

Anionic/cationic complexes in hair care

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Synopsis

The formulation of cosmetic products is always more complicated than studying the individual components in aqueous solution. This is because there are numerous interactions between the components, which make the formulation truly more than the sum of the parts. This article will look at interactions between anionic and cationic surfactants and offer insights into how to use these interactions advantageously in making formulations.

BACKGROUND

Products sold into the hair care market are a combination of many individual ingredients that interact with each other often in unpredictable ways. The ability to understand these interactions and to use them to make products with synergistic interactions is one major area of research. One such area of interest is the interaction between cationic and anionic surfactants.

Fatty quaternaries have been known for many years. Because of their fatty nature and positive charge, these compounds find application in a variety of areas including as conditioners for hair and skin. Despite the fact these materials have been recognized as key cosmetic additives, there is little published on the structure function relationship on basic properties. For example, some quats are very insoluble when added to anionic surfactant, others have improved compatibility. The ability to select quats that have optimum compatibility with anionic systems offers the formulator flexibility in formulating heretofore unavailable. There is also much confusion related to deposition of cationic material onto hair as measured by a number of red dye uptake tests. These tests merely measure cationic on the surface of the hair. Since deposition on hair made from a solution containing cationic and anionic, contains no free cationic, no red color is observed with these tests. This does not mean however there was no deposition, it simply means the deposited material does not have an overall positive charge and consequently does not bind dye.

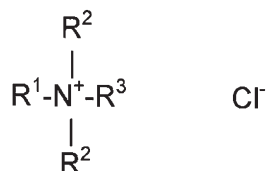
Anyone that has added stearylalkonium chloride to sodium lauryl sulfate and observed the white sticky solid that results knows anionic and cationic surfactants can be incompatible. We have begun to call anionic and cationic materials that produce a white gunky solid when mixed together *hard complexes*. As the expression implies the cationic and anionic compound possess properties which when added together form insoluble complexes (salts). We set out to determine if there are cationic materials

having different structures which could be more soluble in the presence of anionic surfactants. The terms used here for quats and anionic materials are an adaptation of the work of Pearson used to describe acids and bases. Pearson proposed that "hard acids bind strongly to hard bases and soft acids bind softly to soft bases" (1). The interaction between anionic and cationic materials has been studied prior to this work (2-4).

The structural changes that can be made to cationic molecules can "soften" them, making them more compatible with anionic systems. Alternatively, there should also be the possibility of developing an anionic material that has increased compatibility with cationic surfactants, perhaps a more highly ethoxylated sulfate or a sulfosuccinate. However, this concept of modifying the anionic, is a topic for another investigation.

A study was undertaken to determine (1) the compatibility of specific quats with SLS and SLES, (2) the foam properties of the combinations with SLS and SLES, (3) the substantivity of these combinations in aqueous and anionic surfactant delivery systems, and (4) the combing force needed.

The quats studied conform to the following structure:



The preferred definitions for the study groups are (Table I):

R¹ 1. Alkyl (C12)

2. Ricinoleylamidopropyl

3. Dilinoleylamidopropyl

4. Cocamidopropyl

R² 1. Methyl -CH₃

2. 2-hydroxy ethyl -CH₂CH₂OH

R³ 1. Methyl -CH₃

2. Benzyl -CH₂-C₆H₅

3. Glyceryl -CH₂-CH(OH)-CH₂-OH

(A) COMPATIBILITY WITH ANIONIC SURFACTANTS

A determination of compatibility of a variety of quats with two anionic surfactants, sodium lauryl sulfate and sodium laureth-3-sulfate was made. The compatibility was determined by titration. The point at which an anionic solution containing 10% anionic either became hazy or formed a precipitate was determined.

Table I
Compounds Studied

Name	R ¹	R ²	R ³	Description
AMB	Alkyl (C 12)	CH ₃	Benzyl	Coco dimethyl benzyl ammonium chloride
AME	Alkyl (C 12)	CH ₂ CH ₂ OH	CH ₃	Coco di-2 hydroxyethyl methyl ammonium chloride
AMG	Alkyl (C 12)	CH ₃	Glyceryl	Coco dimethyl glyceryl ammonium chloride
AMM	Alkyl (C 12)	CH ₃	CH ₃	Coco tri-methyl ammonium chloride
AEB	Alkyl (C 12)	CH ₂ CH ₂ OH	Benzyl	Coco di-2 hydroxyethyl benzyl ammonium chloride
AEG	Alkyl (C 12)	CH ₂ CH ₂ OH	Glyceryl	Coco di-2 hydroxyethyl glyceryl ammonium chloride
CaMB	Castor amido	CH ₃	Benzyl	Ricinoleylamidopropyl dimethyl benzyl ammonium chloride
CaMG	Castor amido	CH ₃	Glyceryl	Ricinoleylamidopropyl dimethyl glyceryl ammonium chloride
DMB	Dimer amido	CH ₃	Benzyl	Dilinoleylamidopropyl dimethyl benzyl ammonium chloride
DMG	Dimer amido	CH ₃	Glyceryl	Dilinoleylamidopropyl dimethyl glyceryl ammonium chloride
DMM	Dimer amido	CH ₃	CH ₃	Dilinoleylamidopropyl trimethyl ammonium chloride
MMB	Cocamido	CH ₃	Benzyl	Cocamidopropyl dimethyl benzyl ammonium chloride
MMG	Cocamido	CH ₃	Glyceryl	Cocamidopropyl dimethyl glyceryl ammonium chloride
MMM	Cocamido	CH ₃	CH ₃	Cocamidopropyl trimethyl ammonium chloride

PROCEDURE—SOLUTION PREPARATION:

(1) Prepare 50g of a 10% active test solution of surfactant. Record pH.

The surfactants are sodium lauryl sulfate and sodium laureth sulfate.

Ingredient	w/w
Surfactant	34.00%
Distilled water	65.50%

Combine the ingredients listed with slow to medium agitation. Mix until uniform at 20°-25°C. Prepare test solutions for both SLS and SLES (10% active SLS and 10% active SLES).

(2) Prepare 100 g of a 10% active test solution for each quat sample.

Preparation of 10% active quat:

Ingredient	w/w
Stock quat solution (35% w/w)	28.50%
Distilled water	71.50%

Combine ingredients listed with slow to medium agitation. Mix at 20°-25°C until uniform. Then,

- (1) Using a hot plate and stir bar set on medium agitation, slowly titrate surfactant test solution with quat solution using a 5-ml disposable pipette, at a rate of one drop per second. Continue adding quat solution until a precipitate is observed (subjective evaluation).
- (2) The solution will appear cloudy and translucent at this point. Record the amount (grams) of quat solution added at the cloud point, final pH, and the viscosity. Repeat for remaining quat solutions. Store at 20°-25°C. Observe solutions after 24 hours. If solution remains cloudy, then titration is complete. If solution is clear, then repeat step 2. Perform titration for each quat using SLS and SLES individually. Titration data is shown in Tables II–V.

Calculations

$$\% \text{Quat added} = \frac{\text{grams of quat added}}{(50 + \text{grams of quat added})} \times 100$$

Table II
Titration Data (SLS)

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Final pH	Viscosity (cps)	Notes
AMB	9.75	7.6	4,400	Formed an opaque, pearlescent gel beyond the haze point
AME	6.28	7.1	<10	Did not form a gel
AMG	30.49	8.1	<10	Did not form a gel
AMM	17.63	7.8	<10	Did not form a gel
AEB	14.58	7.9	<10	Did not form a gel
AEG	29.53	7.7	<10	Did not form a gel
CaMB	25.72	7.6	1,000	Formed a gel
CaMG	44.47	7.1	1,000	Formed a gel
DMB	18.33	7.6	<10	Did not form a gel
DMG	40.25	7.6	12,000	Formed a gel
DMM	23.85	7.6	6,000	Formed a gel
MMB	15.28	7.4	14,000	Formed a gel
MMG	31.02	8.0	13,000	Formed a gel
MMM	21.25	8.0	13,400	Formed a gel

Table III
Titration Data (SLS)

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AMB	9.75	<10	Did not form a gel
AME	6.28	<10	Did not form a gel
AEB	14.58	<10	Did not form a gel
AMM	17.63	<10	Did not form a gel
DMB	18.33	<10	Did not form a gel
AEG	29.53	<10	Did not form a gel
AMG	30.49	<10	Did not form a gel

Soft Quats

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
MMB	15.28	14,000	Formed a gel
MMM	21.25	13,400	Formed a gel
DMM	23.85	6,000	Formed a gel
CaMB	25.72	1,000	Formed a gel
MMG	31.02	19,200	Formed a gel
DMG	40.25	12,000	Formed a gel

Table IV
Titration Data (SLES)

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Final pH	Viscosity (cps)	Notes
AMB	18.67	6.6	<10	Did not form a gel
AME	4.47	7.0	<10	Formed a gel
AMG	25.04	7.2	1,000	Formed a gel
AMM	17.44	7.2	<10	Did not form a gel
AEB	18.35	7.2	<10	Did not form a gel
AEG	38.72	7.1	1,000	Formed a gel
CaMB	24.31	7.6	1,000	Formed a gel
CaMG	46.23	7.3	1,000	Formed a gel
DMB	11.09	7.3	<10	Did not form a gel
DMG	28.37	7.9	6,800	Formed a gel
DMM	20.00	7.0	6,200	Formed a gel
MMB	25.00	7.1	<10	Formed a gel
MMG	26.68	7.1	40,000	Formed a gel
MMM	20.23	7.3	50,000	Formed a gel

Table V
Titration Data (SLS)

Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AMB	18.67	<10	Did not form a gel
AMM	17.44	<10	Did not form a gel
AEB	18.35	<10	Did not form a gel
DMB	11.09	<10	Did not form a gel
Soft Quats			
Quat Sample	Amount of quat solution added to achieve haze point in SLS (g)	Viscosity (cps)	Notes
AME	4.47	7,000	Formed a gel
DMM	20.00	6,200	Formed a gel
MMM	20.23	50,000	Formed a gel
CaMB	24.31	1,000	Formed a gel
AMG	25.04	1,000	Formed a gel
MMB	25.00	9,800	Formed a gel
MMG	26.68	40,000	Formed a gel
DMG	28.37	6,800	Formed a gel
AEG	38.72	1,000	Formed a gel
CaMG	46.23	1,000	Formed a gel

RESULTS

The quats that showed the best compatibility and gellation properties with sodium lauryl sulfate were the amido quats. The only exception was the amido quat that contained an aromatic group (DMB).

There was improved compatibility with sodium laureth-3-sulfate when compared to sodium lauryl sulfate. This leads to the conclusion that SLES is a softer anionic than SLES.

All quat compounds reached a cloud point when titrated into anionic. However, the amount necessary to reach the haze point were different and the nature of the end point were different. The so-called hard quats have very little tolerance for anionic, forming insoluble precipitates with very little addition. Quaternary compounds having intermediate hardness show compatibility with anionic surfactants at near stoichiometric amounts, but do eventually haze. Soft quats do not exhibit a haze, but rather show a clear gel.

(B) FOAM HEIGHT AND STABILITY

It has been generally assumed that a gel made using an anionic and cationic combination would not foam. An evaluation of the gelled system was therefore undertaken to see if this is true.

PURPOSE

Determine the height and stability of foam produced from aqueous solutions of anionic surfactant containing quaternium compounds (Tables VI–VIII).

PROCEDURE

Quat solutions: Titrated quat solutions

Controls:

INCI: Polyquaternium-10

Sodium lauryl sulfate

Sodium laureth sulfate

Name	ARL-4-84A	ARL-4-84B	ARL-4-84C	ARL-4-84D
Polyquaternium 10	1.00%	1.00%	—	—
Deionized water	91.00%	91.00%	92.00%	92.00%
Sodium lauryl sulfate	8.00%	—	8.00%	—
Sodium laureth sulfate	—	8.00%	—	8.00%

- (1) Prepare ARL-4-84A and B by mixing polyquaternium 10 and deionized water with a prop mixer set on low speed until uniform (1-5 min, 20°-25°C).
- (2) Add surfactant and mix with medium agitation until uniform (1-2 min 20°-25°C).
- (3) Prepare ARL-4-84C and D by combining deionized water and surfactant. Mix with medium agitation until uniform (1-2 min 20°-25°C).

Table VI
Foam Heights of SLS Titrations

Quat Sample	Foam height _{max} (ml)	Foam height _{initial} (ml)	Foam height _{final} (ml)	Foam stability (min)
AMB	—	—	—	Does not foam
AME	190	90	140	30.0
AMG	500	400	300	30.0
AMM	600	500	350	15.0
AEB	300	200	200	40.5
AEG	200	100	150	40.0
CaMB	250	150	175	95.0
CaMG	200	100	150	79.0
DMB	400	300	250	14.0
DMG	300	200	200	8.0
DMM	250	150	150	13.0
MMB	400	300	250	29.0
MMG	400	300	250	97.0
MMM	400	300	250	1440.0

Table VII
Foam Heights of SLES Titrations

Quat Sample	Foam height _{max} (ml)	Foam height _{initial} (ml)	Foam height _{final} (ml)	Foam stability (min)
AMB	150	50	100	141.0
AME	250	150	175	1440.0
AMG	350	250	225	240.0
AMM	200	100	150	1440.0
AEB	200	100	150	47.0
AEG	300	200	200	1440.0
CaMB	150	50	125	8.50
CaMG	150	50	125	6.0
DMB	150	50	125	5.5
DMG	200	100	150	75.0
DMM	150	50	125	9.0
MMB	200	100	150	1440.0
MMG	250	150	175	146.5
MMM	300	200	200	1440.0

Table VIII
Foam Heights of Controls

Control	Foam height _{max} (ml)	Foam height _{initial} (ml)	Foam height _{final} (ml)	Foam stability (min)
ARL-4-84A	200	100	100	31.0
ARL-4-84B	200	100	150	1440.0
ARL-4-84C	600	500	350	25.0
ARL-4-84D	450	350	275	180.0

RESULTS

Quat solutions titrated with sodium lauryl sulfate (SLS) produced higher levels of foam than those titrated with sodium laureth sulfate (SLES). However, the quat solutions that were titrated with SLES exhibited greater foam stability than those titrated with SLS. In some cases the quats titrated with SLES had a half-life greater than 24 hours (1440 minutes), including the control. After running all controls, it can be concluded that the addition of quaternium compound had a negative effect on the foaming capabilities of SLS and SLES. Stock SLS produced a foam height of 600 ml, while the average foam height produced from quat/SLS was around 250 ml.

Quat AMB (SLS) produced no foam. Unlike all the other quats that were titrated with SLS, which formed translucent, cloudy, gels at their respective cloud points, quat AMB produced a white, opaque paste. This is evidence that a complex is forming between this quat and SLS. This did not occur when quat AMB was titrated with SLES.

Controls for this experiment produced expected results. ARL-4-84A, which contained 1% polyquaternium 10, produced a higher foam height than ARL-4-84B, which also contained 1% polyquaternium 10, but in SLES. This also proved true for ARL-4-84C and

D as well, which produced the same results. Based on these test results, SLES produced greater foam stability than SLS, however SLS produced higher levels of foam.

Quat AMM and MMM performed superior in SLS and SLES compared to all the samples tested, including the controls. AMM showed superior foaming capabilities, by achieving the greatest foam height in SLS (500 ml), as well as having one of the best foam stabilities in SLES (over 1440 minutes). This stability was roughly ten times greater than all other quats and controls tested, with the exception of AEG, CaMB, MMG, and MMM, which all had foam stabilities of over 1440 minutes. It can be concluded that these quaternium compounds did not have a great effect on the expected foaming capabilities of SLS or SLES, with the exception of AMM and MMM. These two quat solutions increased foam stability by a factor of ten without suppressing foam height.

(C) SUBSTANTIVITY (AQUEOUS DELIVERY SYSTEM)

PURPOSE

Determine the substantivity of quaternium compounds in an aqueous delivery system to human hair.

PROCEDURE

Test solution: ARL-2-73A₁ LOT#: 020604

Stock solution: ARL-2-73A LOT#: 020604

Direct red 80 (Aldrich 365548-25G, LOT#: 04927)

Glacial acetic acid (Aldrich 338826-25ML, LOT#: 12405LA)

Treatment solutions

Name	w/w	Formula #
35% active quat solution	0.5%	ARL-4-85A-N
Deionized water	99.5%	

Control: Polyquaternium-10

RESULTS

All quat solutions, with the exception of three (AEG, AMG, CaMG) exhibited cationic substantivity when delivered to hair tresses in a 0.5% aqueous solution (see Table IX, p. 218; Figures 1 and 2, pp. 222, 223). It is likely that these quat solutions did not exhibit substantivity because of their glyceryl groups. However, quat DMG, which also contained a glyceryl group, did exhibit cationic substantivity. It is also possible that the quat group was damaged, or reacted out somewhere in the study, because they were no longer cationic.

Table IX
Cationic Substantivity: 0.5% Quat Solutions

Quat solution	Tress sample	Treatment	Result	
			Positive	Negative
AMB	A	ARL-4-85A	Pink	—
AME	B	ARL-4-85B	Purple	—
AMG	C	ARL-4-85C	—	No color change
AMM	D	ARL-4-85D	Purple	—
AEB	E	ARL-4-85E	Purple	—
AEG	F	ARL-4-85F	—	No color change
CaMB	G	ARL-4-85G	Purple	—
CaMG	H	ARL-4-85H		No color change
DMB	I	ARL-4-85I	Purple	—
DMG	J	ARL-4-85J	Purple	—
DMM	K	ARL-4-85K	Purple	—
MMB	L	ARL-4-85L	Purple	—
MMG	M	ARL-4-85M	Purple	—
MMM	N	ARL-4-85N	Purple	—
—	O	Positive control	Pink	—
—	P	Negative control	—	No color change

(D) SUBSTANTIVITY (ANIONIC SURFACTANT SYSTEM)

PURPOSE

Determine the substantivity of quaternium compounds in an anionic surfactant delivery system to human hair.

PROCEDURE – STM – PE#4

Quat solutions:

Titrated quat solutions

INCI: Polyquaternium-10

Surfactants:

Sodium lauryl sulfate

Sodium laureth sulfate

Lot #	Name	ARL-4-86A	ARL-4-86B	ARL-4-86C	ARL-4-86D
565720	Polyquaternium 10	0.5%	0.5%	—	—
0321605	Sodium lauryl sulfate	40.00%	—	40.00%	—
04107056	Sodium laureth sulfate	—	40.00%	—	40.00%
062906	Deionized water	59.50%	59.50%	60.00%	60.00%

Table X
Substantivity of Titrated Quat Solutions in SLS

Tress sample	Treatment	Result	
		Positive	Negative
A	Test	—	No color change
B	Test	—	No color change
C	Test	—	No color change
D	Test	—	No color change
E	Test	—	No color change
F	Test	—	No color change
G	Test	—	No color change
H	Test	—	No color change
I	Test	—	No color change
J	Test	—	No color change
K	Test	—	No color change
L	Test	—	No color change
M	Test	—	No color change
N	Test	—	No color change
O	Positive control	—	No color change
P	Negative control	—	No color change

Table XI
Substantivity of Titrated Quat Solutions in SLES

Tress sample	Treatment	Result	
		Positive	Negative
A	Test	—	No color change
B	Test	—	No color change
C	Test	—	No color change
D	Test	—	No color change
E	Test	—	No color change
F	Test	—	No color change
G	Test	—	No color change
H	Test	—	No color change
I	Test	—	No color change
J	Test	—	No color change
K	Test	—	No color change
L	Test	—	No color change
M	Test	—	No color change
N	Test	—	No color change
O	Positive control	—	No color change
P	Negative control	—	No color change

No substantivity was observed (Tables X, XI) when quat solutions were delivered from a 10% active, anionic solution of surfactant (SLS and SLES). The test measures cationic deposition as opposed to deposition of a compound of any nature. Since the quat and anionic form a complex, the deposited material is not cationic and consequently does not provide a color when tested with the dye test. More representative of the deposition is combing force.

(E) INSTRUMENTAL ANALYSIS OF COMBING FORCE

PURPOSE

Determine the force needed to comb wet and dry hair tresses treated with 0.5% active quaternium compound by instrumental analysis.

PROCEDURE

Treat hair tresses

- (1) Treat hair tresses by soaking them in 10-15ml of 0.5% active quat solution for two minutes at 20°-25°C.
- (2) Rinse hair tresses under running tap water (2.0-2.5 gallons/min, 35°-40°C), for one minute. Allow hair tresses to air dry for 24 hours at 20°-25°C and 40-50% relative humidity

RESULTS

The instrumental analysis of 0.5% active quat compounds (Tables XII, XIII, p. 221) showed that blue (MMM), performed the best followed by yellow (MMG), black (deionized water), and red (polyquaternium 10).

CONCLUSIONS

Quaternium compounds can be classified as hard or soft by their ability to form gelled systems with anionic systems. Cationic systems that form a gel at near stoichiometric amounts are classified as "soft", those that form precipitates of haze without appreciable viscosity build are classified as "hard" quats. "Soft quats" can produce foam in the systems they gel, albeit at levels below the volume of foam generated by the anionic per se.

Quaternium compounds titrated with sodium laureth sulfate (SLES) produced greater viscosities with amido quats. The exception was amido quats containing a benzyl group, which exhibited a low viscosity in SLES.

Compounds that contained a benzyl group, or were a alkyl rather than amido, (i.e. AMB, AME, AMG, AMM, AEB, AEG), precipitated at lower levels of titration and are consequently classified as "hard quats."

Overall, all quat/anionic solutions tested had less foam than when the anionic itself was tested. This was true for both SLS and SLES.

With the exception of quats AEG, AMG, and CaMG, and the negative control, all 0.5% active, aqueous solutions of quaternium compounds produced positive results for cationic substantivity, when evaluated per se.

In aqueous solutions of anionic surfactants, all quat solutions, including the positive control (polyquaternium 10), produced negative results. This is thought to be due to the fact

Table XII
Measured Combing Force (grams)

Subject A	1 st Combing	2 nd Combing	3 rd Combing	Average
Blue	10.0	15.0	13.0	12.6
Yellow	25.0	19.0	15.0	19.6
Red	30.0	13.0	13.0	18.6
Green	40.0	38.0	30.0	36.0
Black	12.0	13.0	15.0	13.3
<i>Subject B</i>	<i>1st Combing</i>	<i>2nd Combing</i>	<i>3rd Combing</i>	<i>Average</i>
Blue	25.0	13.0	15.0	17.6
Yellow	29.0	20.0	10.0	19.6
Red	30.0	28.0	20.0	26.0
Green	45.0	40.0	35.0	40.0
Black	25.0	15.0	10.0	16.6
<i>Subject C</i>	<i>1st Combing</i>	<i>2nd Combing</i>	<i>3rd Combing</i>	<i>Average</i>
Blue	10.0	12.0	10.0	10.6
Yellow	15.0	10.0	10.0	11.6
Red	15.0	25.0	20.0	20.0
Green	22.0	24.0	25.0	23.6
Black	30.0	23.0	30.0	27.6
<i>Subject D</i>	<i>1st Combing</i>	<i>2nd Combing</i>	<i>3rd Combing</i>	<i>Average</i>
Blue	10.0	10.0	12.0	10.6
Yellow	35.0	22.0	25.0	27.3
Red	15.0	15.0	10.0	13.3
Green	43.0	40.0	35.0	39.3
Black	20.0	10.0	13.0	14.3
<i>Subject E</i>	<i>1st Combing</i>	<i>2nd Combing</i>	<i>3rd Combing</i>	<i>Average</i>
Blue	27.0	16.0	10.0	15.0
Yellow	40.0	20.0	20.0	26.6
<i>Subject E</i>	<i>1st Combing</i>	<i>2nd Combing</i>	<i>3rd Combing</i>	<i>Average</i>
Red	20.0	20.0	12.0	17.3
Green	38.0	40.0	45.0	41.0
Black	23.0	20.0	15.0	19.3

Table XIII
Average Values of Combing Force (grams)

Tress color	Total score
Blue	13.20
Yellow	17.02
Red	19.04
Green	35.98
Black	18.22

that there is no net positive charge of the hair, due to the fact that the anionic and cationic in combination have a new zero charge. This is not to be confused with no deposition. Instrumental dry combing analysis of human hair tresses treated with aqueous quat solutions

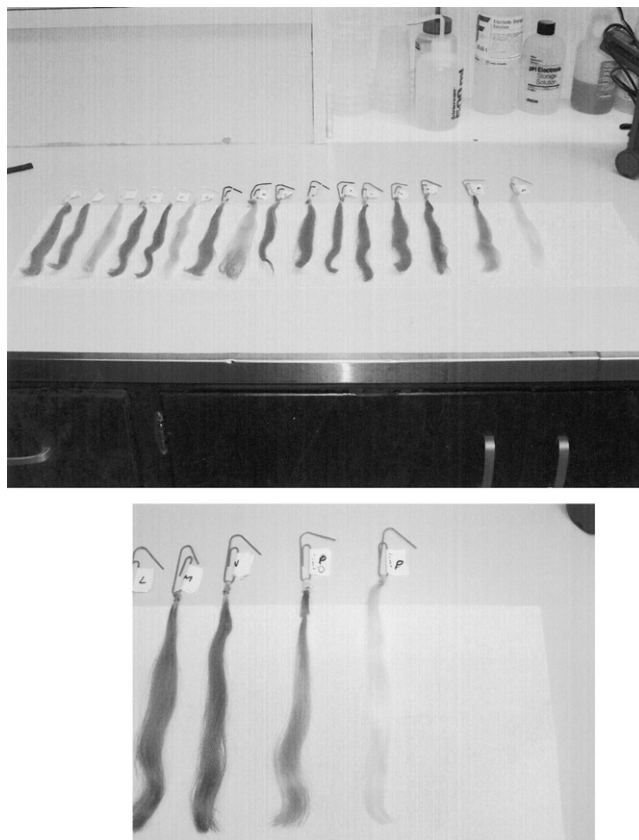


Figure 1. Positive and negative controls for 0.5% quat solutions.

confirmed conditioning, showing that quat MMM indeed performed the best, followed closely by MMG, polyquaternium 10, and the negative control. Again, quat DMG did not show any improvement in performance.

Quat AMB concluded to be the poorest performer yielding opaque surfactant mixtures at low levels. Foam height and stability was dramatically suppressed. Although AMB was substantive to human hair when delivered from an aqueous solution, no substantivity was observed from an anionic mixture.

Quat MMM concluded to be the best performer, yielding a thick, translucent gel with a viscosity well over 10,000 cps for both SLS and SLES titrations. MMM/anionic solutions produced an above average foam height without suppression and extended foam stability well over 24 hours or, ten times greater than SLS and SLES, controls, and positive controls (polyquaternium 10 and SLS/SLES). MMM performed equally as well in substantivity tests when delivered from an aqueous system. Like all other quat solutions, no substantivity was observed when delivered from an anionic mixture. Because of its performance, MMM was chosen for subjective and combing analysis. Like quats DMG and MMG, quat MMM performed poorly in the wet combing test. However, it did perform slightly better in the dry combing test. Quat MMM turned out to perform slightly better in the dry combing test. Quat MMM turned out to perform the best in the instrumental analysis of combing force. The average performance of quat MMM was superior to all quats in this study, including the positive control, polyquaternium 10.

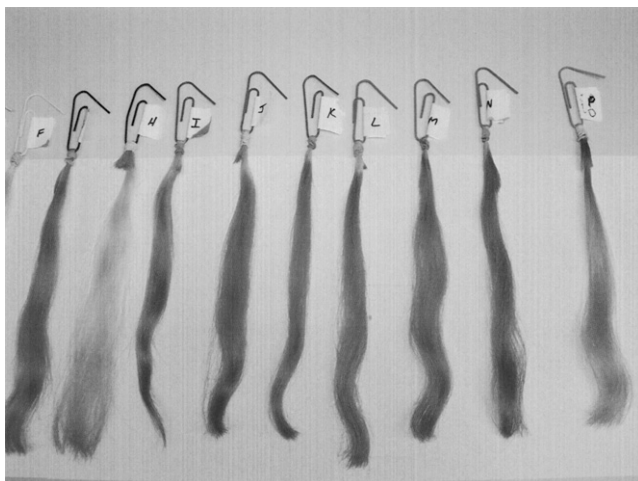


Figure 2. Hair tresses that exhibit substantivity with 0.5% quat solution.

SILICONE COMPLEXES

The data above was presented to show the basic theory of making complexes and optimizing them for hair care applications. The application of this technology to silicone complexes results in an ability to improve deposition of silicone conditioning agents on hair. The structure of silicone quaternium 20 is shown in Figure 3.

By making the complex of the anionic and cationic silicone a more effective conditioner is achieved. Silicone quaternium 20 has been developed to maximize the disruption of the hydrogen bonding between water molecules, yet still maintaining water solubility. The result is a complex that despite its water solubility achieves the lowest free energy by deposition on the hair and skin. The result is a very effective conditioning of the hair and skin.

SALON EVALUATION:

1. Silquat[®] J208-1B Silicone quat
2. SilPlex[®] J2-S Silicone quat complex

Shampoo base

Ingredients	%
Water	Qs
Sodium laureth-2 sulfate	30.00
Cocamidopropyl betaine	7.00
Cocamide DEA	4.00
Na ₂ EDTA	0.10
Silquat [®] J208-1B or SilPlex [®] J2-S	2.50
Germaben II	1.00
Citric Acid (25% soln)	Qs

All formula pH adjustments ranged from 6.65 to 6.80, specs being 6.30 to 6.80.

Table XIV
Wet Combing Evaluation

	(Control) Water only	Silicone quat	Silicone complex
Wet comb	1.0	4.0	5.0
Rinse off	3.0	4.0	5.0
Clean feel	1.0	4.0	5.0
Shine	3.0	4.0	5.0
Average	2.0	4.0	5.0

Table XV
Dry Combing Evaluation

	(Control) Water only	Silicone quat	Silicone complex
Dry comb	2.0	4.0	5.0
Feel	2.0	4.5	5.0
Manageability	2.0	4.0	5.0
Shine	3.0	5.0	5.0
Clean look	2.0	4.0	5.0
Flyaway	2.0	3.0	4.5
Static	2.0	3.0	4.5
Residual feel	3.0	4.5	5.0
Average	2.25	4.00	4.88

CONCLUSION

The silicone complex is an excellent product for use in a 2 in 1 shampoo and for adding sheen and softness to color treated hair. It left the hair silky soft with no residual feel and the combing was without any tugging or pulling. The comb slipped easily through the swatches, providing significant shine.

COACERVATE TECHNOLOGY

Silplex J-2S (Figure 4) has been found to be an effective agent for the formation of coacervate shampoos. The use of Silplex J-2S allows one to formulate a shampoo (Table XVI, p. 227) with outstanding foam and conditioning using natural oils and castor isostearate succinate, a natural ECOCERT polymer, available from Zenitech.

Silplex J-2S is used in baby shampoo at 0.5% to make a family product, is used in body wash, and is very effective for Asian hair.

The ability to choose specific anionic and cationic materials that interact to build viscosity, provide foam and act to make coacervates offer the formulator unique possibilities.

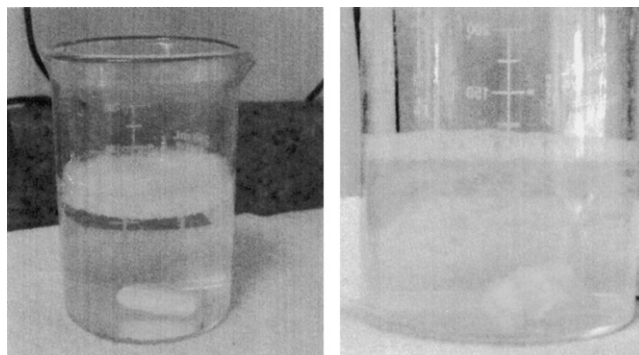


Figure 4. Silplex J2S and Silquat J208.

PROCEDURE

- (1) Into a clean and sanitized stainless steel container equipped with propeller mixer, add water in Phase B
- (2) Add SLES and betaine, heat up to 70° to 75°C, slowly add cocamide MEA and EGDS, mix slowly while minimizing air incorporation. Mix until uniform, then cool down to room temperature.
- (3) In another clean and sanitized stainless steel tank equipped with propeller mixer, add water and the rest of ingredients of phase A one by one while minimizing air incorporation. Mix until uniform.
- (4) Add phase B slowly into Phase A. Mix until uniform
- (5) Premix Silplex J2-S and Cosmosurf CE-100 until uniform, then add into Phase A+B, mix well. Add the rest of ingredients in Phase C one by one into Phase A+B until homogeneous while minimizing air incorporation.
- (6) Add ingredients in Phase D one by one. Adjust pH by using citric acid to pH = 5.5 ~ 6.5, and adjust viscosity to 6,000 cps ~ 12,000 cps by adding q.s. NaCl and Crothix. Add fragrance if necessary.

PROPERTIES

Viscosity (cps)	12,000
pH	5.70
Appearance	Opaque white cream

FOAM

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. 1.00 gram

Table XVI
Shampoo Formulation: Two-in-One Shampoo (Coacervate) FH183D

	Description (Supplier)	INCI Name	Weight %
A	D.I. water	Aqua	22.000
	Carbopol Aqua SF-1 polymer (1%)	Acrylates copolymer	2.500
	TEA 99%	Triethanolamine	0.200
	Na ₂ EDTA	Disodium EDTA	0.100
	Sodium laureth sulfate	Sodium laureth-2 sulfate	27.500
	Cocamidopropyl betaine	Cocamidopropyl betaine	6.000
B	D.I. water	Aqua	18.000
	Sodium laureth sulfate	Sodium laureth-2 sulfate	5.500
	Cocamidopropyl betaine	Cocamidopropyl betaine	4.000
	Ninol COMF	Cocamide MEA	1.200
	EGDS	Ethylene glycol distearate	3.000
C	Silplex J2-S (Siltech LLC)	Silicone quaternium-20	2.000
	Cosmosurf CE-100 (SurfaTech Corporation)	Octyldodecyl citrate crosspolymer	
	Wheat protein	Wheat protein	0.500
	Hemp seed oil	Cannabis sativa (Hemp) Seed oil	1.000
	Nipaguard DMDMH	DMDM hydantoin	0.500
D	Decyl glucoside	Decyl glucoside	3.000
	Amphosol 2C	Disodium cocoamphodiacetate	3.000
	Citric acid (40% aq)	Citric acid	q.s.
	Sodium chloride (if needed)	Sodium chloride	q.s.
	Crothix (Croda) (if needed)	PEG-150 pentaerythrityl tetrastearate	q.s.
	Fruity Herbal	Fragrance	q.s.
		Total	100.000

of test material was used and 100 ml of 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 air pump was sited on the bottom of the cylinder to generate the bubbles. After recording the foam height within 20 seconds for each test material, each material was evaluated three times and their averages were documented. The scale for foam height of 1000 ml is outstanding and 100 ml is very poor. The type of foam was also noted as tight or loose. Bubbles were generated by an electronic air pump.

Sample [Bubble for 20 sec]	Initial reading [average, ml]	Two minute reading [average, ml]	Five minute reading [average, ml]
FH183D	700	690	670

Foam was tight and uniform.

WET COMB

All products were evaluated on 10-inch virgin brown hair. Two x 2-gram swatches were used for each material tested, all from the same lot. All swatches were wet with 25°C water and one gram of test material was used for each swatch. Swatches were washed and then rinsed for at least one minute per swatch. Wet comb evaluation was then performed. No blow-drying of hair was done. All swatches airdried then the dry comb evaluation was performed once hair was completely dry. Scale used is 1 to 5, 5 being the best. Used for wet and dry combing.

Sample/Evaluation	Wet comb	Rinse-off	Clean feel (Scroop)	Shine	Residual feel	Average
Control water only	1.0	3.0	2.0	2.0	2.0	2.0
FH183D	4.5	4.5	4.5	3.0	3.0	3.9

DRY COMB

Sample/ Evaluation	Dry comb	Dry feel	Clean feel/ look	Shine	Fullness/ manageable	Fly-away	Residual feel	Static	Average
Control water only	3.0	3.0	2.0	1.0	1.0	1.0	1.0	2.0	1.750
FH183D	4.4	4.5	4.0	4.0	4.4	4.2	3.5	4.0	4.125

SALT TOLERANCE, PH, VISCOSITY, EASE OF FORMULATION, AND EFFECT ON FORMULATION STABILITY

The scale used is 1 to 5, 5 being the best, only for salt tolerance, ease of formulation, and effect on formulation stability. Viscosity was tested by using a Brookfield, LVT, #4 spindle, 12 rpm.

Formula/ Evaluation	Salt tolerance	pH	Viscosity, cps	Ease of formulation	Effect on formulation stability	Average
FH183D	2.5	5.70	12,000	4.0	4.5	3.67

REFERENCES

- (1) R. G. Pearson, *J Am Chem Soc.*, **85**, 335 (1963).
- (2) E. Lucassen and D. Giles, *J. Colloid Interface Sci.*, **81**(1), 150–157 (1981).
- (3) A. J. O'Lenick, *J. Surfact. Deterg.* **3**(2), 229 (2000).
- (4) G. Kume, M. Gallott, and G. Nunes, *J. Surfact. Deterg.*, **11**, 1–1 (2008).