Switch color ingredient: an amazing way to change static make-up

Pirovano, Claudio[1]; Galotto-Galotto, Nella[1]; Distefano, Gaetano[1]; Valagussa, Carola[1]; Fiorellini, Manuela[1]; Beverina, Luca[2]; Bettinelli, Sara[1]; Depta, Gabriele[1]; **Valsesia, Patrizia[1]**

[1] Research & Innovation Department, Intercos S.p.A., Agrate Brianza, Italy;
[2] Università degli Studi Milano Bicocca U5, Milano, Italy

*Valsesia Patrizia, via Marconi 84, 20864 Agrate Brianza (MB) - Italy, +39 039 655 8342, patrizia.valsesia@intercos.com

Background:

A unique photochromic ingredient was designed and developed, opening the way to the obtainment of amazing dynamic cosmetic products.

Methods:

The photochromic cosmetic polymer was synthesized, inserting in the polymeric backbone of a siliconic oil a tailor-made spiropyran photochromic molecule. An in-depth study on the UV-induced color transition was carried on in order to evaluate its potential application in cosmetics.

Results:

The new ingredient is born from the conception of a material able to take the make-up towards the trends of the next future. Functionality and safety make the oil an actual cosmetic ingredient, while the ability to change color with UV under sunlight makes it unique and dynamic, distinctive from the usual static cosmetic raw materials. Very catchy cosmetic prototypes can be obtained, showing the transition between two different colors.

Conclusion:

The resulting photochromic products, able to modify their color in response to sunlight radiation, can be conceived both to amaze and surprise with an impressive color change and to convey an extremely natural effect, darkening outdoors under the direct sun rays where their appearance on the skin is unnaturally white.

Keywords: photochromic oil, color, switch, emollient oil, silicone

Introduction.

Make-up represents a way to answer new needs and adapting to the new communication channels. The concept of make-up has to embody the evolution of our lives, fitting in a fluid way between contrasting scenarios and following dynamically the rapid changes of beauty trends.

Playing in a creative and sophisticated way with color finishes and the other functional ingredients enables the creation of a kaleidoscope, in which anyone can found the right make-up with the right texture for the day mood.

This work will show an answer to new customer needs, with the possibility to break staticity to color cosmetics by taking advantage of material science and photochromism. A unique photochromic ingredient was designed and developed, opening the way to the obtainment of amazing dynamic cosmetic products.

The resulting photochromic products, able to modify their color in response to sunlight radiation, can be conceived both to amaze and surprise with an impressive color change and to convey an extremely natural effect, darkening outdoors under the direct sun rays where their appearance on the skin is unnaturally white.

Materials and Methods.

A photochromic cosmetic raw material was synthesized, inserting in the polymeric backbone of a cosmetic oil traditional, photochromic molecules like spiropyrans and spirooxazines.

The photochromic molecule was designed specifically in order to have a chemical bond with the selected cosmetic oil. The starting molecule belongs to the spiropyrans family and it was functionalized following the synthetic approach reported in the dedicated patent [1]. The obtained precursor was then reacted with a cosmetic silicon oil (INCI: bis-hydroxyethoxypropyl dimethicone) *via* transesterification reaction. The synthesis was performed at 145°C under vacuum for 6 hours in the presence of a catalyst. Bis-hydroxyethoxypropyl dimethicone is used in excess, acting directly as a reaction solvent other than as a reactant.

An in-depth study was performed in order to assess the color transition of the obtained photochromic oil and to evaluate its switching properties under UV light and sunlight.

An UV lamp (UV nail lamp, 36 Watt power, Nail Star Professional) was used to induce the color switch of the material and the analyses of the color were performed using UV-Vis Spectroscopy (UV-Vis Spectrometer Lambda 850+, PerkinElmer). The UV-Vis spectra were collected using quartz cuvettes, filled with a solution of 10 μl of the oil in 10 ml of THF. The so prepared sample was analyzed scanning the range between 700 and 200 nm, 1mm pathlenght, scan speed 240 nm/min.

Colorimetric measurements were made on the photochromic oil using a Spectrophotometer X-Rite Macbeth I7. More specifically, color coordinates (CIELAB color space) were determined by spectrophotometric analysis on a film of the material. The sample was prepared using an Automatic Draw Down Apparatus to apply a uniform film on a Laneta Black & white card.

The color of the material was evaluated in its stable state A and in its state B, reached after undergoing to UV lamp radiation. Furthermore, the switching properties of the photochromic cosmetic raw material were assessed measuring the UV-Vis spectra after cycles of different steps of exposure at UV light. In particular, the measurements of the UV-Vis absorption were carried out in order to study the timing and the intensity of the transition and the lifetime of the switching. In the first case, the UV light exposure was increased in 10 seconds intervals for each step, starting from 10 seconds for the first step to 2 minutes, jumping then to 5 minutes and finally 15 minutes. In the second case, the time of UV light exposure was fixed to 20 seconds and several exposures were performed.

The compatibility of the new raw material with selected powders and waxes was studied in order to find the right combination with other ingredients and enhance the photochromic effect in a formula. Some prototypes of cosmetics were then formulated in order to evaluate the potentialities in terms of color switching.

The color shift of the obtained formulations was studied in terms of color coordinates. The coordinates were recorded using the VS450 X-Rite spectrophotometer, a benchtop spectrophotometer that operates in a non-contact mode, ideal for measuring wet and dry cosmetic samples including liquids, pastes or powders.

The color of the formulations containing the photochromic oil was evaluated in its stable state A and in its state B, reached after undergoing to UV lamp radiation, likewise the raw material. Furthermore, the switching properties of the formulation were assessed measuring

the color coordinates after different steps of exposure at UV light, using the same time setting as the tests with the raw material.
An anhydrous lip fluid, a face powder and an eyeshadow formulated with the switch color ingredient as the main character were declined in several shifting shades.

Results.
The photochromic oil was successfully synthesized combining a conventional cosmetic silicone emollient with a tailor-made photochromic molecule (Figure 1) [1].

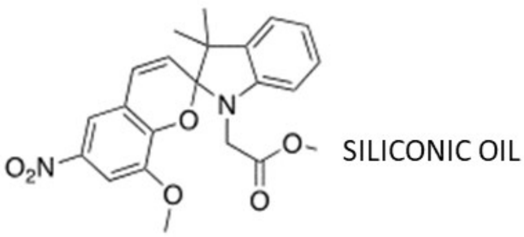


Figure 1: The photochromic oil

The photochromic starting molecule belongs to the family of the spiropyrans, able to guarantee the requested performances in terms of photochromatic contrast. The functional chain inserted on the indolic nitrogen makes the covalent anchoring to the macrodiol possible by catalytic transesterification reaction. The presence of nitro and methoxy groups on the phenyl residue ensures a correct position of the photostatic equilibrium both under irradiation conditions and dark conditions and a better photochemical stability, respectively.
The material obtained by transesterification reaction of the photochromic precursor with the bis-hydroxyethoxypropyl dimethicone was characterized in terms of physico-chemical properties (NMR, GPC, FT-IR). The assigned INCI name is Polysilicone-37.
The reversible switch occurs when the material is irradiated by sunlight and the oil changes from an almost colorless to a strongly colored (blue) phase. In particular, the color change is promoted by UV-A radiation of sunlight. Figure 2 shows the UV-Vis spectra of the photochromic oil before (red profile) and after (blue profile) exposure to UV lamp light. An absorption band appears in the yellow-orange-red region of the spectrum (maximum around 625nm), explaining the blue color observation of the irradiated material.

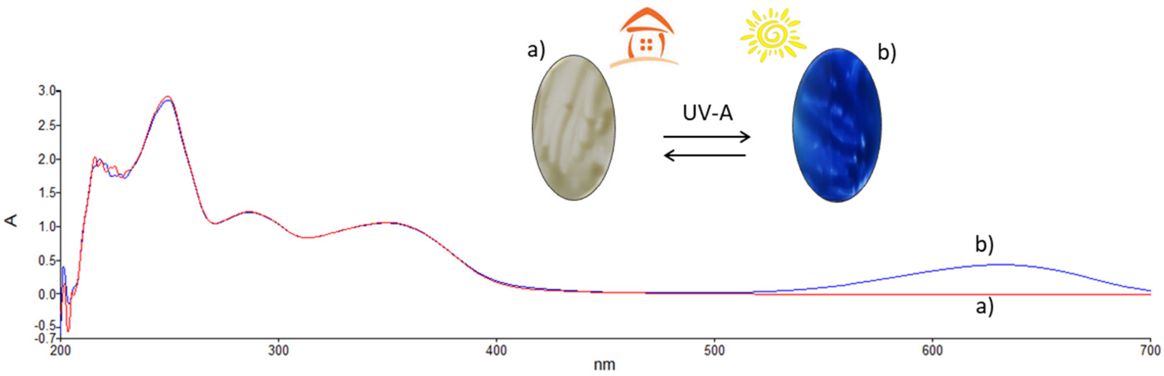


Figure 2: UV-Vis red profile, photochromic oil in its state a); UV-Vis blue profile, photochromic oil after UV light exposure b). The reversible switch occurs from an almost colorless to a strongly colored (blue) phase.

The timing and the intensity of the switching were studied having the sample undergo to a cycle of different steps of UV light exposure, increasing in 10 seconds intervals for each step, starting from 10 seconds for the first step to 2 minutes, jumping then to 5 minutes and finally 15 minutes. The color shift from state A to state B was measured both by UV-Vis absorption and by colorimetric analysis after every step of exposure. Figure 3 shows that the maximum intensity of color change is reached after 20 seconds of UV light exposure. The colorimetric analysis is reported in Figure 3 a). Every rectangle represents the color of the sample after being exposed the respective time reported on it. The UV-Vis absorption of some selected time of exposure is reported in Figure 3 b).

It results clear that the sample that shows the highest color intensity is the one exposed to UV light for 20 seconds. Up to 1 minute of exposure, the intensity of the blue color of the photochromic oil doesn't change in a significant way, while a further increase of exposure affects negatively the color transition, likely due to the deactivation of the photochromic power of the material. After 15 minutes under UV lamp, the light absorption of the sample changes totally, remaining quite close to the sample in the starting state.

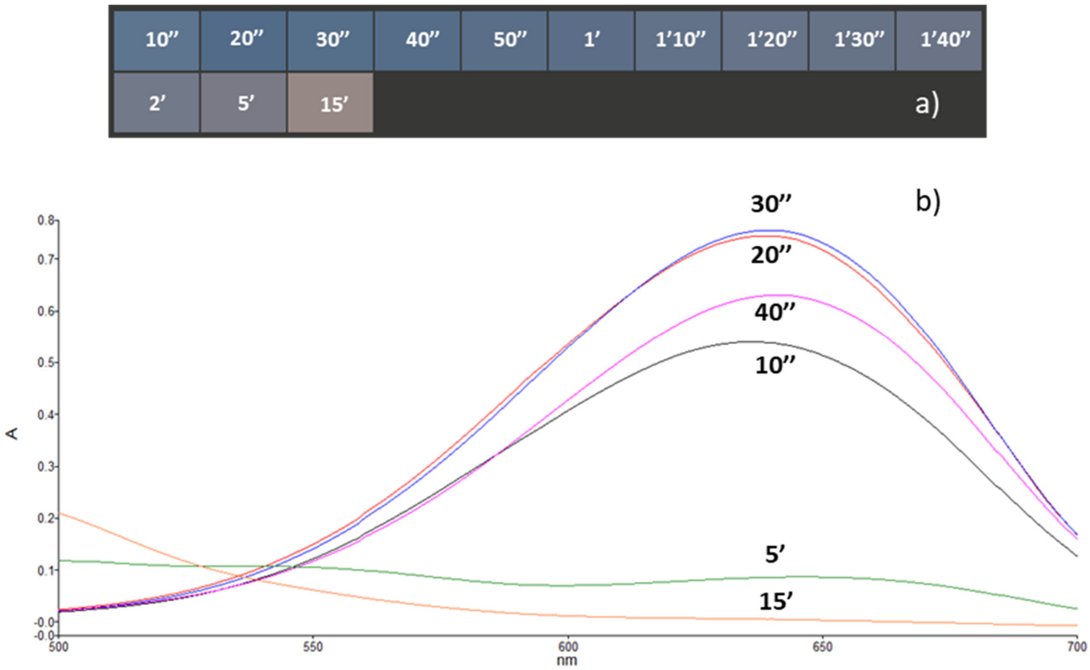


Figure 3: a) Colorimetric analysis of the photochromatic oil at different UV light exposure times a); b) UV-Vis spectra (500-700 nm range) of the 10 seconds exposure sample (black profile), 20 seconds exposure sample (red profile), 30 seconds exposure sample (blue profile), 40 seconds exposure sample (pink profile), 5 minutes exposure sample (green profile), 15 minutes exposure sample (orange profile)

The lifetime of the switching was then assessed by monitoring the UV absorption of the same sample after several cycles of 20 seconds of UV light exposure.

After every step of exposure and after having collected the UV-Vis spectrum, the following exposure was made when the sample was back to the initial state A (colorless). The ability to switch starts to fade after the ninth cycle of exposure. Moreover, a shift of the color in the excited state was observed, changing from a blue tone to a reddish and then, after more than ten exposure cycles, to a yellowish tone.

The compatibility of the new raw material with common powders was studied in order to assess the potentiality of the color switch and to find the right combination with other ingredients. In the tables below are reported the compatibility of the photochromic oil with powders and treated powders (Table 1) and the compatibility with selected waxes (Table 2). The chemical surface nature of powders influences the color change, impacting negatively the intensity of the switch. On the other hand, the presence of specific coating agents on the surface of powders can mask the blocking effect of the powders and make the photochromic transition possible to occur.

Table 1: Compatibility of the photochromic oil with powders and treated powders (5% photochromic oil)

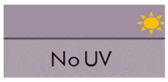
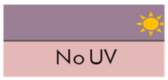
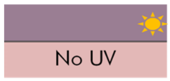
Powder and Treated Powder INCI	**Color switch under sunlight?**	
Synthetic Fluorphlogopite	**N**	
Synthetic Fluorphlogopite and Triethoxycaprylylsilane and C20-24 Olefin	**Y**	
Synthetic Fluorphlogopite and Hydrogenated Vegetable Oil and Sorbitan Tristearate	**Y**	
Mica	**N**	
Mica and Dimethicone	**N**	
Mica and Hydrogenated Vegetable Oil and Sorbitan Tristearate	**Y**	
Talc	**Y**	
Lauroyl Lisine	**Y**	
Boron Nitride	**N**	
Silica	**N**	
Calcium Sodium Borosilicate	**Y**	
Zinc Stearate	**Y**	

Table 2 shows the compatibility of the photochromic oil with selected waxes. It is clearly visible that the presence of waxes from different chemical nature does not block the dynamic color change of the new ingredient.

Table 2: Compatibility of the photochromic oil with waxes

INCI	Wax: Phothocromic Oil : Siliconic Oil = 20:10:70	
	Appearance at RT	**Color switch under sunlight?**
Helianthus Annuus (Sunflower) Seed Wax	very hard structure, homogeneous	**Y**
Oryza Sativa (Rice) Bran Wax	very hard structure, not homogeneous	**Y**
Synthetic Wax and Copernica Cerifera (Carnauba) Wax	hard structure, homogeneous	**Y**
Polyethylene	hard structure, homogeneous	**Y**
Synthetic Wax 1	soft structure, homogeneous	**Y**
Synthetic Wax 2	not homogeneous	**Y**

Based on the characterization and the assessment of the color shift made on the new raw material, a series of prototypes of make-up products were formulated, trying to balance the combination of the photochromic oil with other cosmetic ingredients, especially pigments, in order to emphasize the dynamic transition between two different colors by changing the light conditions.

A lip gloss in three different red shades containing 1% of photochromic oil and a fluid eyeliner formulated with 4 % of the new ingredient were tested, and the color shift was studied in terms of color space, recording the color coordinates of a sample after a cycle of different steps of UV light exposure (Figure 4). The cycle was set increasing in 10 seconds intervals for each step, starting from 10 seconds for the first step to 2 minutes, jumping then to 5 minutes and finally 15 minutes, similarly to the analyses made on the raw material. No recover time was applied to the sample between one step to another, besides the time required for the colorimetric analysis.

The colorimetric analyses of the most significative steps are reported in Figure 4: t 0 (before UV light exposure), 10, 20, 30, 40, 50 seconds, 1, 5, 15 minutes and finally the analysis of the sample 5 minutes after the last step of UV exposure.

A value of ΔE is reported for every step with respect to t0 color.

ΔE is the total color difference and it is based on ΔL*, Δa*, and Δb* color values, all of which provide a complete numerical descriptor of the color in the CIELAB color space. ΔE is measured on a scale from 0 to 100, where 0 is less color difference, and 100 indicates complete distortion. The meanings are as follows: ≤ 1,0, not perceptible by the human eye;

1-2, perceptible through close observation, 2-10, perceptible at a glance; 11-49; colors are more similar than the opposite; 100, colors are exactly the opposite.

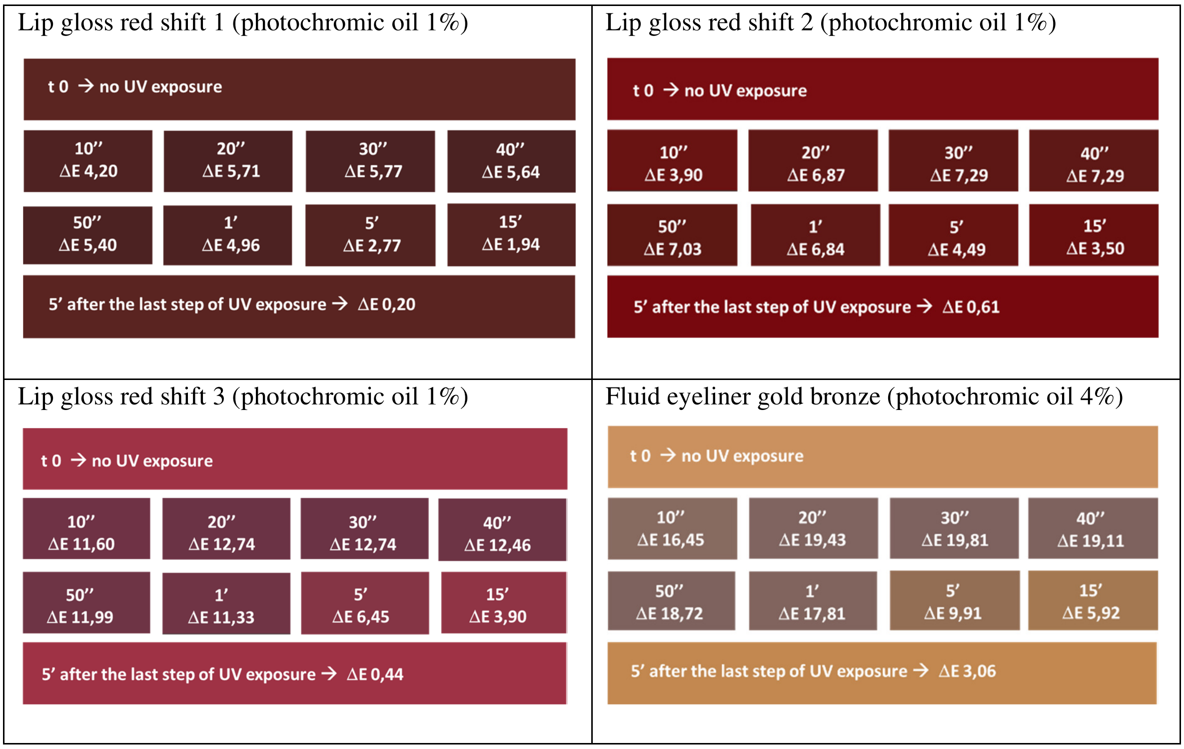


Figure 4: Colorimetric analysis of different formulations containing the photochromic oil at different UV light exposure times. Every rectangle represents the color of the sample after being exposed the respective time reported on it; t0 is the sample before the cycle of UV light exposure; ΔE represents the total color difference with respect to t0 color.

In general, for all the examples reported, it is well noticeable that the maximum of ΔE is reachable when the sample is directly irradiated for 20 seconds to 1 minute. More than 1 minute of direct UV radiation affect negatively the color switch and the photochromic oil tends to come back to the colorless state.

Understandably, the amount of photochromic oil in formula together with the starting color tone of the product affect the intensity of the color switch. Darker is the starting color, less intense will be the color change (ΔE lip gloss red shift 1 < ΔE lip gloss red shift 2 < ΔE max lip gloss red shift 3). Higher is the amount of the photochromic oil in the formula, more visible would be the color switch. In the "fluid eyeliner gold bronze" that contains 4% of photochromic oil, ΔE max is almost 20.

ΔE values of the last step, where the colorimetric analysis was made on the sample 5 minutes after the last UV exposure, show that the switch is completely reversible. Just in the case of the fluid eyeliner, the ΔE indicates that the color difference is perceptible ($\Delta E = 3,06$).
The reported results were obtained using a UV lamp to study the color change. This direct and standardized source of UV allowed to study the chromatic transition of the material, making the color comparison among different samples and conditions possible, in order to evaluate the best combinations with the other cosmetic ingredients and find the best way to emphasize the dynamic effect of color change.
The chromatic transition of the new raw material, stand alone or contained in a formulation, happens also under direct sunlight, with a behavior like what observed with the direct UV light of the lamp. This study opened the way to the formulation of several cosmetic products, designed with the idea to play with color and the dynamicity of the chromatic transformation.

Discussion.

The new photochromic oil was conceived with the aim to obtain a cosmetic ingredient that would be functional, easy to use, safe and disruptive at the same time.
The ability to change color with UV is designed on a cutting-edge material able to fulfill all the necessary requirements of the formulation in the modern cosmetic science.
The introduction of new molecules in cosmetics is always a delicate operation, because substances with low molecular weights, such as that of a molecule, could be absorbed by the skin. So, the synthetic protocol was created, starting from the need to obtain a cosmetic polymer with photochromic properties.
A tailor-made photochromic molecule was synthesized with specific functional groups useful for creating a chemically link with a long polymer chain. A conventional siliconic emollient oil was then selected among those polymers with the appropriate reactive functional groups and with the suitable cosmetic properties.
The material, obtained by the combination of the silicone emollient and the tailor-made photochromic molecule, is a functional and safe cosmetic oil, with unique and dynamic ability to change color with UV. The photochromic functionalization does not affect the original sensorial properties of the silicon emollient and the optimized concentration of the

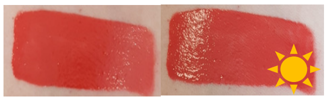
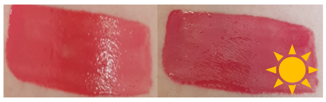
oil in formula and the appropriate combinations with the other raw materials were individuated.

The new photochromic oil can change the color of a cosmetic formulation under natural sunlight, allowing the adaptation of the makeup to indoor and outdoor situations.

The studies performed on the color switch of different cosmetic prototypes under different conditions helped to understand the potentialities of the material inside a product. Amazing color shifts can be created smartly combining the traditional cosmetic pigments with the oil. On one hand, it is possible to obtain make-up products with stunning effects, focusing on marked chromatic transitions, on the other hand, just slight and functional color change can be obtained whenever the photochromic switch is useful for tuning the tone and keeping the skin complexion equilibrated between indoor and outdoor, avoiding the unnatural whiteness of make-up.

Some examples of products and chromatic effects that can be obtained are reported in Table 3 and in Figure 5. These examples represent the starting point of a new era of dynamic cosmetics, able to adapt and modify their aspect in response to external inputs, expanding the sensorial experience that consumers would not ever expect from a cosmetic product.

Table 3: The effect of the photochromic oil in formulation

Product	Amount of phothocromic oil and color transition effect in the formula	
Lip Gloss shades shift	7%	
	1%	
	1%	
	1%	
Bronzer shades shift	10%	
	15%	
	17%	

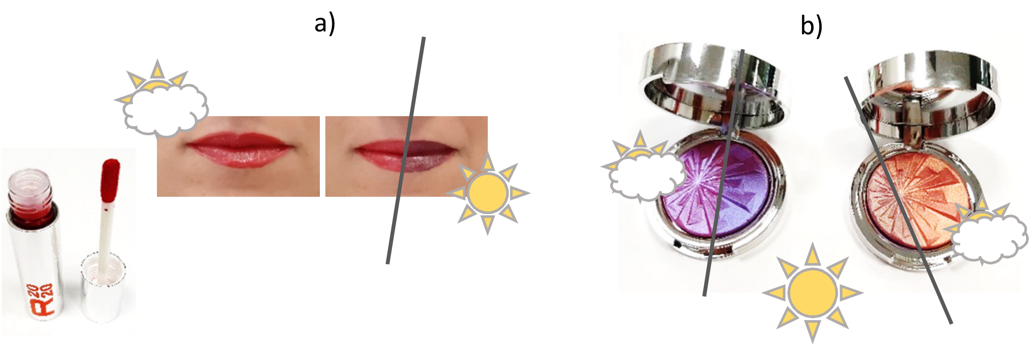


Figure 5: Cosmetic products with the photochromic oil: lip gloss a) and two switching shade of eyeshadow b)

Conclusion.

A new photochromic oil is born from the conception of a material able to take the make-up towards the trends of the next future. Functionality and safety make the oil an actual cosmetic ingredient, while the ability to change color with UV makes it unique and dynamic, distinctive from the usual static cosmetic raw materials. Very catchy cosmetic prototypes can be obtained (an anhydrous lip fluid, a face powder and an eyeshadow), showing the transition between two different colors. The colors can be well balanced by the intelligent combination with other cosmetic colorants and the transition can occur for an almost infinite number of times. The shift of shades can be both well visible on the skin or just a fine and sophisticated color tune, depending on the desired effect and the concentration of the oil in formula. In every case, the make-up breaks its normal staticity and becomes fluid and kaleidoscopic.

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Conflict of Interest Statement. NONE.

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