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Refractive index modification of silicone polymers

ABSTRACT

Silicone compounds are becoming a commonly used raw material in many cosmetic products. They find applications where they provide properties that cannot be obtained from other less costly raw materials. One of the properties that can be modified in this class of materials that is often overlooked is refractive index. Refractive index is important in making clear emulsions, used in cosmetic formulations.

The use of organo-silicone polymers in cosmetic products has grown dramatically over recent years. This is due to the specific extraordinary properties that these silicones can render to a product. These desirable properties include:

- Surface tension reduction
- Foaming hydro-alcoholic solutions
- Emulsification
- Feel enhancement
- Film formation.

Of the many properties that can be varied in an organo-silicone compound, refractive index is one that is largely overlooked. The refractive indexes of materials used in cosmetic formulations can be used to 'RI match' and create a clear emulsion.[1]

The importance of a clear emulsion is not easily overlooked in the cosmetic application. As seen by most marketing advertisements, a cosmetic product not only has to perform but also look attractive. The ability to produce a clear emulsion can be accomplished by either micro-emulsion[2] or refractive index matching. The refractive index of alkyl silicones can be altered by modifying the type and percentage of the organo-functionality on the molecule. This leads to a new advantage in using alkyl silicones in that they can be modified to match the RI of a cosmetic formulation.

The refractive index (or index of refraction, RI) of a substance is a number that describes how light propagates through that substance. Simply put, light will travel at different speeds depending on the density of the substance it is moving through. When the beam of light enters a material of different density, the beam bends. Everyone who has ever used a straw from which to drink water has seen this phenomenon. Another example is observed in Figure 1. If a pen is placed into water, the pen appears to bend as shown.[3]

Figure 1: *Example of refraction.*

As seen in the illustration, the pen appears to be bent where it enters the water. We all know that the pen is not bent and that the illusion is the result of the RI difference between the water and air. Another example is the illusion of a wavy appearance on a highway. This is caused by the difference in refractive index between hot and cooler air.

Refractive index is defined as the factor by which the wavelength and the velocity of the radiation are reduced with respect to their vacuum values. Refractive index of materials varies with the wavelength. This is called dispersion; it causes the splitting of white light in prisms and rainbows, and chromatic aberration in lenses. In opaque media, the refractive index is a complex number: while the real part describes refraction, the imaginary part accounts for absorption.[4] The RI values of some commonly used materials are listed in Table 1.[5]

So why should cosmetic chemists be interested in refractive index? Mark Garrison, a noted cosmetic chemist points out: "Cosmetic chemists are interested in refractive index because, if the refractive index on a polar and oil phase match, the resulting oil in water separation will look homogeneous." This observation has been used to make 'clear emulsions'.[6]

Table 1: RI values of common materials.

Material	Refractive Index (*n*)
Acetic Acid	1.37
Acetone	1.36
Alcohol, ethyl (ethanol)	1.36
Alcohol, methyl (methanol)	1.33
Carbon disulfide	1.63
Decane	1.41
Dodecane	1.41
Ether	1.35
Ethylene glycol	1.43
Heptane	1.38
Hexane	1.37
Octane	1.40
Propane	1.34
Propylene	1.36
Propylene glycol	1.43
Water	1.33

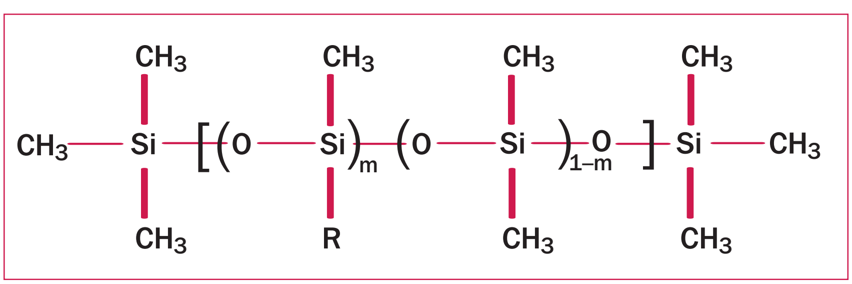

Figure 2: *Comb-type dimethicone slicone polymer.*

US Patent 5,290,555 states: 'When two transparent, immiscible liquids are mixed, the combination is often cloudy. If, however, the liquids have the same refractive index, the mixture will be substantially transparent to the human eye and appear to be homogenous'.

Matching RI values can be tricky, so how do chemists know how to match RI values? Sun JZ *et al*[1] point out: 'Current consumer trends favour clear products in the cosmetic market.'[4] The former has been widely explored, leading to many microemulsion-conditioning products in the market. In contrast, the latter has not been widely explored because the physical principle is not well explained and there has been no practical methodology to follow to realise many different applications.

In our exploration of refractive index matching in formulation of cosmetics, a practical method has been developed and leads to many unique formulations. RI matching enables chemists to make many unique formulas that cannot be achieved by other methods. RI matching should become a common technique for formulation chemists.[7]

Refractive index matching can be difficult since it requires judicious control of the materials used in formulation. The RI values have to be very close in value to obtain a clear and transparent emulsion. Typically, the refractive indices of the two phases within the emulsion must be matched to within about 0.0078 units of each other.[8] The ability to match refractive index of the two phases can be addressed by two different approaches:

- Formulation manipulation
- Ingredient manipulation.

The first method involves matching of the refractive indices by addition of two different ingredients depending upon the refractive index of the two phases. While useful, this approach is limited to the range of refractive indices available to the formulator. There are several strategies associated with this method, Dow Corning describes a procedure for manipulation of the RI values in Formulation 1.[9]

From this procedure, it is clear to see how a formulating chemist can shift the RI of both phases. This is a useful and effective technique to change the RI, the only drawback is the addition of the water/glycerin to the formulation. These additions can affect the formulation.

The second approach deals with the chemical manipulation of a polymer backbone to achieve a desired RI value. There are simple and precise ways to alter the polymer to change the RI. This article will deal with this chemical manipulation, making modifications of organo-functional silicones resulting in different refractive index values. This will allow for added flexibility in formulation.

Formulation 1.

Phase	Trade name	INCI	%wt
A	DC 9011 Silicone Elastomer Blend[1]	Cyclopentasiloxane (and) PEG-12 dimethicone crosspolymer	10.0
	Xiameter PMX-2000 Silicone Fluid 10 cSt	Dimethicone	3.5
	DC 556 Cosmetic Grade Fluid[1]	Phenyl Trimethicone	0.5
	Xiameter PMX-0245 Cyclopentasiloxane	Cyclopentasiloxane	6.0
B	Reach 301 Solution[2]	Aluminum Sesquichlorohydrate	42.0
		Deionised water	17.5
	Propylene Glycol[1]	Propylene Glycol	12.5
	Glycerin[3]	Glycerin	6.5
	Alcohol[4]	Ethyl Alcohol	1.5

Procedure
Combine phase A and phase B separately. Match the refractive index of phase A to that of phase B. If the refractive index of phase A is higher than that of phase B, add water to the aqueous phase to match. If lower, add glycerin to match. With rapid mixing, add phase B to phase A very slowly, using a separatory funnel.

Suppliers
1 Dow Corning 2 Reheis Inc 3 Fisher Chemical Company 4 Equistar

Formulation 2: Transparent antiperspirant gel.[10]

Phase	Material	%
A	Cyclomethicone	7.5
	Isopropyl Myristate	0.2
	Cyclomethicone/Dimethicone	9.0
	Ethanol	1.0
	Fragrance	0.2
B	Aluminum Chlorohydrate	50.0
	Dipropylene Glycol	14.0
	Demineralised water	17.7
	Imidazolinyl Urea	0.3
	PPG 5-Ceteth-20	0.1

Refractive Index
Phase A: 1.3987 Phase B: 1.3986
Gel: 1.3986 Clarity: 14 NTU

Formulation 3: Transparent Hair Gel[11]

Phase	Material	%
A	Deionised water	17.3
	Disodium EDTA	0.1
	Carbomer	0.5
	Sucrose Laurate (38% sol.)	4.0
	Hydrolysed wheat protein	1.0
	Glycerin	12.0
	PEG-8	12.0
B	Cyclopentasiloxane	35.0
	Phenyl Trimethicone	5.0
	Caprylic/Capric Triglyceride	11.5
	Masking Fragrance	0.3
C	Sodium Hydroxide (18% sol.)	1.4

Refractive index matching by chemical manipulation

Silicone polymers

A study was undertaken to determine how to modify organo-functional silicones to provide a range of refractive indices by varying the type of different types of groups on a silicone backbone. The silicone polymer chosen was a comb-type dimethicone conforming to the structure shown in Figure 2.

The R group of this polymer can be quickly and easily modified to drastically change the polymer performance. To test how the pendant group of the polymer affects the RI, a series of experiments were conducted and RI values were tested. Three pendant groups were tested: ethylene oxide (EO), fluoro-containg groups, and aromatic groups. These groups were reacted onto the silicone backbone through the same reaction, specifically hydrosylation, and the RI was compared. The concentration of these pendant groups (% by weight) was also examined to test its effect on the refractive index.

Results

The refractive index of various silicone compounds were evaluated using aromatic substituted silicone compounds, fluoro silicone compounds and silicone compounds containing polyoxyethylene groups. The results are shown in Figures 3 to 5. The results of combining the data in one graph is shown in Figure 6.

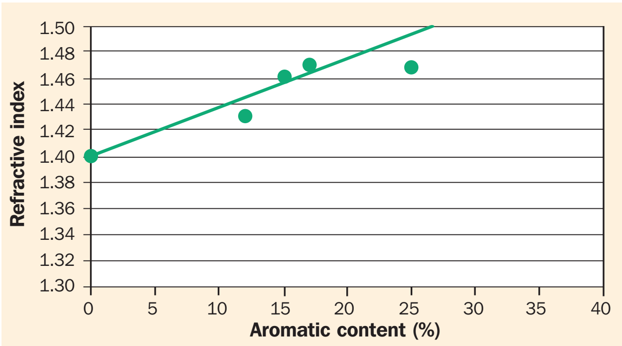

Figure 3: *Number aromatic groups* vs. *refractive index.*

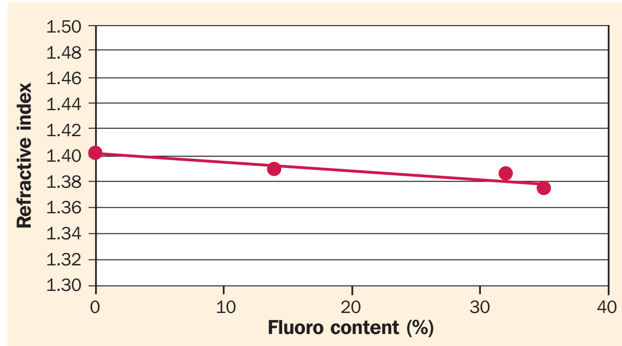

Figure 4: *% fluoro groups* vs. *refractive index.*

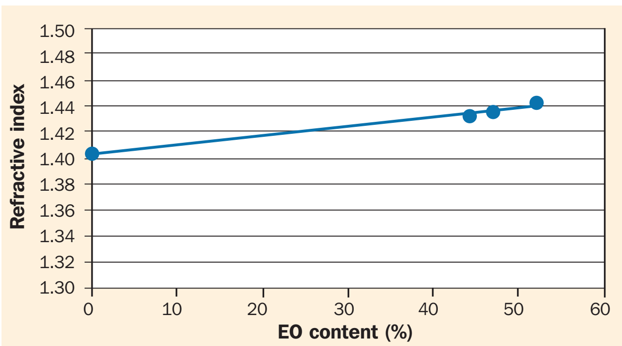

Figure 5: *% EO* vs. *refractive index.*

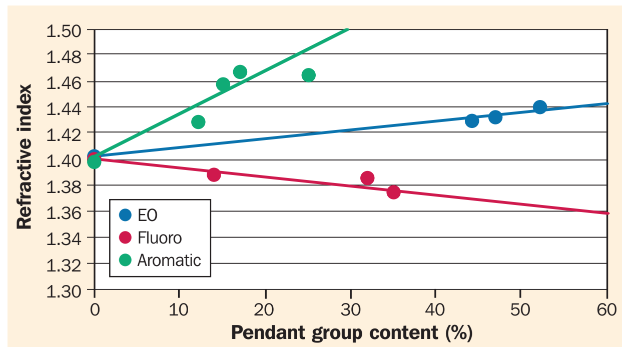

Figure 6: *Combined data.*

Conclusion

When one considers that the RI values of the two phases within the emulsion must be matched to within about 0.0078 units of each other in order to obtain a clear emulsion and that common organic compounds have a limited range of refractive index values available, the data offers a wide range of possibilities to formulators. This leads to chemical modification to alter RI.

One significant finding is the range within a homologous series. Silicone compounds having fluoro groups range from 1.30-1.40, while those with polyoxyethylene groups range from 1.40-1.44; finally those that have aromatic groups range from 1.40-1.55.

Another significant finding is that there is overlap in some of the values when one considers homologous series. This allows the formulator to have more than one option from a functional group point of view as to which silicone to choose. In fact, all three classes of compounds have candidate molecules that meet that refractive index. PC

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17 US Patent 7,217,778 – High refractive index flexible silicone.
18 US Patent 6,780,826 – Oil-containing personal wash compositions or emulsions comprising particles of high refractive index and defined thickness, geometry and size.

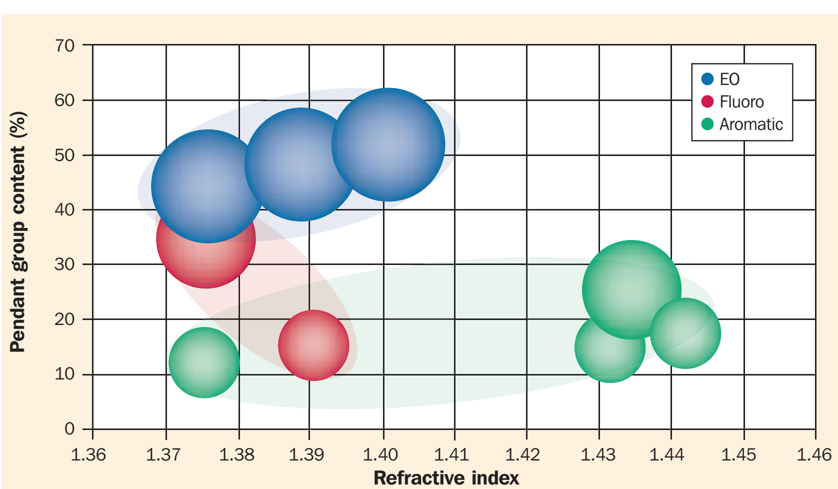

Figure 7: *Compounds that have candidate molecules that meet that refractive index.*