Lip color that lasts! A novel, multiple emulsion liquid lipstick with outstanding rub-off and wash-off resistances

***D. Almeida[1], C. Urio[2], D. Iwasso[2], N. Polidoro[1]*, L. Carmona[2], M. Padilha[2], M. Baptista[2], C. Sasson[2], G. Diemant[2]**

[1] *The Dow Chemical Company, São Paulo, Brazil*
[2] *Grupo Boticário, Curitiba, Brazil*

ABSTRACT

Consumers are increasingly looking for lip colored products capable of lasting the full day without the need to reapply, while delivering comfort, color intensity and ease of use. This work describes the development of a multiple emulsion system having silicone polymers as the continuous phase, water as the intermediate phase (W/Si emulsion) and an acrylate (O/W) or silicone polymer (Si/W) as the internal phase. The outstanding resistance to rub-off and wash-off is obtained by adding a silicone and/or acrylate film former to both hydrophobic phases. Rub-off and wash-off resistances were evaluated based on instrumental techniques. Rub-off was evaluated dry and in presence of olive oil, measuring color fade by CIELab colorimetry, and the wash-off was performed with Diastron® Wash-off Simulator and panel analysis. Data from dry rub-off resistance indicates a linear correlation between concentration and color retention performance, analyzing Delta E values compared to a Placebo for both film formers in internal phase. In presence of olive oil, concentration dependency was also validated but in an inversed relationship: the lower the concentration of the film former, the better the color retention.

1. Introduction

This work describes the development and validation of a multiple emulsion system having silicone polymers as the continuous phase, water as the intermediate phase (W/Si emulsion) and an acrylate (O/W) or silicone polymer (Si/W) as the internal phase. Performance of the proposed liquid lipstick was validated by means of rub-off and wash-off resistance, as well as film flexibility.

2. Experimental

2.1. Equipments and Materials

2.1.1. Silicone and Organic Film Formers

A crosspolymer of silanol and trimethylsiloxysilicate (INCI: Dimethiconol/Trimethylsiloxysilicate Crosspolymer) supplied at 40% in isododecane was added to the continuous phase at a fixed concentration of 20% wt. (as supplied). An alkyl-modified T-propyl silicone resin (INCI: C30-45 Alkyldimethylsilyl Polypropylsilsesquioxane) was studied in combination with the silicone crosspolymer at a fixed concentration of 9% wt., in order to better understand its impact on the film. At the same time, two different film formers were added to the internal phase, separately, at two different concentrations, to study dose-dependency. The first one is an emulsion-polymerized acrylic polymer (INCI: Acrylates Copolymer), provided in a non-ionic O/W emulsion with 45% internal phase. The second one is a silicone-modified, linear acrylic polymer, also emulsion-polymerized (INCI: Acrylates/ Polytrimethylsiloxymethacrylate Copolymer) and provided as an anionic O/W emulsion with 30% internal phase. Both polymers were studied at 5% and 15% concentration (as supplied) in the liquid lipstick.

2.1.2. Formulation Design

Table 1 describes formulations F1 to F10 included in this study, and the range comprises a placebo, two different film formers at two different concentrations in the internal phase (as previously explained in section 2.1.1) and formulations with and without the alkyl-modified T-propyl silicone resin.

2.1.3. Inverse Optical Microscopy

To validate the hypothesis that a multiple emulsion was formed when selected film formers are combined in both external and internal phases, a Nikon Ti3 Inverted Light Microscope was used, with a 100x magnitude lens immersed in oil. For video capturing, a high speed Hamamatsu camera at 30us/frame was coupled to the microscope.

2.1.4. Membranes/Substrates

The substrate of choice for running all rub-off analysis was Vitro-Skin®, which is a testing substrate that mimics the surface properties of human skin (ref site). It was purchased from IMS Inc., USA. Latex-made elastic bands were selected for the flexibility evaluation, and were purchased in local department stores in Brazil.

2.1.5. Film Applicator

The 25 um side of a quadruplex film applicator from TQC (serial number VF2167-108) was used to produce the films on Vitro-Skin® and latex-made elastic bands.

2.1.6. Mechanical Mixers

All emulsions were prepared using high speed mechanical mixers purchased from Mathis, in Brazil. A double-sided straight blade was coupled to the mixer to ensure enough turbulence and shearing force to the emulsion under formation. Speed was set to 1500 rpm during the emulsification process.

Table 1. Quantitative composition of the liquid lipstick formulations

INCI Name	Formulation									
PHASE A	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
INCI Name										
Disiloxane	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Red 7 Lake	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Red 7	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Red Iron Oxides	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Titanium Dioxide	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
PHASE B										
INCI Name										
Trimethylsiloxysilicate/ Dimethiconol Crosspolymer (and) Isododecane	-	20.0	20.0	20.0	20.0	-	20.0	20.0	20.0	20.0
C30-45 Alkyldimethylsilyl Polypropylsilsesquioxane	-	-	-	-	-	9.0	9.0	9.0	9.0	9.0
Diimethicone 350 cS	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
PEG/PPG-18/18 Dimethicone (and) Cyclopentasiloxane	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
Diimethicone 1 cS	20.0	-	-	-	-	42.0	22.0	22.0	22.0	22.0
PHASE C										
INCI Name										
Acrylates Copolymer	-	15.0	-	5.0	-	-	15.0	-	5.0	-
Acrylates/ Polytrimethylsiloxymethacrylate Copolymer	-	-	15.0	-	5.0	-	-	15.0	-	5.0
Water	61.0	46.0	46.0	56.0	56.0	30.0	15.0	15.0	25.0	25.0

2.1.7. CIELab Colorimeter

A handheld spectrophotometer obtained from Konica Minolta Inc., model CM-2600d, was used to objectively measure color in between rub-off cycles. The equipment was set to operate in the $L^*a^*b^*$ space and to perform triplicates, providing the average automatically.

2.1.8. Rub-Off Tester

A washability tester purchased from Elcometer, model 1720, was used to rub-off the films with felt bands attached to the test site. Both speed and cycle were set to 1.

2.1.9. Wash-off Simulator

A Wash-off simulator 700 from Diastron Inc. was used to simulate wash cycles with 0.5% Sodium Lauryl Ether Sulfate solution on subjects' arms. The equipment was prepared in a way that the probe avoid touching the skin during the procedure. Speed was set to 500 rpm, rotation to 360º and timer to 30s.

2.1.10. Optical Tensiometer

A high precision optical tensiometer was used to calculate the contact angle between water and treated Vitro-Skin®. It was purchased from Bioscientific, under the brand Attension Theta. A 1 mL syringe from Hamilton was coupled to the tensiometer.

2.2. Methods

2.2.1. Film Preparation

Films on Vitro-Skin® and latex-made elastic bands were carefully prepared using a rigid metallic back plate to ensure a completely flat and wrinkle-free surface. After attaching the membranes to the back plate with adhesive tapes, the quadruplex film applicator was positioned at the top of the membrane, with the 25 um mark facing downside, and the formulation was added on top of it. Finally, the operator pulled down the applicator and cleaned the excess of lipstick formulation. The films were then left to dry overnight.

2.2.3. Rub-off Assessment

Vitro-Skin® films were manually cut in circles with approximately 3.5 cm in diameter and attached to the probe. The initial color was measured with the Minolta CIELab colorimeter at 3 different points and the average was reported. A virgin felt was then attached to the bottom of the Elcometer 1720 washability tester with double-face adhesive tape and the probe was positioned inside the arm and on the felt. The equipment was then activated and one rub-off cycle was performed. After the rub-off, the felt was replaced by another one, the probe was removed and the color was measured again, following the same methodology. Twenty-five consecutive rub-offs were performed, and color measurements were done after 1, 2, 3, 4, 5, 10 and 25 rub-off cycles. For the rub-off resistance in the presence of oil, 2g of olive oil was added to the center of the felt before each insult.

2.2.4. Wash-off Assessment

Three circles with 5 cm of diameter were drawn in both forearms of 2 subjects, after cleansing the areas with a 9% Sodium Lauryl Ether Sulfate solution. Approximately 0.06g of each liquid lipstick included in the test group was added to the individual circular areas, spread over by a qualified facilitator and left to dry at environmental conditions for 1 hour. After the drying period, each subject was taken to the Diastron Wash-Off Simulator by the facilitator and each area was washed 5 times with a 0,5% Sodium Lauryl Ether Sulfate solution at controlled conditions (refer to section 2.1.9.), one at a time. Forearms were gently dried out with toilet paper, and 19 non-trained panelists ranked visually the test areas in terms of color intensity and homogeneity after the 5th wash cycle (One to three scale).

2.2.5. Film Flexibility

Pictures of the latex-made elastic bands were taken to register its original appearance before the flexibility test. The bands were then manually stretched 2 times its initial size and pulled back to its original position, and another picture was taken. The integrity of the film was assessed based on the presence of cracks, fractures and discontinuations, compared to the initial image.

2.2.6. Hydrophilicity Evaluation

Vitro-Skin® films previously used in the dry rub-off resistance were also used to measure the contact angle with water, as an indication of the presence of film formers after the 25th rub-off cycle. The films were placed on the sample holder of the Attension tensiometer and contact angles were measured in 5 different sections of the film. The average was reported.

3. Results and Discussions

3.1. Validation of Emulsion Morphology

It was expected that the addition of an emulsion-polymerized acrylic or silicone-acrylate polymers to the water phase of a W/Si system would generate a multiple emulsion. Three formulations with different compositions were evaluated microscopically to assess the morphology of the resulting emulsion. Figures 1, 2 and 3 are representative microscopic images of F1, F2 and F3, respectively.

Formulation F1, which did not contain any emulsion-polymerized film former in the aqueous phase, presented a high size polydispersity, with micelles ranging from several microns up to 30um. There is no evidence of a multiple emulsion configuration, as expected. In the other hand, formulations F2 and F3 have a much smaller particle size with a narrower distribution, with average around 10um.

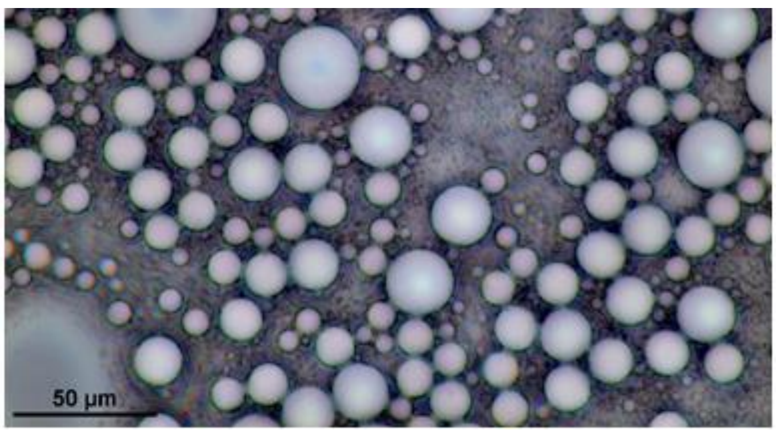

Figure 1. Representative image of formulation F1, obtained at 100x magnification

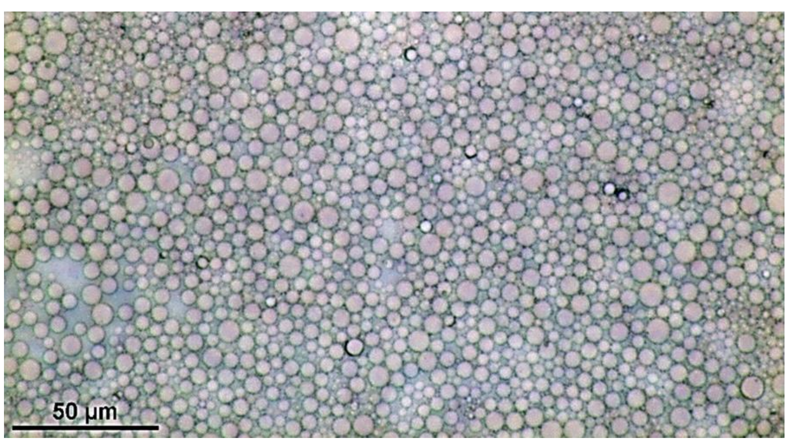

Figure 2. Representative Image of formulation F2, obtained at 100x magnification

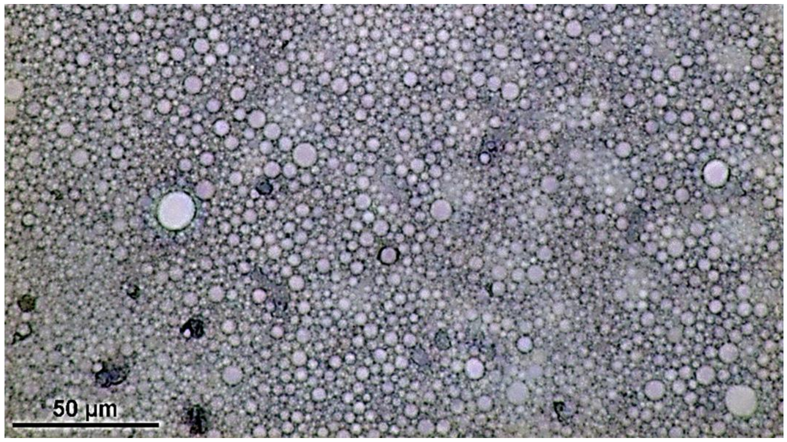

Figure 3. Representative Image of formulation F3, obtained at 100x magnification

There is an evidence of a multiple configuration with the presence of very small particles inside the micelles containing the aqueous phase, which is confirmed by observing the frenetic movement of such particles in the video captured with the Hamamatsu camera. The addition of an emulsion-polymerized film former in the aqueous phase favors the formation of outer micelles with smaller particle sizes, leading as well to the formation of O/W/Si or O/W/O emulsions.

3.2. Rub-Off Resistance

Changes in color of the liquid lipstick applied to the test substrate are expected to happen as it gets successively rubbed against a given surface. Such changes were objectively measured through CIELab colorimetry and analyzed based on specific color parameters calculated with the L^*, a^* and b^* coordinates, always using delta numbers with the original color as reference.

Delta E is the most widely used measure of difference in color between two objects and takes into consideration all coordinates. Mathematically it is defined as:

$$dE = \sqrt{(dL^*)^2 + (da^*)^2 + (db^*)^2}$$

Very objectively, hue is perceived as an object's color and is commonly specified by familiar names describing broad tonal families of the visible spectrum. Mathematically it is defined as:

$$Hue = dh^o = tan^{-1}\left(\frac{b^*}{a^*}\right)$$

Chroma is an equivalent designation to color saturation, describing the vividness or dullness of a color. In other words, it express how close the color is to either gray or the pure tone. Mathematically it is defined as:

$$Chroma = dC^* = \sqrt{(da^*)^2 + (db^*)^2}$$

And finally, lightness describes the luminous intensity of a color or, in other words, how light or dark it seems to be. Mathematically it is defined as:

$$Lightness = dL_i = (L^*{}_i - L^*{}_1)$$

Considering the color selected for the liquid lipsticks in this study, which is a combination of Iron Oxides and organic pigments (Red 7 and Red 7 Lake), it is expected negative variations in Chroma and Hue, and a positive variation in Lightness and Delta E. It is a result of the progressive removal of the red film formed on the substrate and the arising of the original Vitro-Skin®'s bright and yellowish tone.

3.2.1. Rub-Off Resistance - Dry

Table 2 reports delta colorimetric data for all liquid lipsticks after 1, 2, 3, 4, 5, 10 and 25 rub-off cycles, for color parameters defined in section 3.2.

Experimental data can be separated in two groups to facilitate analysis of the variables influencing the results. The first group, comprised of formulations F1 to F5, did not contain C30-45 Alkyldimethylsilyl Polypropylsilsesquioxane in the composition. The second group with formulations F6 to F10 contained it.

For the first group, results are reported in Figure 4. All formulations containing silicone and/or organics film formers (F2 to F5) had significant lower dE^* ($p<.05$) compared to F1 after cycles 5, 10 and 25. Only formulation F3 presented a significantly lower dE^* ($p<.05$) after the 1st rub-off cycle.

Films prepared with Formulation F3 were significantly ($p<.05$) darker (lower dL^*) and with improved Hue (lower dh^o) compared to F1 after rub-off cycles 10 and 25, meaning that colors did not move far away from the original red color. Formulations F2 to F5 inhibited the increase in dullness compared to Placebo. Analyzing the dose-dependency of the film formers in the internal phase, both Acrylates Copolymer and Acrylates/Polytrimethylsiloxymethacrylate Copolymer tend ($.10<p<.05$) to have lower dL^* and dC^* at 15% compared to 5%, even though differences in dE* was not statistically significant. In summary, higher concentrations seemed to be favorable to achieve better results in terms of dry rub-off, leading to more vivid tones.

Table 2. Colorimetric data for formulations F1 to F10 under dry conditions

	Deltas per color coordinate			Deltas per color parameter			Deltas per color coordinate			Deltas per color parameter		
	Formulation / Design Point											
	F1						F2					
Insult Cycle	dL*	da*	db*	dE*	dhº	dC*	dL*	da*	db*	dE*	dhº	dC*
1	4.01	0.90	-5.45	6.82	-0.06	-2.82	1.54	0.52	-0.97	1.89	-0.01	-0.23
2	4.76	-0.74	-10.98	11.99	-0.11	-7.46	2.64	0.57	-2.44	3.64	-0.03	-1.12
3	4.96	-1.47	-15.88	16.70	-0.17	-10.80	2.77	0.64	-4.27	5.12	-0.05	-2.22
4	5.35	-2.72	-18.49	19.43	-0.19	-13.22	2.33	0.29	-4.09	4.71	-0.04	-2.38
5	6.33	-4.03	-19.73	21.10	-0.20	-14.98	2.14	-0.20	-5.44	5.85	-0.05	-3.60
10	7.11	-6.09	-24.25	25.99	-0.25	-18.98	2.07	0.09	-6.54	6.86	-0.07	-4.04
25	8.46	-8.54	-27.62	30.12	-0.29	-22.67	2.55	0.02	-9.06	9.41	-0.09	-5.58
	F3						F4					
Insult Cycle	dL*	da*	db*	dE*	dhº	dC*	dL*	da*	db*	dE*	dhº	dC*
1	-0.15	-0.86	-1.87	2.06	-0.01	-1.85	0.39	-0.54	-4.70	4.75	-0.04	-3.31
2	0.04	-0.89	-2.62	2.76	-0.02	-2.35	0.47	-1.42	-6.78	6.94	-0.06	-5.25
3	-0.19	-1.16	-4.99	5.12	-0.04	-4.04	0.26	-1.47	-7.37	7.52	-0.07	-5.63
4	-0.14	-1.28	-5.42	5.57	-0.04	-4.40	0.87	-1.62	-8.46	8.65	-0.08	-6.37
5	0.34	-1.72	-6.33	6.56	-0.05	-5.30	0.64	-1.29	-8.02	8.14	-0.07	-5.85
10	-0.06	-1.61	-6.46	6.66	-0.05	-5.30	-0.93	-2.88	-7.61	8.19	-0.06	-6.92
25	0.26	-2.03	-9.46	9.67	-0.08	-7.41	-0.06	-2.41	-7.91	8.27	-0.06	-6.71
	F5						F6					
Insult Cycle	dL*	da*	db*	dE*	dhº	dC*	dL*	da*	db*	dE*	dhº	dC*
1	0.84	-0.90	-2.16	2.48	-0.01	-2.06	2.38	-4.70	-5.50	7.61	-0.05	-6.46
2	0.67	-1.74	-3.42	3.90	-0.02	-3.50	3.65	-11.14	-11.77	16.61	-0.11	-14.62
3	0.45	-1.88	-4.18	4.60	-0.03	-4.08	7.78	-24.97	-19.67	32.73	-0.20	-30.05
4	1.30	-1.96	-5.00	5.52	-0.04	-4.65	12.19	-32.33	-22.61	41.29	-0.24	-37.85
5	0.99	-2.04	-5.24	5.70	-0.04	-4.85	20.35	-38.66	-23.53	49.62	-0.23	-44.24
10	1.66	-2.27	-8.45	8.90	-0.07	-6.95	24.30	-49.19	-24.68	60.16	-0.17	-54.77
25	1.84	-2.22	-10.71	11.09	-0.10	-8.20	24.77	-54.35	-25.90	65.09	-0.15	-60.06
	F7						F8					
Insult Cycle	dL*	da*	db*	dE*	dhº	dC*	dL*	da*	db*	dE*	dhº	dC*
1	0.59	0.32	-4.16	4.21	-0.04	-2.35	0.26	-0.50	-4.66	4.69	-0.04	-3.34
2	0.15	-0.65	-6.57	6.60	-0.06	-4.56	0.97	-1.18	-7.14	7.30	-0.06	-5.39
3	0.39	-0.54	-6.62	6.65	-0.06	-4.51	0.65	-1.39	-8.11	8.25	-0.07	-6.14
4	-0.04	-1.13	-7.38	7.46	-0.07	-5.43	0.85	-1.56	-8.76	8.93	-0.08	-6.66
5	-0.47	-2.07	-7.89	8.17	-0.06	-6.49	0.78	-2.24	-11.05	11.30	-0.10	-8.55
10	-0.11	-2.58	-11.98	12.25	-0.11	-9.25	1.77	-2.29	-11.83	12.17	-0.10	-9.04
25	0.17	-3.07	-11.24	11.65	-0.09	-9.24	3.59	-3.00	-15.42	16.11	-0.14	-11.62
	F9						F10					
Insult Cycle	dL*	da*	db*	dE*	dhº	dC*	dL*	da*	db*	dE*	dhº	dC*
1	0.93	-0.34	-7.09	7.16	-0.07	-4.26	-0.08	-0.85	-7.68	7.72	-0.07	-5.10
2	1.10	-0.95	-8.25	8.38	-0.08	-5.38	0.08	-1.11	-8.86	8.92	-0.09	-5.96
3	0.84	-1.03	-9.60	9.69	-0.10	-6.15	0.43	-1.13	-10.25	10.32	-0.10	-6.71
4	0.95	-1.64	-10.62	10.79	-0.11	-7.19	0.17	-1.77	-10.21	10.36	-0.10	-7.23
5	1.13	-1.74	-10.74	10.94	-0.11	-7.34	0.65	-1.89	-11.58	11.75	-0.11	-8.05
10	1.20	-2.13	-10.55	10.83	-0.10	-7.58	0.44	-3.09	-12.12	12.51	-0.11	-9.35
25	1.24	-3.12	-10.42	10.94	-0.09	-8.36	0.41	-3.86	-12.35	12.94	-0.11	-10.13

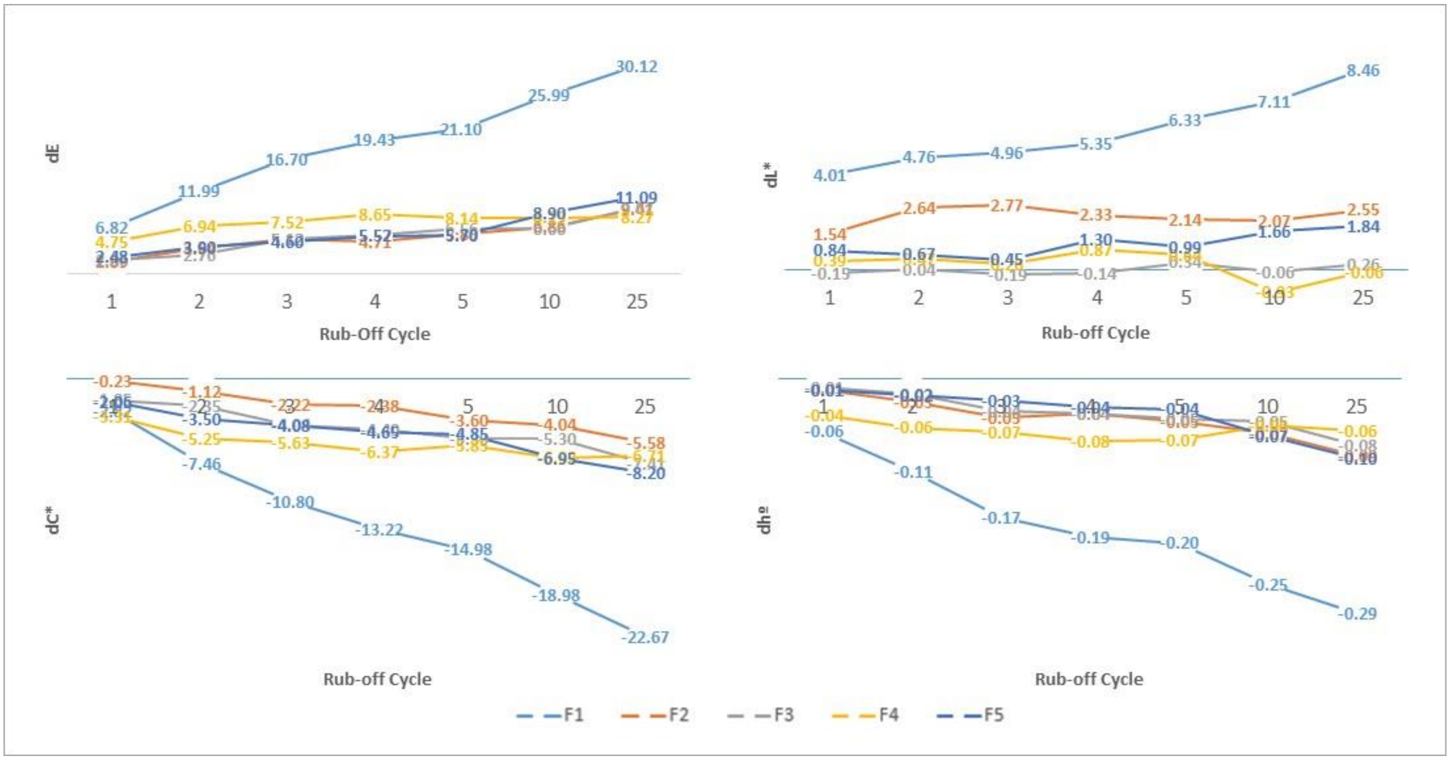

Figure 4. dE, dL*, dC* and dhº for each colorimetric reading for Formulations F1 to F5 under dry rub-off*

For the second group, results are reported in Figure 5. Formulations, F7, F8, F9 and F10 presented a significantly lower dE* compared to F6 ($p<.05$) after rub-off cycles 10 and 25. The same performance was observed after rub-off cycle 1 for F7 and F8.

Films produced with formulations F7 to F10 are darker compared to F6 after rub-off cycles 10 and 25 and also presented significantly ($p<.05$) lower dC* compared to F6. Differences in dhº are negligible.

The dose-dependency effect is similar to both film formers. In summary, when C30-45 Alkyldimethylsilyl Polypropylsilsesquioxane is present in the continuous phase, raising the concentration of Acrylates Copolymer or Acrylates/Polytrimethylsiloxymethacrylate Copolymer from 5% to 15% leads simultaneously to a better performance in short term and to a worse performance in long term.

Pictures of the films after the 25th rub-off cycles are illustrated in Figure 6.

3.2.2. Rub-Off Resistance – Olive Oil

Table 3 reports delta colorimetric data for all liquid lipsticks after 1, 2, 3, 4, 5, 10 and 25 rub-off cycles, all performed in presence of olive oil, which was added directly to the felt band.

Once again colorimetric data was divided in two groups to facilitate visualization and interpretation of the numbers, and the groups are the same as described in section 3.2.1.

Overall delta numbers are significantly higher compared to the ones obtained in a dry condition, as the presence of olive oil represents one of the greatest challenges in terms of resistance, leading to faster and more aggressive color variation over cycles.

For the first data group, results are graphically reported in Figure 7. All formulations presented significantly lower dE* and dC* ($p<.05$) after cycles 5, 10 and 25, and significantly lower dhº after all cycles. The presence of film formers drastically reduced the color loss and maintained color vividness and trueness, when compared to formulation F1, which is free of film formers.

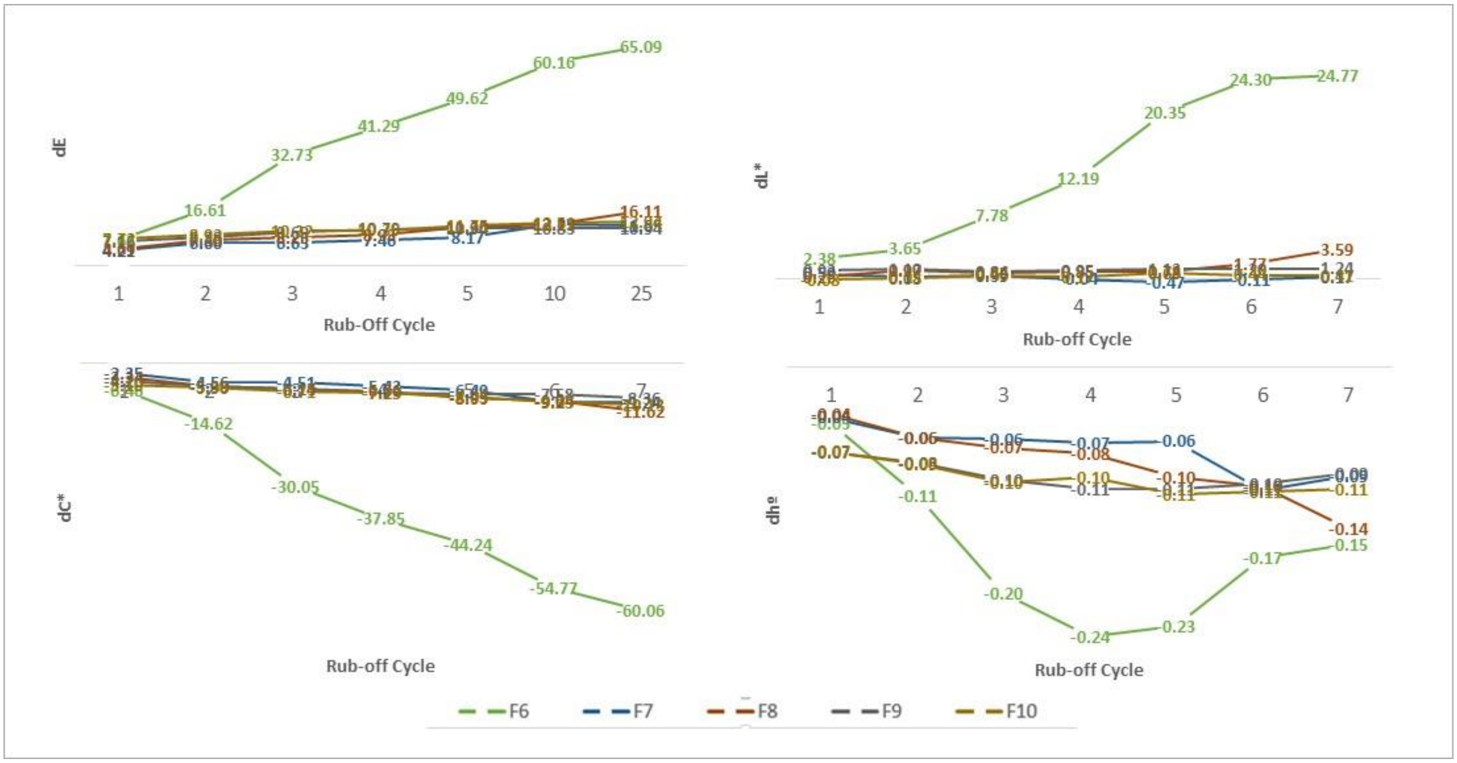

Figure 5. dE, dL*, dC* and dhº for each colorimetric reading for Formulations F6 to F10 under dry rub-off*

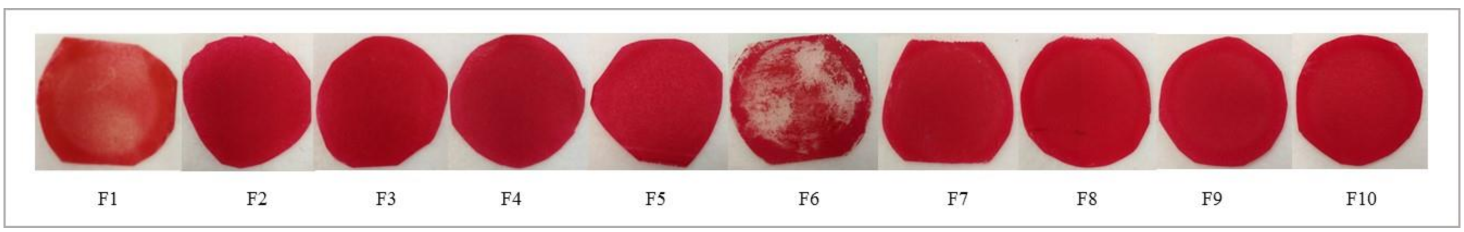

Figure 6. Pictures of the films on Vitro-Skin® after the 25th rub-off cycle (dry)

In terms of lightness (dL*), formulations F2 to F5 presented significantly lower numbers ($p<.05$) after rub-off cycle 25.

Analyzing the dose-dependency impact on colorimetric data, higher levels of Acrylates Copolymer significantly lowered variation in lightness after cycles 1 and 25 ($p<.05$), as well as lowered dE* after cycle 10. For the Acrylates/ Polytrimethylsiloxymethacrylate Copolymer, the impact of raising the concentration from 5% to 15% is much more discrete, with a lower variation in dL* after cycle 5. It is possible to conclude that in lipstick formulations where C30-45 Alkyldimethylsilyl Polypropylsilsesquioxane is not present in the continuous phase, dose-dependency effect is stronger for the Acrylates Copolymer.

For the second group, results are reported in Figure 8. The impact of adding silicone and organic film formers when C30-45 Alkyldimethylsilyl Polypropylsilsesquioxane is present in the continuous phase is even stronger compared to the previous group of formulations. Compared to formulation F6, which is free from film formers, F7 to F10 presented significantly lower dL*, dE*, dC* and dhº in between rub-off cycles 3 and 25 ($p<.05$).

Table 3. Colorimetric data for formulations F1 to F10 with olive oil

	Deltas per color coordinate			Deltas per color parameter			Deltas per color coordinate			Deltas per color parameter		
	Formulation / Design Point											
	F1						F2					
Insult Cycle	dL*	da*	db*	dE*	dh°	dC*	dL*	da*	db*	dE*	dh°	dC*
1	4.41	-1.71	-21.25	21.77	-0.24	-14.14	-0.16	-3.03	-3.77	4.84	-0.01	-4.71
2	5.51	-5.57	-28.67	29.72	-0.32	-20.99	0.25	-2.88	-6.71	7.31	-0.05	-6.35
3	6.94	-8.13	-33.02	34.71	-0.38	-25.08	-0.06	-3.09	-5.53	6.33	-0.03	-5.81
4	7.19	-11.96	-36.80	39.35	-0.42	-29.99	0.35	-3.37	-6.39	7.23	-0.04	-6.55
5	7.71	-14.25	-38.38	41.66	-0.44	-32.67	0.81	-3.90	-5.71	6.96	-0.03	-6.58
10	14.73	-22.27	-43.85	51.34	-0.52	-41.88	1.04	-3.12	-6.72	7.48	-0.05	-6.55
25	19.43	-34.83	-47.41	61.95	-0.55	-54.92	1.47	-3.37	-12.05	12.60	-0.11	-9.74

	F3						F4					
Insult Cycle	dL*	da*	db*	dE*	dh°	dC*	dL*	da*	db*	dE*	dh°	dC*
1	0.84	-3.19	-8.49	9.11	-0.07	-7.59	0.92	-1.59	-4.69	5.04	-0.04	-4.08
2	1.14	-3.58	-9.24	9.97	-0.07	-8.33	2.39	-1.63	-6.97	7.55	-0.06	-5.42
3	0.83	-3.83	-10.46	11.17	-0.08	-9.21	2.34	-3.09	-5.20	6.48	-0.03	-5.59
4	1.24	-3.93	-10.93	11.68	-0.09	-9.55	2.25	-2.24	-6.96	7.65	-0.06	-5.91
5	1.00	-3.83	-11.01	11.69	-0.09	-9.51	2.17	-2.88	-7.38	8.21	-0.06	-6.68
10	0.77	-3.92	-11.26	11.94	-0.09	-9.72	2.59	-2.43	-7.98	8.73	-0.07	-6.64
25	0.97	-4.80	-12.62	13.54	-0.10	-11.19	2.36	-2.87	-8.94	9.68	-0.08	-7.54

	F5						F6					
Insult Cycle	dL*	da*	db*	dE*	dh°	dC*	dL*	da*	db*	dE*	dh°	dC*
1	0.14	-2.49	-6.01	6.50	-0.04	-5.70	6.42	-25.40	-19.93	32.91	-0.18	-30.89
2	0.55	-3.00	-7.67	8.25	-0.06	-7.11	26.76	-55.81	-24.37	66.52	0.24	-60.60
3	1.26	-3.13	-8.94	9.55	-0.07	-7.96	29.17	-58.66	-24.66	70.00	0.47	-62.80
4	1.44	-3.46	-10.05	10.72	-0.08	-8.87	29.17	-58.66	-24.66	70.00	0.47	-62.80
5	1.89	-3.59	-11.18	11.89	-0.09	-9.63	29.17	-58.66	-24.66	70.00	0.47	-62.80
10	0.54	-4.06	-10.60	11.36	-0.08	-9.68	29.17	-58.66	-24.66	70.00	0.47	-62.80
25	1.28	-3.93	-11.62	12.33	-0.09	-10.17	29.17	-58.66	-24.66	70.00	0.47	-62.80

	F7						F8					
Insult Cycle	dL*	da*	db*	dE*	dh°	dC*	dL*	da*	db*	dE*	dh°	dC*
1	0.73	-1.28	-9.53	9.64	-0.10	-6.66	0.09	-2.69	-18.29	18.49	-0.17	-13.12
2	0.95	-1.42	-10.52	10.65	-0.11	-7.33	0.16	-2.90	-20.68	20.88	-0.20	-14.53
3	2.40	-0.68	-11.06	11.34	-0.12	-6.99	1.00	-3.21	-21.28	21.54	-0.20	-15.10
4	2.64	-1.03	-12.80	13.10	-0.14	-8.20	1.08	-3.42	-22.09	22.38	-0.21	-15.68
5	1.83	-1.93	-13.87	14.12	-0.14	-9.52	0.93	-4.33	-23.61	24.02	-0.23	-17.21
10	0.46	-3.37	-13.89	14.30	-0.13	-10.77	1.47	-5.21	-25.99	26.54	-0.25	-19.10
25	1.19	-5.80	-18.31	19.24	-0.17	-15.09	2.07	-7.21	-29.81	30.74	-0.29	-22.58

	F9						F10					
Insult Cycle	dL*	da*	db*	dE*	dh°	dC*	dL*	da*	db*	dE*	dh°	dC*
1	-0.18	-5.15	-14.66	15.54	-0.14	-12.09	0.27	-5.82	-14.12	15.27	-0.11	-12.71
2	0.33	-5.52	-14.70	15.71	-0.14	-12.44	0.85	-5.98	-16.13	17.22	-0.14	-13.85
3	0.13	-5.99	-15.20	16.33	-0.14	-13.09	1.07	-6.61	-17.74	18.96	-0.16	-15.18
4	1.01	-7.39	-18.14	19.61	-0.17	-15.66	2.08	-7.51	-19.79	21.26	-0.18	-16.93
5	1.95	-9.53	-21.60	23.68	-0.21	-19.05	2.48	-7.85	-20.62	22.20	-0.19	-17.60
10	3.54	-13.63	-25.75	29.35	-0.25	-24.42	3.68	-11.39	-25.93	28.55	-0.24	-23.05
25	9.73	-23.99	-34.15	42.85	-0.35	-36.92	8.20	-19.49	-33.66	39.75	-0.32	-33.38

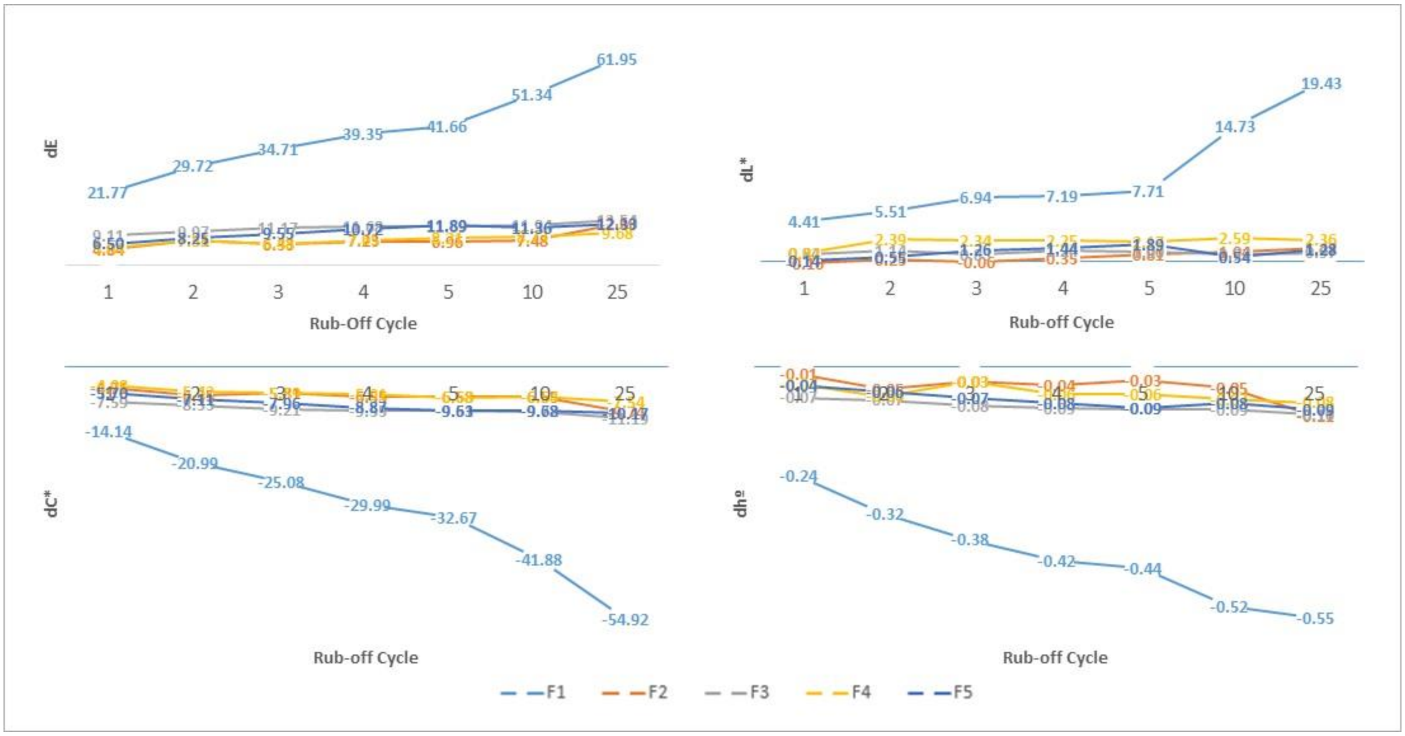

Figure 7. dE, dL*, dC* and dhº for each colorimetric reading for Formulations F1 to F5 with olive oil*

In terms of dose-dependency, Acrylates Copolymer tends (.10<p<.05) to preserve dL*, dC* and dhº when used at higher levels. No significant difference in short term was observed for this film former. In the other hand, Acrylates/Polytrimethylsiloxymethacrylate Copolymer at higher levels performs better long term, and worse short term. Pictures of the films after the 25th rub-off cycles are illustrated in Figure 9.

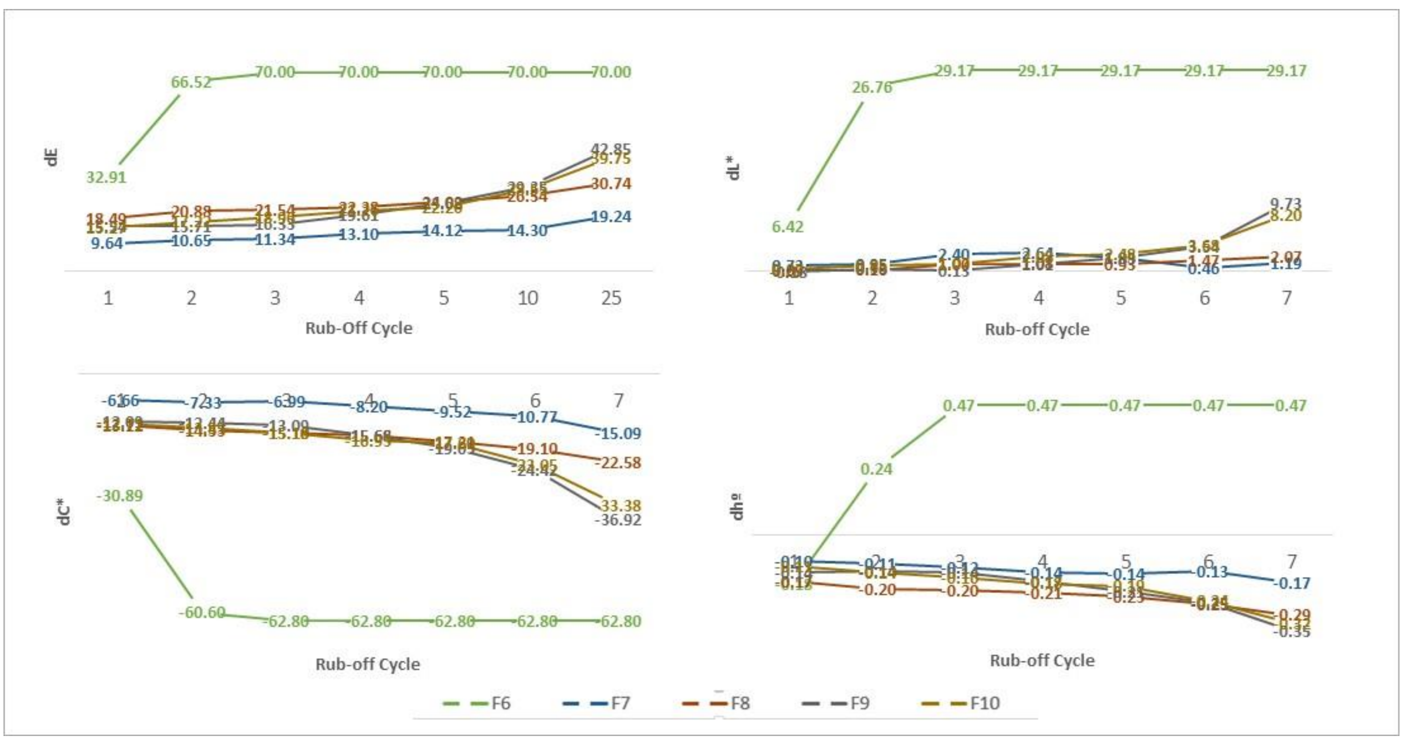

Figure 8. dE, dL*, dC* and dhº for each colorimetric reading for Formulations F6 to F10 with olive oil*

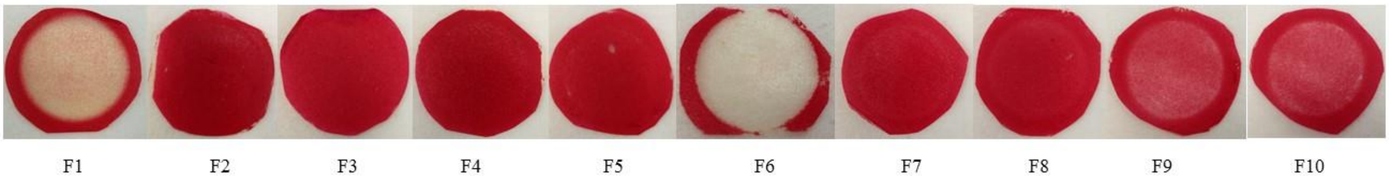

Figure 9. Pictures of the films on Vitro-Skin® after the 25th rub-off cycle (olive oil)

3.2. Wash-Off Resistance

In this study, formulations were evaluated in groups of 3 on subjects' forearms, as detailed in section 2.2.4. The objective was to evaluate the impact of film formers in wash-off resistance, as well as the dose-dependency effect. Once again, formulations were divided in 2 groups: the first one did not contain C30-45 Alkyldimethylsilyl Polypropylsilsesquioxane, and the second one contained it.

Statistical significance was analyzed based on Friedman Test and Wilcoxon Signed Rank Test to validate differences.

3.2.1. Group 1 – without C30-45 Alkyldimethylsilyl Polypropyl silsesquioxane

3.2.1.1. Sub-group 1: formulations F1, F2 and F4

Individual scores from each panelist, means and standard deviations are reported in Table 4. A picture of one of the subjects' forearms after the 5th wash is reported in Figure 10.

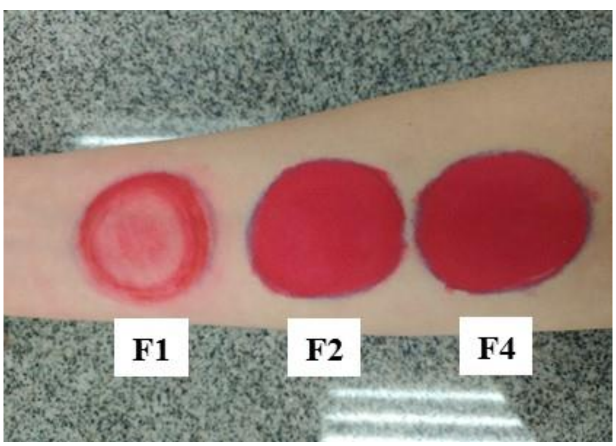

Figure 10. Individual's forearm illustrating the test sites after the 5th wash cycle (F1, F2, F4).

The data shows a significant difference in color intensity and homogeneity between formulations F1-F2, and between formulations F1-F4 ($p<0.001$). However, the panelists did not perceive a significant difference between formulations F2-F4, thus not validating a dose-dependency effect for Acrylates Copolymer.

Table 4. Individual scores per panelist for wash-off resistance for sub-group 1 (F1, F2, F4).

Subject	Panelist	Formulations		
		F1	F2	F4
S1	P1	1	3	2
	P2	1	2	3
	P3	1	2	3
	P4	1	3	2
	P5	1	2	3
	P6	1	3	2
	P7	1	2	3
	P8	1	2	3
	P9	2	3	2
	P10	1	2	3
S2	P1	1	2	3
	P2	1	2	3
	P3	1	3	2
	P4	1	2	3
	P5	1	2	3
	P6	1	3	2
	P7	1	3	2
	P8	1	3	2
	P9	1	3	2
Mean		1.05	2.47	2.53
SD		0.23	0.51	0.51

3.2.1.2. Sub-group 2: formulations F1, F3 and F5

Individual scores from each panelist, means and standard deviations are reported in Table 5. A picture of one of the subjects' forearms after the 5th wash is reported in Figure 11.

Liquid lipsticks with silicone or organic film formers performed significantly better than placebo (F1) after 5 wash cycles ($p<0.001$).

Comparing formulations F3 and F5, the later one was perceived by panelists as being significantly different ($p<0.001$), with a more vivid and intense red color. There is a dose-dependency indicating that higher levels of Acrylates/ Polytrimethylsiloxymethacrylate Copolymer lead to better wash-off resistance of the liquid lipstick formulation.

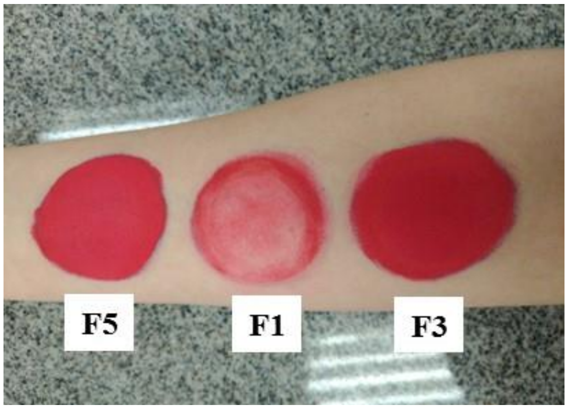

Figure 11. Individual's forearm illustrating the test sites after the 5th wash cycle (F1, F3, F5)

Table 5. Individual scores per panelist for wash-off resistance sub-group 1 (F1, F3, F5).

Subject	Panelist	Formulations		
		F1	F3	F5
S1	P1	1	3	2
	P2	1	3	2
	P3	1	2	3
	P4	1	3	2
	P5	1	3	2
	P6	1	3	2
	P7	1	3	2
	P8	1	3	2
	P9	1	2	3
	P10	1	3	2
S2	P1	1	3	2
	P2	1	3	2
	P3	1	3	2
	P4	1	3	2
	P5	1	3	2
	P6	1	3	3
	P7	1	2	2
	P8	1	3	2
	P9	1	2	3
Mean		1.00	2.79	2.21
SD		0.00	0.42	0.42

3.2.2. Group 2 – with C30-45 Alkyldimethylsilyl Polypropyl silsesquioxane

3.2.2.1. Sub-group 1: formulations F6, F7 and F9

Individual scores from each panelist, means and standard deviations are reported in Table 6, and picture of one of the subjects' forearms after the 5th wash is reported in Figure 12.

As opposed to the results obtained for formulations without the alkyl-modified Polypropylsilsesquioxane, there is a dose-dependency effect observed for Acrylates Copolymer. Panelists significantly ($p<.001$) preferred the film containing 15% (F9) compared to the one containing 5% (F7). Both performed significantly ($p<.001$) better than F6.

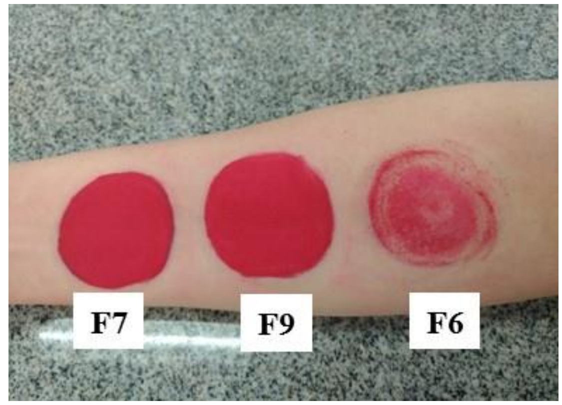

Figure 12. Individual's forearm illustrating the test sites after the 5th wash cycle (F6, F7, F9)

Table 6. Individual scores per panelist for wash-off resistance sub-group 1 (F6, F7, F9).

Subject	Panelist	Formulations		
		F6	F7	F9
S1	P1	1	3	2
	P2	1	3	2
	P3	1	3	2
	P4	1	3	2
	P5	1	3	2
	P6	1	3	2
	P7	1	3	2
	P8	1	3	2
	P9	1	3	2
	P10	1	3	2
S2	P1	1	3	2
	P2	1	3	2
	P3	1	3	2
	P4	1	3	2
	P5	1	3	2
	P6	1	3	2
	P7	1	2	3
	P8	1	3	2
	P9	1	3	2
Mean		1.00	2.95	2.05
SD		0.00	0.23	0.23

3.2.2.2. Sub-group 2: formulations F6, F8 and F10

Individual scores from each panelist, means and standard deviations are reported in Table 7, and picture of one of the subjects' forearms after the 5th wash is reported in Figure 13.

Performance and significance relationships among treatments are the same as observed for Acrylates/ Polytrimethylsiloxymethacrylate Copolymer in Group 1 – both formulations with film formers performed better than placebo (F6) ($p<.05$), and the level of 15% in the internal phase provided the best wash-off resistance. Red color is more vivid and intense compared with 15% to 5% concentration ($p<0.05$).

Table 7. Individual scores per panelist for wash-off resistance sub-group 2 (F6, F8, F10).

Subject	Panelist	Formulations		
		F6	F8	F10
S1	P1	1	3	2
	P2	1	3	2
	P3	1	3	2
	P4	1	3	2
	P5	1	3	2
	P6	1	3	2
	P7	1	3	2
	P8	1	3	2
	P9	1	3	2
	P10	1	3	2
S2	P1	1	3	2
	P2	1	3	2
	P3	1	2	3
	P4	1	3	2
	P5	1	3	2
	P6	1	3	2
	P7	1	2	3
	P8	1	3	2
	P9	1	3	2
Mean		1.00	2.89	2.11
SD		0.00	0.32	0.32

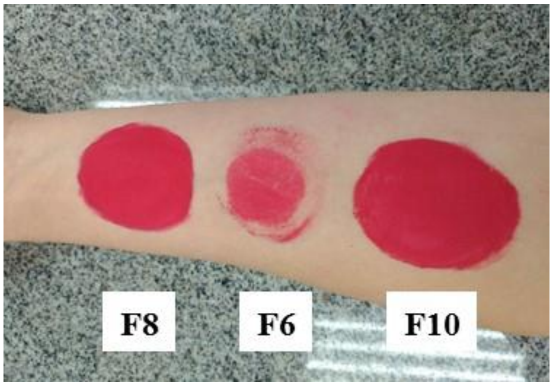

Figure 13. Individual's forearm illustrating the test sites after the 5th wash cycle (F6, F8, F10)

3.3. Film Flexibility

Lip products must be as comfortable as possible to consumers, as this is an area with frequent and extreme movements during the whole day. Thinking about long lasting, film former polymers included in the formulations must be flexible enough to provide such comfort, and the flexibility was assessed in this study applying the methodology described in section 2.2.5.

Figure 14 contains pictures of the latex-made elastic bands covered with 50 um films, from F1 to F10.

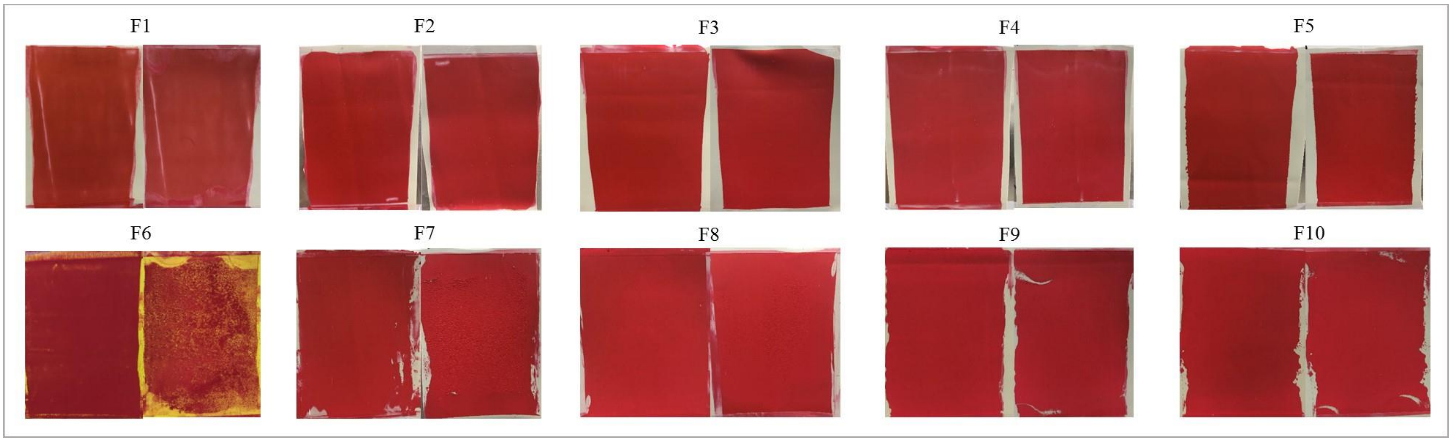

Figure 14. Pictures of latex-made elastic bands with formulations F1 to F10 applied on top of it, before the 200% stretch (left) and after the stretch (right)

Left hand pictures of each pair represent the film before the 200% stretch, and the right side ones represent the film pulled back after the stretch. The film was then assessed visually looking for cracks, fractures or discontinuities coming from the mechanical action.

Formulations F1 to F5, which did not contain C30-45 Alkyldimethylsilyl Polypropylsilsesquioxane in the composition, did not show any sign of damage to the films. Both film formers added to the water phase performed as well as the placebo (formulation F1), and there is no significant dose-dependency effect.

However, when only C30-45 Alkyldimethylsilyl Polypropylsilsesquioxane was added to the continuous phase (Formulation F6), a very crackly and powdery film was obtained after the stretch, compromising completely its adhesion to the elastic band.

Both Acrylates Copolymer and Acrylates/ Polytrimethylsiloxymethacrylate Copolymer improved significantly the resistance to stretch when added to the formulation at 5% (F9, F10), especially the later one. At 15% (F7, F8) performance was still much better than F1, but not as good as F9 and F10.

3.4. Contact Angle

The objective of this technique was to study the impact of the proposed formulations in the contact angles of the films with water after the 25th rub-off cycle. Vitro-Skin® is naturally a very hydrophobic substrate, with contact angle measured as 115.7º ± 1.2.

Results are reported in Table 7 and example pictures obtained with the optical tensiometer are illustrated in Figure15.

Substrates coated with formulation F1 presented a significantly (p<.05) lower contact angle after the insult cycles, with mean 107.18º, as a result of the abrasion itself, or due to the absence of film formers in the composition. In the other hand, substrates coated with formulations F2 to F5 presented significantly (p<.05) higher contact angles, closer to Vitro-Skin® itself. Increasing Acrylates Copolymer from 5% to 15% significantly increased contact angles. For Acrylates/ Polytrimethylsiloxymethacrylate Copolymer, dose-dependancy presented significance level of .10<p<.05, trending to better performance at 15%. For formulations with C30-45 Alkyldimethylsilyl Polypropylsilsesquioxane in the composition, there was no significant difference among all formulations (F6 to F10).

Table 7. Contact angles between water and Vitro-Skin® coated with the formulations F1 to F10

	Contact Angle (º)				
Replicate	F1	F2	F3	F4	F5
1	113.49	116.94	116.22	123.93	113.09
2	109.84	113.94	117.6	121.07	114.55
3	99.32	119.12	127.07	116.11	123.12
4	100.27	116.83	115.21	120.06	114.29
5	112.98	112.29	113.82	117.47	115.91
Mean	107.18	115.82	117.98	119.73	116.19
SD	6.89	2.70	5.26	3.07	4.00
Replicate	F6	F7	F8	F9	F10
1	116.94	112.74	112.51	112.68	115.33
2	121.18	111.89	115.03	119.21	112.26
3	112.92	119.87	110.69	117.33	118.11
4	117.8	114.09	115.05	113.94	113.69
5	114.9	109.72	119.04	124.71	116.93
Mean	116.75	113.66	114.46	117.57	115.26
SD	3.12	3.82	3.15	4.76	2.37

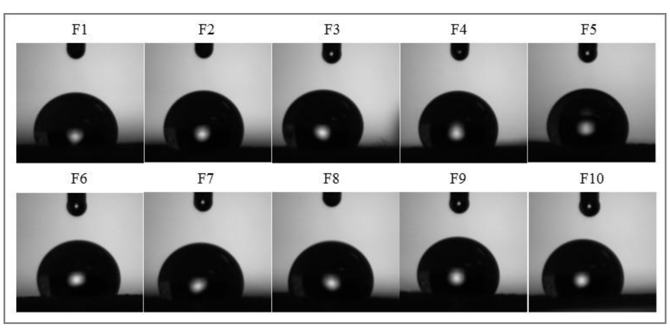

Figure 15. Example images of contact angle with water

3.5. Impact of organic pigments in the rub-off resistance:

The intense red color observed on the felts after the rub-off cycles leads to the hypothesis that organic pigments are most likely to be the ones coming off the film.

To investigate this hypothesis, formulations F1 and F3 were re-formulated removing Red 7 Lake from the composition and decreasing dramatically the concentration of Red 7, generating formulations F11 and F12. The total amount of pigments (inorganics + organics) was kept constant. The new compositions are quantitatively described in Table 8.

Table 8. *Quantitative composition of the liquid lipstick formulations F11 and F12*

INCI Name	Formulation	
PHASE A	F11	F12
INCI Name		
Disiloxane	4.0	4.0
Red 7	0.4	0.4
Red Iron Oxides	1.0	1.0
Titanium Dioxide	2.6	2.6
PHASE B		
INCI Name		
Trimethylsiloxysilicate/ Dimethiconol Crosspolymer (and) Isododecane	-	20.0
C30-45 Alkyldimethylsilyl Polypropylsilsesquioxane	-	-
Diimethicone 350 cS	2.0	2.0
PEG/PPG-18/18 Dimethicone (and) Cyclopentasiloxane	9.0	9.0
Diimethicone 1 cS	20.0	-
PHASE C		
INCI Name		
Acrylates Copolymer	-	15.0
Acrylates/ Polytrimethylsiloxymethacrylate Copolymer	-	-
Water	61.0	46.0

Films from formulations F11 and F12 were prepared on Vitro-Skin®, as described in section 2.2.1, and the rub-off resistance was assessed based on the methodology described in section 2.2.3, both in dry and oily conditions.

Pictures of the Vitro-Skin® films after the 25th rub-off cycle are illustrated in Figure 16, and colorimetric data is given in Table 9 and Figure 17, both dry and in presence of oil.

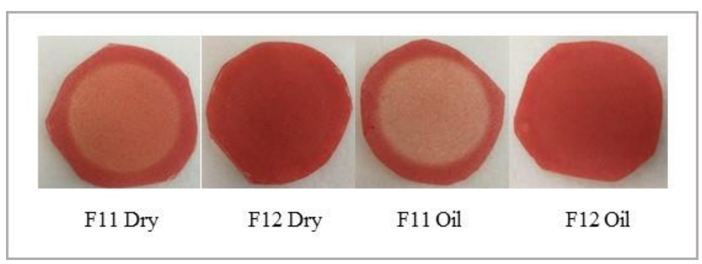

Figure 16. Pictures of the films with F11 and F12 on Vitro-Skin® after the 25th rub-off cycle (dry and olive oil)

The lower concentration of organic pigment changed the original color, as absolutely predicted, but also reduced dramatically color variations from rub-off in all conditions, even for the formulation without film former (F11), validating the hypothesis. Comparing both to understand the impact of the film formers, it is possible to conclude that in dry conditions, films made with F12 presented significantly ($p<.05$) lower dhº from cycle 4 to 25. Color after the last insult was more vivid and closer to the original for the formulation with film formers ($p<.05$). When olive oil was added to the test, differences between F11 and F12 were even more significant – parameters dE^*, dL^* and dC^* were all significantly ($p<.05$) lower for formulation F12 compared to F11, for all colorimetric readings.

It is possible to conclude that organic pigments, specifically Red 7 and Red 7 Lake, play an important role in the rub-off resistance. The higher its concentration, the higher will be the color variation.

Table 9. Colorimetric data for formulations F11 and F12 in dry and oily conditions

	Deltas per color coordinate			Deltas per color parameter			Deltas per color coordinate			Deltas per color parameter		
	Formulation / Design Point											
	F11 (dry)						F12 (dry)					
Insult Cycle	dL*	da*	db*	dE	dhº	dC*	dL*	da*	db*	dE	dhº	dC*
1	0.30	-1.30	-0.65	1.48	0.00	-1.44	0.52	-0.99	-1.66	2.00	-0.02	-1.69
2	1.05	-1.86	-1.29	2.49	0.00	-2.25	0.73	-1.11	-2.19	2.56	-0.03	-2.05
3	1.54	-2.92	-1.32	3.55	0.01	-3.18	1.05	-1.46	-2.55	3.12	-0.03	-2.53
4	1.99	-3.92	-1.46	4.63	0.02	-4.10	1.34	-1.99	-2.97	3.81	-0.03	-3.20
5	2.25	-4.29	-1.55	5.08	0.02	-4.46	1.30	-2.05	-3.09	3.92	-0.04	-3.31
10	2.81	-5.88	-1.57	6.70	0.04	-5.80	1.74	-2.71	-4.09	5.20	-0.05	-4.37
25	4.77	-9.64	-2.64	11.07	0.07	-9.52	1.89	-3.02	-4.12	5.44	-0.05	-4.65
	F11 (olive oil)						F12 (olive oil)					
Insult Cycle	dL*	da*	db*	dE	dhº	dC*	dL*	da*	db*	dE	dhº	dC*
1	0.97	-0.79	-2.32	2.63	-0.04	-1.88	0.87	-1.05	-1.21	1.82	-0.01	-1.53
2	1.52	-2.46	-2.67	3.93	-0.02	-3.49	0.98	-1.23	-1.46	2.14	-0.01	-1.81
3	2.41	-4.28	-2.97	5.74	-0.01	-5.20	1.17	-1.81	-1.85	2.83	-0.01	-2.50
4	3.48	-6.07	-3.38	7.77	0.01	-6.93	1.20	-2.01	-2.00	3.08	-0.01	-2.75
5	3.95	-7.17	-3.92	9.07	0.01	-8.15	1.26	-2.20	-2.07	3.27	-0.01	-2.95
10	6.08	-11.30	-5.32	13.88	0.05	-12.35	1.52	-2.47	-2.20	3.64	-0.01	-3.25
25	11.10	-18.95	-7.67	23.26	0.14	-19.86	1.84	-3.35	-2.36	4.48	-0.01	-4.08

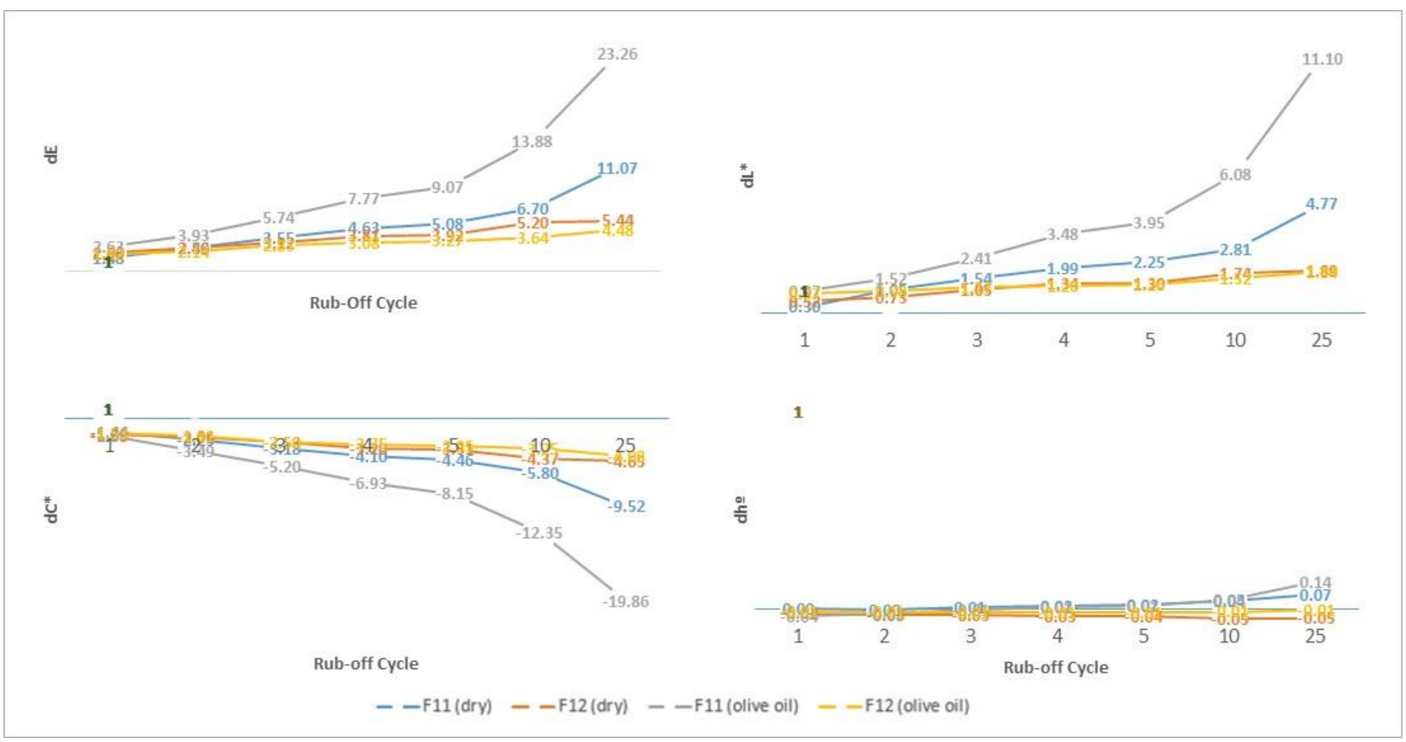

Figure 17. dE^*, dL^*(lightness), dC^* and dhº for each colorimetric reading for Formulations F11 and F12 (dry and olive oil)

4. Conclusions

The addition of an emulsion-polymerized acrylic or silicone-acrylate polymer in the water phase of a W/Si emulsion creates a multiple emulsion system, containing film formers in both internal and external phases, as observed by microscopy techniques. Once pigmented with organic and inorganic pigments, this system represents a novel possibility as a liquid lipstick formulation to the cosmetic market.

Outstanding rub-off resistance was validated using instrumental techniques, and it was observed that systems free of Alkyl-modified T-propyl silicone resin are more efficient to inhibit color loss in presence or absence of olive oil in the proposed chassis. Different film formers at different levels provided different performance in terms of the colorimetric parameters evaluated, as adequately discussed in each section.

The presence of film formers drastically improved resistance to wash-off and there is a significant dose-dependency effect, where higher levels of film formers led to higher resistance.

For the flexibility of the film, all formulations free from Alkyl-modified T-propyl silicone resin, including F1 which is the placebo, has shown total flexibility and no signs of damage to the film after stretching it. In the other hand, formulation with the waxy resin and free of film formers (F6) was excessively cracky and lost adherence to the latex-made elastic band. Addition of 5% of film formers to the internal phase and the silicone film former to the external phase improved significantly this behavior.

Formulators looking for very low variations in color should consider working with the lowest level as possible of organic pigments, like Red 7, for example. Data shown in this study proves that it plays a significant role on color loss. The lower its concentration, the better the performance will be.

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