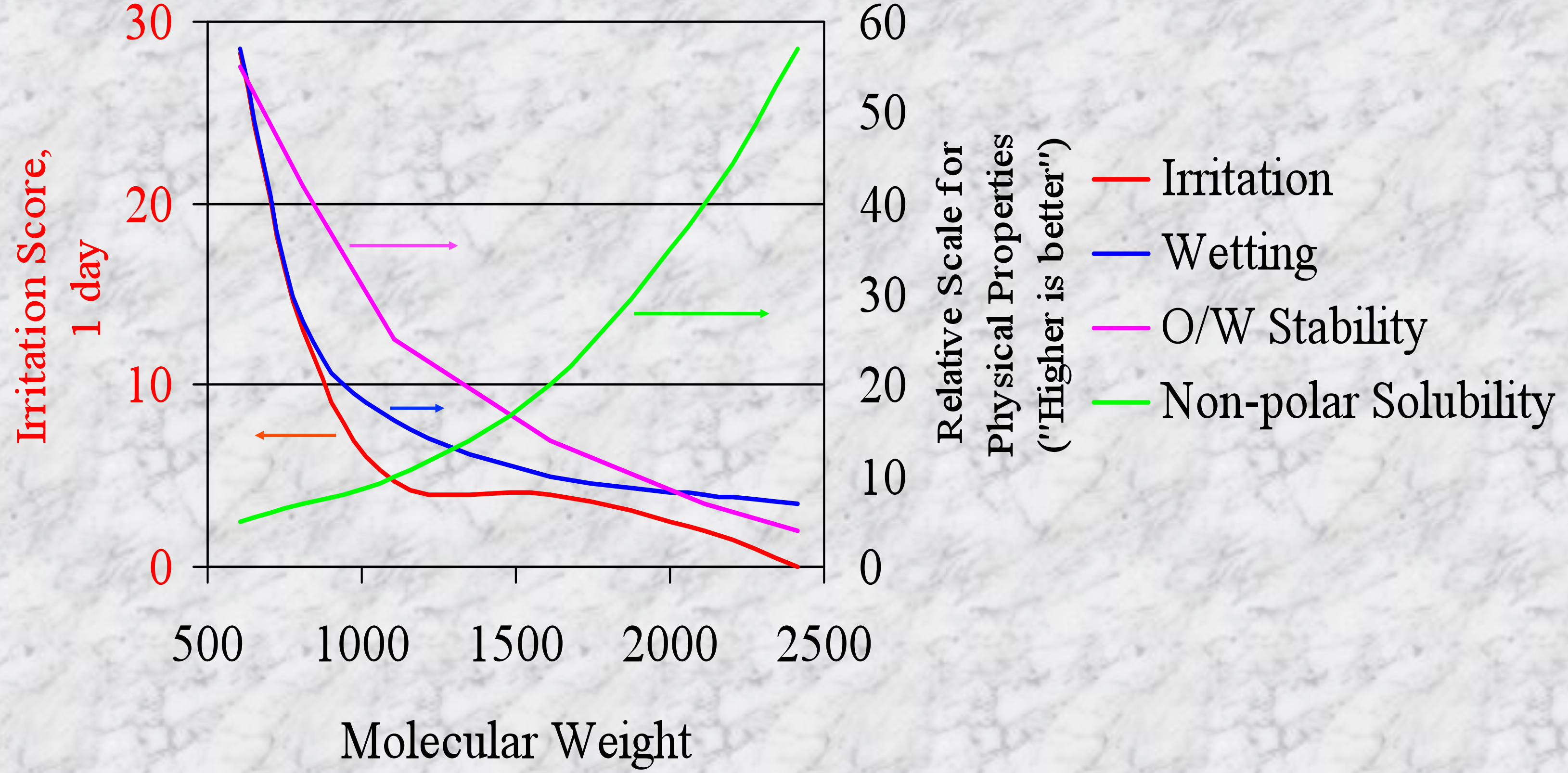
- There is a strong relationship between molecular weight and wetting. The lower molecular weight materials have faster wetting times.

- The smaller molecule allows for more efficient packing efficiency and dynamics. The materials with lower molecular weight were extremely effective at the higher concentration.

Draize Primary Ocular Irritation



Correlation of Ocular Irritation and Physical Properties



Summary

- Solubility in polar media seems to relate to the length of the polyoxyethylene group.
- Products with higher molecular weight had better dispersibility in nonpolar oils.
- The cloud point is related to the length of the polyoxyethylene group in the molecule and was rather independent of the silicone portion of the molecule.
- The molecules studied spread slightly better than water but cannot be considered superspreaders.

Summary

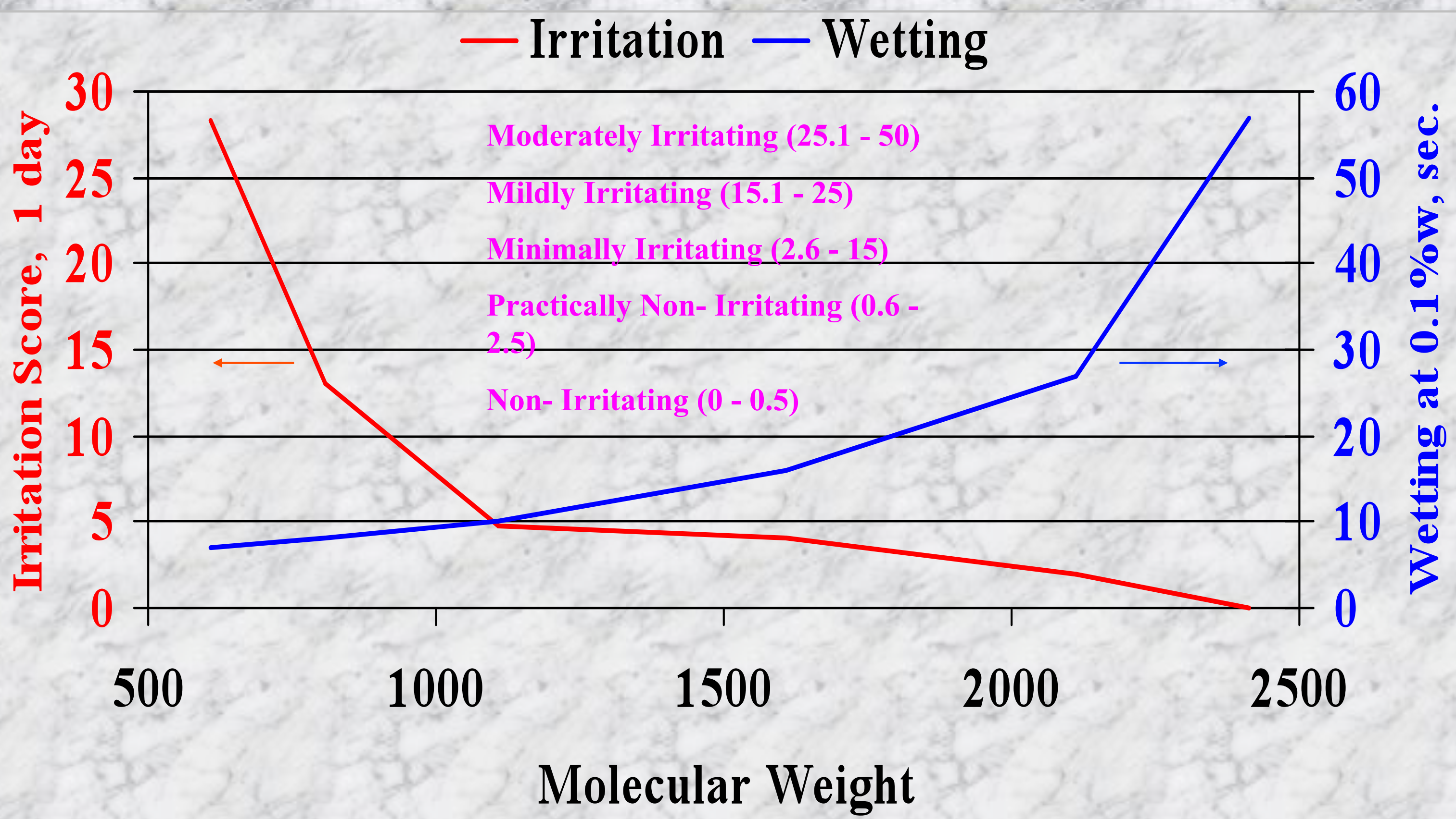
- The lower molecular weight materials have faster wetting times.
- The higher the molecular weight the lower the ocular irritation.
- The proper selection of a dimethicone copolyol can result in a product that has a desirable combination of properties.
- The properties, when correlated to the irritation data, allow for selection of cost-effective materials that are both effective and possess low irritation potential.

Draize Primary Ocular Irritation

Designation	1 day	3 days	7 days
MD*M	28.3	17.0	4.3
MD*DM	13.0	9.3	2.0
$MD_2{*}D_8M$	9.2	4.7	1.3
$MD_3{*}D_5M$	4.0	2.0	0.0
$MD_4{*}D_7M$	2.0	0.7	0.0
$MD_4{*}D_8M$	0.0	0.0	0.0

The higher the molecular weight the lower the ocular irritation.

Correlation of Ocular Irritation with Wetting



QUESTIONS?