

A general formulation strategy toward long-wear color cosmetics with sebum resistance

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Abstract

We propose a “Soft” + “Hard” formulation strategy for long-wear and sebum/oil-resistant makeup. The ratios of “Hard” nonvolatile components (e.g., resins, particulates, and solid emulsifiers) and compatible “Soft” nonvolatile components (e.g., nonvolatile oils and liquid emulsifiers) may be carefully adjusted to create desired long-wear performance and sensory. For a given formulation chassis, we recommend studying compatibility and viscoelastic profiles of blends made of “Hard” polymeric resins and “Soft” structuring polymers to gain fundamental understanding of the polymer matrix for pigment adhesion. Enhanced oil/sebum resistance may be achieved, where there is good compatibility among the “Soft” and “Hard” polymeric components and where there is considerable immiscibility between oil/sebum and each nonvolatile component. Our strategy may help promote cosmetic formulation development based on rational design and understanding interactions among components, develop novel long-wear formulation chassis, and properly evaluate emerging new technologies.

INTRODUCTION

Since the early 1990s, the product category of long-lasting facial makeup has grown from just a few niche lines to cover mainstream mass-market offerings and many premier brands. With the selfie craze, high-definition cameras, and multimedia displays, consumers nowadays want to look flawless on social media and in person throughout the day. As a result, our industry has been investing a considerable amount of resources for technical breakthroughs at this frontier (1,2). Recent formulation advances have transformed the perception of these products from drying/tacky and paint-like sensory and appearance to that of regular makeup (1–3).

Sebum is recognized as a major cause for makeup deterioration over time. Secreted from human sebaceous glands, sebum is mainly made of triglyceride oils, fatty acids, wax, and squalene. Sebum may not only lead to uneven facial makeup application, but also excessive plasticization of cosmetic films, wetting of pigments, and weakened makeup adhesion to the skin. This can result in oily appearance, makeup shade change, and easier transfer.

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While there is a great amount of formulation knowledge on how to achieve water resistance and rub-off resistance, our industry has fewer technical advances in oil/sebum resistance (1–4). Previously, we developed a set of simple, semiquantitative, yet highly relevant nonhuman test methods for understanding color cosmetics' oil resistance. Those test methods not only enabled us to make comprehensive assessments of makeup formulations' lasting performance when exposed to oil (grease or sebum), but also helped reveal each ingredient's subtle impact to a finish formulation's oil resistance efficacy (4). Based on our learnings, we propose here a “Soft” + “Hard” formulation strategy toward long wear and sebum/oil resistance. For illustration, we apply here the “Soft” + “Hard” formulation strategy to silicone-based makeup formulations.

MATERIALS AND METHODS

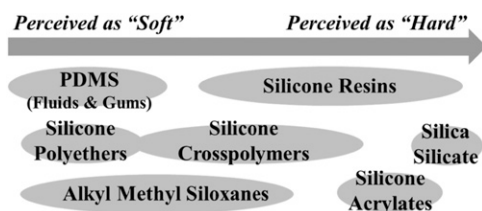
“SOFT” + “HARD” FORMULATION STRATEGY FOR SILICONE-BASED FORMULATIONS

To apply the “Soft” + “Hard” strategy to silicone-based formulation chassis, we created a conceptual map of silicone materials' “hardness” and charted several types of silicone materials, including polydimethylsiloxanes, silicone resins, silicone polyethers (SPEs), silicone crosspolymers, alkylmethylsiloxanes, silicone acrylates, and silica silicate (Scheme 1). The perceived “hardness” is largely based on materials' glass transition temperature or softening temperature. For instance, low-viscosity silicone fluids would be considered very “Soft,” while materials like commercial MQ resins with a glass transition temperature over 200°C would be at the very “Hard” end of the conceptual map.

MATERIALS

An important type of “Soft” components we investigated are SPE fluids used for creating W/Si or W/O formulations. With typical Tg values well below -100°C, most silicone emulsifiers were placed on the “soft” end of the conceptual “hardness” map. SPEs in this study include a block copolymer with an INCI name of “Bis-Isobutyl PEG/PPG-10/7/ Dimethicone Copolymer,” two random copolymers with INCI names of “PEG/PPG-19/19 Dimethicone” and “Lauryl PEG-10 Tris(trimethylsiloxy)silylethyl Dimethicone.”

A silicone acrylate (SiAc) copolymer (INCI name: “Acrylates/Polytrimethylsiloxymethacrylate Copolymer”) was selected to illustrate a type of “Hard” silicone components. The silicone acrylate technology is currently used for long-lasting lip products and durable liquid foundations with comfortable wear. The particular silicone acrylate (Acrylates/Polytrimethylsiloxymethacrylate Copolymer) referred to throughout this study is a brittle



Scheme 1. A conceptual map of silicone materials' “hardness,” charting several types of silicone materials.

solid at room temperature and has a distinct melting transition with onset of $\sim 75^{\circ}\text{C}$ and peak at $\sim 90^{\circ}\text{C}$ based on differential scanning calorimetry (DSC) study. Blends of silicone acrylate and SPE at various ratios were prepared by mixing and evaporating volatile solvent. We prepared and tested two sets of simple makeup prototypes to further illustrate our “Soft” + “Hard” strategy for achieving sebum resistance. In our study, artificial sebum, a mixture of organic oils, was used (4).

METHODS AND RESULTS

Visual assessment and cross-section transmission electron microscopy (TEM) were performed to help understand compatibility between and silicone acrylate and different SPEs. After removing volatile carrier fluids, silicone acrylate and “PEG/PPG-19/19 Dimethicone” blended at 7:3 ratio formed an optically transparent plastic material. The compatibility between silicone acrylate and “PEG/ PPG-19/19 Dimethicone” in the blend was further suggested by cross-section TEM (Figure 1A). No distinct phase domain was observed at 5-nm scale and above. On the contrary, silicone acrylate and “Lauryl PEG-10 Tris(trimethylsiloxy)silylethyl Dimethicone” blended at a 7:3 ratio formed an opaque solid. Distinct phase domains, sized from several nanometers to over 100 nm, were observed under cross-section TEM (Figure 1B). All indicate incompatibility between the two materials.

Viscoelastic properties of compatible silicone acrylate/SPE blends were further investigated. Shown in Figure 2A are temperature sweep measurements of elastic modulus (G') of silicone acrylate (SiAc) and “PEG/PPG-19/19 Dimethicone” (an SPE) blends at different ratios. Figure 2B shows damping factor of related blends. G' level of SiAc/SPE at a 7:3 ratio was lower than that of neat silicone acrylate at the entire temperature range tested. Also, the addition of SPE shifted the damping factor peak to a lower temperature, which is indicative that thermal transition occurred at a lower temperature. At room temperature, the blend of SiAc/SPE at a 7:3 ratio showed a significantly higher dumping factor (more “viscous”) than neat silicone acrylate. Clearly, more pronounced effects were observed from the SiAc/SPE (6:4) blend. These systematic changes signify that this particular SPE worked as an effective plasticizer in the blends. DSC study (data not shown)

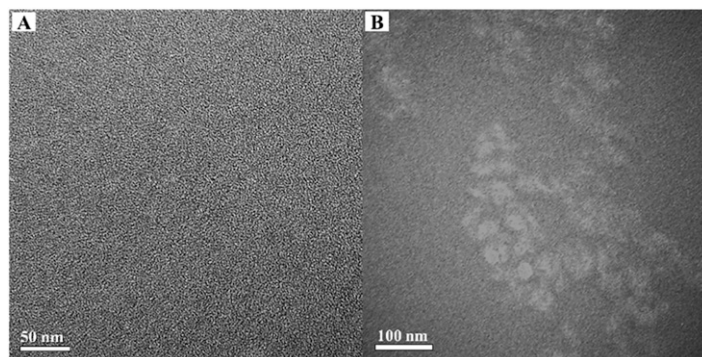


Figure 1. Cross-section TEM images of blends. (A) A blend of silicone acrylate and “PEG/PPG-19/19 Dimethicone” at 7:3 ratio. (B) A blend of silicone acrylate and “Lauryl PEG-10 Tris(trimethylsiloxy)silylethyl Dimethicone” at 7:3 ratio.

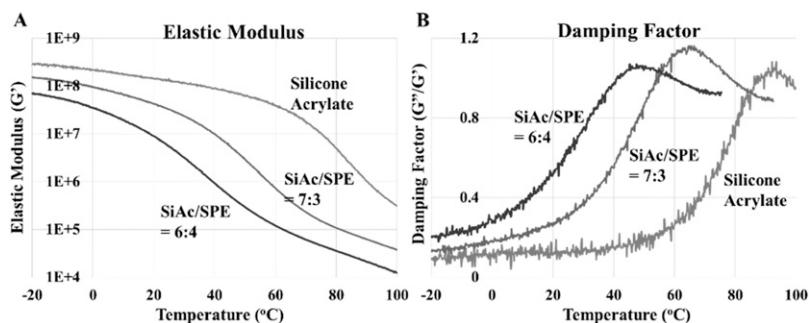


Figure 2. Viscoelastic profile of “Soft” + “Hard” blends. (A) Temperature sweep elastic modulus measurement on several blends of silicone acrylate and SPE with different ratios. (B) Damping factors of related blends.

further confirmed the SPE’s plasticization effect. For the SiAc/SPE (7:3) blend, DSC indicates a melting transition with onset of 43°C and peak at 68°C, broader and lower than that of neat silicone acrylate.

Film properties of compatible blends of “Hard” silicone acrylate and “Soft” SPE may be tuned by the ratio of “Hard” to “Soft.” Figure 3 shows film hardness and tack of silicone acrylate and “Bis-Isobutyl PEG/PPG-10/7 Dimethicone Copolymer” blends at different ratios. Film hardness was studied by pendulum film hardness test, where a higher count is correlated to a harder film. Film tackiness was measured by texture analyzer. A higher maximum tack force is generally correlated to a more tacky film. Figure 3A suggests a correlation between softer film and higher fraction of “Soft” SPE in the blends. Within the “Soft” to “Hard” ratio studied, film becomes tackier with increasing the fraction of SPE (Figure 3B).

Cracking and flexibility of color cosmetic films containing silicone acrylate/SPE blends were further investigated. For a formulation using silicone acrylate as the sole polymeric nonvolatile, dried film exhibited visible cracks (data not shown). On the other hand, the formulation with a combination of nonvolatile silicone acrylate and “Bis-Isobutyl PEG/PPG-10/7/Dimethicone Copolymer” (an SPE) at 7:3 wt ratio yielded a dry film exhibiting no observable cracks (data not shown). Stretching test was conducted by drying these prototype formulations on a flexible rubber band. After the rubber band was elongated, films were assessed for cracking. Figure 4 showed that films with an adequate fraction of

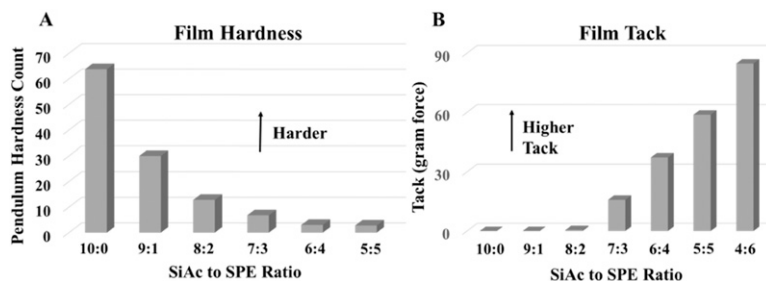


Figure 3. Film hardness and tack. (A) Pendulum film hardness measurement on blends of silicone acrylate (“Hard”) and SPE (“Soft”) at different “Hard” to “Soft” ratios. (B) Related films’ maximum tack force measured by texture analyzer.

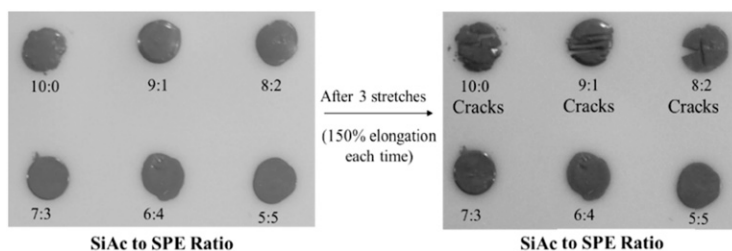


Figure 4. Stretching test showing film flexibility. Images were taken before and after stretching test, showing cracking of films made with silicone acrylate and SPE blends at different ratios.

SPE did not crack under the test condition, suggesting more flexible than films' based on lower fractions of SPE.

Sebum/oil abrasion test was conducted to understand a makeup film's rub-off resistance in the presence of sebum (3). Figure 5A shows compositions of anhydrous makeup prototypes containing blends of silicone acrylate and SPE at different "Hard" to "Soft" ratios. After dried on collagen, cosmetic films were subjected to abrasion test. Figure 5B shows a digital camera image of both abrasion cloths and cosmetic films after given 100 rubs. The top row shows, in duplicate, abrasion cloth and cosmetic films after abrasion without artificial sebum treatment. The bottom row shows, in duplicate, abrasion cloths and cosmetic films after abrasion with sebum pretreatment. Figure 5C shows abrasion clothes' color increase after 100 rubs as measured by colorimeter. Figure 5D shows makeup films' color loss as measured by colorimeter. With the understanding that sebum is a culprit leading to poor wear performance of color cosmetics, abrasion testing of the substrate pretreated with artificial sebum oil confirmed more color transfer than without sebum. Importantly, we found ideal "Hard" to "Soft" ratios may exist for improved performance. When higher levels of the SPE (soft component) were incorporated, considerable rub-off and transfer were observed, especially in the presence of sebum. On the other end, at very

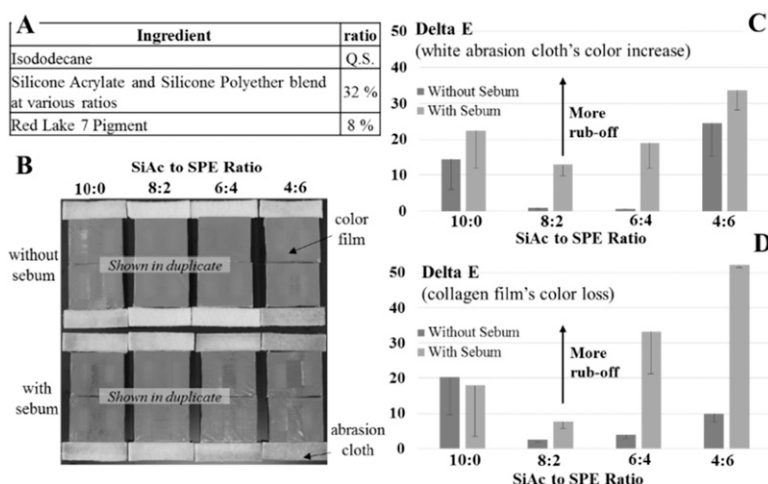


Figure 5. Sebum abrasion test. (A) Anhydrous makeup prototypes containing a silicone acrylate and a SPE at different ratios. (B) A digital camera image of both abrasion cloths and cosmetic films (on collagen) after given 100 rubs, with or without artificial sebum pretreatment. (C) Abrasion clothes' color increase after 100 rubs. (D) Makeup films' color loss after 100 rubs.

high ratios of silicone acrylate (hard) to SPE (soft), shown here 10:0 (all silicone acrylate), color films are brittle and can be chipped off through abrasions.

Contact transfer test was conducted to understand the extent of pigment transfer from color cosmetic films to white substrates upon contact (3). Shown in Figure 6 are four water-in-oil liquid foundation prototypes with the same amount of “Hard” silicone acrylate and the same “Hard” to “Soft” ratio (3:1), varying only silicone emulsifiers (all fluids). Emulsifiers A and B both showed incompatibility with silicone acrylate and decent miscibility with artificial sebum oil (data not shown). Emulsifiers C and D both showed good compatibility with the silicone acrylate; however, Emulsifier D showed the highest degree of immiscibility with artificial sebum oil. For the test, liquid foundations were coated and dried on nylon filter papers. In some cases, cosmetic films dried on filter papers were impregnated with artificial sebum prior to the test. Figure 6B shows a digital camera image taken after contact transfer tests with both cosmetic films and pigment traces transferred. As shown in the top row, without sebum, there is no observable pigment transfer for all four foundation films. However, shown in the bottom row of Figure 6B, with a sebum pretreatment, four formulations showed different degrees of pigment transfer, which were documented by colorimeter measurement (see Figure 6C). Emulsifier D, having both good compatibility with the silicone acrylate and the highest degree of immiscibility with artificial sebum oil, led to formulation with best sebum resistance.

DISCUSSION

While there are different technical approaches toward long-lasting performance, today’s prevailing technologies in color cosmetics are based on using various polymeric “film

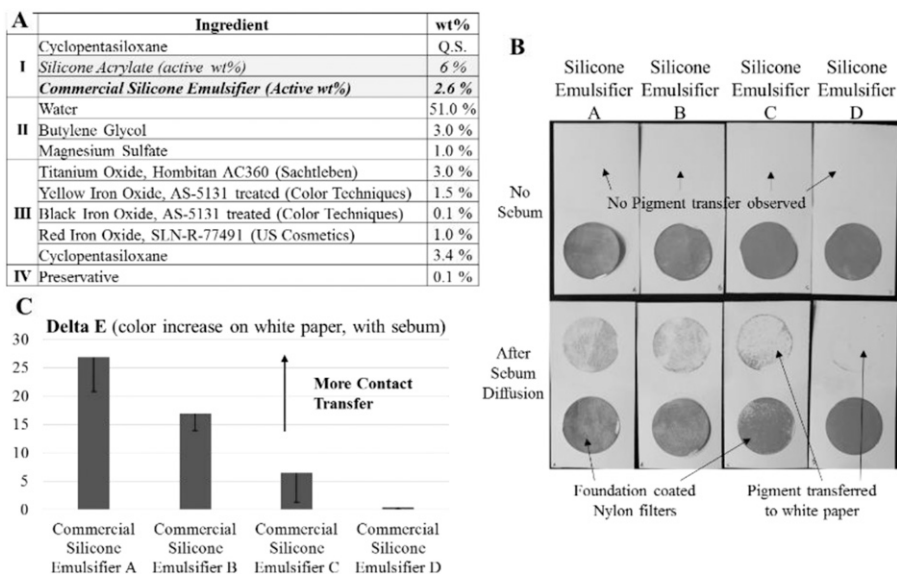


Figure 6. Contact transfer test. (A) Compositions of water-in-silicone liquid foundations, varying only silicone emulsifiers. (B) A digital camera image taken after contact transfer tests, having both cosmetic films (on filter paper) and pigment traces transferred to white substrates. (C) White substrates’ color increase after contact transfer test (with sebum impregnation, the bottom row in B).

formers.” Virtually, every color cosmetic currently on the market with “long lasting” claims contains at least one organic or silicone “film former,” such as PVP-type copolymers, acrylate-type copolymers, polyethylene, silicone MQ resins, silicone resin waxes, and silicone acrylates (1–2). Despite all the developments, to date, no general formulation guidelines have been clearly articulated to achieve the benefits of long wear. Regarding silicone-based technologies, over the past decades, researchers from Revlon, Procter & Gamble, L’Oreal, Estee Lauder, Shiseido, and others adopted a variety of silicone materials for long-wear color cosmetics, including silicone gums, silicone waxes, silicone resins, silicone polyamide, and silicone pressure-sensitive adhesives (5–9). However, other than a vague concept of “MQ + plasticizer,” fundamental understandings and formulation knowledge remain in the minds of very few skilled cosmetic chemists (1–3).

Our “Soft” + “Hard” formulation strategy focuses on studying interactions among non-volatile components, especially polymeric nonvolatiles, in a given formulation chassis. Our definition of “Hard” components includes a number of materials such as MQ resins, acrylates, resin waxes, silica silylates, and different tackifiers. “Soft” components include the other ingredients typically found in formulations, e.g., liquid emulsifiers, rheology modifiers, and shine-enhancing fluids. Understanding the intrinsic material properties of “Soft” + “Hard” nonvolatile blends may enable us to better interpret/predict relevant cosmetic films’ long-wear properties.

For instance, for prototypes in Figures 5A and 6A, upon application on skin and evaporation of volatile fluids, we hypothesized that the combination of SPE and silicone acrylate are the main components of a polymer matrix that is responsible for adhering pigments onto the skin. The particular silicone acrylate studied is a hard and relatively brittle material in its neat form. Our results suggest that the silicone acrylate is able to form compatible blends with several SPEs, with good miscibility at polymer chain segment level. Rheology and DSC studies show that a “soft” SPE (compatible with silicone acrylate) is able to lower the blends’ glass transition temperature, making it an effective plasticizer of silicone acrylate. Conversely, the silicone acrylate is able to raise the glass transition temperature, making silicone acrylate an effective “tackifier” for compatible SPE. In a sense, consistent to our film properties and flexibility studies, the SPE may effectively mobilize the “hard” acrylate segments, increasing flexibility to the film. Likewise, the “hard” acrylate segment can effectively “toughen” the “soft” SPE, introducing cohesion strength to the film. At right ratios, these combined polymeric nonvolatiles may form an optimized matrix to “glue” pigment particles on the skin. Insights around the intrinsic properties of a given pigment “glue” blend can be gained through its viscoelastic profile.

Consistently with the understanding that sebum negatively impacts long-wear performance of color cosmetics, our studies confirmed that *in vitro* testings with artificial sebum oil pretreatment lead to more color transfer than without sebum pretreatment. Perspiration and sebum may alter a blend of nonvolatiles’ pigment “gluing” efficacy. If sebum is miscible with nonvolatile components, it effectively reduces the “Hard” to “Soft” ratio, further plasticizes the blend of nonvolatiles, and results in a “softer” and more “fluidic” matrix on skin. This leads to weakened pigment binding to skin, easier removal upon rub-off, and more color transfer upon contact. On the other hand, if each component of a nonvolatile blend can be carefully selected with reduced sebum miscibility, the nonvolatile matrix formed for pigment binding may be less prone to sebum’s plasticization, thus may reduce the detrimental effects of sebum. Based on all our learnings, we developed a systematic formulation strategy for longer wear and sebum resistance benefits.

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