ONE-STEP LONG-LASTING COLOR/SHINE LIP GLOSS VIA LIQUID LIQUID PHASE SEPARATION

Huang, Tsang-Min[1]; Ebanks, Jody[1], Bui, Hy[1]; Li, Chunhua [1]; Roulier, Veronique[2]; Weinkauf, Ronni[1]; Lee, Yan[1]; Abed, Mira[1]; Gineston, Sylvie[2]; Servais-Dealet, Annabelle[2]; Singh, Malaya[1]

[1] L'Oréal Research & Innovation, Clark, United States
[1] L'Oréal Research & Innovation, Chevilly-Larue, France

*Tsang-Min Huang, 111 Terminal Ave, Clark, NJ 07066, 732 850 7736, tsangmin.huang@rd.loreal.com

Abstract

One-step long-wear color liquids or solid lipsticks are known not to provide a long-lasting gloss or shine. Incorporating glossy ingredients into a single step lipstick will disrupt the long wear efficiency. Thus, a separate topcoat is required to protect the color coat and provides shine and comfort. However, the shiny topcoat is usually not long-lasting and reapplication overtime is needed. Therefore, a true one-step long wear and lasting shine lipstick is a key need for consumers.

To achieve the one-step lipstick with long-lasting color and shine or comfort, a unique and unstable formulation containing two partially compatible phases or completely incompatible phases of silicone-silicone polymer dispersions was utilized. This unique architecture phase separates and re-organizes upon application, delivering an adhesive layer to the skin and an outermost shine and non-transfer layer.

In vitro assay evaluations of the wear and shine show excellent performance, and a good correlation between in vitro and in vivo results is observed for the product. The long-lasting wear of the product is well perceived by consumers and the shine is observed to last at least 4 hours during daily activities, including eating and drinking. This novel product addresses a key consumer need and delivers the performance of a two-step product in a single step application.

Introduction.

Many liquid lipsticks have been formulated to deliver long-lasting wear and shine in a single step application. Unfortunately, many of these products generally do not possess both good non-transfer and lastingness while simultaneously providing good comfort and good appearance (ie: long lasting shine). Oftentimes, ingredients incorporated to deliver acceptable long wear are more matte or become uncomfortable with time, and vice versa ingredients incorporated to deliver shine/comfort compromise the wear. Historically, to address this technical gap, two step products utilize a basecoat for wear and a topcoat to continually re-new the shine and improve the comfort [1].

Therefore, the desire to have a single-step long-wear and shine lipstick remains a challenge in color cosmetics due to the technical difficulty of balancing the adhesion/cohesion of the film-formers to the lip substrate. This adhesive/cohesive balance is paramount to have good transfer resistance without sacrificing the comfort/shine.

To deliver wear/comfort/shine in one-step application, scientists at L'Oreal have explored multiple pathways to create a single-step liquid or solid lipstick [2-13]. By using a phase separation concept, a one-of-kind silicone-silicone unstable dispersion has been developed to deliver these challenging requirements for a single-step lipstick [13]. The formulation contains two partially compatible phases or completely incompatible phases. Upon application and after solvent evaporation the product spontaneously forms a bilayer film structure to provide long lasting color, renewable/lasting shine and comfort.

Materials and Methods

Sample Preparation

A prototype formulation was prepared by mixing pigment and different silicone resins of various type/level organo-modification and molecular weight. The samples were at rest for 24 hours before any evaluation was performed. The morphology of the samples was examined under polarized optical microscope (Nikon ECLIPSE LV100N).

Performance Evaluation

In Vitro Wear Assay

A 25.4 μm wet thickness of prototype was coated on abrasion paper and allowed to sit on the benchtop for 24 hours to dry. One piece of ASTM tape was placed on the dried film, adhered with light finger pressure, and removed, by pulling back the film at a 180-degree angle. In another test, droplets of olive oil, artificial saliva, and acetic acid were placed on the dried films for 10 min and then were wiped off with cotton pads for 15 times each. Both the film quality and color transfer to the cotton pads were assessed for wear.

Arm Test

Several shades of the prototype formulation were painted onto the forearm area (1.5"x1.5" size) with a doe foot applicator. The samples were allowed to dry for 5 minutes before spraying with water and being wiped with a dry cloth. The procedure was also repeated using avocado oil instead of water. The wear of color was evaluated by checking the amount of product left on skin after wiping with the dry cloth.

Stretching Test

Prototype formulation and benchmark products were painted separately on pre-cut rubber bands and allowed to dry at ambient temperature for 2 hours. The rubber bands were stretched to twice its original length for 10 times. The film integrity of the product indicates the flexibility and cohesiveness of the film. The result of this test was used to predict whether the product would peel/flake during the wearing of the product.

Renewable shine

A wet film of 76.2 μm was coated on an abrasion paper and dried in a 37°C oven to simulate the lip environment. A cylinder weight of 70 grams was placed on top of the film for 10 seconds to disrupt the film surface. The film was then placed back into the 37°C chamber and sequential images were taken in 5 minutes increments to record the self-leveling behavior of the product surface.

Consumer Test

The prototype formulation was tested by consumers against a lip gloss benchmark product. The benchmark was selected as a single step/wear product using traditional wear technology found on the market. A panelist size of >150 individuals were evaluated over a 7-day time frame in a monadic test design. A questionnaire on performance was completed on day 7 of the test.

Results

Prototype Formula

Figure 1a visually shows that the prototype formulation is not stable and phase separates at rest over time. The color phase is settled down on the bottom and clear phase rises to the top. The morphology of the fresh sample is shown in the microscopic image (**Figure 1b**). Numerous discrete internal pigmented domains are dispersed within a clear and continuous phase. Compared to the internal phase, the external phase is more mobile, showing the different viscosity between the internal and external phases. The phase separation is driven by the key immiscibility between two silicone polymers as shown in **Figure 1c**.

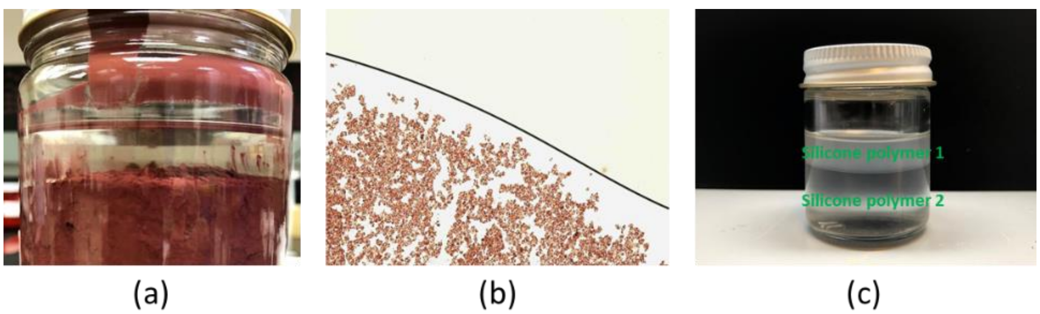

Figure 1. (a) Phase separation of at-rest prototype formula, (b) Microscopic image of fresh-made prototype formula, (c) Immiscibility between two silicone polymers.

Performance Evaluation

Renewable Shine

Figure 2 shows the film surface was disrupted and recovered after 5 and 20 minutes. As seen in the initial sample (**Fig. 2a**), the circular area was compromised by applied weight. The inset picture shows the weight surface is not pigmented and shows minimal transfer with a clear residue. This suggests that the pigmented dispersed phase settles on the substrate and the clear external phase rises to the surface. As the film was treated in a 37°C oven for 5 minutes (**Fig. 2b**), the disrupted surface became glossy again, showcasing the self-leveling behavior of the film surface. As the film continued to anneal in the oven, the pressed mark became lighter, and the shine of the film recovered.

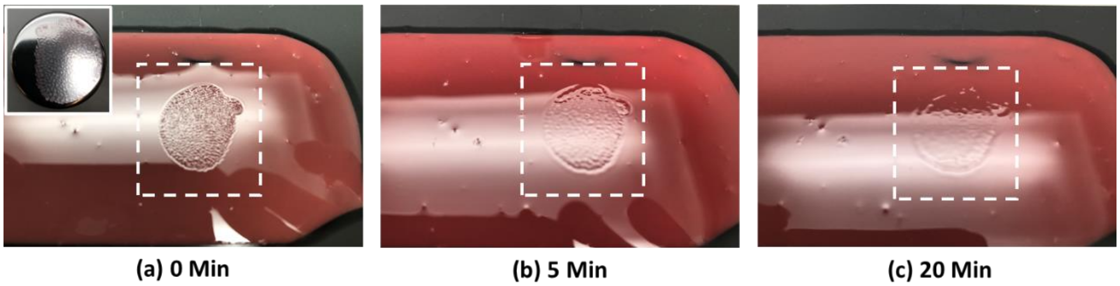

Figure 2. Self-healing shine of disrupted film at 37°C. (a) Initial, inset: residual on the weight surface after pressing, (b) 5 min, (c) 20 min

In Vitro Wear Assay Evaluation

Figure 3 shows the result from the wear assay evaluation of the film integrity after wiping was assessed for disruption of the film. The transfer of color to the cotton pads was assessed holistically to give an indication of the transfer proof nature of the film. As can be seen in **Figure 3**, the film was not visually disrupted after being exposure to olive oil, acetic acid or artificial saliva. Furthermore, there was minimal color transfer to the cotton pads following wiping. This result indicates a good wear performance and a transfer proof nature of the formulation in the presence of common film disrupting food components.

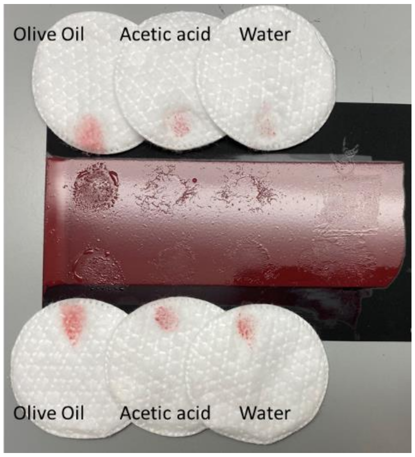

Figure 3. In vitro wear assay of prototype under water, acetic acid and olive oil, showing good wear performance and transfer proof nature of the formula in the presence of common film disrupting food components.

Arm Test

Figure 4 reveals the oil/water resistance of the prototype formulation with different type (shades) of pigments. The rationale behind using different types of pigment is to check how of the pigment chemistry affects the overall performance. As shown in **Figure 4**, all samples show minimal or no change on the film appearance on skin after wiping, indicating the current test formulation provides an excellent long- wear performance regardless of pigment type.

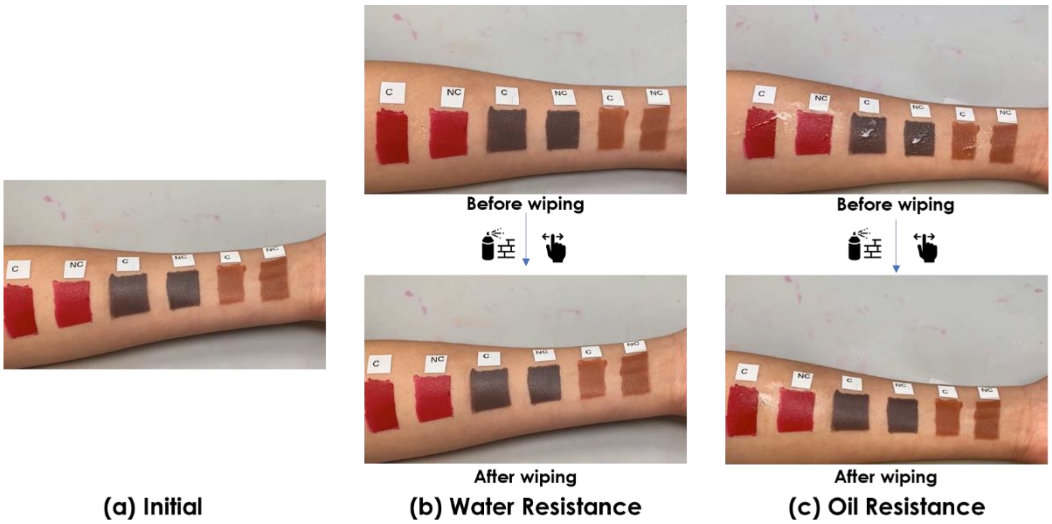

Figure 4. Arm test of different shades of prototype formulation exposed to different medium. (a) initial application, (b) wiping with water and (c) wiping with avocado oil.

Stretch Testing

Figure 5 shows the films of prototype formulation and benchmark product after stretching. The purpose of stretching test is to simulate how the films behave during the movement of lip. The benchmark is a MQ technology-based one-step product which provides long-wear and satin shine finish according to the product claims. It is observed that the benchmark is brittle/flaky and peels after stretching (**Fig 5**). This phenomenon indicates that the film is less cohesive under strain/ deformation due to the loss of solvent or other ingredients over time. On the other hand, the prototype formulation still stays on the rubber band without flaking and peeling, suggesting that the product is more cohesive, resilient and may adapt to lip movement to provide good wear.

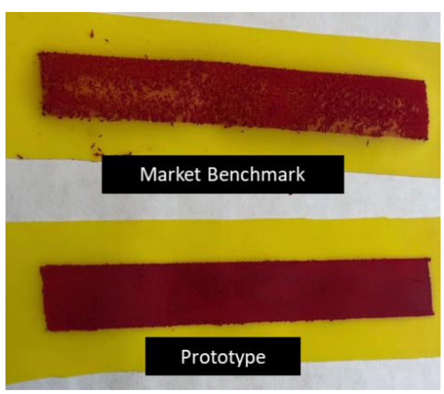

Figure 5. Stretching test of prototype formula and benchmark.

Consumer Test

Figure 6 demonstrates the wear and transfer resistant performance of this technology with mask in the course of time. During the test, panelists do not reapply the product and maintain their regular daily activity. The initial finish of this specific prototype is highly pigmented and satin shine. As time passes, the prototype fades evenly and maintains the satin finish, resulting in good cosmeticity /appearance. Also, the color transfer from lip to mask is minimal.

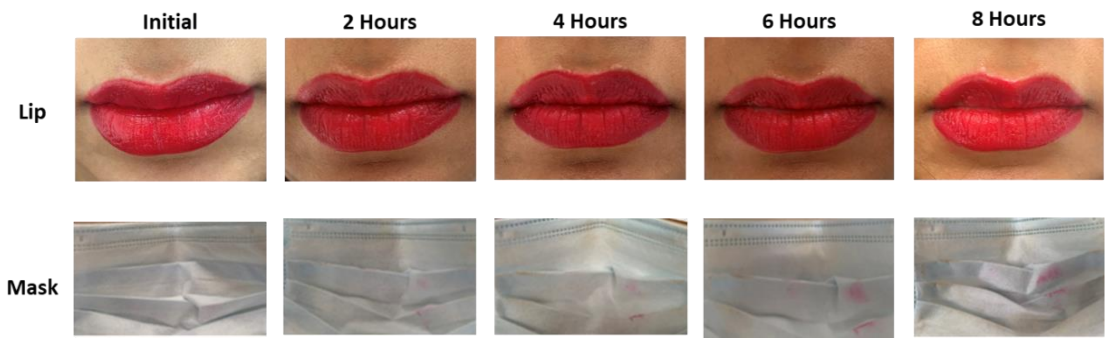

Figure 6. In vivo wear and mask proof test of prototype formulation.

Table 1 shows the performance summary of prototype formulation vs. Long-wear gloss benchmark on the market. Compared to the benchmark, the prototype is superior on overall liking on the main Lux/Mass users with all ages groups. Its performance is superior on application liking, end look liking and wear. Additionally, the consumer test is pretty aligned with the in vitro evaluation result.

-

	Prototype formula	
	vs. Longwear Gloss Benchmark	
Main Sample	Better application Better end look, coverage Better wear	SUPERIOR
Longwear Users	Better lightweight Better lasting, shine all day	PARITY (With advantages)
Lux users	Better color intensity Better breathability Better wear	SUPERIOR
Mass users	Better color intensity Better breathability Better wear and shine all day	SUPERIOR
Younger (18 - 35 y.o.)	Better on fuller results Better wear Inferior on "Lips do not look dry after removal"	SUPERIOR
Older (>35 y.o.)	Better application, Better end look and coverage Better wear	SUPERIOR

Table 1. Performance summary of prototype formula vs. Long-wear gloss benchmark.

Discussion

The prototype is a unique and unstable silicone-silicone polymer dispersion mixture. The phase separation is driven by the different level of organo-modification between two silicone film formers.

Figure 7a is the schematic drawing of this architecture. The internal phase mainly contains the first silicone polymer with pigments and solvents. The first silicone polymer serves as binder to glue pigments together and ensures the uniform color in the film during the film formation on substrate. On the other hand, the external phase includes the second silicone film former and solvent.

The film formation of the prototype on substrate is strongly determined by the kinetic competition between phase separation and solvent evaporation. **Figure 7** shows the two extreme cases of how the kinetic competition affects the film structure. If the film is dried prior to the completion of the phase separation, the film former in the external phase will prevent the internal phase from settling and coalescence to form a continuous film on lip surface. This results in a sea-and-island structure as depicted in **Figure 7b**. On the other hand, if the phase separation is faster than drying process, the internal domains can quickly settle on lip surface and coalesce to form a continuous film, while simultaneously, the external phase forms a transparent film to protect the color coat (**Figure 7c**).

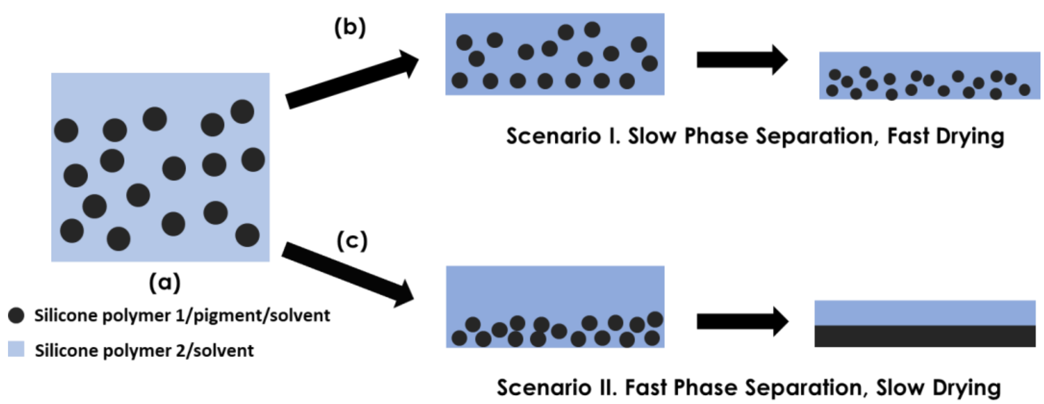

Figure 7. Film formation mechanism of unstable silicone-silicone polymer dispersion. (a) the morphology of the re-mixed prototype, (b) Sea-and-Island structure formed through fast drying/slow phase separation, (c) bilayer structure via slow drying/fast phase separation

In this prototype, according to the renewable shine and arm test experiments, the prototype forms a bilayer film on substrate. That is, a pigmented layer is at the bottom, and a colorless layer is formed on top of the adhesive layer to provide shine and comfort. The long-lasting color suggests the dispersed phase forms a well adhesive film which is robust enough to resist common food ingredients including with tissue/napkin wiping. The renewable shine is attributed to the well-balanced viscoelastic behavior of silicone polymer in the top layer. Moreover, the long-chain silicone polymer can anchor or be entrapped at the interface between the two layers during the film formation to promote good interlayer adhesion. Therefore, due to the above mechanism, the long-lasting/self-healing shine is achieved.

The excellent performance in vitro is well perceived by consumers in the large-scale consumer study against relatively long-wear lip gloss. Compared to the benchmark, the prototype is superior on application liking, end look liking and wear across Lux/Mass users, all ages groups. Especially, during the COVID-19 pandemic, wearing mask in the public for many hours is required, which can interfere with the face/lip makeup product performance. Therefore, the demand of high transfer resistant or transfer proof makeup under mask wearing condition has greatly increased [14, 15]. However, due to the high temperature and high humidity environment in the enclosed mask space, face/lip makeup products can transfer to the mask much easier. In the mask transfer test, the prototype proves excellent long wear performance with low color transfer for at least 8-hour of continuous wear.

Furthermore, the technology shows the flexibility to achieve to different shades and finish. **Figure 8** shows the adjustability of the technology to achieve satin and glossy finishes without compromising its long color lasting and shine retention.

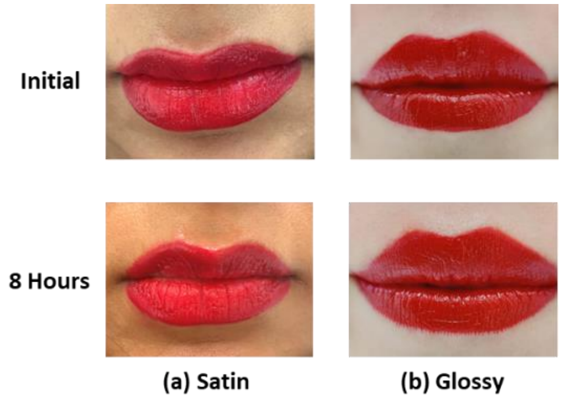

Figure 8. The capability of achieving different finish without comprising long-wear performance under mask condition. (a) satin, and (b) glossy finish.

Conclusion

In conclusion, the performance of our single-step long-lasting technology requires a good balance between polymer physics, phase separation kinetic and packaging design. Its excellent long-wear performance and shine retention are demonstrated by a series of *in vitro* evaluation and proven by a large-scale consumer test against lip gloss benchmark, showing superior on application liking, end look liking and the overall performance of wear.

Acknowledgments.

We wish to thank Hubert Lam for supporting raw material and supplier needs. For the consumer test, we would like to thank Jennifer Hobby, Sarah Barret, Donna Dooley, and Ildi Vazan. We want to thank Simon Dutton and Ariel Ziegler for pack support. In addition, these studies would not have proceeded without the strong support of Sarah Gauer.

Conflict of Interest Statement.

L'OREAL funded this study.

References

1. H. Bui and D. Coleman-Nally, Film-Forming Technology and Skin Adhesion, in: Long-Wear Cosmetics in *Adhesion in Pharmaceutical, Biomedical and Dental Fields*, K. Mittal (Ed.), p. 141–166, Scrivener Publishing LLC (2017).
2. US Pat 7,879,316, Cosmetic composition containing a polyorganosiloxane polymer**,** V. Ferrari, F. Toumilhac, W. Yu, S. X. Lu, X. Blin, J. Mondet, I. Hansenne, A. Shah and A. Galdi., assigned to L'OREAL (Feb 1, 2011)
3. US Pat 7,842, 285, Cosmetic compositions and methods of use, S. Lu, W. H. Yu and H.S. Bui, assigned to L'OREAL (Nov 30, 2010)
4. US Pat 10, 272,027 Lipstick composition having improved comfort, H. S. Bui, R. J. El-Khouri, and M. Trivedi**,** assigned to L'OREAL (April 30, 2019)
5. US Pat 9,649,270, Color cosmetic composition, R. J. El-Khouri, R. Debeaud**,** M. Vicic, and H. S. Bui**,** assigned to L'OREAL (May 16, 2017)
6. US Pat 10, 426, 722 Compositions containing an alkylated silicone acrylate copolymer, H. S. Bui, and R. J. El-Khouri, assigned to L'OREAL (Oct 1, 2019)
7. US Pat 10,576,025, Composition comprising polymer particles, a hydrocarbon-based oil and a hydrocarbon-based block copolymer, and process using the same, L. Daubersies; C. Lison, S. Douezan, H. S. Bui, and R. J. El-Khouri, assigned to L'OREAL (Mar 3, 2020)
8. US Pat 10, 675, 226 Lip compositions capable of forming a multilayer structure after application to lips, R. J. El-Khouri, assigned to L'OREAL (June 9, 2020)
9. US Pat 10, 772, 806 Liquid lipstick compositions capable of forming a multilayer structure after application to lips, R. J. El-Khouri, assigned to L'OREAL (Sept 15, 2020)
10. US Pat 10, 780, 040 Cosmetic compositions which are homogenous in the bulk and capable of forming a multilayer structure after application to a keratinous material, R. J. El-Khouri, assigned to L'OREAL (Sept 22, 2020)
11. US Pat 10, 881, 601 Cosmetic compositions capable of forming a multilayer structure after application to a keratinous material, R. Rosario-Melendez, and R. J. El-Khouri, assigned to L'OREAL (Jan 5, 2021)
12. US Pat publication 20200345613 LIP COMPOSITIONS CAPABLE OF FORMING A MULTILAYER STRUCTURE AFTER APPLICATION TO LIPS, XZ. Zhou; TM Huang, J. Ebanks, M. Hasebe; H. S. Bui, and C. Li, assigned to L'OREAL (Nov 5, 2020)
13. US Pat publication 20210038495 LIP COMPOSITIONS CAPABLE OF FORMING A MULTILAYER STRUCTURE AFTER APPLICATION TO LIPS, XZ. Zhou; TM Huang, J. Ebanks, M. Hasebe; H. S. Bui, and C. Li, R. J. El-Khouri, and R. Ahmad, assigned to L'OREAL (Feb 11, 2021)
14. Messaraa, C,; Mangan, M.; Lasting Impression: A consumer-centric Approach to Measure Transfer-proof Lipstick, March 1, 2021; https://www.cosmeticsandtoiletries.com/testing/efficacy/article/21836041/cosmetics-toiletries-magazine-lasting-impression-a-consumercentric-approach-to-measure-transferproof-lipstick
15. THE BEST TRANSFER PROOF FOUNDATIONS FOR FACE MASKS {AND THE ONES TO AVOID!}, https://www.anniesnoms.com/2021/02/04/the-best-transfer-proof-foundations-for-face-masks/