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Analysing silicone quaternary compounds

Traditional cationic compounds, referred to as quats, are used very commonly in the personal care industry as conditioners and softeners on the hair and skin. This is due to the fact that hair and skin have a net negative charge due in part to oxidation of sulfur containing amino acids. As a result of ionic interactions, the positively charged quats become substantive to the hair and skin.[1] Cationic surface active compounds have performed a variety of functions in personal care applications including conditioning, antimicrobial activities, emulsification, and improving both wet and dry comb.

It is therefore not surprising that the silicone analogues of traditional quats are likewise important compounds in personal care vis-à-vis conditioning and softening. The structure of the compound and the balance of silicone, fatty and water-soluble groups determines the properties of silicone quats, as is the case with all other silicone compounds. In the instance of these compounds the cationic group is a water-soluble group.

Silicone quats are not new materials, in fact one early patent goes back over 30 years. This patent[2] issued in 1980 discloses hair care compositions containing one or more quaternary nitrogen derivatives of trialkylamino hydroxy organosilicon compounds have superior conditioning capability for hair. Specifically, the compounds disclosed have the structure shown in Figure 1a:

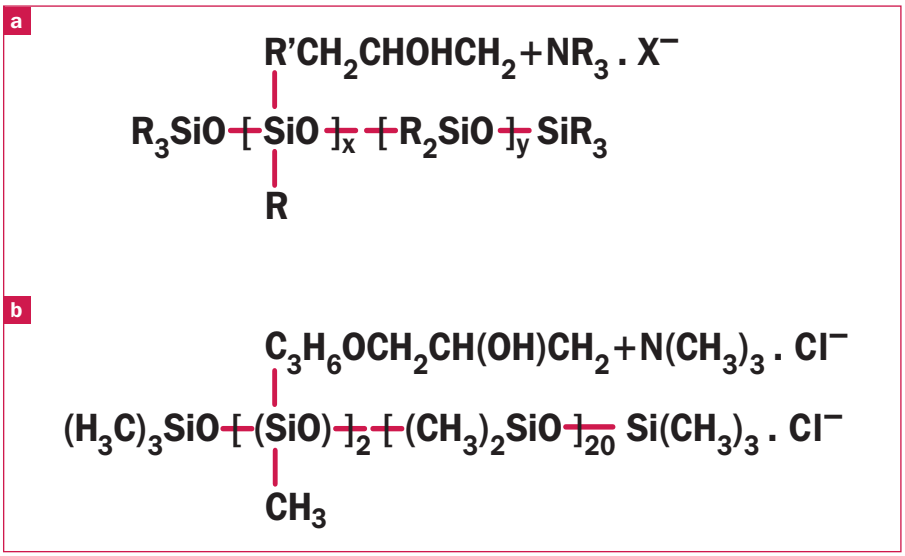


Figure 1: *Silicone quat structures.*

Wherein:

- R is a monovalent hydrocarbon radical having from 1 to a18 carbon atoms.
- R' is a divalent hydrocarbon radical having from 1 to 18 carbon atoms as a divalent hydrocarbonoxy radical having from 1 to 18 carbon atoms wherein the oxygen of said hydrocarbonoxy radical is in the form of an ether linkage.
- X^- is a halide anion
- X has an average value from 2 to 20
- Y has an average value of from 20 to 200.

While the 'R' definition is defined widely, in actuality the compounds disclosed all three 'R' groups are CH_3 (Fig. 1b).

The aqueous hair conditioning compositions described by Morlino are:

- From about 0.1 to about 10.0 weight per cent of a quaternary nitrogen derivative of a trialkylamino hydroxy organosilicon compound.
- From about 75 to about 99.9 weight per cent water.
- From about 0 to about 30 weight per cent of one or more surfactants selected from the group consisting of amphoteric, polar non-ionic, anionic, cationic, non-ionic, zwitterionic surfactants or a combination thereof.

Another silicone quaternary patent goes back 20 years and relates to terminal silicone quats.[3]

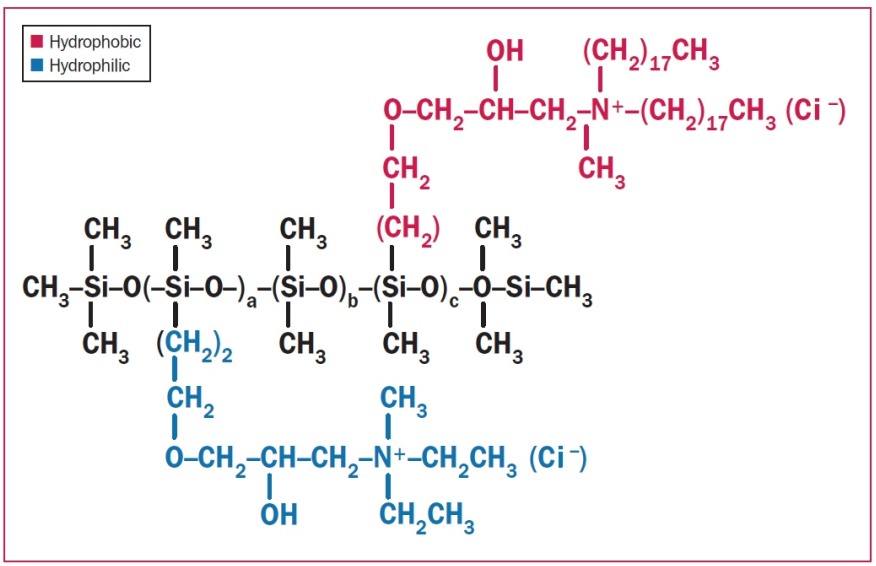


Figure 2: *Combination of diethyl quat (a) and distearyl quat (c) structure.*

Multi-domain silicone quaternary polymers

It has recently been discovered[4] that a new series of silicone quaternary compounds can be prepared using two very different silicone quaternary groups in one polymer. When lower alkyl groups (C3 or below) are placed on the nitrogen in the silicone polymer they act as water loving (hydrophilic) groups, improving water solubility. When higher alkyl groups (C16 and above) are placed on the nitrogen in the silicone polymer they act as oil loving (oleophobic) groups, improving oil solubility. Compounds of this type have been

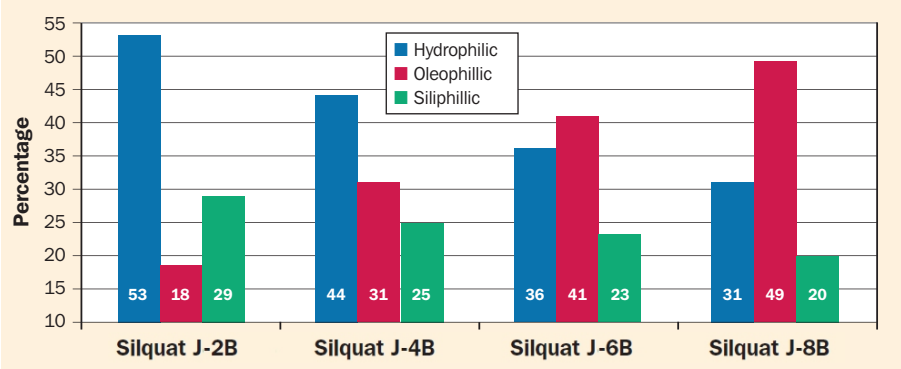


Figure 3: *Composition of multi-domain quats.*

Table 2: Solubility of Silquat J2-B Series.

Solvent	Material		Silquat J2-2B	Silquat J2-4B	Silquat J2-6B	Silquat J2-8B
Highly polar	Water	1% in solvent	Soluble	Dispersible	Dispersible	Dispersible
		5% in solvent	Dispersible	Dispersible	Dispersible	Insoluble
Non-polar hydrocarbons	Mineral oils	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
	Isododecane	1% in solvent	Dispersible	Dispersible	Soluble	Soluble
		5% in solvent	Dispersible	Soluble	Soluble	Soluble
	Isoparaffin	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
Esters	C8/C10 triglycerides	1% in solvent	Dispersible	Dispersible	Soluble	Soluble
		5% in solvent	Insoluble	Dispersible	Soluble	Soluble
	Isopropyl myristate	1% in solvent	Dispersible	Dispersible	Soluble	Soluble
		5% in solvent	Insoluble	Dispersible	Soluble	Soluble
	Trioctyldodecyl citrate	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
	$C_{12\text{-}15}$ alkyl benzoate	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
Ethers	PPG-14 butyl ether	1% in solvent	Dispersible	Soluble	Soluble	Soluble
		5% in solvent	Dispersible	Soluble	Soluble	Soluble
	Dicaprylyl ether	1% in solvent	Dispersible	Dispersible	Dispersible	Soluble
		5% in solvent	Insoluble	Dispersible	Soluble	Soluble
SIlicones	Cyclopentasiloxane	1% in solvent	Dispersible	Dispersible	Dispersible	Dispersible
		5% in solvent	Insoluble	Dispersible	Soluble	Soluble
	Dimethicone	1% in solvent	Dispersible	Dispersible	Dispersible	Dispersible
		5% in solvent	Dispersible	Dispersible	Dispersible	Dispersible
	Phenyl trimethicone	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
	Trimethylsiloxysilicate	1% in solvent	Dispersible	Dispersible	Dispersible	Dispersible
		5% in solvent	Dispersible	Dispersible	Dispersible	Dispersible
Natural oils	Olive oil	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
	Sunflower oil	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
	Castor oil	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
Alcohols	Octyldodecanol	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
	Isopropanol	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
	Ethanol	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
Glycols	Glycerin	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
	Propylene glycol	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
	Butylene glycol	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble
	Hexylene glycol	1% in solvent	Soluble	Soluble	Soluble	Soluble
		5% in solvent	Soluble	Soluble	Soluble	Soluble

Table 3: Specifications of O/W cationic rich and repairing hair conditioners.		
Specifications	**FC362B w/J2-4B**	**FC362 control**
Viscosity (cps)	13,500	16,500
pH	4.50	4.50
Appearance	White Cream	White Cream
Stability @45∞C	Good	Good
Feel (1-10, 10 the best)	9.4	9.0
Compatibility	Good	Not Good

dubbed multi-domain silicone quats. It should be clear that the ability to control the solubility of the quat will allow the formulator a greater degree of latitude in formulation of products containing these polymers.

Structure

The silicone quaternary product used is a combination of diethyl quat (a) and distearyl quat (c) on the same silicone backbone with varying ratios of a and c (see Fig. 2).

The difference between the various products is the ratio of a to c, with b kept constant. The composition is shown in Figure 3.

The fact that the molecules have different ratios of oil loving, water loving and silicone loving groups, results in different solubilities. Table 2 shows the

Formulation 1: O/W cationic skin care cream formula.					
Phase	**Ingredients**	**FC360A w/J2-2B W/W%**	**FC360B w/J2-4B W/W%**	**FC360C w/J2-6B W/W%**	**FC360D w/J2-8B W/W%**
A	D.I. Water	74.80	74.80	74.80	74.80
	Hydroxyl Ethyl Cellulose	1.00	1.00	1.00	1.00
	Glycerin	7.50	7.50	7.50	7.50
B	Silquat J2-2B	4.75	0	0	0
	Silquat J2-4B	0	4.75	0	0
	Silquat J2-6B	0	0	4.75	0
	Silquat J2-8B	0	0	0	4.75
	Isopropyl Myristate	8.40	8.40	8.40	8.40
	Dimethicone, 10 cts	3.55	3.55	3.55	3.55
C	Citric Acid	q.s.	q.s.	q.s.	q.s.

Procedure

Disperse cellulose in water until uniform and add glycerine and heat up to 75~80˚C. Combine phase B and mix well, heat up to 75~80˚C. Add phase B into phase A while agitating quickly to obtain a homogeneous mixture; continue to mix for 5 minutes. Cool batch down to room temperature and adjust pH to ~4.5 using citric acid if necessary.

Formulation 2: O/W cationic rich and repairing hair conditioner formula.			
Phase	**Ingredients**	**FC362B w/J2-4B (W/W%)**	**FC362 control (W/W%)**
A	D.I. Water	74.00	74.00
	Hydroxyl Ethyl Cellulose	1.00	1.00
	Glycerin	5.00	5.00
B	Silquat J2-4B	4.00	0
	Isopropyl Myristate	11.70	11.70
	Silmer Q25	1.00	1.00
	Silquat CR 4000	1.00	1.00
	Silwax D0-MS	1.00	1.00
	Phenonip	0.30	0.30
C	Siltech 105	1.00	1.00
	Citric Acid	q.s.	q.s.

Procedure

Disperse cellulose in water until uniform and add glycerine and heat up to 80˚C. Combine phase B and mix well, heat up to 80˚C. Add phase B into phase A while agitating quickly to obtain a homogeneous mixture; continue to mix for 5 minutes. Cool batch down to room temperature and adjust pH to ~4.5 using citric acid if necessary

differences in solubility. These differences allows the formulator to add a silicone quaternary polymer into the phase of a formulation to provide benefits to that phase. Additionally, differences are seen as a function of concentration (that is at 1% and 5%).

Emulsification

The first set of experiments were to evaluate these polymers as cationic emulsifiers. Three per cent of each cationic emulsifier was used to make the cream, the creams with Silquat J2-4B/6B/8B were stable at room temperature, but the cream made with Silquat J2-2B separated after 2 weeks at room temperature.

Cationic O/W skin care cream formulas have unique sensory properties such as a soft, powdery feel and long lasting effects. A higher percentage of di-stearyl in the molecule helped increase the dry powdery feel.

Microscopic study of cationic O/W skin care creams

The cationic skin care cream formulas shared the same viscosity (11,000 cps - viscosity was tested by using Brookfield, LVT, #4 spindle, and 12 rpm), pH (4.50), appearance (white cream), Stability @RT/45˚C (Good/Good), Feel: 1-10, 10 the best (9.2), and compatibility (Good). (Formulation 1)

Method: Barska AY11374 digital microscope was used to take pictures of emulsion particles of the products. The images were taken at 100x and 400x magnifications at multiple spots on each microscopy glass slide. Pictures were processed by using Adobe Photoshop 7.0. Full scale of the image is 400 µm and 100 µm for 100x magnification and 400x magnification respectively. A selction of these images is shown in Figure 4.

FC360C with J2-6B has the smallest average particle size for all these cationic O/W skin care creams; this is also confirmed by the fact that the cream with J2-6B is the whitest one.

Cationic O/W hair care cream formulas have unique sensory properties such as soft smooth feel and long lasting effects. Silquat J2-B series can be used as a primary emulsifier and hair conditioning reagent.

Microscopic study of cationic rich and repairing hair conditioner

Method is the same as the above (Formulation 2).

Combining a cationic emulsifier with a traditional organic emulsifier creates an emulsion that has a less oily feel and powdery slippery skin feel for sunscreens. (Table 3)

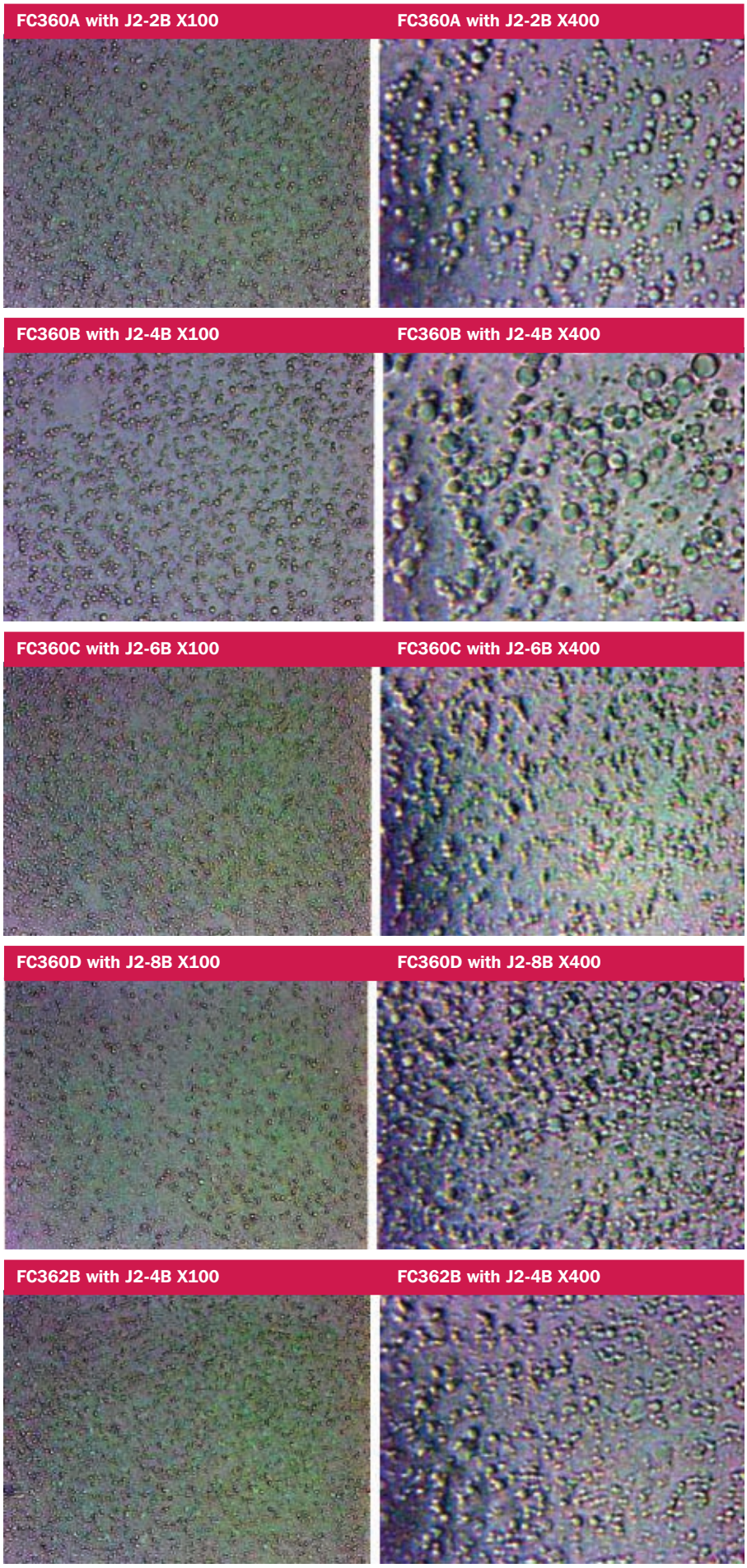


Figure 4

Microscopic Study of Cationic Sun Care Cream

FS415A w/J2-2B has a viscosity of 14,000 cps while FS415B w/J2-4B has a viscosity of 13,500 cps. They share the same pH (5.50), appearance (white cream), stability @45˚C (Good), Feel (9.3), and compatibility (Good). (Formulation 3)

Method is the same as the above.

The average sizes for both sunscreens are similar and less than 5 µm.

O/W cationic foundation formulation

FM626A w/J2-2B has a viscosity of 33,000 cps, its pH is 5.50, appearance is Ivory Makeup, stability @RT/45˚C is Good/good, Feel is 9.3, and its compatibility is Good (Formulation 4).

In an emulsion with pigments, combining a cationic emulsifier with a traditional organic emulsifier creates an emulsion that is very easy to spread on skin and has a less oily feel and very soft powdery slippery skin feel.

In a sunscreen/pigment emulsion system, combining a cationic emulsifier with a traditional organic emulsifier creates an emulsion with that is very easy to spread on skin and has a less oily feel and very soft powdery slippery skin feel.

The cream made with J2-6B is thinner than the cream made with J2-8B. Both have soft powdery skin feel but the latter has more powdery feel.

Formulation 3: Formula of O/W cationic sun care cream.

	Ingredients	FS415A w/J2-2B (W/W%)	FS415B w/J2-4B (W/W%)
A	D.I. Water	65.60	65.60
	Hydroxyl Ethyl Cellulose	0.74	0.74
	Glycerin	2.76	2.76
B	Silquat J2-2B	3.50	0
	Silquat J2-4B	0	3.50
	Silquat J2-6B	0	0
	Silquat J2-8B	0	0
	Glyceryl Stearate	1.50	1.50
	Stearyl Alcohol	1.20	1.20
	C12-15 Alkyl Benzoate	5.00	5.00
	Dioctyl Carbonate	3.00	3.00
	Cetyl Ricinoleate	1.00	1.00
	Microcrystalline Wax	1.20	1.20
	Polyglyceryl-3-Diisostearate	1.50	1.50
	Octyl Methoxycinnamate	7.00	7.00
	Avobenzone	2.00	2.00
	Benzohenone-3	4.00	4.00

Procedure

Disperse cellulose in water until uniform and add glycerine and heat up to 75~80˚C. Combine phase B and mix well, heat up to 75~80˚C. Add phase B into phase A while agitating quickly to obtain a homogeneous mixture; continue to mix for 5 minutes. Cool batch down to room temperature.

Conditioning

Foam performance evaluation of 2-in-1 shampoos

Method: All products were evaluated with the same procedure. A 1000 mL cylinder with 10 mL increments was used. All samples and distilled water was prepared at 25˚C. One gram of test material was used and 100 mL distilled water was added to dissolve the test material in a 250 mL beaker. After the test material was totally dissolved, the solution was transferred into the cylinder. An outlet air pump was sited on the bottom of the cylinder to generate the bubbles. The foam height was recorded within 20 seconds for each test material. Each material was evaluated three times and their averages were documented (Formulation 5, Table 4).

The scale for foam height is 1000 mL is outstanding and 100 mL is very poor. The type of foam was also noted whether it was tight or loose. Bubbles were generated by electronic air pump.

Table 4: Specifications of 2-in-1 shampoo with Silquat J2-B Series

Specifications	FH193A with J2-2B	FH193B with J2-4B	FH193 control
Viscosity (cps)	7,000	6,800	9,000
pH	6.45	6.50	6.45
Appearance	White Cream	White Cream	White Cream
Stability @RT/45 ∞C	Good/good	Good/good	Good/good
Feel (1-10, 10 the best)	9.30	9.30	8.90
Compatibility	Good	Good	Good

Evaluation of performance by hair swatches

Method: ASTM (American Society for Testing and Materials International) E 2082-06: Standard Guide for Descriptive

Table 5: Wet comb evaluations.

Sample	Wet comb	Rinse off	Clean feel	Shine/Softness	Residual feel	Fullness	Average
FH193 w/o J2-B	8.8	9.0	8.9	8.9/8.9	8.9	8.9	8.90
FH193A w/J2-2B	9.3	9.2	9.2	9.2/9.3	9.2	9.2	9.23
FH193B w/J2-4B	9.3	9.2	9.2	9.2/9.3	9.2	9.2	9.23

Table 6: Dry comb evaluations

Sample	Dry comb	Dry feel	Clean feel/ look	Shine	Fullness/ manageable	Fly away	Residual feel	Static	Average
FH193 w/o J2-B	8.8	8.8	8.8	8.8	8.8	8.8	8.8	8.8	8.80
FH193A w/J2-2B	9.4	9.3	9.3	9.3	9.3	9.3	9.3	9.4	9.33
FH193B w/J2-4B	9.4	9.3	9.3	9.3	9.3	9.3	9.3	9.4	9.33

Formulation 4: Formula of O/W cationic foundation.

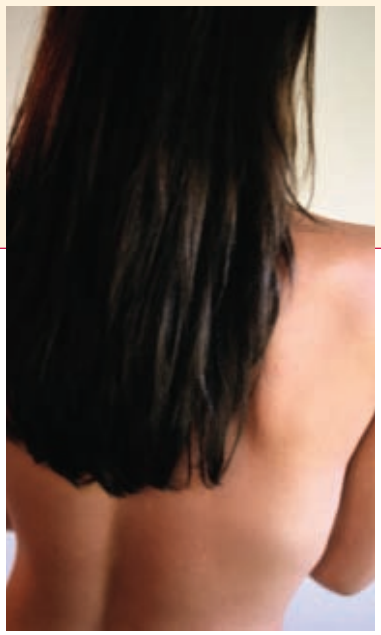
Phase	Ingredients	FM626A w/J2-2B W/W%)
A	D.I. Water	66.30
	Hydroxyl Ethyl Cellulose	1.00
	Propylene Glycol	3.00
	Unipure White LC981 SGP	6.00
	Unipure Yellow LC182 SGP	2.40
	Unipure Red LC381 SGP	0.60
	Unipure Black LC989 SGP	0.20
B	Silquat J2-2B	4.00
	Glyceryl Stearate	2.00
	Isononyl Isononoate	4.00
	Isopropyl myristate	3.00
	Dioctyl Carbonate	2.00
	Silube CR-1	0.50
	Polyglyceryl -3- Diisostearate	1.50
	Cyclopentasiloxane	2.00
	Stearyl Alcohol	1.50
C	Nylone-12	0.50

Procedure
Disperse cellulose in water until uniform and add propylene Glycol and pigments, Blend well then heat up to 75~80˚C. Combine phase B and mix well, heat up to 75~80˚C. Add phase B into phase A while agitating quickly to obtain a homogeneous mixture; continue to mix for 5 minutes. Cool batch down to room temperature.

Formulation 5: Formula of 2-in-1 shampoo with Silquat J2-B Series.

Phase	Ingredients	FH193A w/J2-2B W/W%	FH193B w/J2-4B W/W%	FH193 Control W/W%
A	D.I. Water	59.10	59.10	59.10
	Guar Hydroxypropyltrimonium Chloride	0.80	0.80	0.80
	Na2EDTA	0.10	0.10	0.10
	Sodium Laureth-2 Sulfate	22.00	22.00	22.00
	Cocamidopropyl Betaine	5.00	5.00	5.00
	Genapol TSM	5.00	5.00	5.00
	Disodium Cocoamphodiacetate	2.00	2.00	2.00
	Decyl Glucoside	5.00	5.00	5.00
	Silquat J2-2B	1.00	0	0
	Silquat J2-4B	0	1.00	0
B	Citric Acid (40% aq)	q.s.	q.s.	q.s.
	Sodium Chloride	1.00	1.00	1.00
	Crothix Liquid	q.s.	q.s.	q.s.
	Fragrance	q.s.	q.s.	q.s.

Procedure
Disperse guar Hydroxypropyltrimonium Chloride in water until it is thickened up. Add the rest of phase A one by one, mix slowly while minimising air incorporation. Adjust pH by using citric acid in the range of 4.5 to 5.5; and using NaCl and Crothix to adjust the viscosity (6,000 to 9,000 cps).



Analysis of Shampoo Performance. All products were evaluated on 10-inch virgin brown hair. Two 2-gram swatches were used for each material tested, all from the same lot. All swatches were wet with water (25˚C) and one gram of test material was used for each swatch (Table 5). Swatches were washed and then rinsed for at least one minute per swatch. Wet comb evaluation was then performed. All swatches were air-dried then the Dry comb evaluation was performed once hair was completely dry (Table6). Scale used is 1 to 10, 10 being the best. Used for wet and dry combing. Hair swatches were washed using non-conditioning shampoo before being treated with hair conditioner.

Both J2-2B and 4B are excellent hair conditioning agents in terms of wet comb and dry comb compared with control.

Conclusion

Cationic silicone quats have typically been associated with hair care for conditioning. We have shown that the Silquat J2-2B series of Multi Domain Quats have excellent properties and a unique sensory profile. In this application, they provide unique lubricity, antistatic properties and smoothness to the hair fibres.

These cationic conditioning properties can also be used in skin care formulations which will benefit skin with smooth powdery after-feel, extraordinary softness, unique lubricity and substantivity to the skin.

Most important, Silquat J2-B Series are unique cationic oil-in-water emulsifiers for skin care, hair care, sun care and make-up products. The cationic products can be used as emulsifiers and conditioning reagents in the meantime, this functional transfer of some properties provides an innovative and economical platform to the formulator. Cationic emulsions offer a smooth powdery after-feel that allows high active loadings without sacrificing efficacy. They can offer the formulator a new tool in developing products to meet consumer needs and wants.

These cationic emulsifiers can be also used in combination with a non-ionic organic or a silicone emulsifier to impart some unique sensory properties such as improved softness, smooth powdery dry feel and smooth powdery velvety skin feel.

Cationic emulsifiers can mask the negative sensory properties of high lipophilic loading in skin moisturisation with specific aesthetics, rendering the products with a very soft smooth powdery skin feel.

Cationic emulsifiers offer formulators a means to formulate high lipophilic, high SPF and high concentration of pigments in skin care, sun care and make up products to achieve some enhanced consumer benefits which do not feel oily and have heavy coverage but still spread and feel easy on skin.

Silquat J2-4B has good foam performance in shampoo. PC

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