The Latest Cosmetic Technologies in Japan (Sunscreens and Lipsticks)

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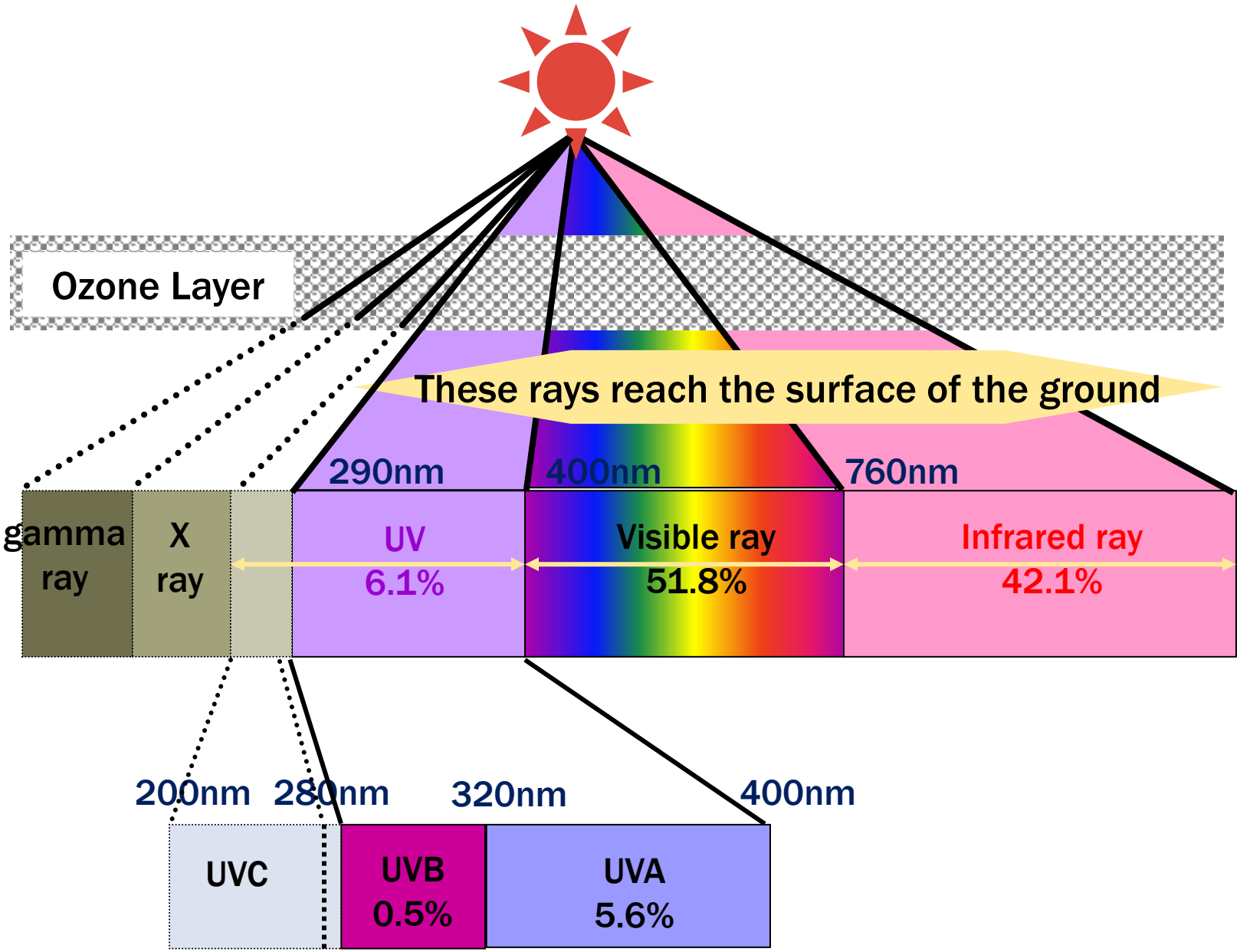
- Development of a Water-resistant / Detergent-washable Sun-care Products Utilizing pH-responsive Polymer

- A Novel, Long-lasting, Non-Smear Lipstick Utilizing a Phase Separation Mechanism is Totally Devoid of Secondary Stain

Development of a Water-resistant / Detergent-washable Sun-care Products Utilizing pH-responsive Polymer

- Introduction (About UV and sunscreens)
- Why do sun-care products have a poor detergent-washability?
- Development of a pH-responsive polymer as a treatment agent for powder
- Development of a sun-care product containing pH-responsive polymer-treated titanium dioxide

What is Ultraviolet Rays (UV)



Penetration of UVB and UVA into skins

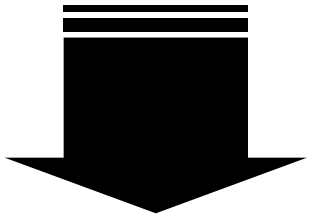
	UVB	UVA
Ratio in Solar Ray	0.5%	5.6%
Skin Penetration	Mostly scattered or absorbed in epidermis	Penetrate to dermis through epidermis

Importance of sun-care products

Awareness of the harmfulness of UV rays

Increasing UV irradiation due to ozone hole

Protecting from UV irradiation is more important.

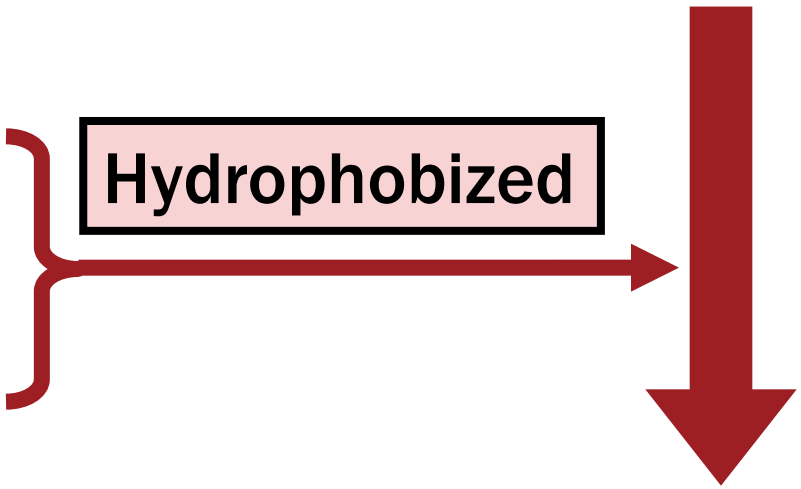


The demand of sun-care products is getting high.

Evolution of sun-care products

Formula of W/O sun-care products
Oil
UV absorbent
UV protective powder (ZnO, TiO_2)
Film-forming polymer
Surfactant agent
Water

Awareness of the harmfulness of UV rays



Water-resistant
(Long lasting character)

Washability of sun-care products

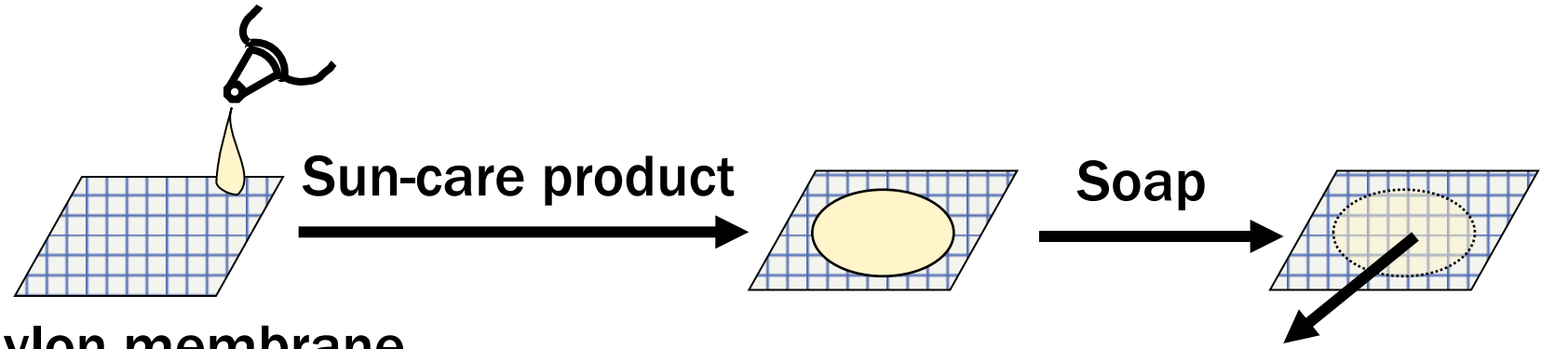
Poor detergent-washability

Wash with a special cleansing agent

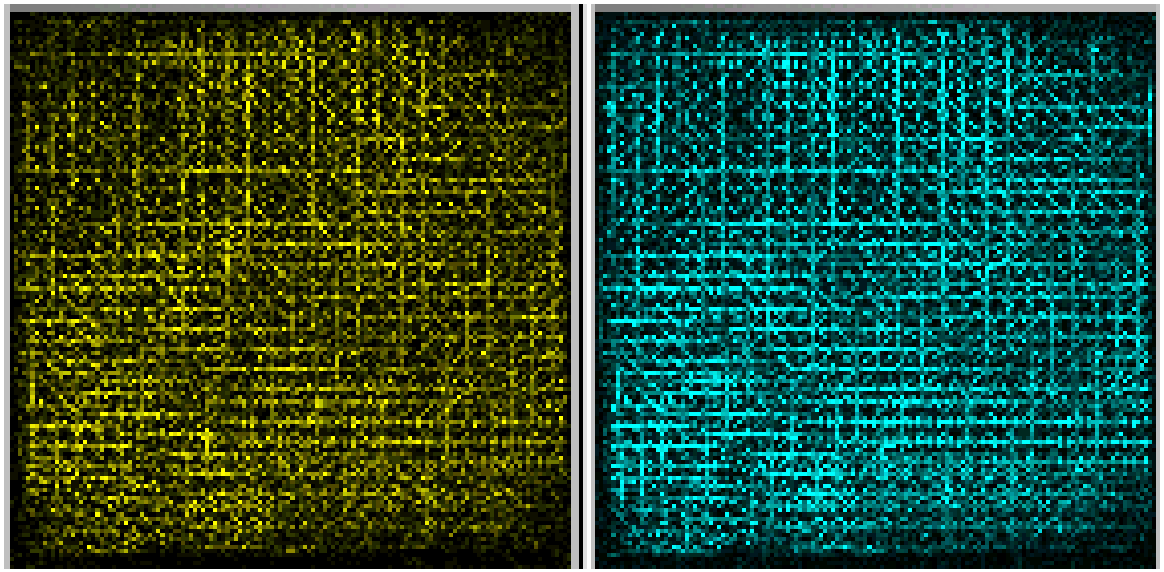
Wash with soap

- White residual
- Squeaky feeling

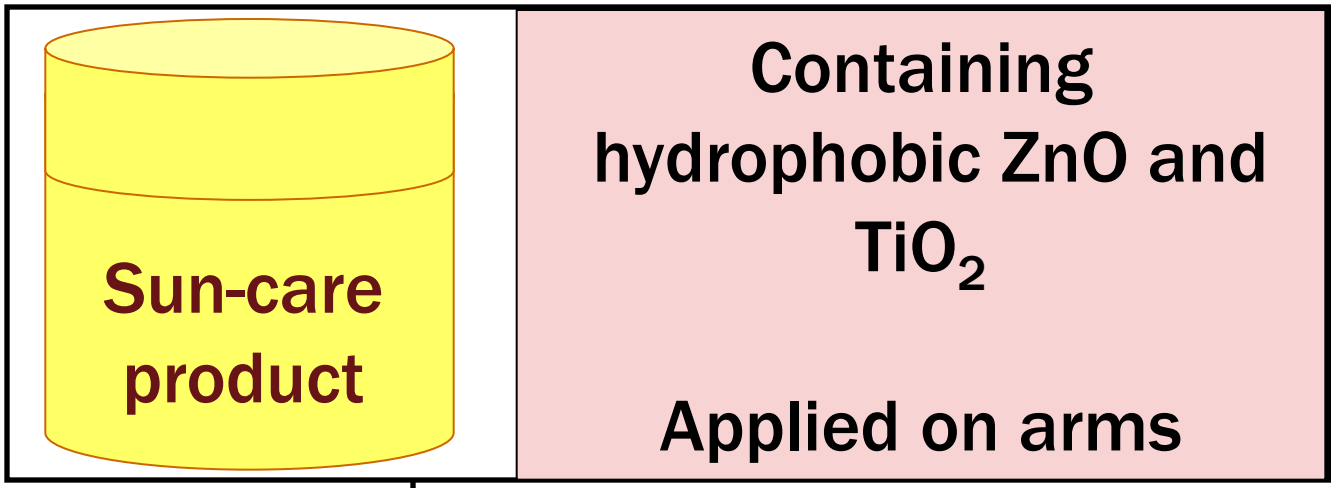
Analysis of the remaining



Hydrophobic TiO_2	Hydrophobic ZnO



Measurement of the residual powder

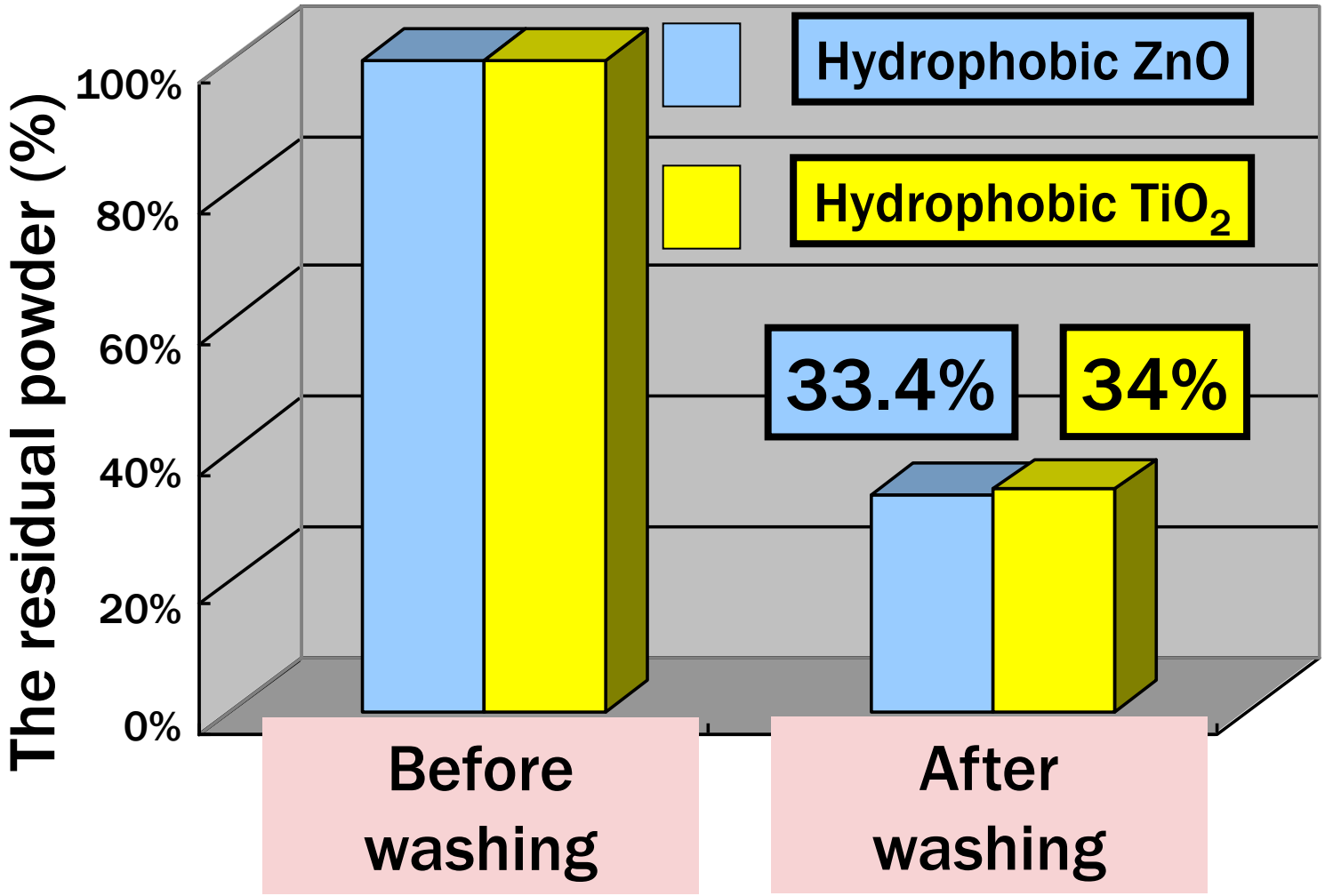


Washing with soap

Peeling of stratum corneum

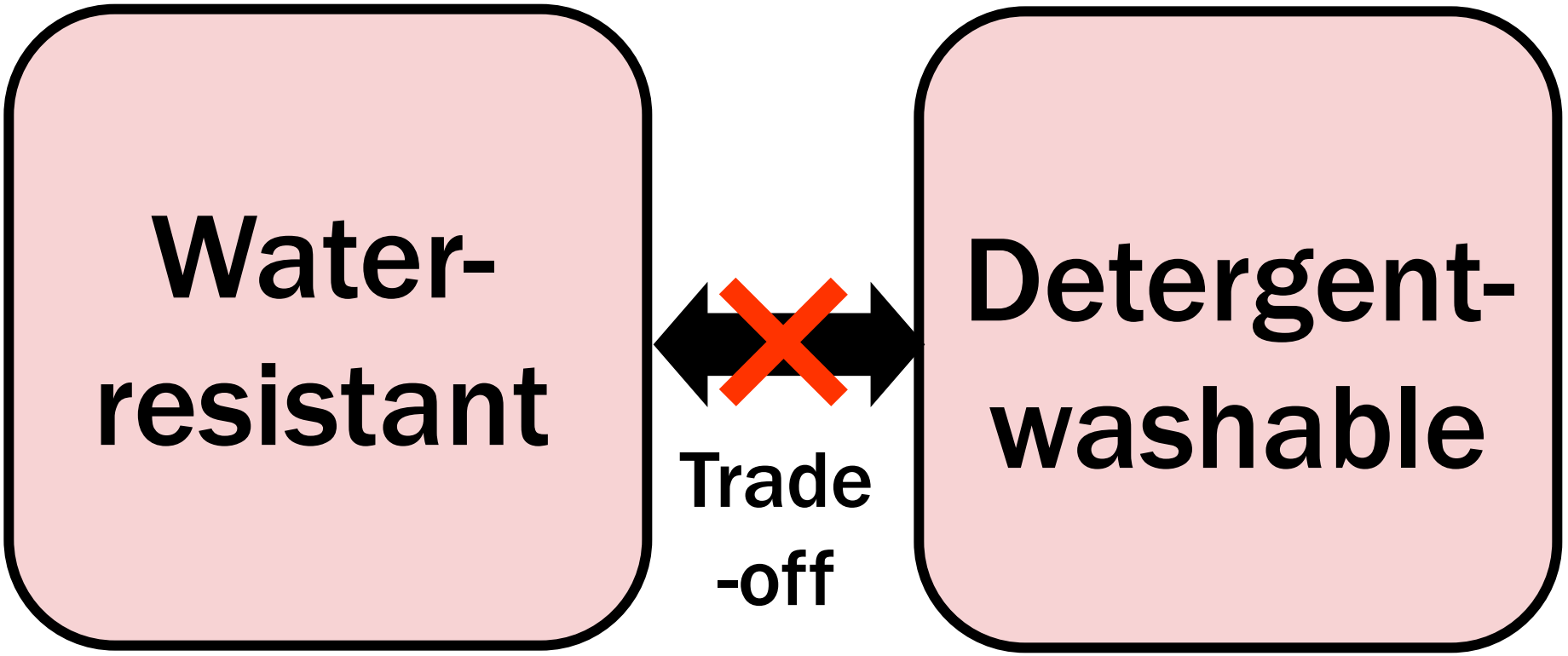
Measurement of the amount of ZnO and TiO_2

Measurement of the residual powder

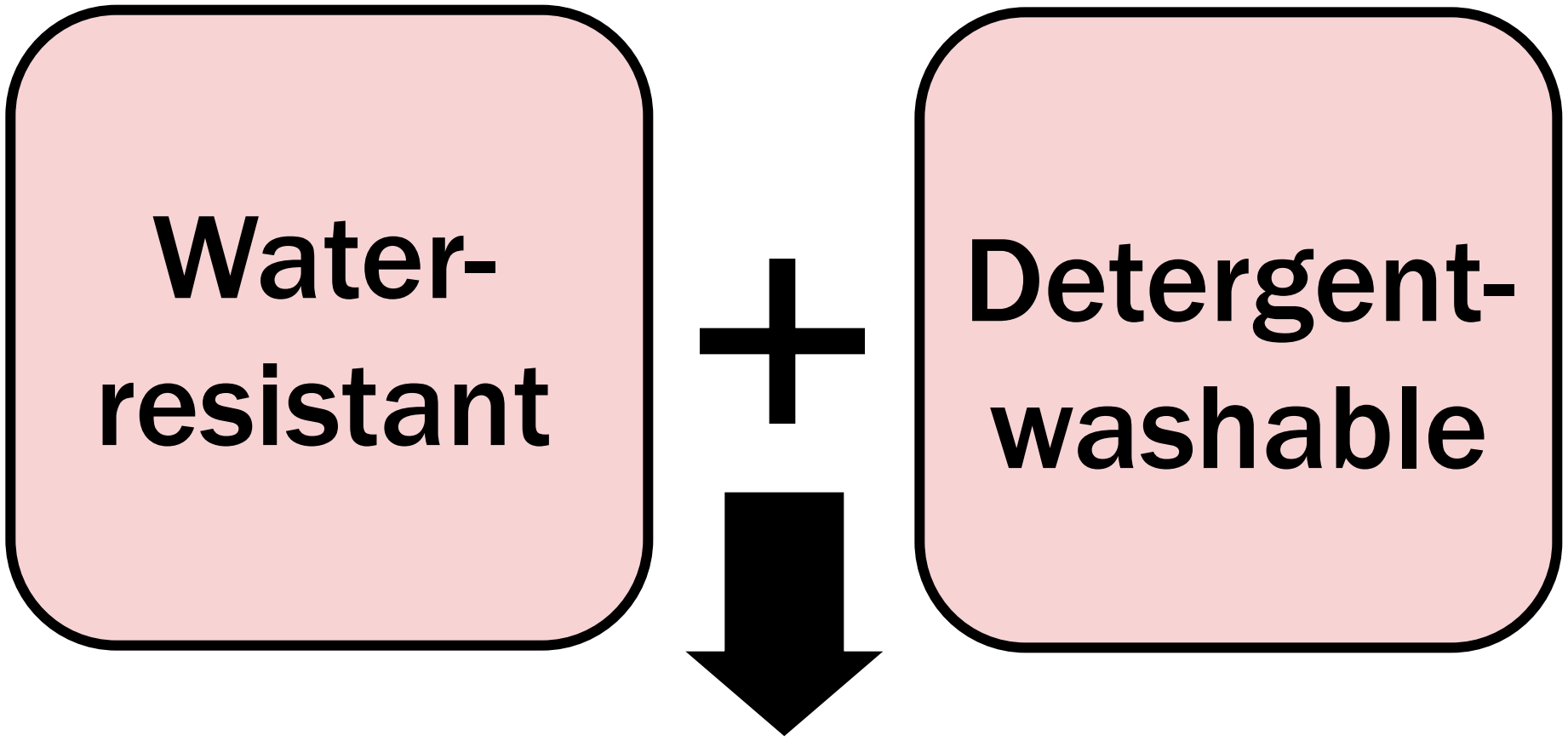


Powder (30%) still remained after washing.

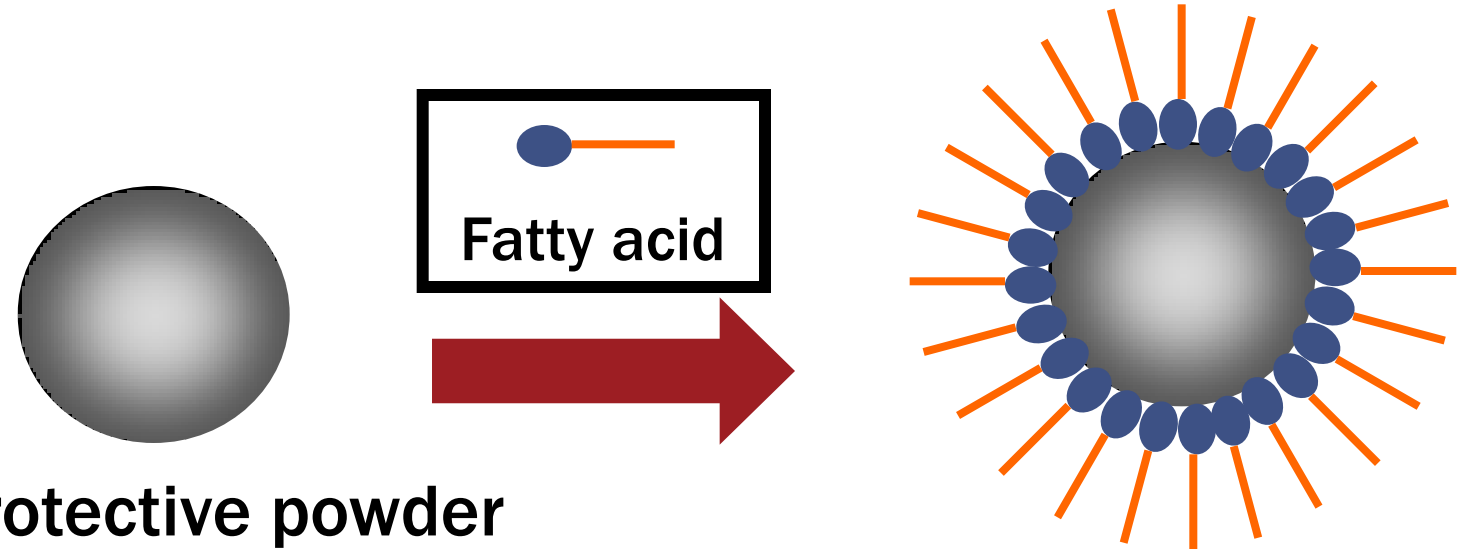
A dilemma found in sun-care products



Purpose


Water-resistant
+
Detergent-washable
Novel sun-care products

Hydrophobic treatment for UV protective powder



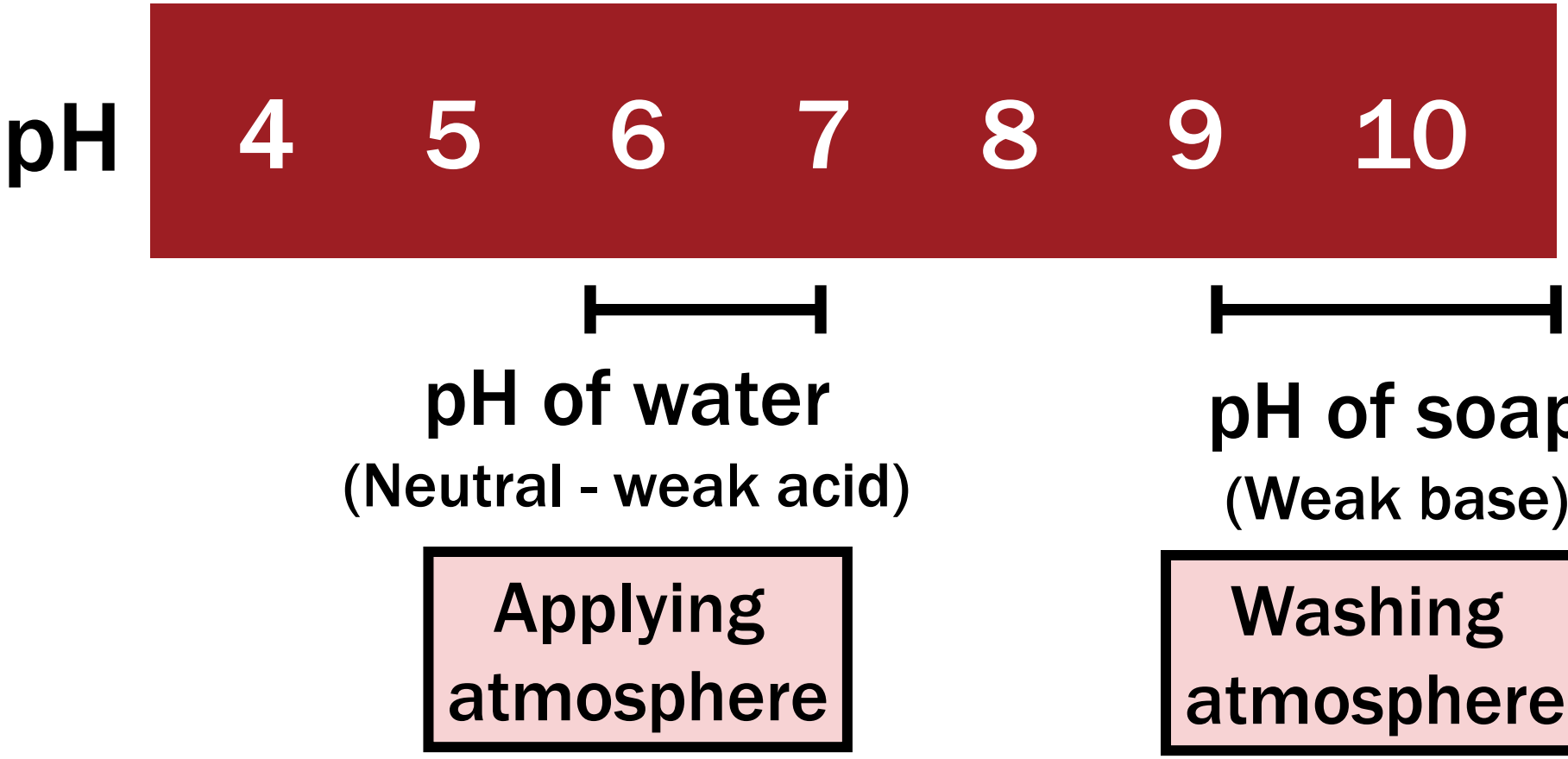
UV protective powder
(Titanium dioxide and Zinc oxide)

Fatty acid-treated powder (Hydrophobic)

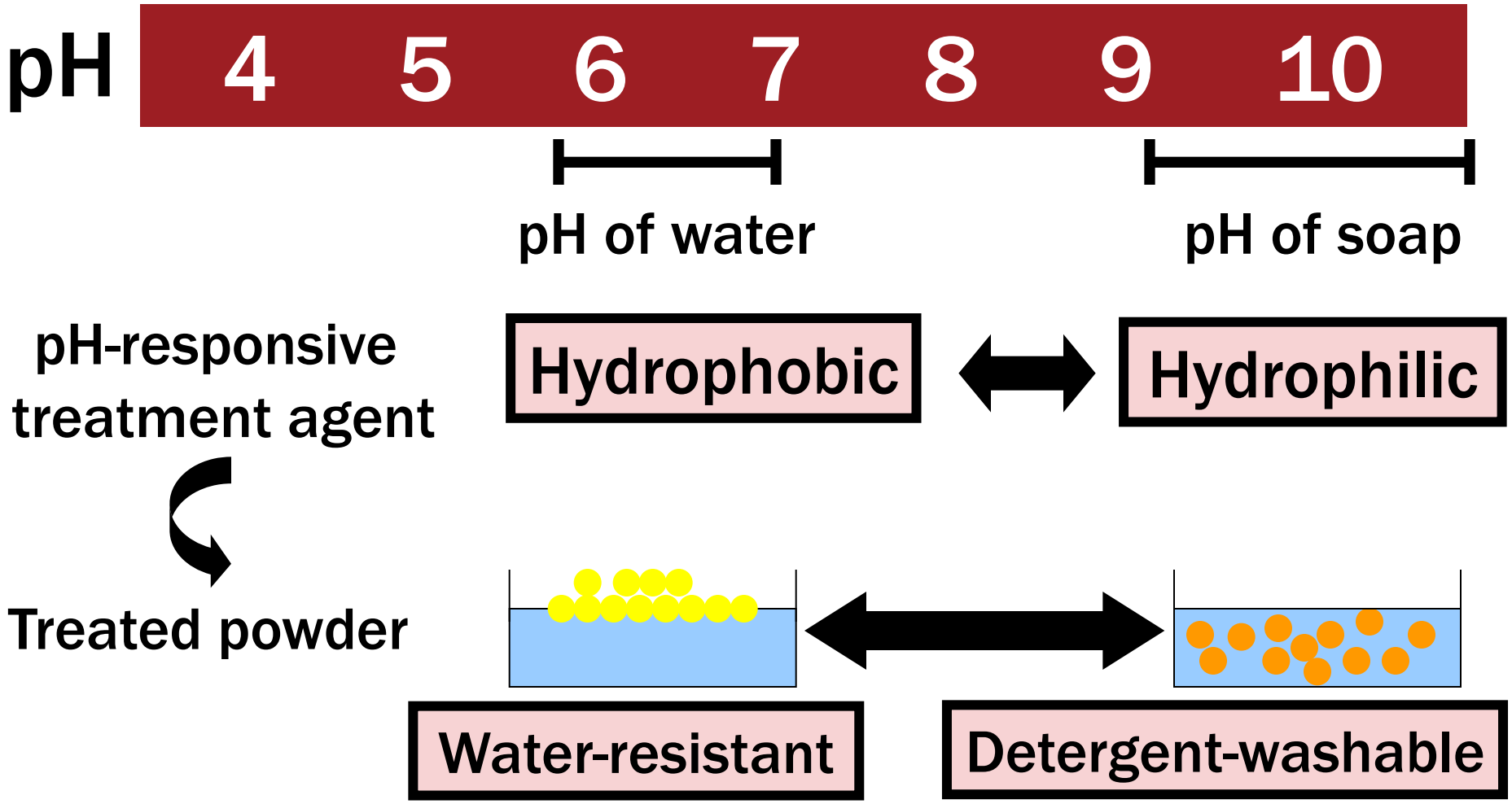
Hydrophobicity causes poor detergent-washability

pH of soap

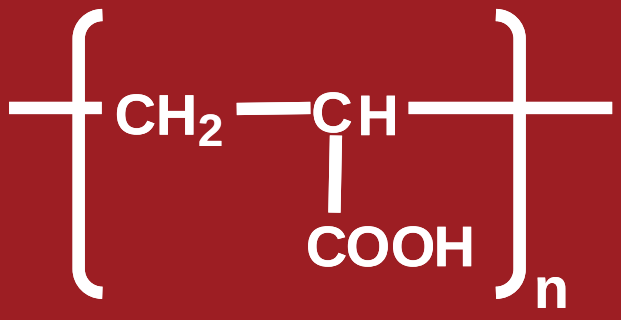
pH of soap ..... weak base



New treatment agent
(pH-responsive agent)



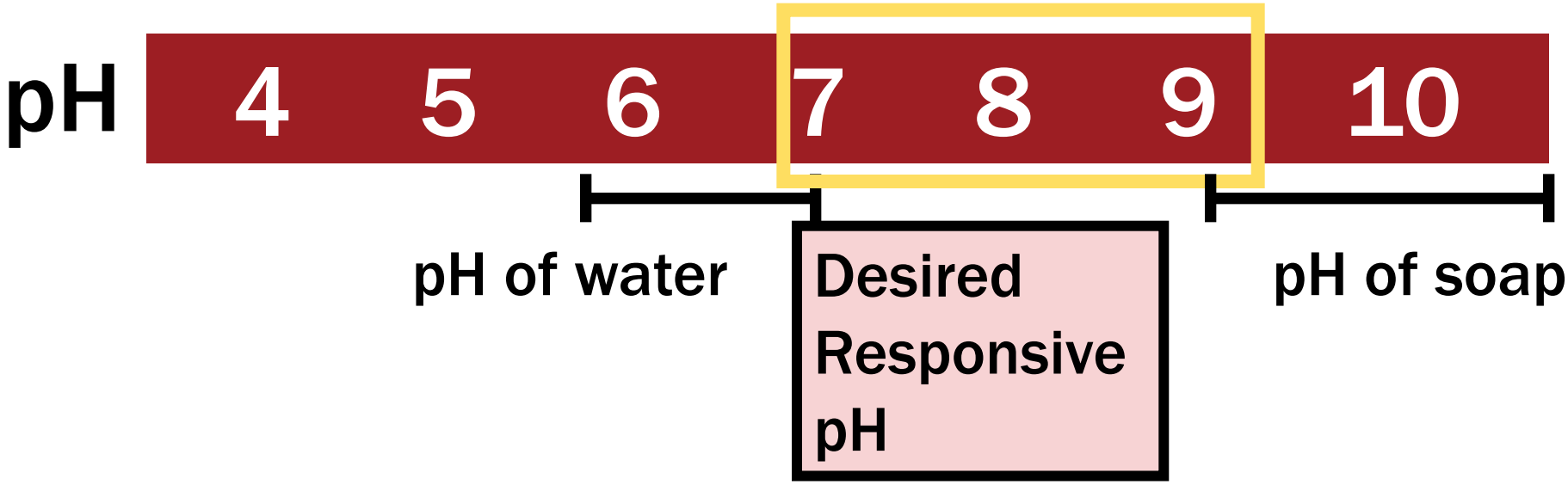
Design of pH-responsive agent



Typical pH-responsive polymer

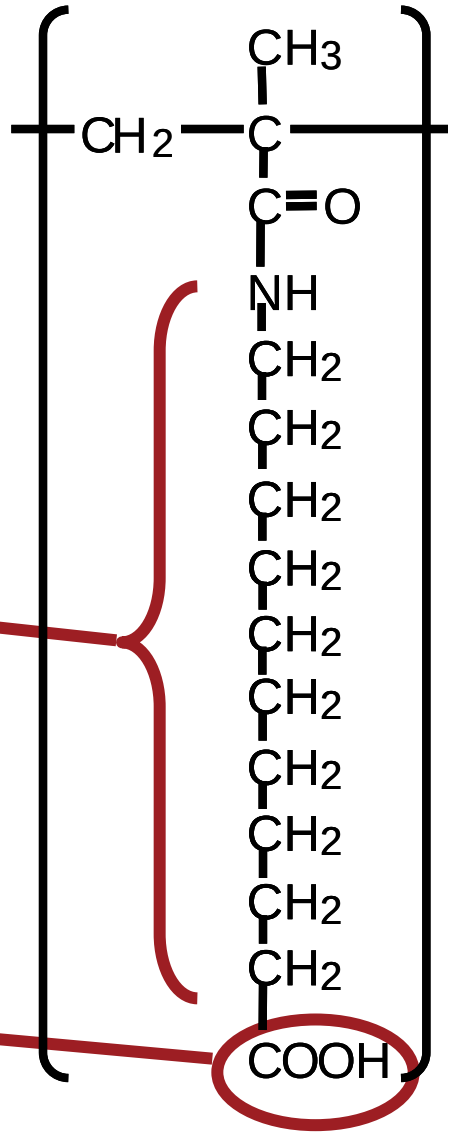
Poly acrylic acid (pKa 5 - 6)

➡More hydrophobic structure



Polymerization of MAU homo polymer

MAU homo polymer
(11-methacrylamidoundecanoic acid)

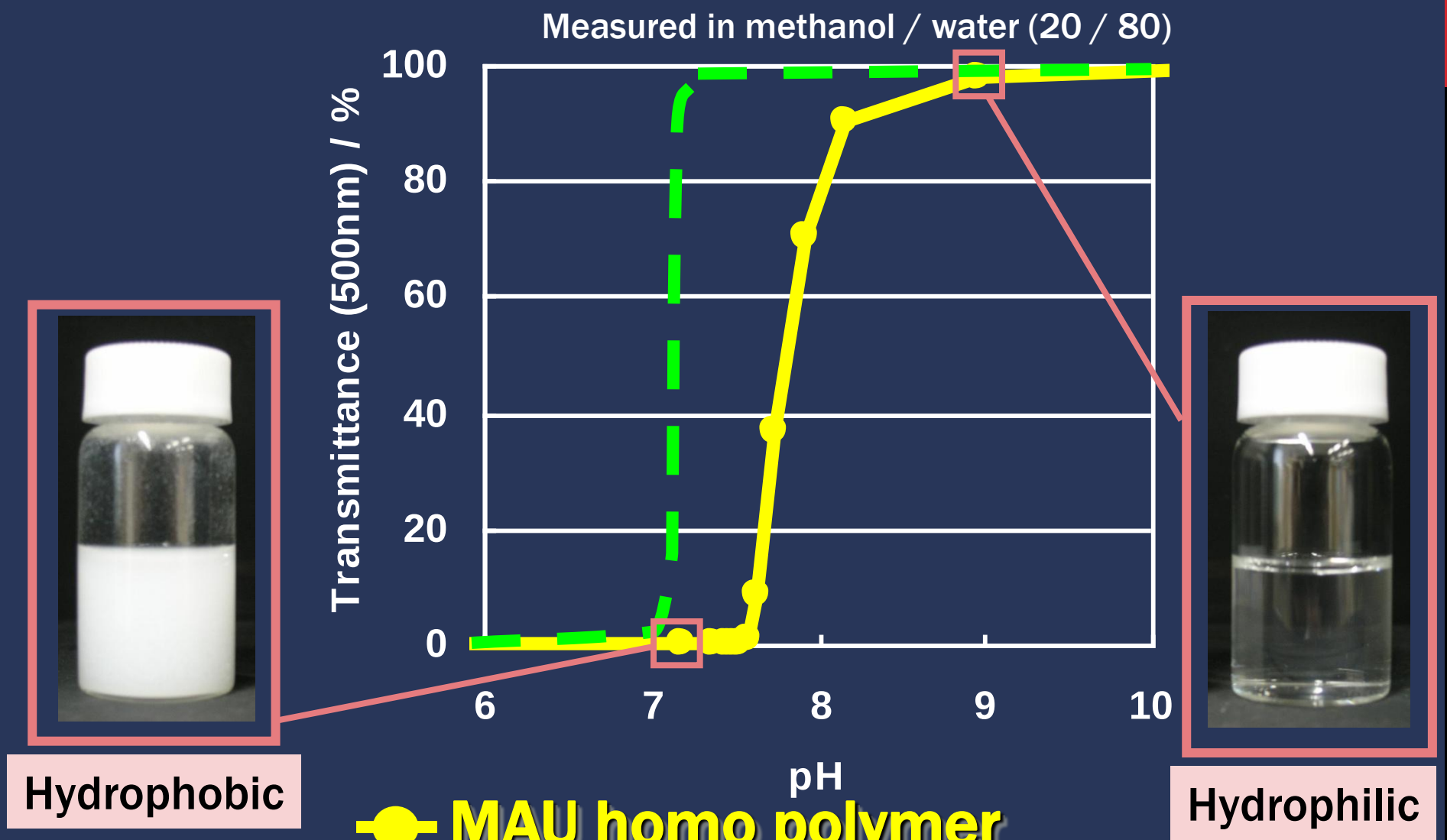


More hydrophobic structure

Long alkyl chain

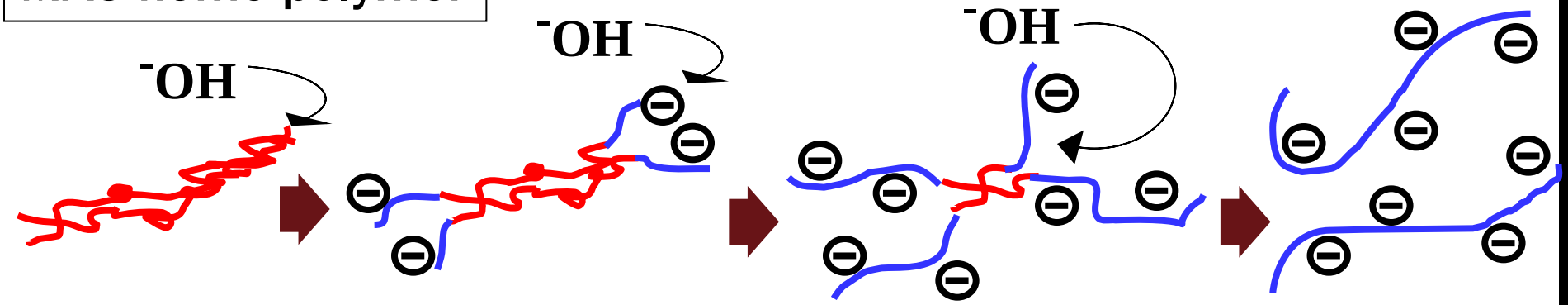
pH-responsive moiety

pH-responsiveness of MAU homo polymer

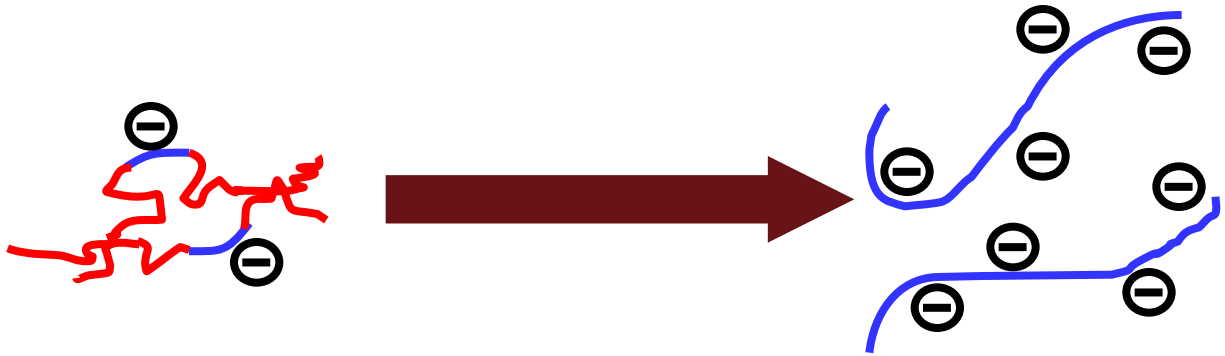


To obtain steep pH-responsiveness

MAU homo polymer



Introduction of strong electrolytes

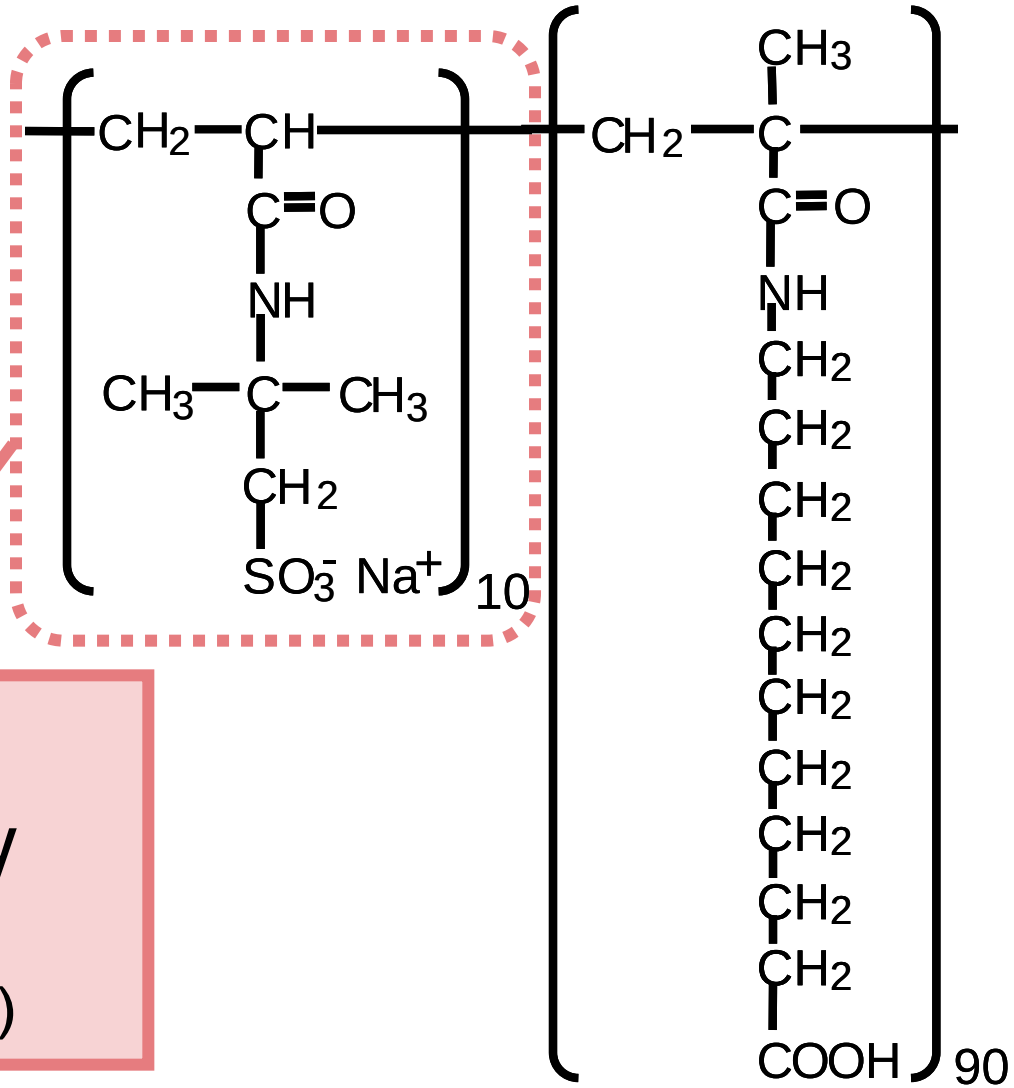


Quick dissociation

Lax structure of aggregating polymers

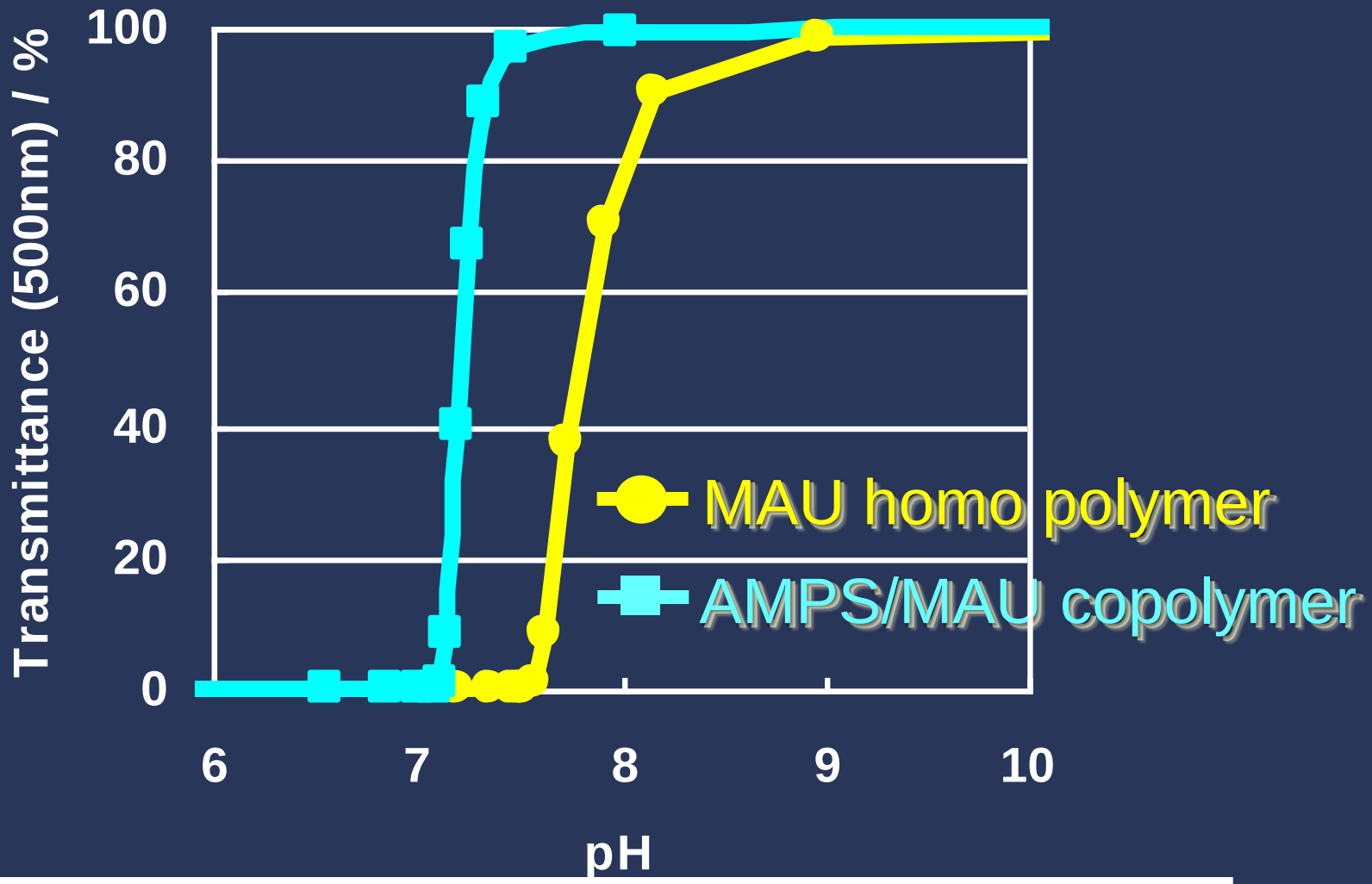
Polymerization of AMPS/MAU

AMPS/MAU copolymer



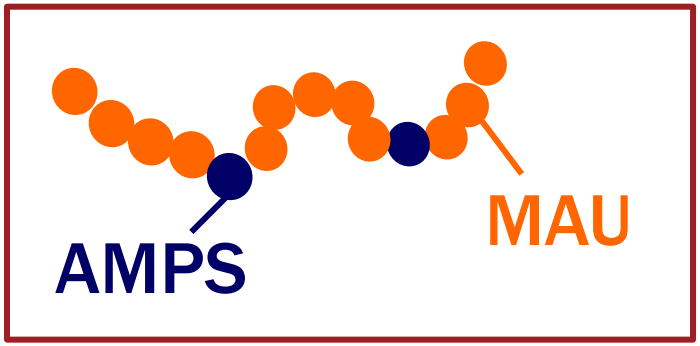
Introduction of a strong acid moiety
(sodium 2-(acrylamido)-2-methylpropanesulfonate)

pH-responsiveness of AMPS/MAU

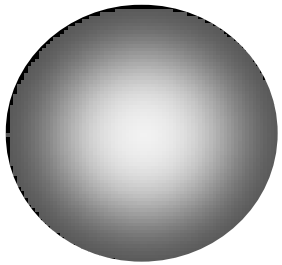


A sharp and quick pH-response found in AMPS/MAU

Development of AMPS/MAU-treated titanium dioxide

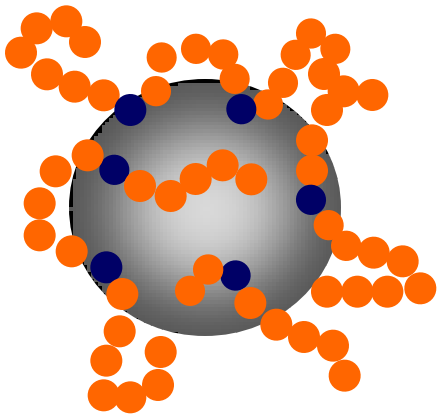


AMPS/MAU
in ethanol / water



Titanium dioxide

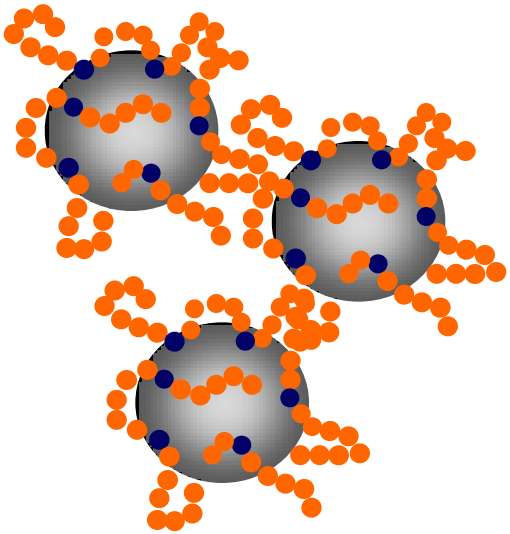
Dry up



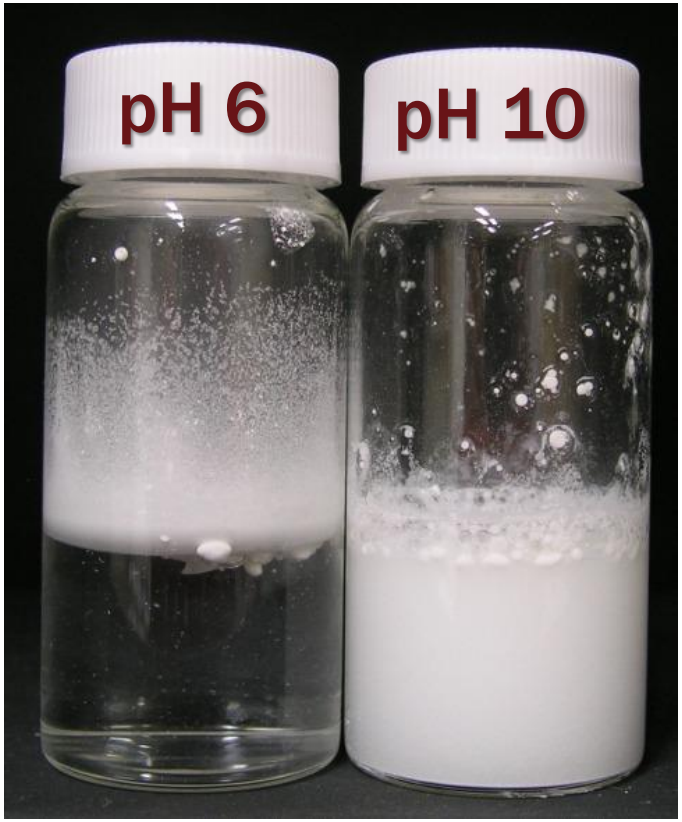
AMPS/MAU-treated titanium dioxide

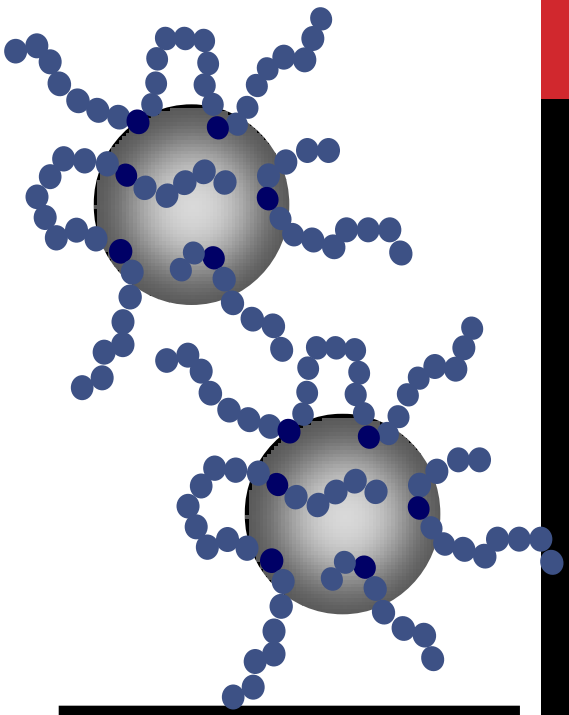
pH-responsiveness of AMPS/MAU-treated titanium dioxide

pH-responsiveness



Hydrophobic





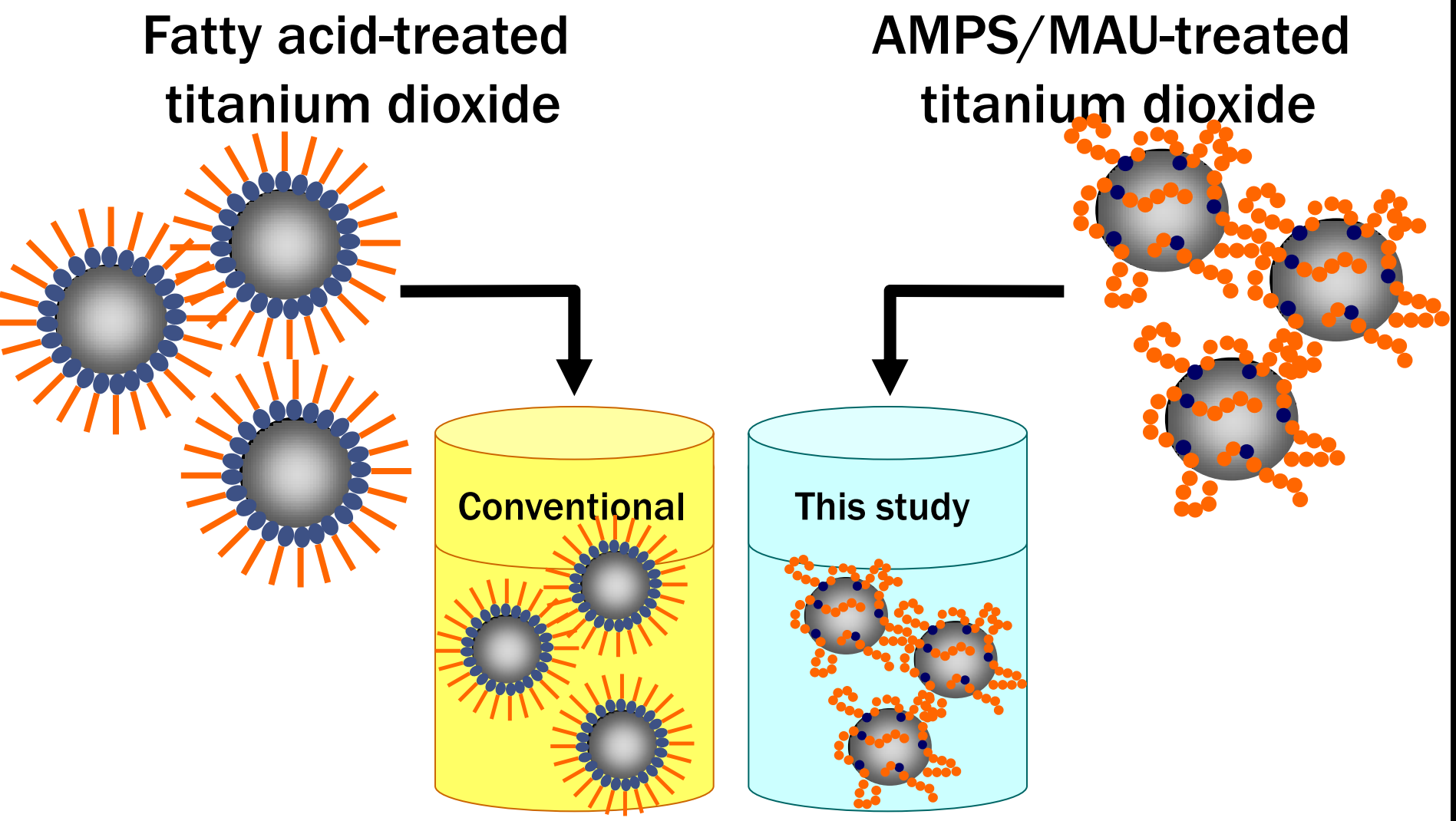
Hydrophilic

pH 4 5 6 7 8 9 10

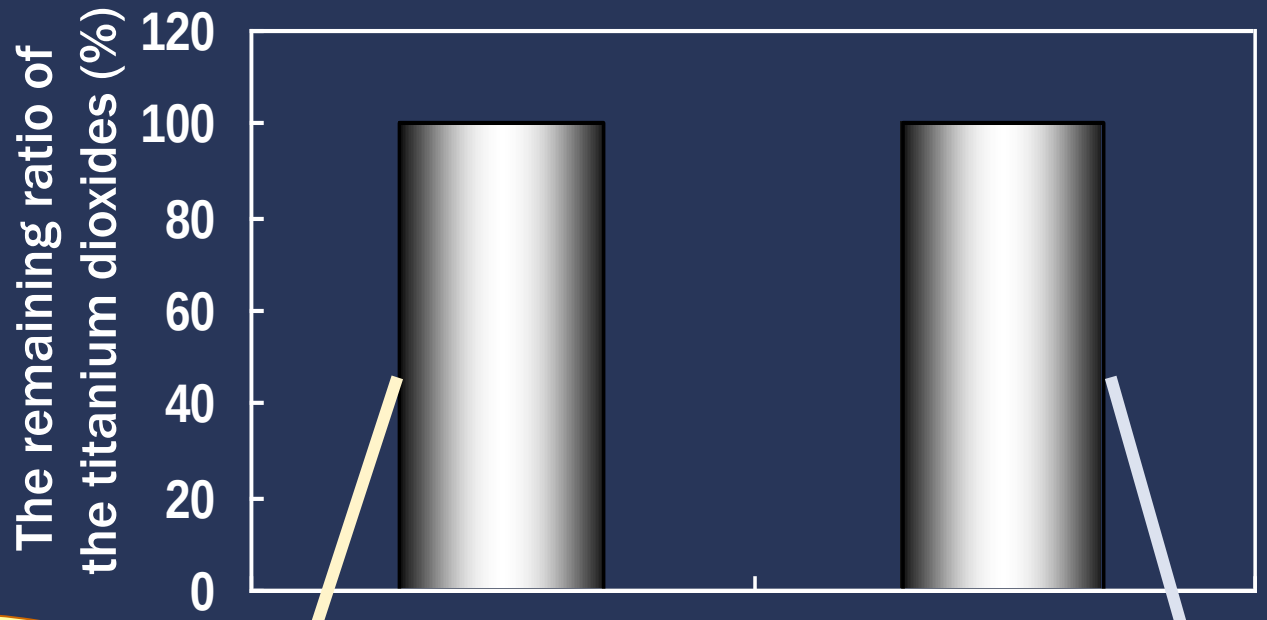
pH of water

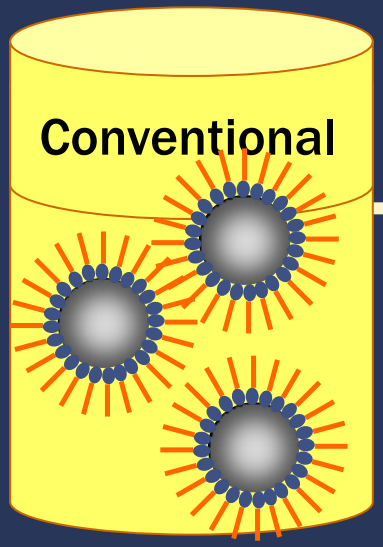
pH of soap

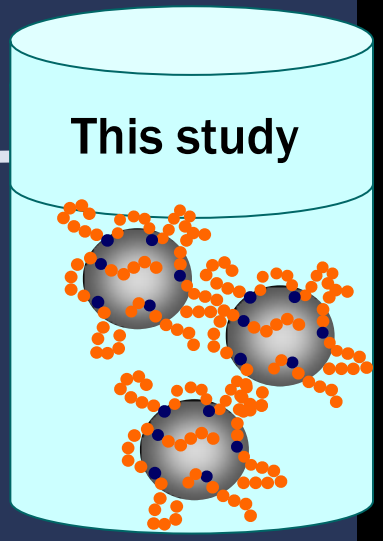
A sun-care product containing AMPS/MAU-treated titanium dioxide



Water-resistance

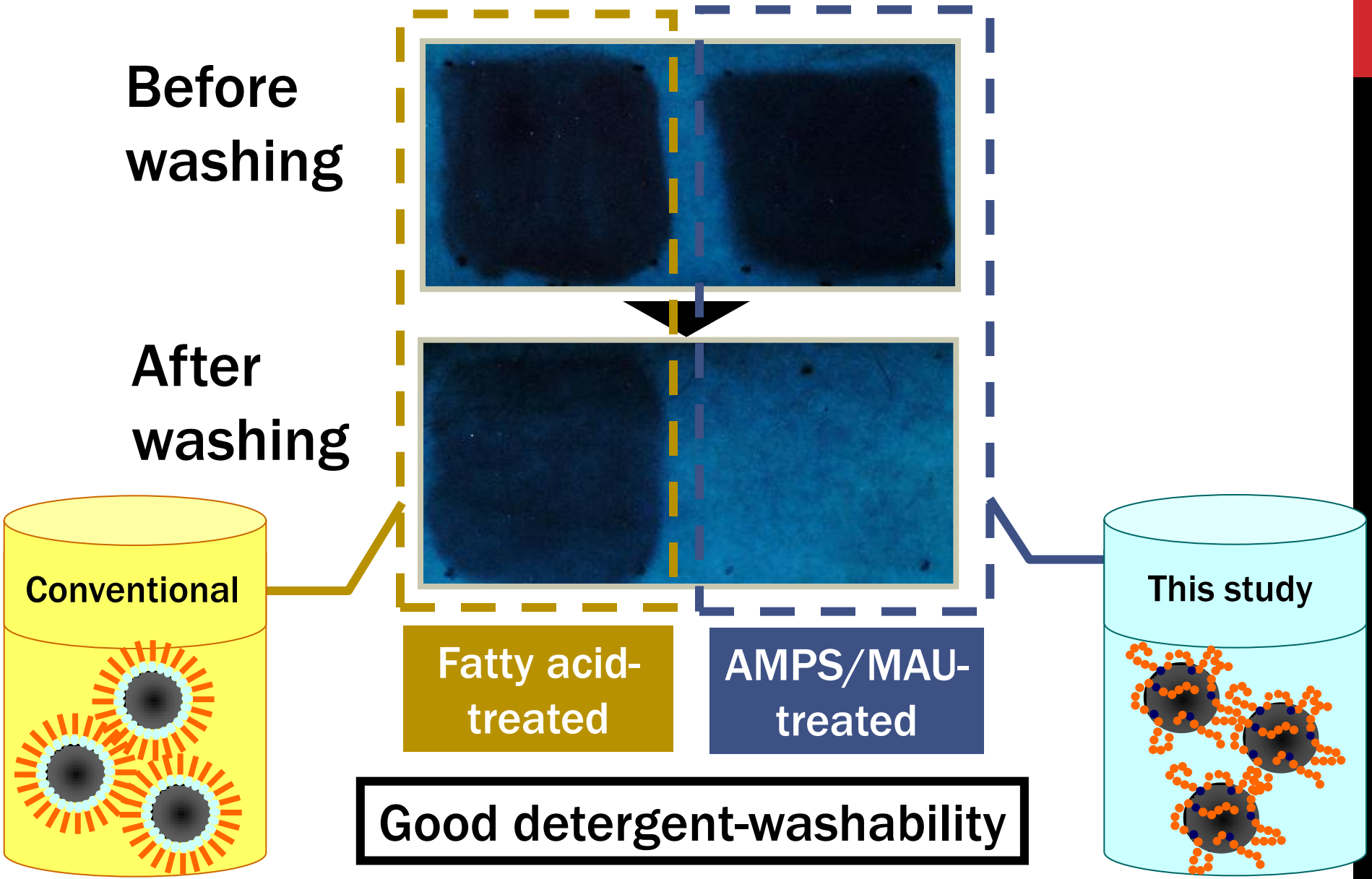






The Same water-resistance with conventional products

Detergent-washability



Conclusion

AMPS/MAU-treated titanium dioxide

Hydrophobic in a weak acid medium

Hydrophilic in a weak basic medium

High pH-responsiveness

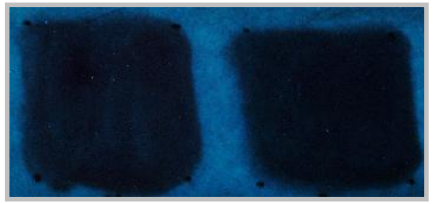
A sun-care product containing AMPS/MAU-treated titanium dioxide

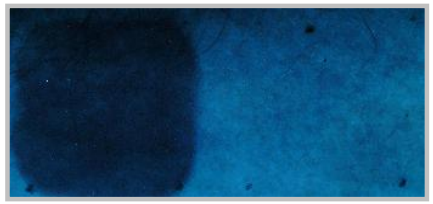
High water-resistance

(It resembles conventional products.)

Great detergent-washability

(It is higher than conventional products.)





A Novel, Long-lasting, Non-Smear Lipstick Utilizing a Phase Separation Mechanism is Totally Devoid of Secondary Stain

- Introduction (Our purpose and ideal lipsticks)
- Liquid crystal instead of film-forming agent
- Design of phase-separation mechanism
- Development of lipsticks
- Efficacy data

	The 50S～	The second half of the 60s	The 70s
Lips	Red Lipsticks	Pink Lipsticks	Natural makeup
Eyes	Eye make-up start		

	The second half of the 80s	The second half of the 90s	
Lips	clarified Lips	Natural makeup	Not color But textures
Eyes	Thick eyebrows	Thin eyebrows	Mascara Eyeliner

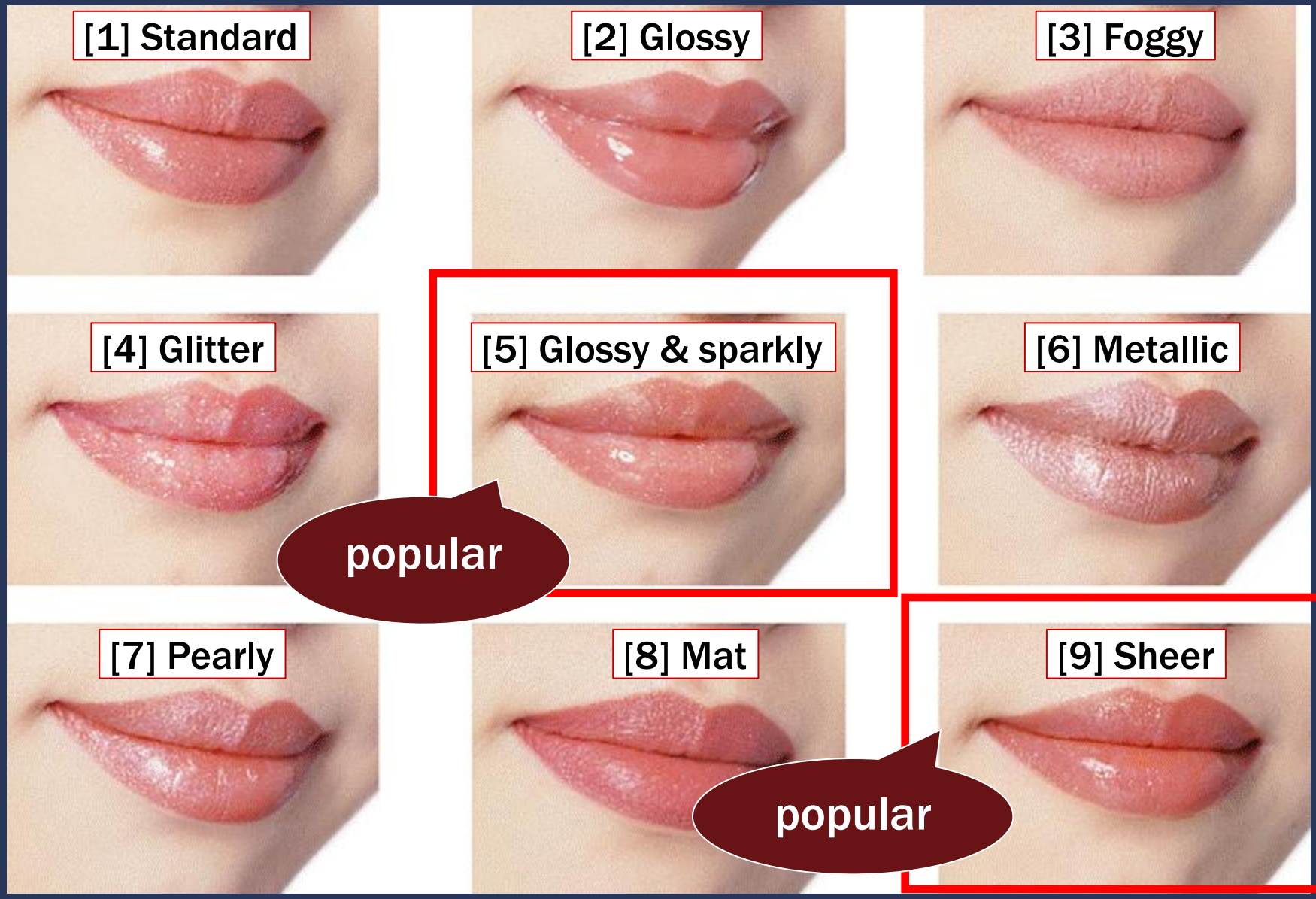
The first half of the 90s

Boom in non-smear lipstick

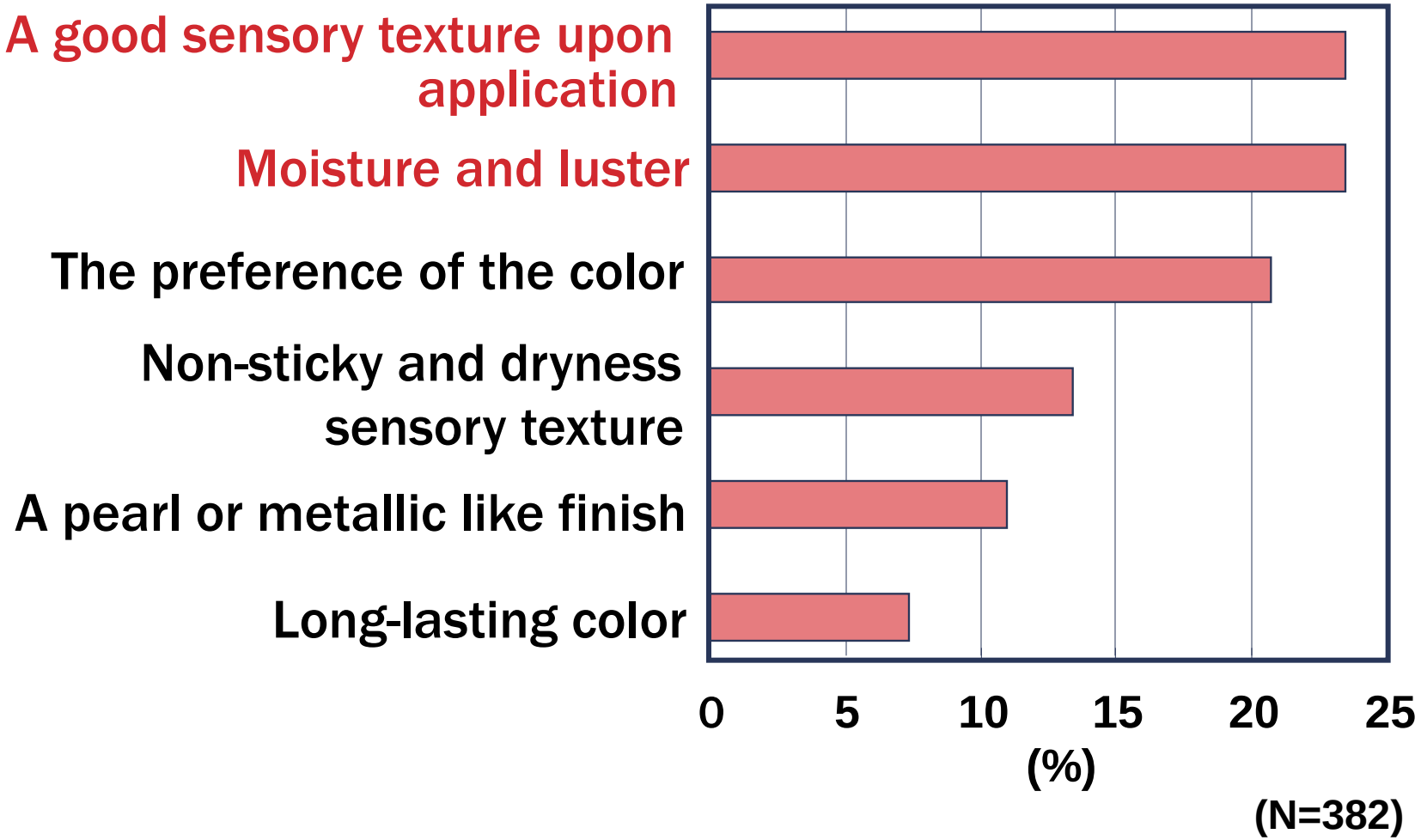
Poor luster
Dry
Stiff

Not perfect

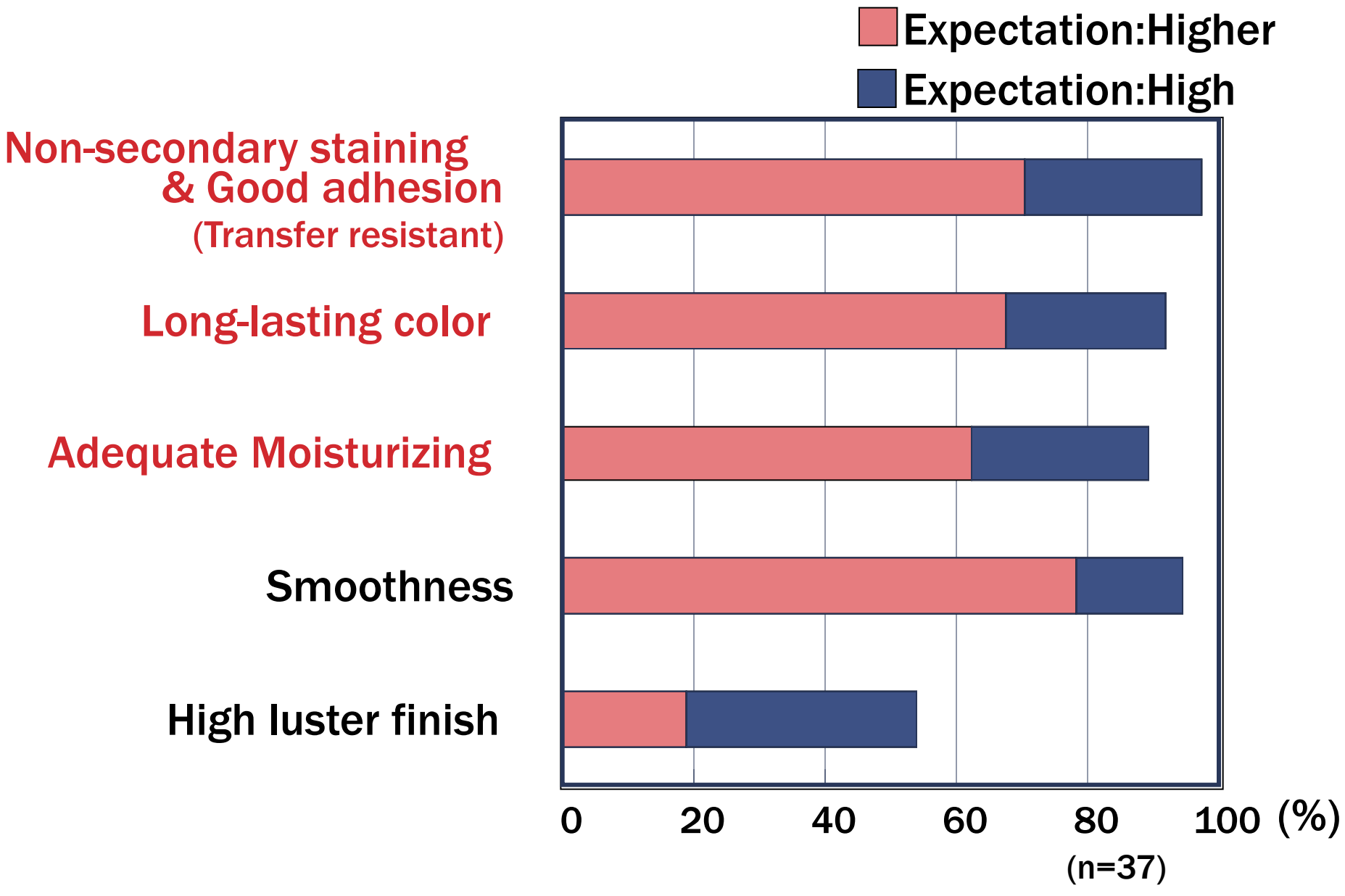
The textures of lipstick



Factors affecting consumers' buying-decisions for lip-stick



Expectations for lip-sticks



An ideal lipstick for consumers

Beautiful high luster

Adequate moisture

Long-lasting color without secondary staining (Transfer resistant)

At the current market

Good

Beautiful luster
Adequate moisture

High-refractive-index polar oils

Not Good

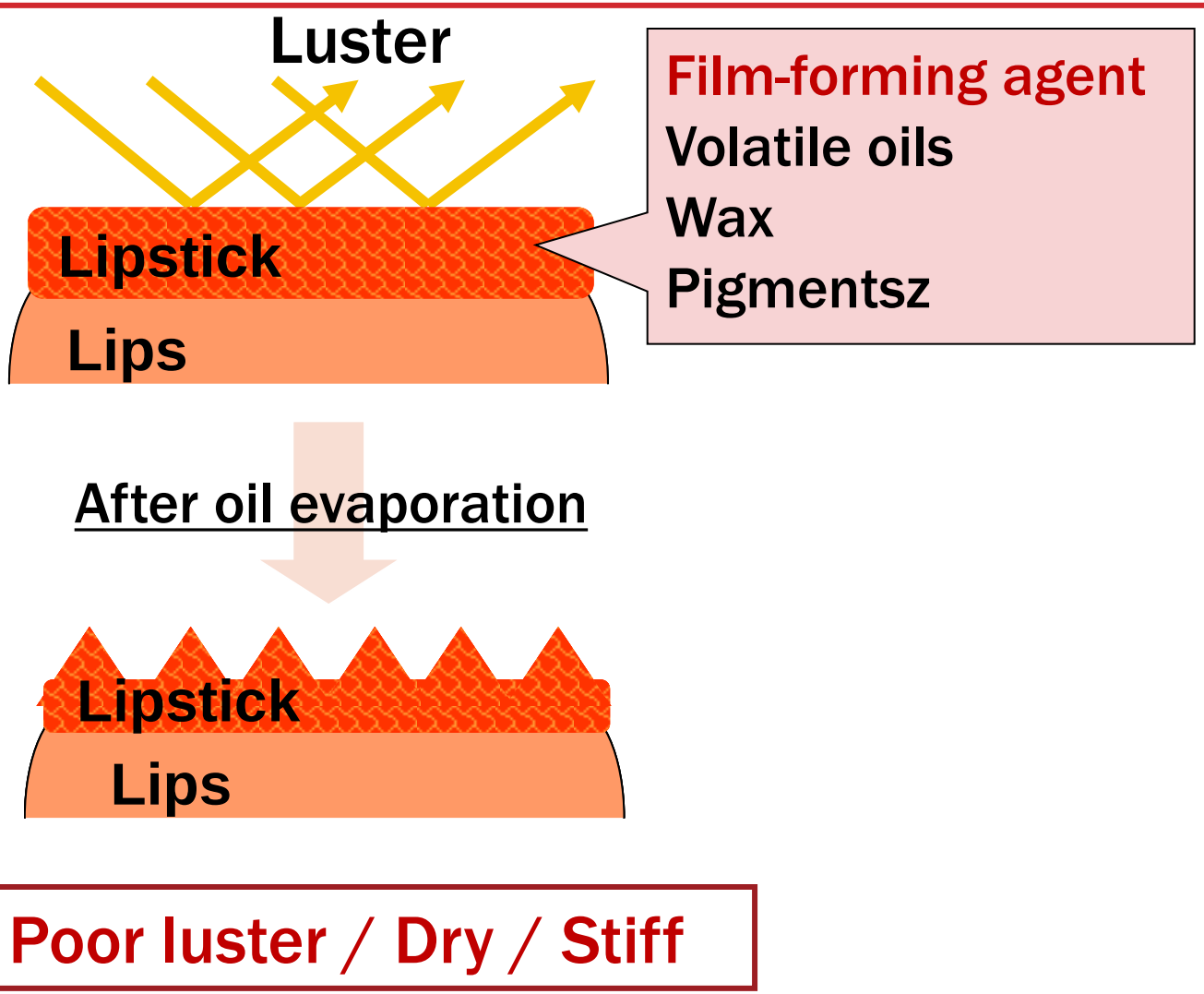
Not Good

Non-Secondary staining

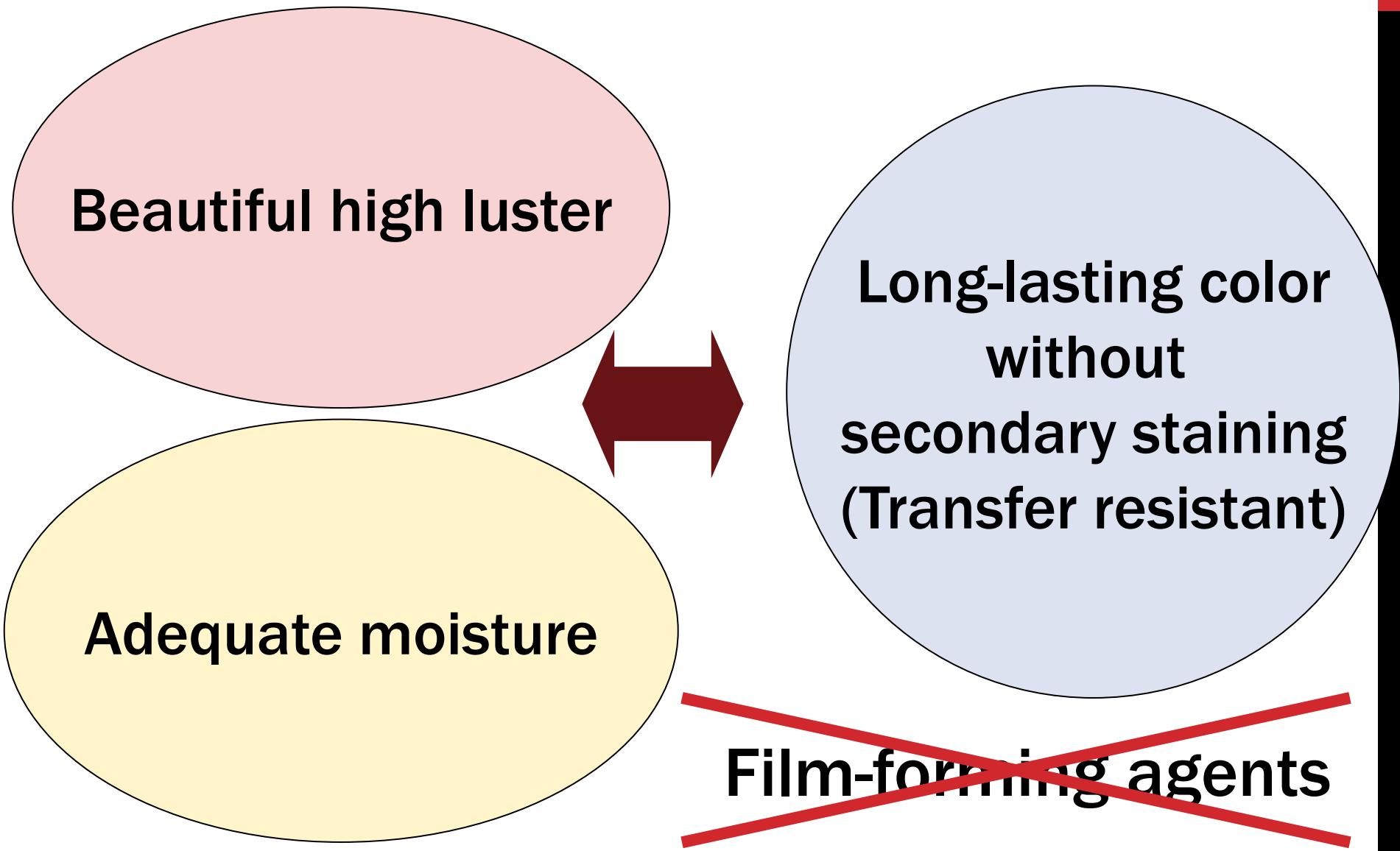
Film-forming agent

Good

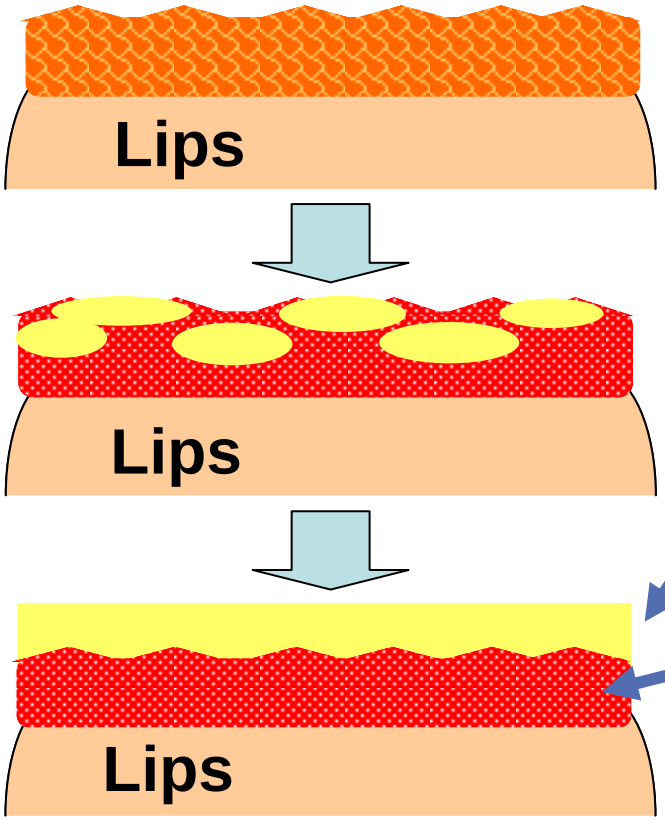
Conventional non-stain lipstick containing film-forming agents



Purpose


Beautiful high luster
Adequate moisture
Long-lasting color without secondary staining (Transfer resistant)
Film-forming agents

Our strategy



Separating oil

- Non-secondary staining
- Luster

Liquid crystal +Pigment

- Luster
- Pigment stabilizer

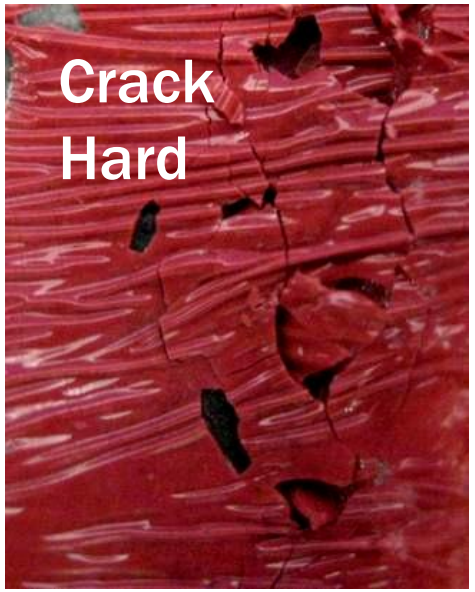
For materializing one step application

Phase separation mechanism

Search for a pigment-stabilizer instead of film-forming agents

Film-forming agent + Pigments

Oil evaporation



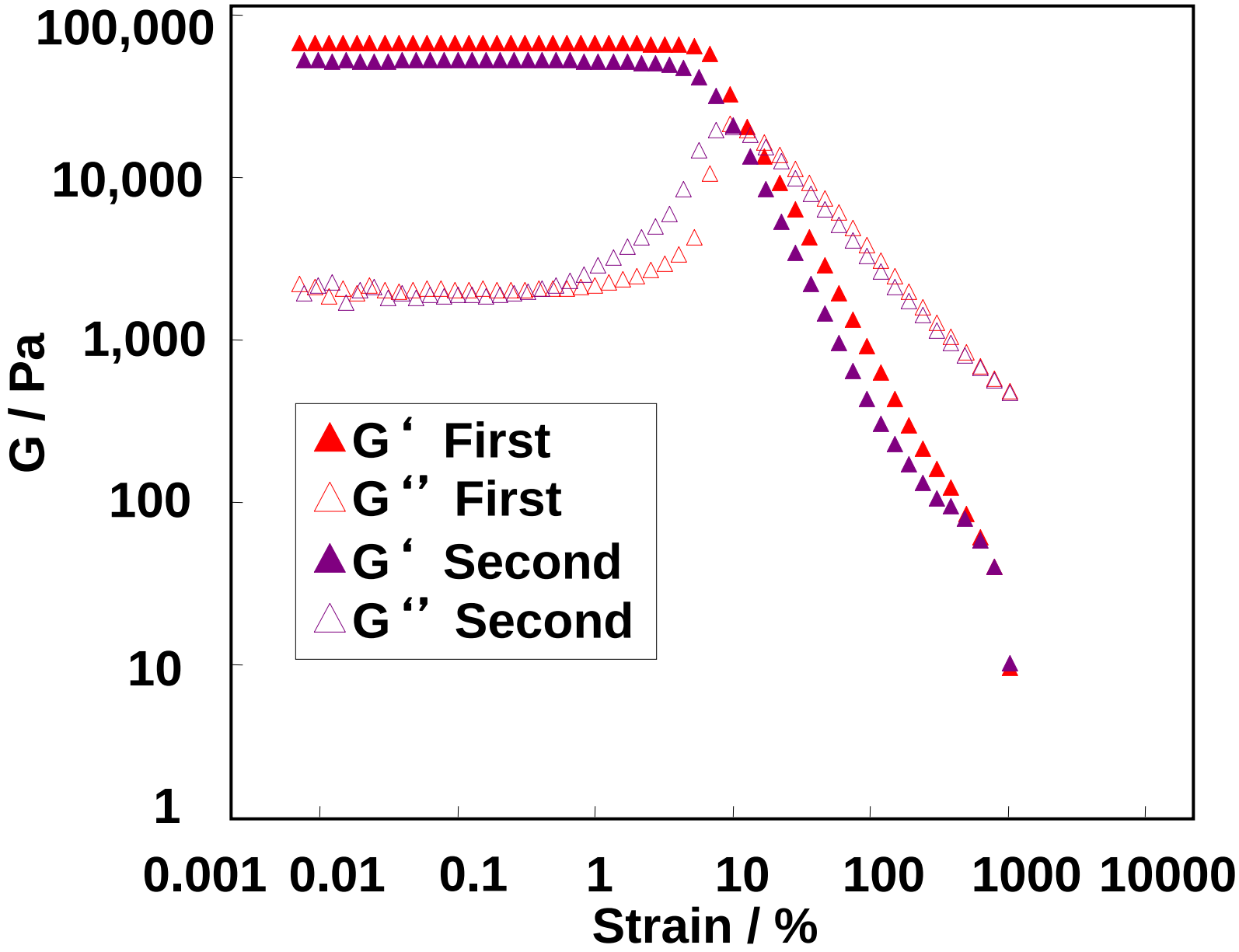
Hard ↓ Flexible

High viscosity oil < Paste-like oil < Gel < Film < Solid oil

↓

(Liquid crystal)

Characteristic of Liquid crystal

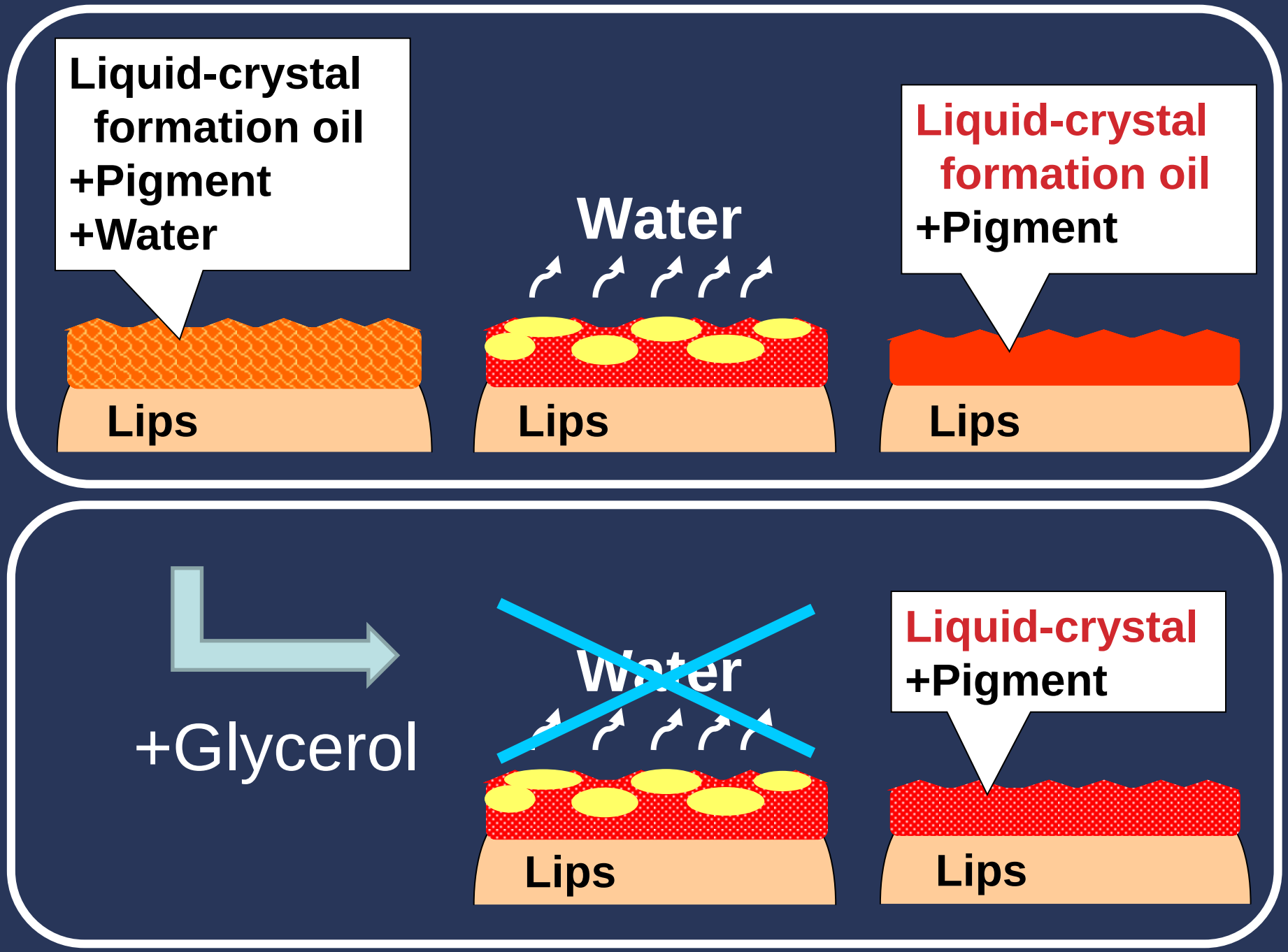


Characteristic of Liquid crystal

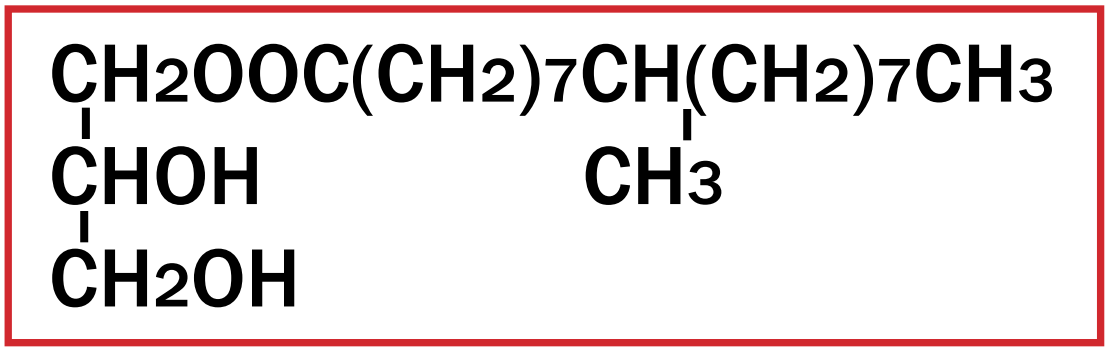
+ Water

Liquid-crystal forming oil + Pigments

Smooth Luster

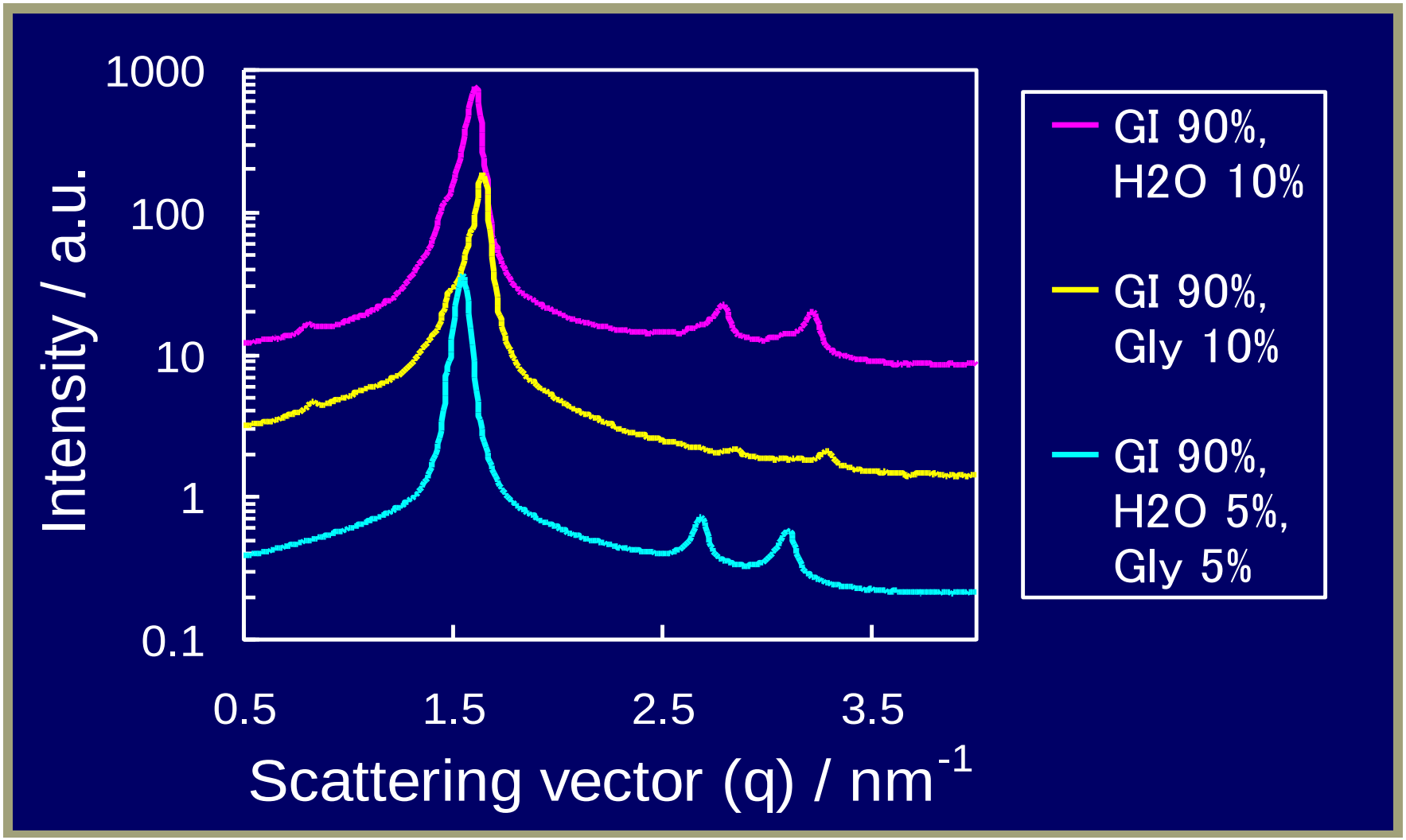

Liquid-crystal
formation oil
+Pigment
+Water
Lips
Water
Lips
Liquid-crystal
formation oil
+Pigment
Lips
+Glycerol
Water
Lips
Liquid-crystal
+Pigment
Lips

The structure of Liquid crystal forming oil

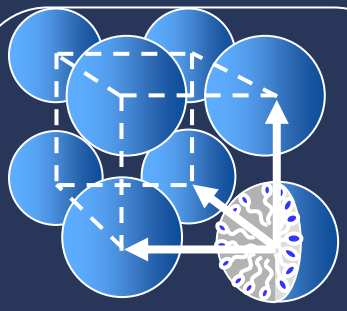


Glyceryl isostearate (GI)

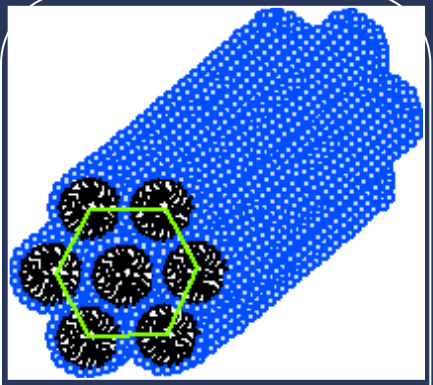
Structure analysis of liquid-crystal By small-angle X-ray scattering



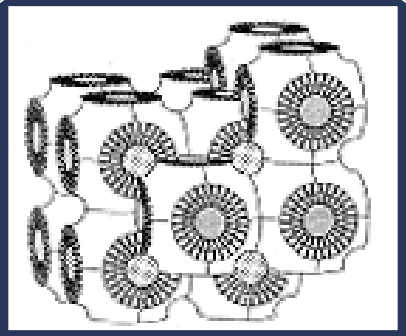
Liquid crystal structures



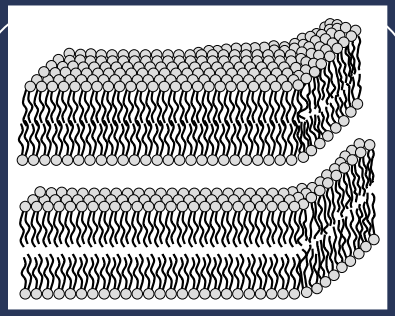
Micelle cubic (I_1)



Hexagonal (H_1)

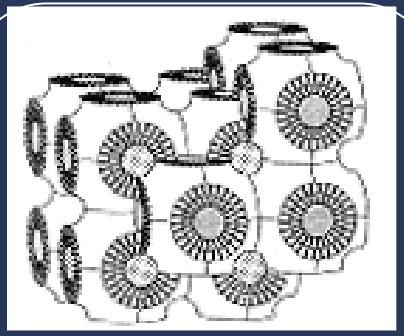


Bicontinuous-cubic (V_1)

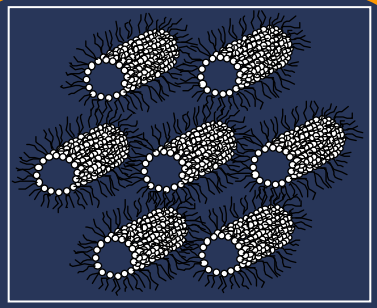


Lamella (L_α)

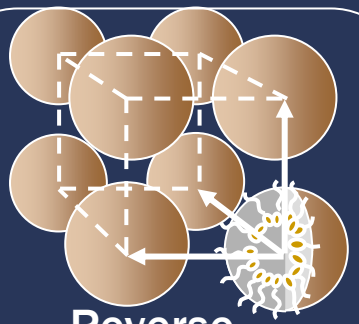
hydrophilic ⟵ ⟶ lipophilic



Bicontinuous-cubic (V_2)

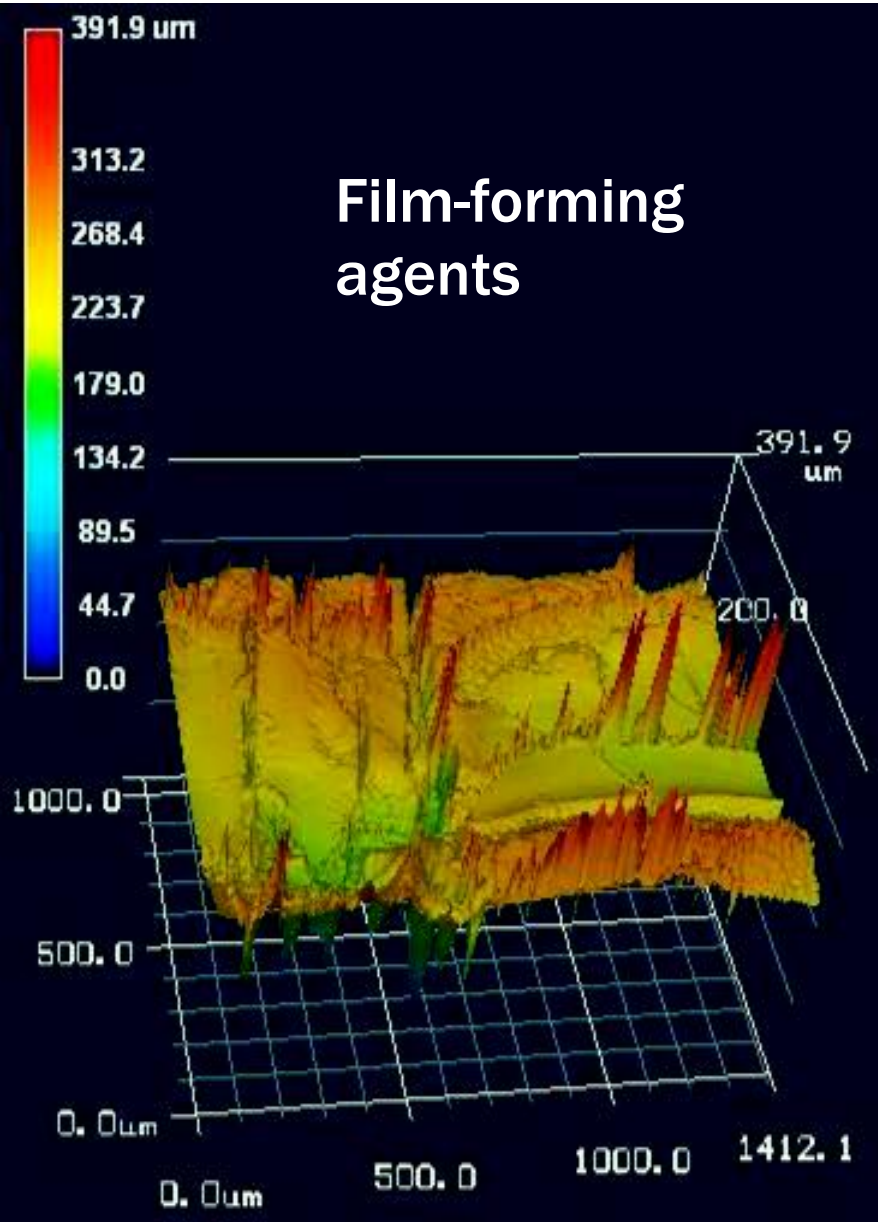


Reverse-hexagonal (H_2)

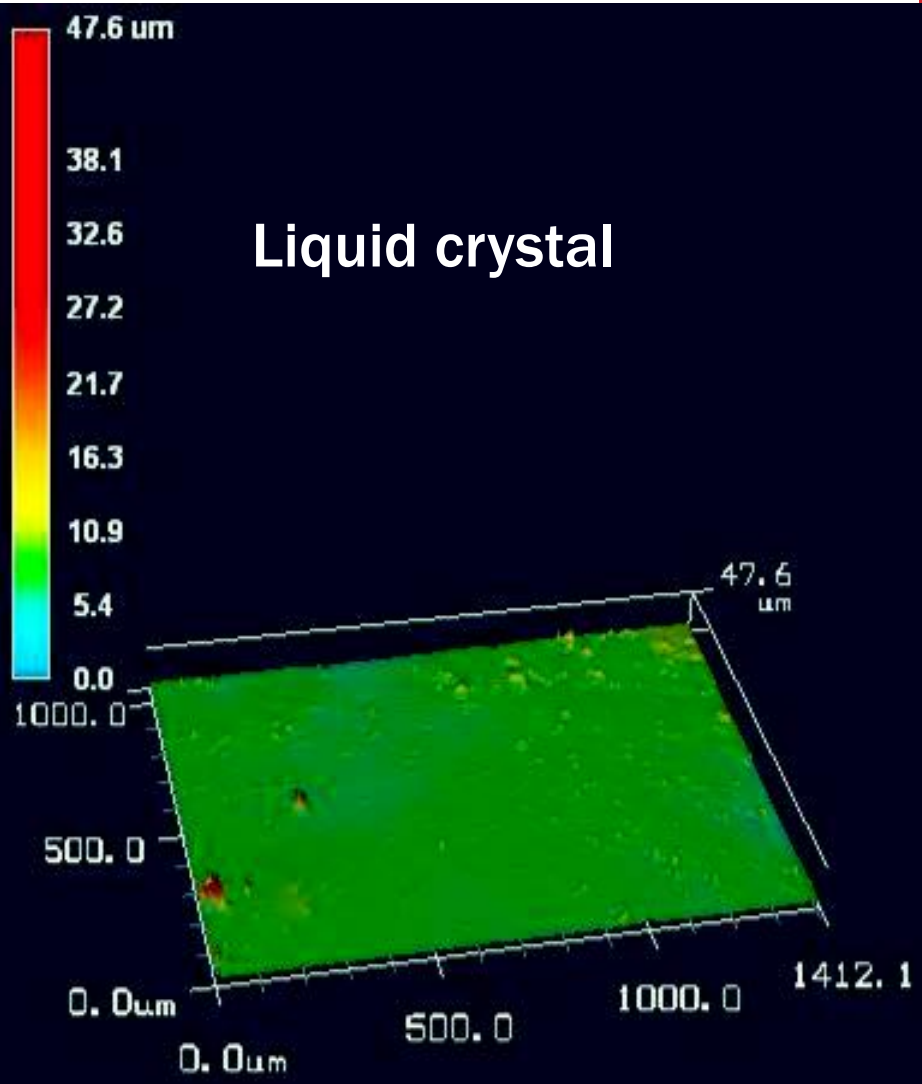


Reverse-micelle cubic (I_2)

The observation of the surface state

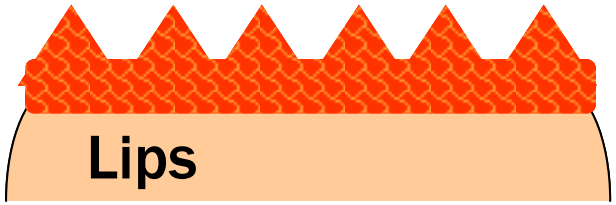


Film-forming agents



Liquid crystal

The protection of the color materials



Conventional
(Film-forming agent)

Luster
<
>
Non-
Secondary
staining

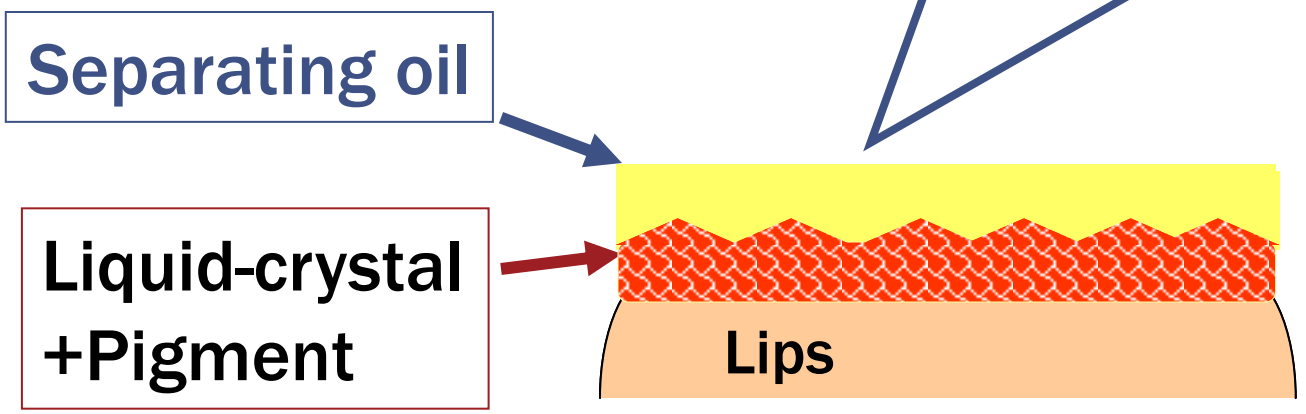
New
(Liquid crystal)

The protection of the color materials was needed

Design of phase-separation mechanism

Separating oil

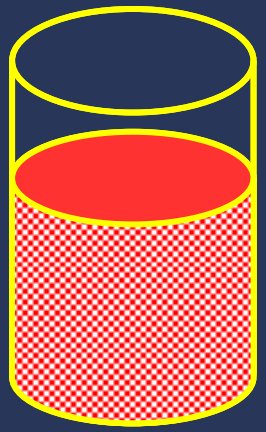
1. Incompatible with the liquid-crystal
2. Incompatible with pigments
3. High-luster
4. High viscosity



Separating oil selection

Method

Liquid-crystal forming oil
Water
Glycerol
Pigment
Various oils



Mixed at 90 °C

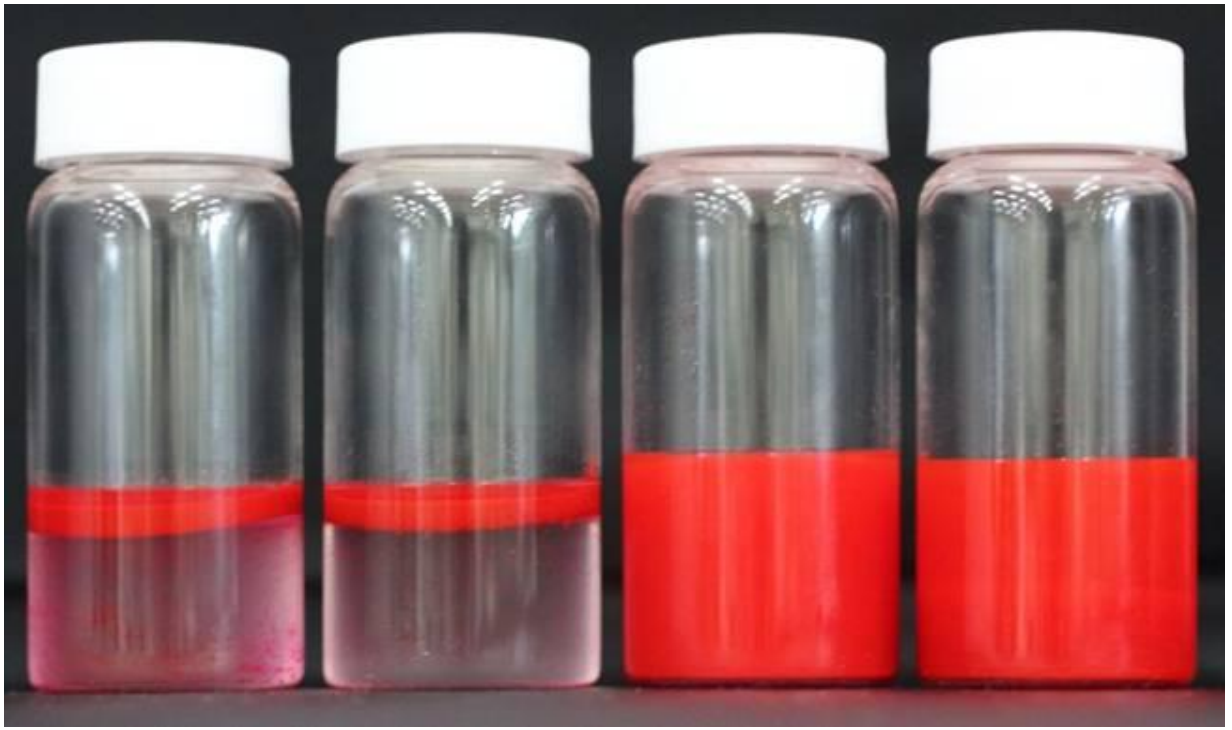
↓

Cooled at room temperature

↓

Centrifugation at 3,000rpm for 30 min

Separating oil selection



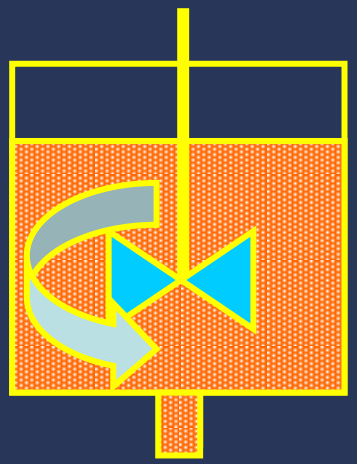
Trimethyl pentaphenyl trisiloxane (TPT)

Diphenyl dimethicone(DDM)

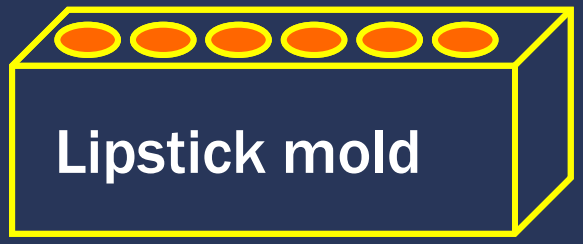
Diisostearyl malate (DIM)

Polyglyceryl-2 triisostearate (PTI)

Preparation method of lipstick



90 ºC
Liquid

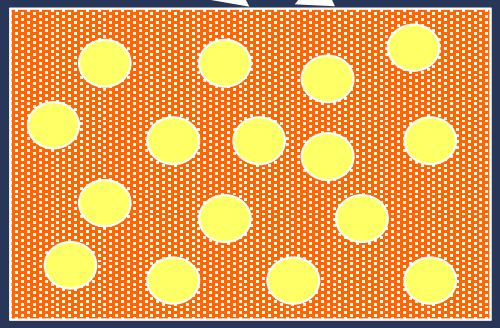


Cooling

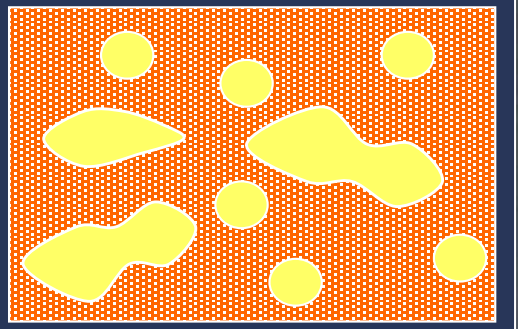
25 ºC
Solid

Liquid-crystal forming oil

Separating oil



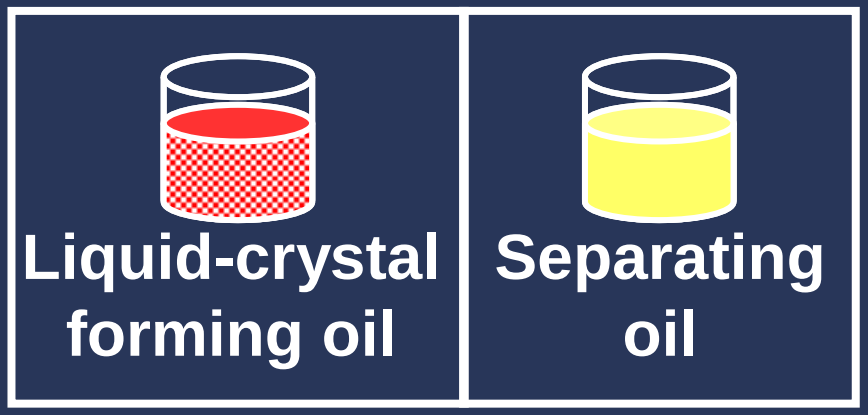
90 ºC

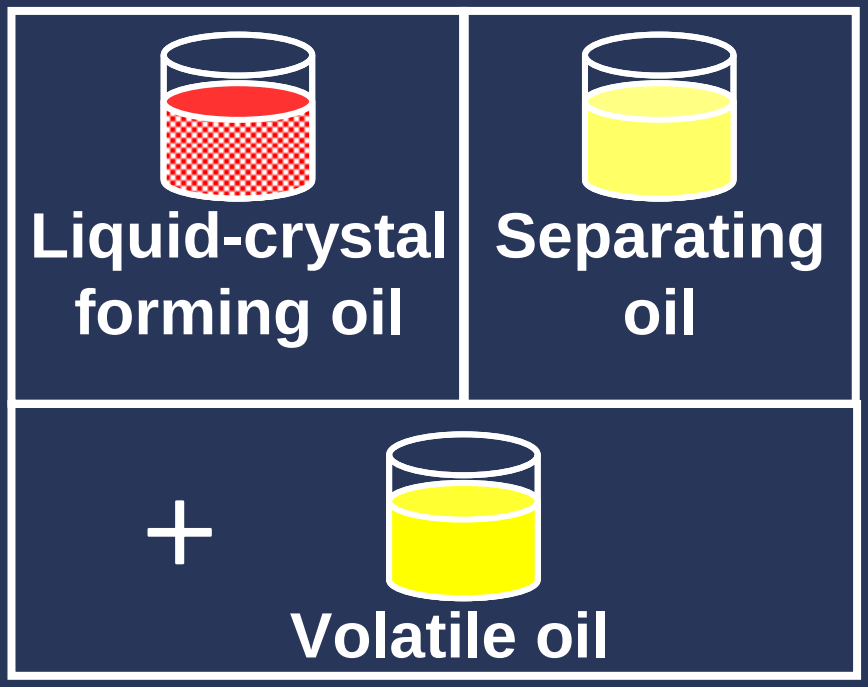


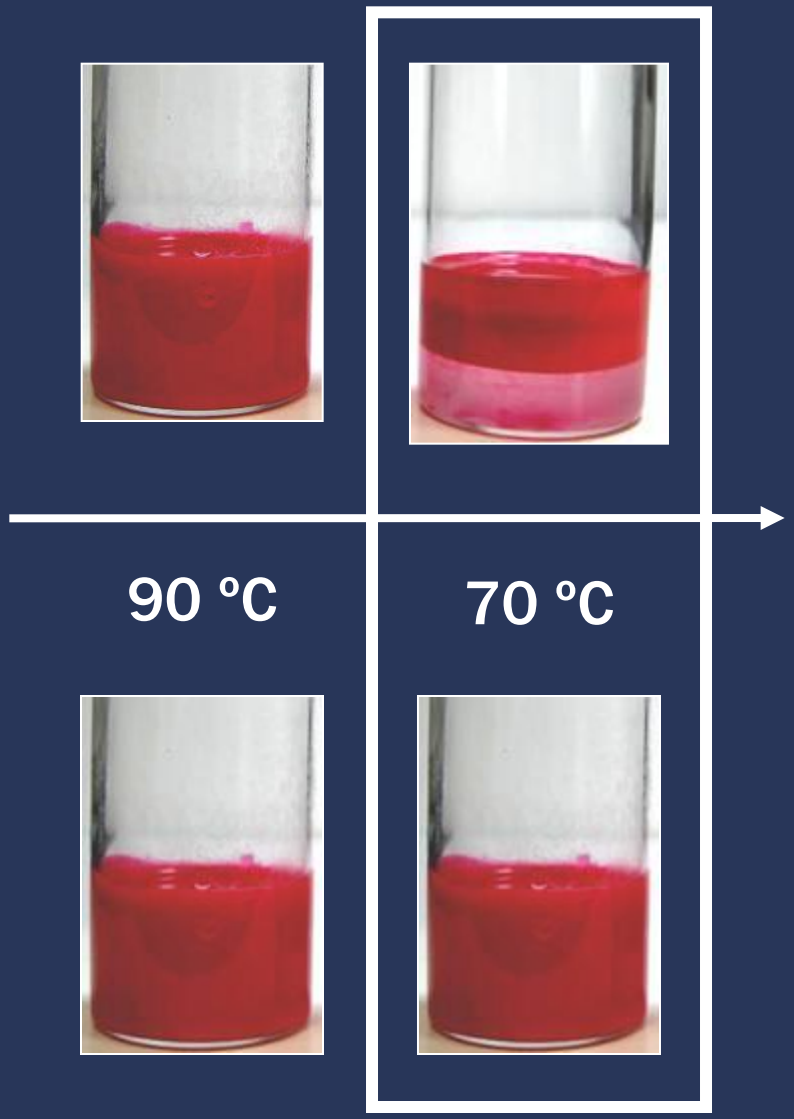
70 ºC

Heterogeneity

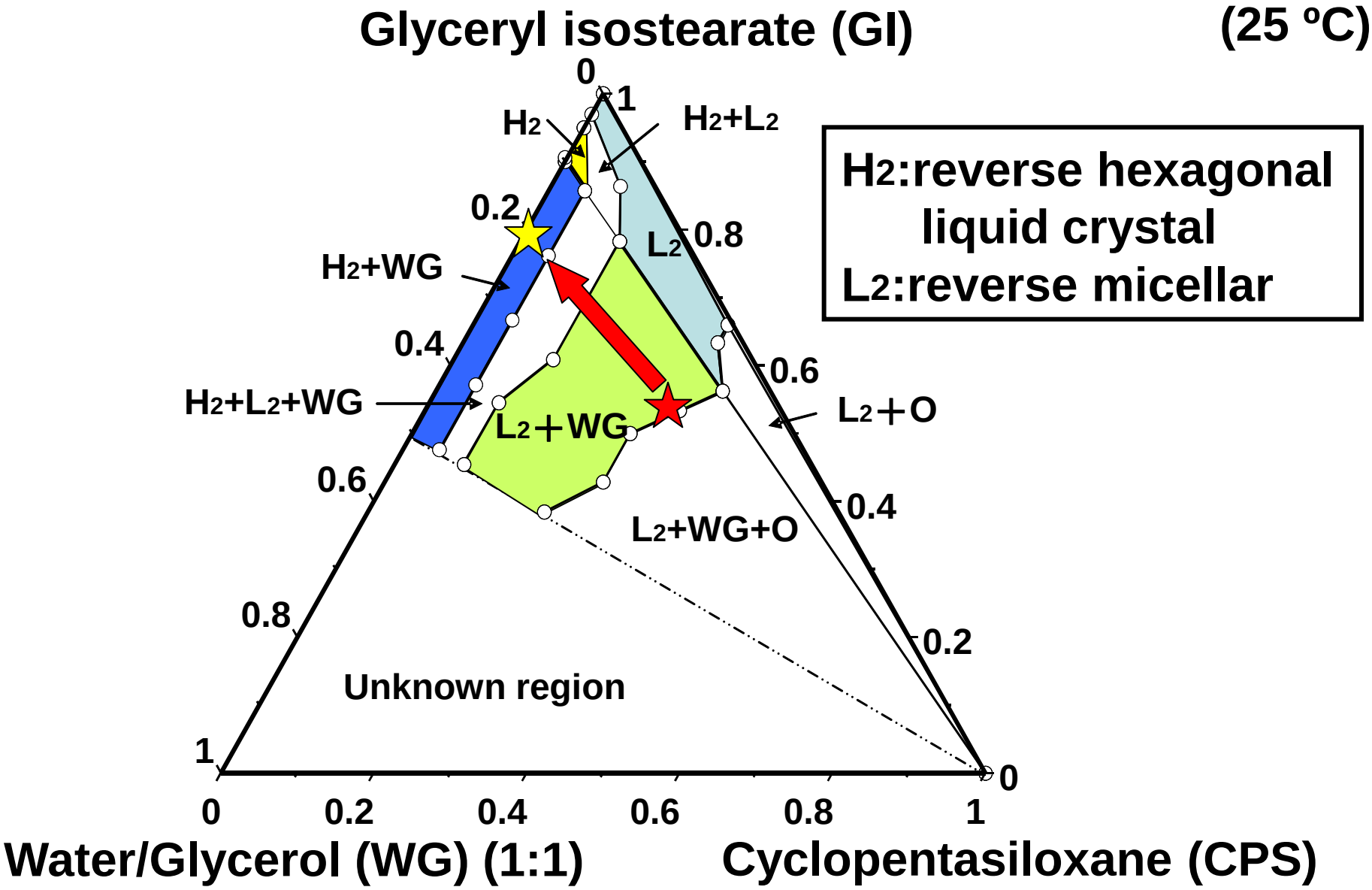
Preparation method of lipstick



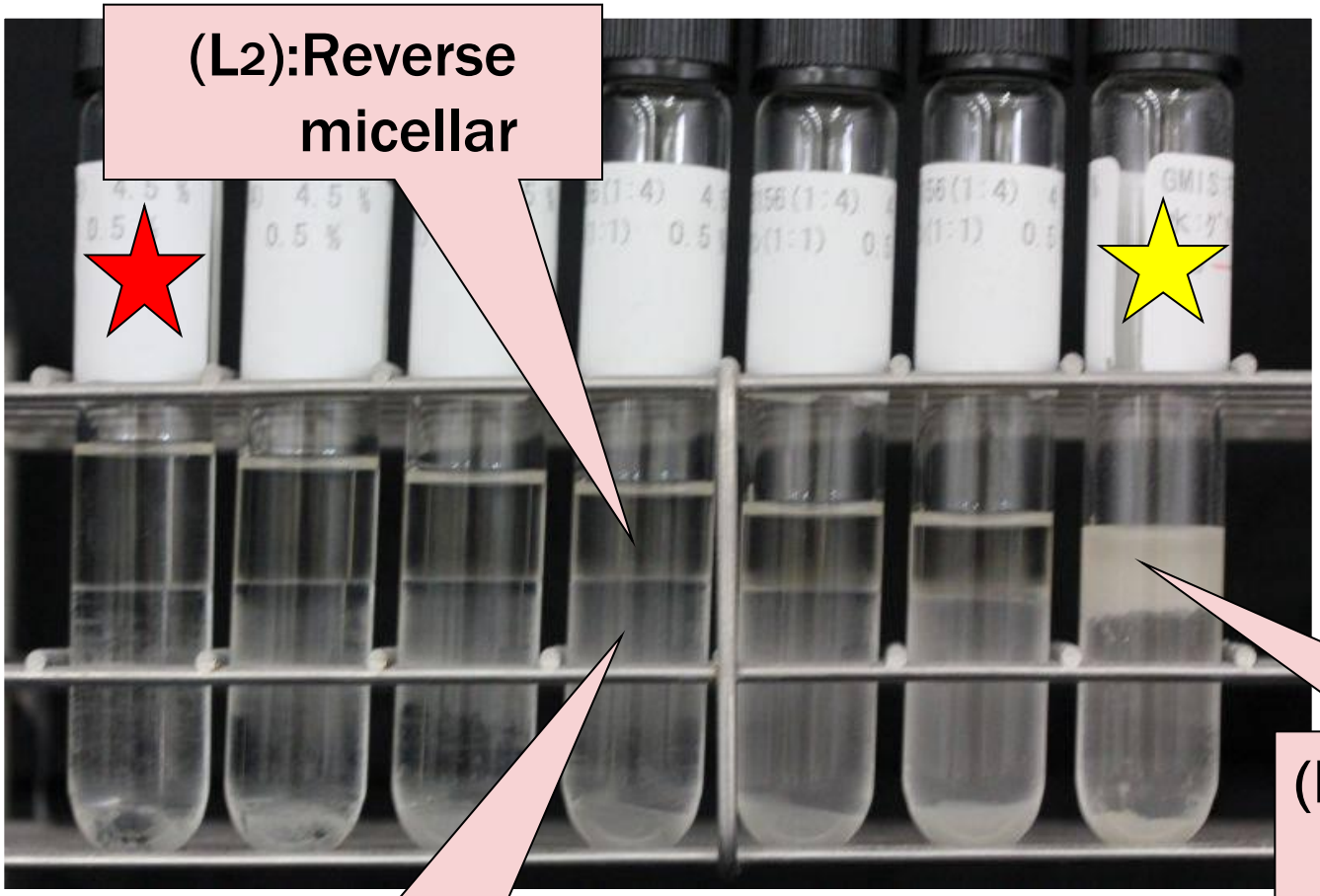




Phase Diagram of GI, W/G, and volatile oil



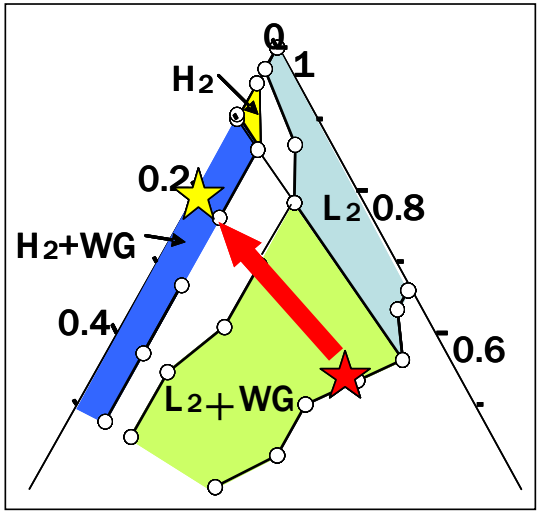
The state of the phase change



(L2):Reverse micellar

Separating oil

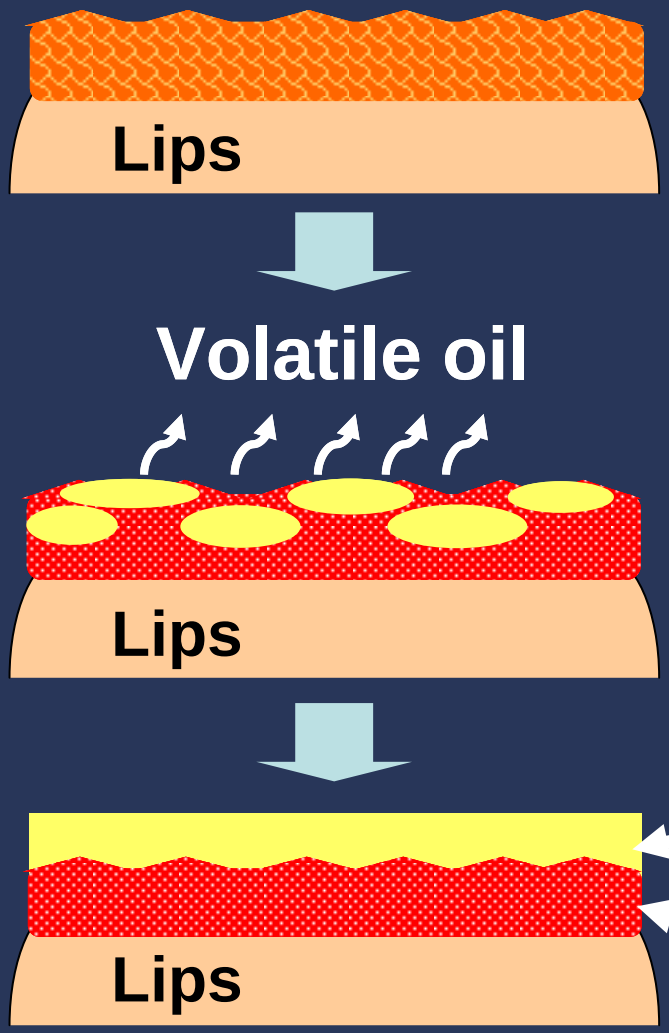
(H2):Reverse hexagonal liquid crystal



Decrease of the volatile oil

Non-secondary stain mechanism

Immediately after the application



Raw materials	Quantity (%)
Liquid-crystal formation oil	14
Separating oil	50
Evaporating oil	13
Wax	8
Water/glycerol	8
Pigments	7

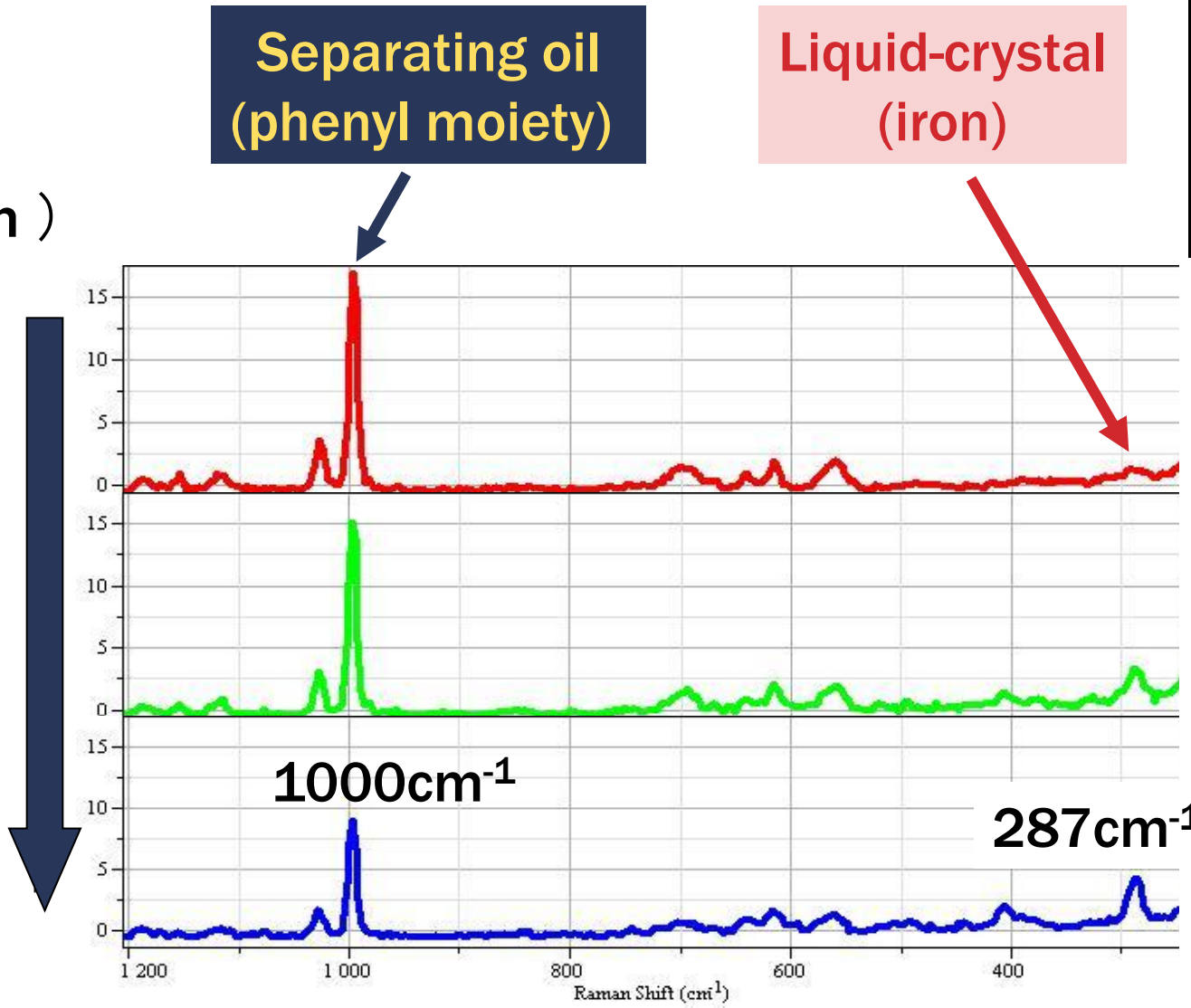
Measurement of the separating-oil layer thickness (Laser Raman)

Scattering
（Interval depth 1 μm ）

Separating oil

Liquid-crystal

PVC Membrane



The continuance of the luster

Application on the lips

Impression of lips on a white ceramic cup

Photograph of cup

Photograph of lips after the impression

Repeat 5 times

Non-secondary staining (Transfer Resistant) character

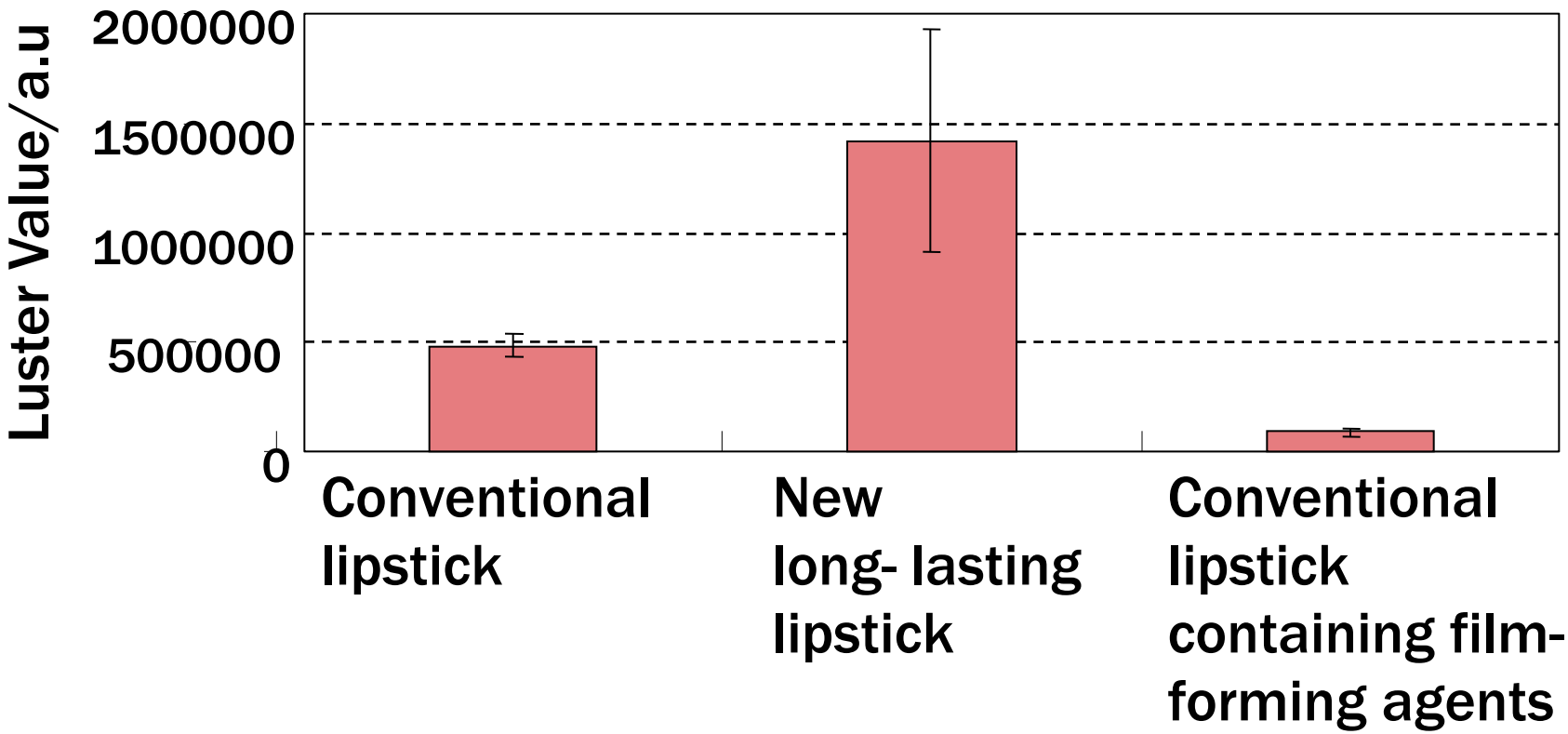
Conventional lipstick

New long-lasting lipstick

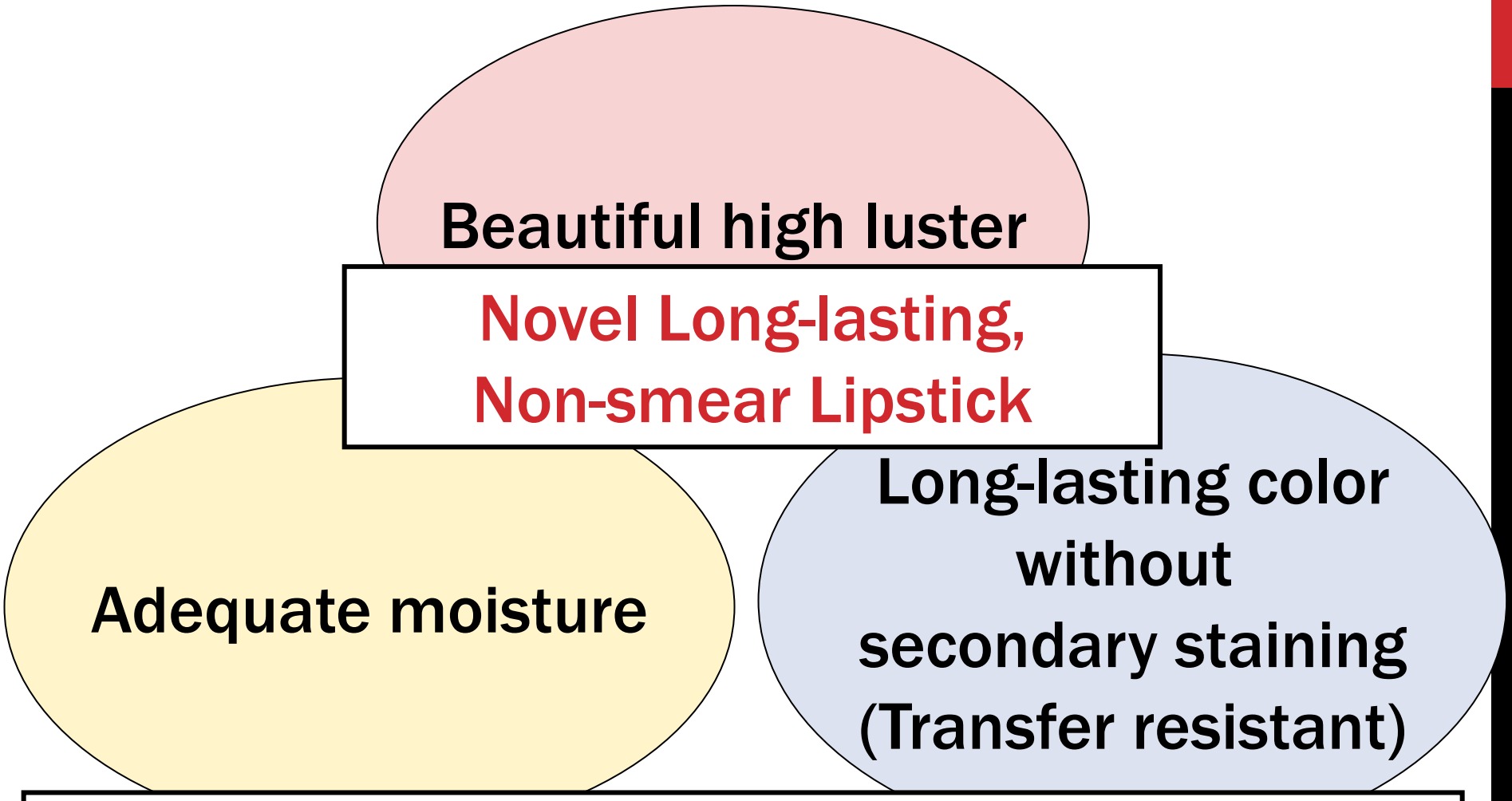
Conventional lipstick containing film-forming agents

Evaluation of luster

After 5 Times



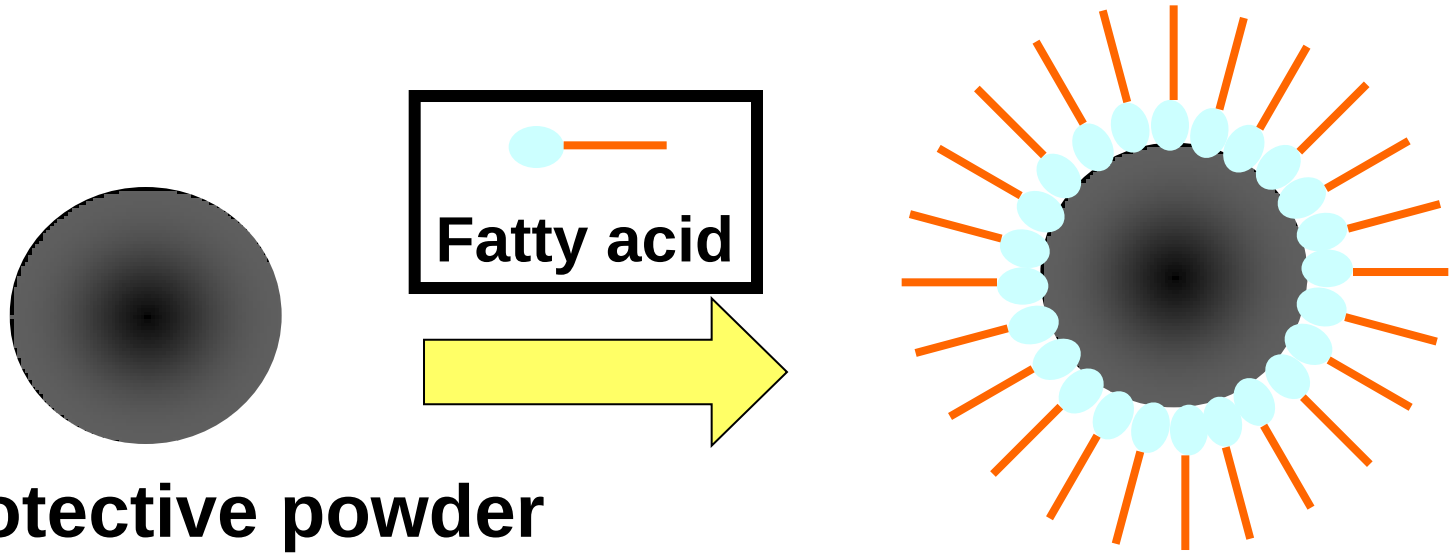
Conclusion



Phase-separation mechanism yielding the formation of Liquid-crystal was used

Support doc.

Hydrophobic treatment for UV protective powder

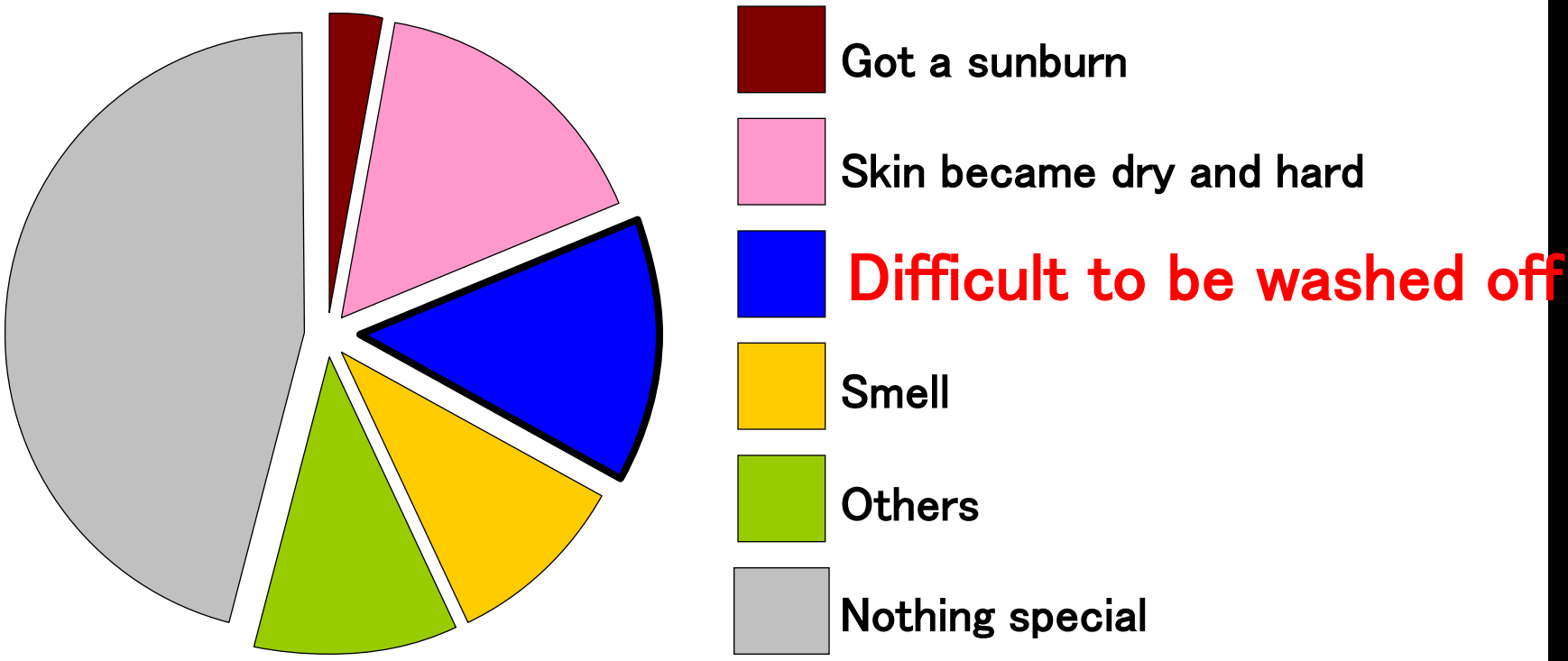


UV protective powder
(Titanium dioxide and Zinc oxide)

Fatty acid-treated powder (Hydrophobic)

Complaint about water-proof sunscreens

Researched by Shiseido



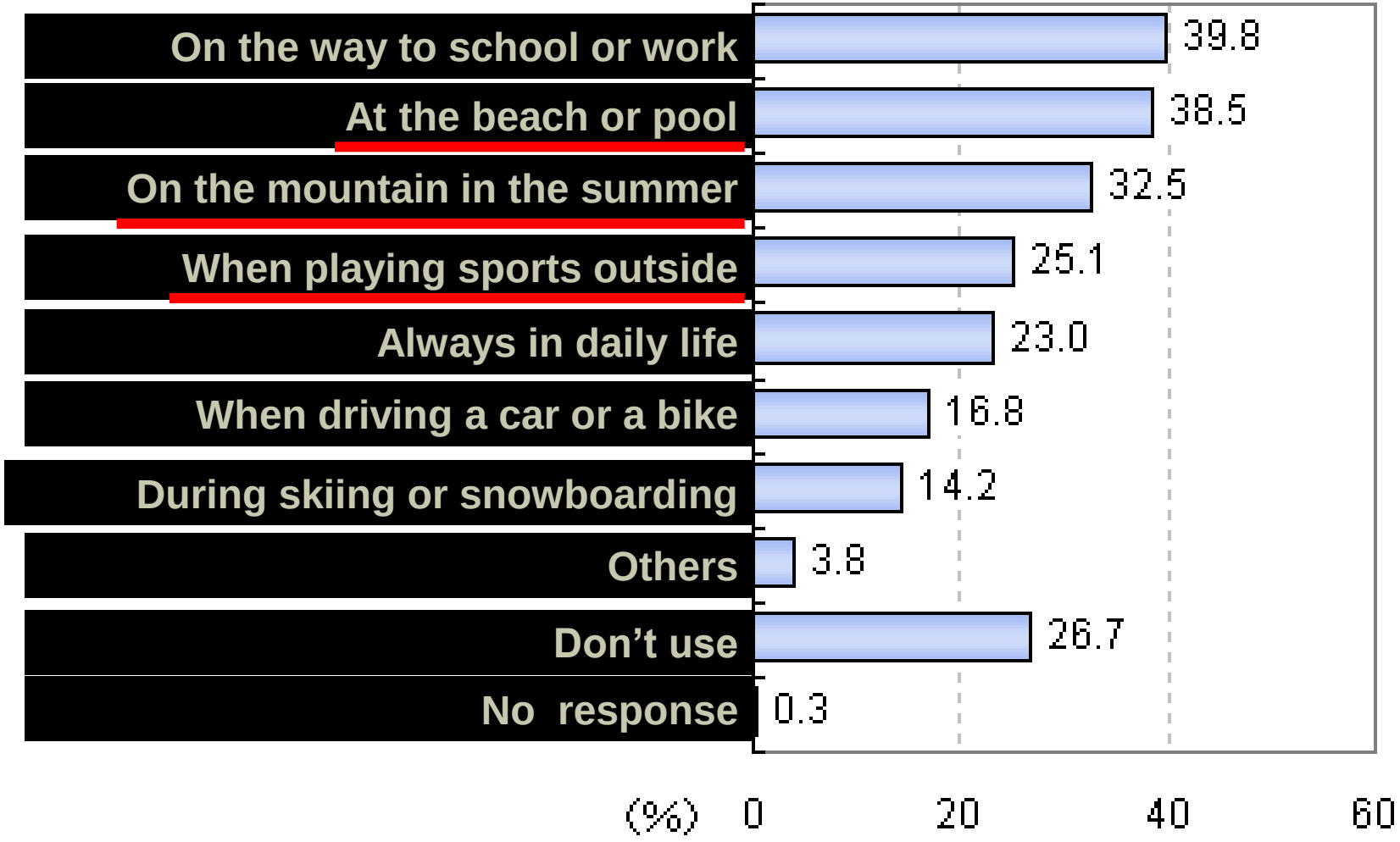
Water-proof sunscreens are so water-resistant that they cause the complaint about the difficulty to be washed off

The difference between UVB and UVA

	UVB	UVA
	Leisure UV	Daily Life UV
Feature	This mainly damages epidermis. Its action is vigorous and causes sunburn leading to spots, freckles and dry skin. The main cause of sun burn in outdoor sports like sea bathing, ski and golf.	Its action is mild, but it reaches dermis. Its damage accumulates because of long-period exposure in daily life. It transmits cloud, fog and glasses, so it damages skins in daily life.

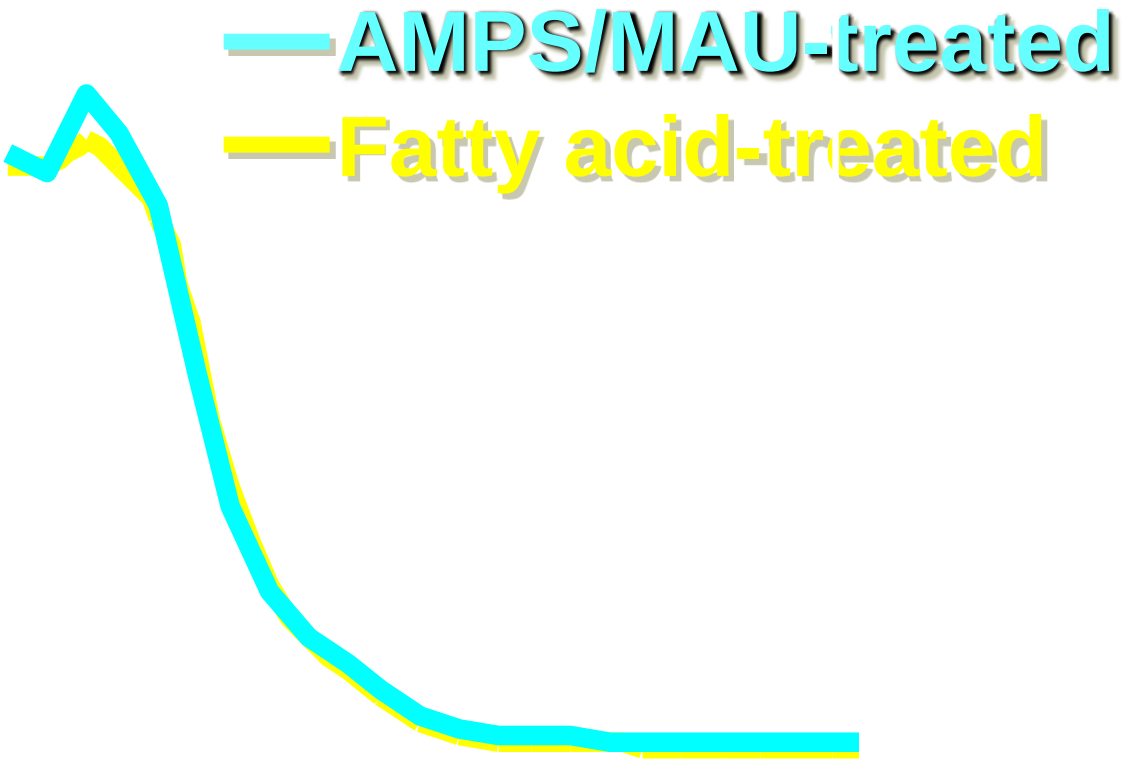
Scene to use sunscreens

Researched by MyVoice Communications, Inc.



Sunscreens are often used when there is water and sweat.

UV protective effect



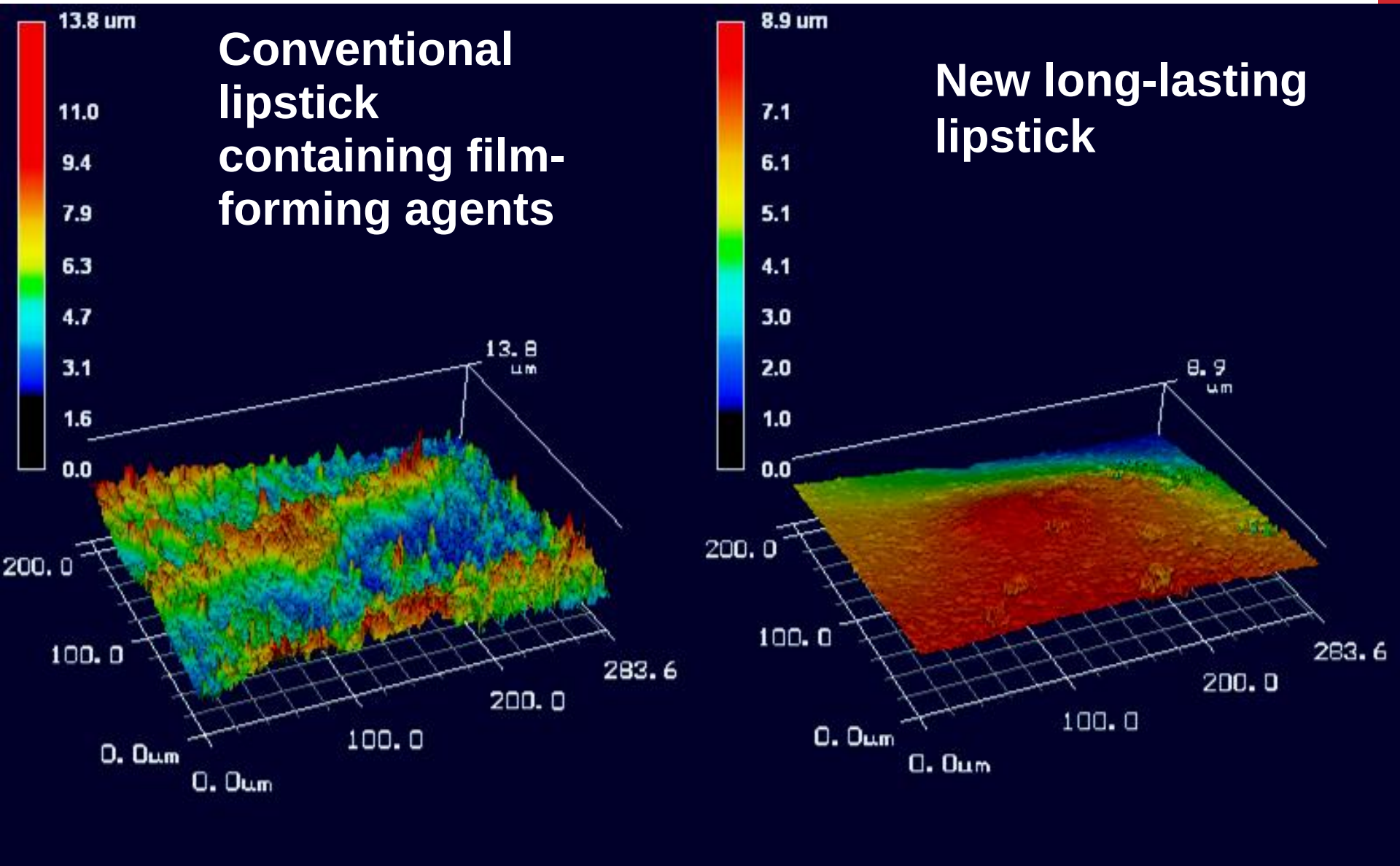
The same UV protective effect

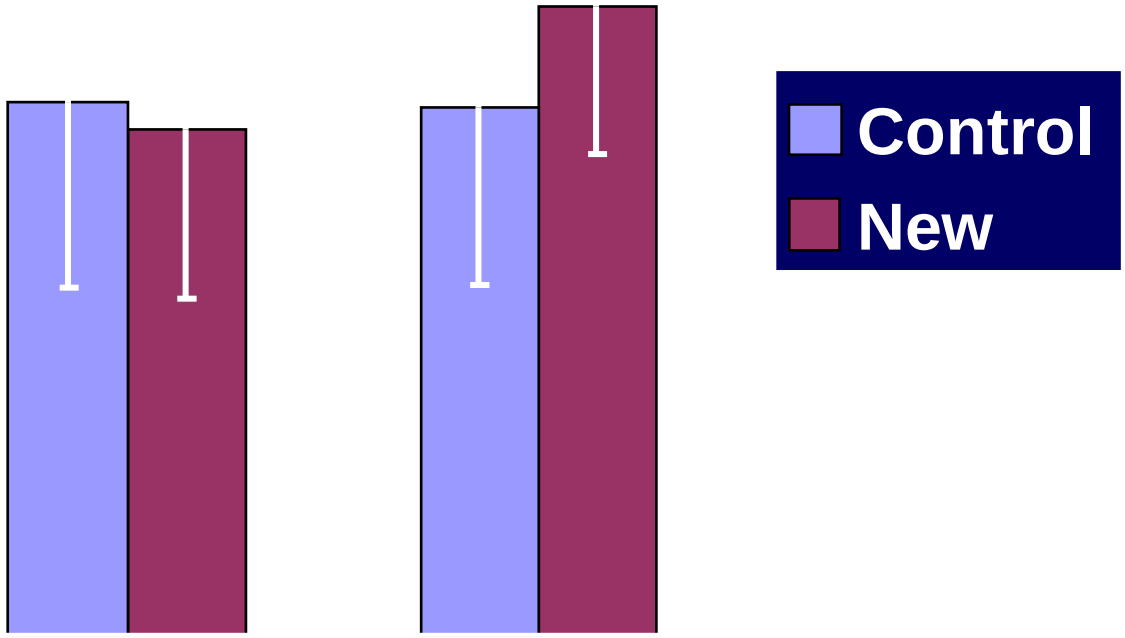
Conclusion

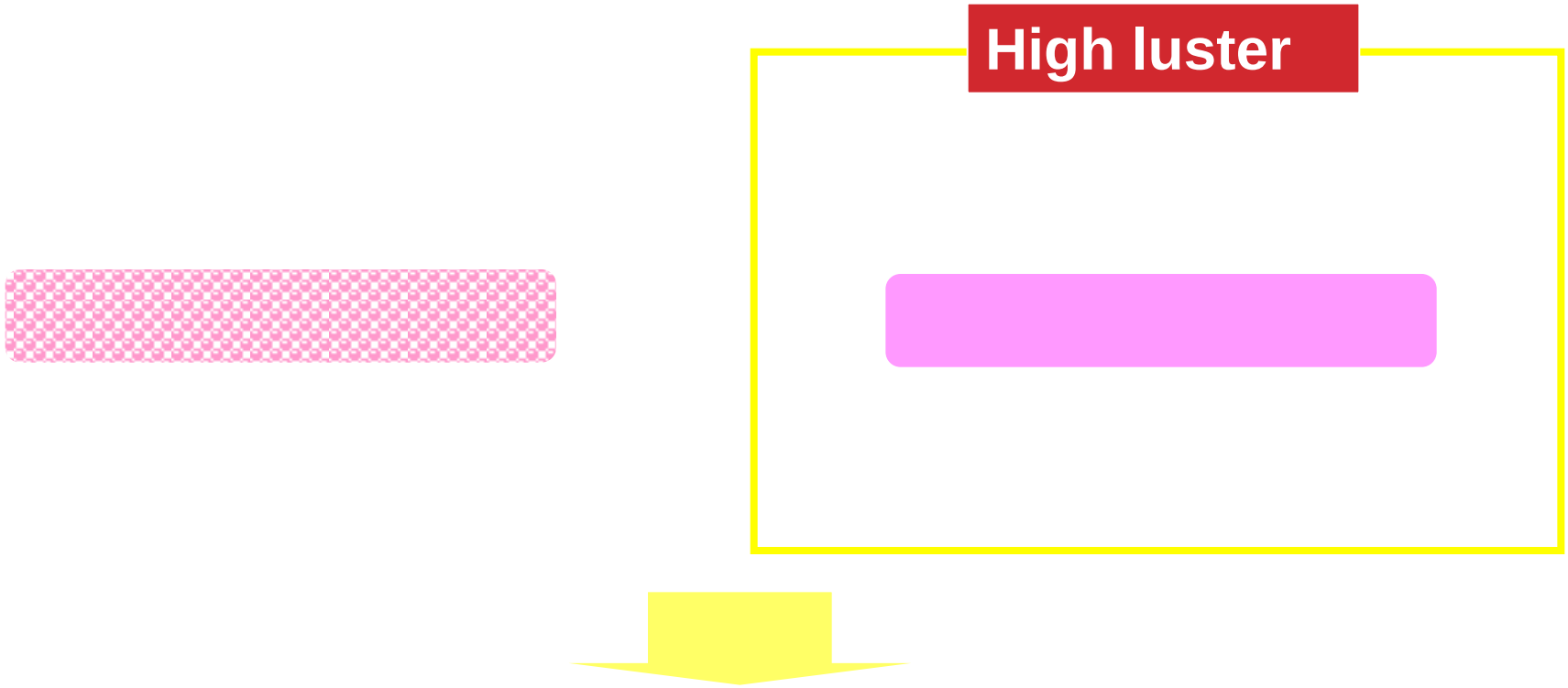
Water-resistant + **Detergent-washable**

Novel sun-care products

AMPS/MAU will be used for various kinds of powders.


Conventional lipstick containing film-forming agents
13.8 um
11.0
9.4
7.9
6.3
4.7
3.1
1.6
0.0
13.8 um
200.0
100.0
0.0um
0.0um
100.0
200.0
283.6
New long-lasting lipstick
8.9 um
7.1
6.1
5.1
4.1
3.0
2.0
1.0
0.0
8.9 um
200.0
100.0
0.0um
0.0um
100.0
200.0
283.6


Control
New



High-refractive-index polar oils

High-refractive-index polar oils

Beautiful high luster

Adequate moisture

Long-lasting color without secondary staining (Transfer resistant)

High-refractive-index polar oils