Application of Perfluoropolymethylisopropyl Ether to Long Wearing Lipstick.

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Key words

Adsorption, Turbo-mill, The new type lipstick, Volatile, Perfluropolymethylisopropyl Ether (PPIE), Volatile gel-network

Abstract

It has been used that fluorinated compounds could be applied to Make-up products. It is that fluorinated compounds are hydrophobicity, lipophobicity and homophobicity. These fluorinated compounds are reported to form a highly protective and effective film against most aggressive chemical and physical agents. In this study we made a success to formulate the new type of lipstick using perfluoropolymethylisopropylether (PPIE, MW = 650, commercial name = Fomblin HC/01 by Ausimont Co.) with low molecular weight which is long wearing and comfortable (excellent) to use. This PPIE was adsorbed more than 90% in this experiment and formed the well-balanced gel networks even if the selected PPIE is 100% volatile at room temperature. On the basis of the adsorption of PPIE, we developed the new type lipstick, which was highly-lip feeling and had long wearing and non coloration. And these characteristics were verified by actual consumer test.

Introduction

Adsorption technology has not been so ordinary in manufacturing lipstick or lipstick base. It is because most of investigators select the components that can be miscible and mixable together when they try to find. Due to these reasons, most of the components are very excellent in miscibility and some of the components are excluded to make lipstick even if it has high functionality on its own. Considering these kinds of reasons, the general manufacturing technology for lipstick so far is to mix lipstick base vs pigment, mica and titanated mica as 90:10 wt% or 80:20 wt%. But these kinds of technologies are very poor in adhesive strength and long-wearing strength because it is easily erased due to low oil-absorption and is easily migrated to other surfaces and is not hygienic and needs more frequent make-up correction, while it is easily manufactured. For this, investigators have tried to improve this property and put a lot of new products on market. Since 1992, a lot of lipsticks have been developed focusing on long-lasting strength in accordance with consumers' needs. But these kinds of lipsticks have been weakness of rough and too deep painting and poor painting when it is repainted or overprinted and heavy coloration causing some consumers to stop using. To meet several consumers' needs explained above, we have put a lot of time into this development and have been finally successful the new type lipstick using kind of perfluorinated compound with perfluoropolymethylisopropylether. Perfluorinated compounds have been long used for make-up cosmetics even if they are very expensive materials because they have hydrophobicity and lipophobicity. The reasons that we select PPIE for this investigation are that in addition to hydrophobicity and lipophobicity, PPIE has homophobicity and is colorless, odorless, tasteless, non-greasy and water-like polymer. Besides, PPIE forms a highly protective and effective film against most aggressive chemical and physical agents. At present, average molecular weight of commercial PPIE has been ranged from 650 to 6250. We select the liquid polymer with 650 average molecular weight because it provides silky-filling and light-feeling on lip

with long wearing ability. PPIE with 1500 MW (Fomblin HC/04) and PPIE with 3200 MW (Fomblin HC/25) had ever been for lipstick over coat.[2]

Also, PPIE was used skin care cream and moisture diffusion control cream by emulsion.[3] But PPIE with 650MW (Fomblin HC/01) was merely used in cosmetics. Besides, this PPIE with 650 is very volatile in air [1] and is not miscible with oils having ever used for lipstick and is also insoluble. We made success to apply this PPIE to lipstick using physical adsorption despite that PPIE cannot be used with lipstick oils. As for adsorption theory, it utilizes the density difference on surface of two phases (solid vs liquid). This time, density of liquid phase is increased. In this case, solid phase is an adsorbent and liquid phase is an adsorbate. Absorption is adsorbate goes through the inner of adsorbent. Adsorption divides into two classes. They are chemical adsorption and physical adsorption. Our exam process was physical adsorption. Physical adsorption is happened in a low temperature and adsorption rate gets faster and adsorption amount gets slower when temperature goes up. Also the adsorption amount of PPIE was measured using weight method.[5] The thermal stability was measured for test samples in 55°C and strength & hardness were measured using Rheometer. Moisture diffusion restraint test for PPIE adsorption product (the new type lipstick) was measured at the same time, too. In addition long-wearing power to color was measured and finally, consumer test was conducted to check product performances and superiority.

Materials and Methods

The first purpose of this test was to define the matrix of stable lipstick when PPIE was adsorbed into oils, waxes and powders. The applied testers are Moisture analyzer, Image analyzer, Rheometer, CCD camera and SEM (Scanning electron microscope). The second purpose was to measure the product performance using Image Analyzer, Coneometer, Spectrophotometer and the sensuous effect of product through consumer test. PPIE was Fomblin HC/01 (Ausimont Co.). Waxes had been generally used: carnauba wax, Ceresin, Ozokerite. Oils were Octyldodecanol, Lanolin, Oleylalcohol, Phenyltrimethicone and Castor oil. Powders were sericite/boron nitride/ dimethicone, silica/dimethicone. (Please refer to the Table I. for further details).

Volatile ratio of PPIE by temperature

Volatility was measured by the volatile ratio of time vs temperature. Set on 25°C, 50°C, 60°C, 70°C, 80°C, 85°C, 90°C after balancing 1.20g sample to measure volatility by temperature of PPIE with MW 650. Test equipment was Hr73 halogen moisture analyzer made by Mettler toledo. Measurement frequency was 30 seconds. Graph was represented by minutes.

PPIE Adsorption test of the new type lipstick

1 Pulverized the waxes, the powders and colors using industrial atomizer.

2 Melted these compounds.

3 Refined these compounds on turbo-mill designed specially.

4 Mixed the perfume & additives finally. (see the Table I and refer to these Compounds by a-type lipstick formula).

5 Adsorption process was observed using SEM (shimazu alpha 25a) & CCD camera (Thosiba Ik 637k) by phase and analyzed using Image analyzer. (Bummi Image top).

Volatility test of the new type lipstick by temperature

1 Measured the volatility on 25°C, 50°C, 60°C, 70°C, 80°C, 85°C, 90°C after balancing 1.20g sample of the new type lipstick.

2 The test equipment was Hr73 halogen moisture analyzer made by Mettler Toledo. Measurement frequency was 30 seconds. Graph was also represented by seconds.

Moisture diffusion restraint test of the new type lipstick

For this test of the new type lipstick,

1 Manufactured the lipstick using the formula described on Table I. (c: powdery type, b: oily type and a: the new type lipstick).

2 Measured the humidity by one hour after painting it on the forearm (Result was represented by hour on graph).

3 And compared its data with moisture supplementary agents (Sodium hyaluronate, Trehalose, Carboxymethyl chitin). Result was represented by hour on graph.

Physical property & stability test of the new type lipstick

1 Measured heat stability on 55°C using each lipstick manufactured by Table I. (c: powdery type, b: oily type and a: The new type lipstick) after 24hrs aging in the constant temperature incubator at 25°C.

2 Measured Strength & Hardness using Rheometer (Sun rheometer cr-200d).

Color migration test of the new type lipstick

1 To measure the difference of color migration for each formula, mixed the

uniform amount of color ingredients.

2 We measured by Spectrophotometer and Image analyzer in a 10minute after painting.

- For test method using Image analyzer:

  1 Painted the samples to compact sponge.

  2 Photographed the original state by CCD camera.

  3 Put white paper on lipstick-painted sponge and pressed this paper perpendicularly using 1kg weighthorizontal board.

  4 Photographed the first pressure-migrated color paper.

  5 Repeated 3 & 4 2 times.

  6 For these data, photographed the original state and the first pressure-migrated color paper and the third pressure-migrated color paper using CCD camera & Image analyzer.

- For test method using Spectrophotometer

  1 To measure the fixed area of each sample, set up a datum point to forearm.

  2 Snap-shot 5 times for each area by spectrophotometer in 10 minutes after painting each lipstick to forearm.

  3 Calibrateed and set the target value after measurement of L^*, a^* ,b^* for the surface of painted area.

  4 Put tissue on lipstick painted forearm; pressed this tissue perpendicularly using a right hand as equal strength.

  5 Snap-shot the degree of the migrated color to the first migrated area; averaged its data, and calculate the difference of color to target using calculation formula:

$$\Delta E^*ab = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

  6 Repeated 4 & 5 2times.

  7 Represented the degree of color (ΔE^*ab) for each sample on graph.

Usage test of model — the new type lipstick

Conducted consumer test for 50 panelists working at the A model institute, S general hospital, C skin care institute. For this questionnaire, Asked consumers to describe as follows:

+3: very highly satisfied

+2: highly satisfied

+1: satisfied,

0: unknown

-1: unsatisfied

-2: highly unsatisfied

-3: very highly unsatisfied

The key questions were color migration, moisture diffusion restraint performance, the degree of convenience.

Results

Volatility test of PPIE by temperature

PPIE was shown the high sensitivity to temperature and 100% volatility as time goes like Fig.1.And when it was stirred or blown, this volatility was accelerated.

And PPIE 650 was proportionate to temperature and was again recognized that it has 100% volatility at room temperature.

PPIE Adsorption test of the new type lipstick

- For result of PPIE adsorption using Image analyzer.

A) Fig. 2 shows the structure containing rosin, waxes, powders and color ingredients. Process of Fig.2 was as follows. 1) pulverized and melted these compounds on industrial atomizer for formula1. 2) scaled up its structure 60 times and photographed it using CCD camera. It shows the very delicate structure.

B) Fig.3 shows the structure containing oils, but excluding PPIE based on Fig.2. It shows the very loose and porous structure so that light can pass through coloress and transparent oils.

C) Fig.4 shows the structure containing PPIE based on Fig.3. This picture shows the very delicate matrix compared with Fig.3. But this structure got unstable because PPIE on edge part got volatile, forming volatile gel-network as time goes on.

D) Fig.5 shows the structure of Fig.4 specially treated by turbo-mill (scientifically designed). This picture was very delicate as PPIE formed the stable matrix. This is the new type lipstick that we developed. This structure is very refined and delicate matrix.

- For result of PPIE adsorption using SEM.

A) Fig.6 is the photograph of sample Fig 2 (waxes&colors&powders) using SEM. It shows the delicate structure. It seems to be a crystalline lump of wax as like Fig.2. B) Fig. 7 is scanning of sample Fig.3 using SEM. This sample was containing oils, but excluding PPIE based on Fig.2. The structure showed very loose and gentle slope. It is possible to consider as the oily type lipstick.

C) Fig.8 is the scanning of sample Fig 4. It shows the structure containing PPIE based on Fig 7. There is a diametrical difference between the two. Fig.8 shows delicate matrix compared with Fig.7. D) Fig.9 is the structure of Fig. 8 treating by Turbo-mill.

We scientifically designed Turbo-mill in accordance with heating & cooling system. The structure was very refined and very delicate as PPIE formed the stable matrix. Found also this structure got more color expression. Finally, this is the new type lipstick that we developed.

Volatility test of the new type lipstick by temperature

Unlike PPIE volatility test, the new type lipstick did not show the sensitivity to temperature; it showed little volatility as time goes on.

As described on graph of Fig 10, the new type lipstick is merely volatile to temperature and turn to be very stable matrix. Volatile ratio does not over 99.55.

Moisture diffusion restraint capability test of the new type lipstick

For this test, c-type, b-type and a-type lipsticks were painted on the forearm uniformly for the same period. We measured the humidity by time for the painted parts as Fig. 11.

The test result shows that a-type lipstick would be superior to b- and c-types of lipsticks. (After 3hrs, moisture measurements were 72 for fresh skin, 43 for a-type, 71for b-type and 62 for c-type). Above all, after erased on forearm, a-type lipstick is much superior to fresh skin in moisture retention as 128 (a-type) vs 73 (fresh skin).

Fig.12 shows the result of comparison for the moisture diffusion restraint capability to moisture supplementary agents (Sodium hyaluronate,Trehalose, Carboxymethyl chitin).

The test results show that the new type lipstick would be superior to moisture-supplementary agents. After 30 minutes, moisture measurements were 69 for fresh skin, 63 for sodiumhyaluronate, 51 for trehalose, 68 for carboxymethylchitin, and 49 for the new type lipstick.

The Physical property & stability test of the new type lipstick

A).We measured Strength, Hardness and Work using Rheometer. Table II shows the result of values for each

type lipstick.

The test result showed that Strength and Hardness of the new type lipstick were average values of b-type plus c-type. The new type lipstick improved both bunching of oily type and roughness of powdery type. Found also work was similar to oily type lipstick.

B).Table III shows the result to heat stability of each type lipstick

The new type lipstick did not change an appreance during 60-80minutes in constant temperature incubator at 55°C. This means that the new type lipstick is excellent for endurance to heat.

Color long-wearing strength & color migration test of the new type lipstick

We analyzed the degree of color long-wearing strength and color migration using spectrophotometer and CCD camera. We took a photograph of the first painted sponge, the first migrated color paper, and the third migrated color paper using CCD camera.

The new type lipstick is better in color migration property than any other type.

Fig. 13 shows the first painted picture by image analyzer. Fig.14 shows the first pressure-migrated color picture by image analyzer. Fig.15 shows the third pressure-migrated color picture. Fig.16 shows the difference of color (ΔE*ab) measured by spectrophotometer. And on the above graph, each detail data was represented on Table IV.

This test result was as follows. ΔE*ab for type a lipstick was 1.62. ΔE*ab for type b lipstick was 3.73. ΔE*ab for type c lipstick was 3.97. The new type lipstick showed the superiority in color-migration property. color for type a lipstick did not be migrated to any counterparts.

Usage test of mode the new type lipstick

Consumers' questionnaire results for each type of lipstick was represented as shown in Table V. The panelists consist of 50 people. And looking at its results, the new type lipstick was absolutely superior except for some questions.

Discussion

We manufactured the high functional lipstick using PPIE adsorption theory. The key points of this study were control of the color-migration and moisture diffusion restraint capability.

1. We succeeded to apply PPIE with 650 MW (Fomblin HC/01) to lipstick using physical adsorption. This PPIE was very volatile in air and was not miscible with oils. The structure was very delicate as PPIE formed the stable matrix.

2. We analyzed color migration using spectrophotometer and CCD camera for each type lipstick. The subtraction values of the first migrated ΔE*ab from the third migrated ΔE*ab were 0.73 for type a, 2.47 for type b and 2.95 for type c. The new type lipstick showed superiority in color migration property. The structure of each type lipstick was represented using image analyzer. Fig. 19 showed the very delicate matrix compared with Fig. 17 & Fig. 18.

3. The lip is composed primarily of muscles covered by skin on the outer surface and mucosa on the inner surface. The lip edge, or vermillion, is covered by non keratinized epithelium made red by numerous hig hly vascular connective tissue papillae.[6] Vermillion is divide by 2 kinds of parts — outside part is dry and inside part is wet. For the moisture restrain capability test, the new type lipstick was much superior to fresh skin. (After 3 hrs, 43 for the new type lipstick vs 73 for fresh skin.) The new type lipstick had finally solved that evaporation of moisture.

4. There was no reference of product using Fomblin HC/01. This PPIE was very volatile in air and was not miscible with oils. To solve these problems, we scientifically designed Turbo-mill in accordance with heating & cooling system. Technology innovation must be create by device of the new equipment or introduction of new ideas. Our study suggests that adsorption of PPIE 650 (Fomblin HC/01) is responsible for the long-wearing effect of high functional lipstick. We examined the efficacy of physical adsorption system in development of lipstick.

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Table. I Formulas of c: powdery type, b: oily type and a: new type lipstick

Lipstick c		Lipstick b		Lipstick a	
Carnauba wax	7.10%	Carnauba wax	2.00%	Carnauba wax	5.00%
Ceresin	10.35	Ceresin	2.80	Ceresin	2.80
Ozokerite	qs	Ozokerite	qs	Ozokerite	qs
Rosin	1.30	Rosin	1.60	Rosin	0.80
Lanolin	7.60	Lanolin	7.60	Lanolin	13.70
Octyl dodecanol	15.20	Octyl dodecanol	19.20	Octyl dodecanol	14.30
Oleyl alcohol	16.20	Oleyl alcohol	17.20	Oleyl alcohol	5.90
Castor oil	qs	Castor oil	qs	PPIE	qs
Phenyl trimethicone	qs	Phenyl trimethicone	qs	Phenyl trimethicone	qs
sericite/boron nitride/dimethicone	2.50	D&C Yellow No.6	2.90	sericite/boron nitride/dimethicone	0.70
silica/dimethicone	4.90	D&C Red No.6	3.60	silica/dimethicone	1.90
D&C Yellow No.6	2.90	D&C Red No.7	2.70	D&C Yellow No.6	2.90
D&C Red No.6	3.60	D&C Red No.21	0.90	D&C Red No.6	3.60
D&C Red No.7	2.70	Tocopheryl acetate	0.20	D&C Red No.7	2.70
D&C Red No.21	0.90	Preservative	0.30	D&C Red No.21	0.90
Tocopheryl acetate	0.20	Fragrance	qs	Tocopheryl acetate	0.20
Preservative	0.30	Total	100.00	Preservative	0.30
Fragrance	qs			Fragrance	qs
Total	100.00			Total	100.00

Table I. Formulas of ⓒ powdery type, ⓑ oily type and ⓐ The new type lipstick

ⓒ type lipstick		ⓑ type lipstick		ⓐ type lipstick	
Carnauba wax	7.10%	Carnauba wax	2.00%	Carnauba wax	5.00%
Ceresin	10.30	Ceresin	2.80	Ceresin	2.80
Ozokerite	qs	Ozokerite	qs	Ozokerite	qs
Rosin	1.30	Rosin	1.60	Rosin	0.80
Lanolin	7.60	Lanolin	7.60	Lanolin	13.70
Octyl dodecanol	15.20	Octyl dodecanol	19.20	Octyl dodecanol	14.30
Oleyl alcohol	16.20	Oleyl alcohol	17.20	Oleyl alcohol	5.90
Castor oil	qs	Castor oil	qs	Ppie	qs
Phenyl trimethicone	qs	Phenyl trimethicone	qs	Phenyl trimethicone	qs
sericite/boron nitride/dimethicone	2.50	D&C Yellow No.6	2.90	sericite/boron nitride/dimethicone	0.70
silica/dimethicone	4.90	D&C Red No.6	3.60	silica/dimethicone	1.90
D&C Yellow No.6	2.90	D&C Red No.7	2.70	D&C Yellow No.6	2.90
D&C Red No.6	3.60	D&C Red No.21	0.90	D&C Red No.6	3.60
D&C Red No.7	2.70	Tocopheryl acetate	0.20	D&C Red No.7	2.70
D&C Red No.21	0.90	Preservative	0.30	D&C Red No.21	0.90
Tocopheryl acetate	0.20	Fragrance	qs	Tocopheryl acetate	0.20
Preservative	0.30	Total	100.00	Preservative	0.30
Fragrance	qs			Fragrance	qs
Total	100.00			Total	100.00

Table II. Values of Strength, Hardness, and Work by Rheometer

Type	Di.mm	Max.g	Strength	Hardness	Work
ⓒ powdery type	3.06	246	241.2	78.5	466.7
ⓑ oily type	2.95	128	125.5	42.5	270.8
ⓐ The new type lipstick	2.61	180	176.5	67.3	292.1

Di.mm=Distance to Max.Point,

Max.g=Max Weight

$$\text{Strength(N/cm2)} = \frac{\text{Max.g} \times 980.665}{\text{Di.mm}}$$

$$\text{Hardness(N/cm2)} = \frac{\text{Strength} \times \text{Sample Height}}{\text{Di.mm}}$$

Work=Max Weight × Di.mm

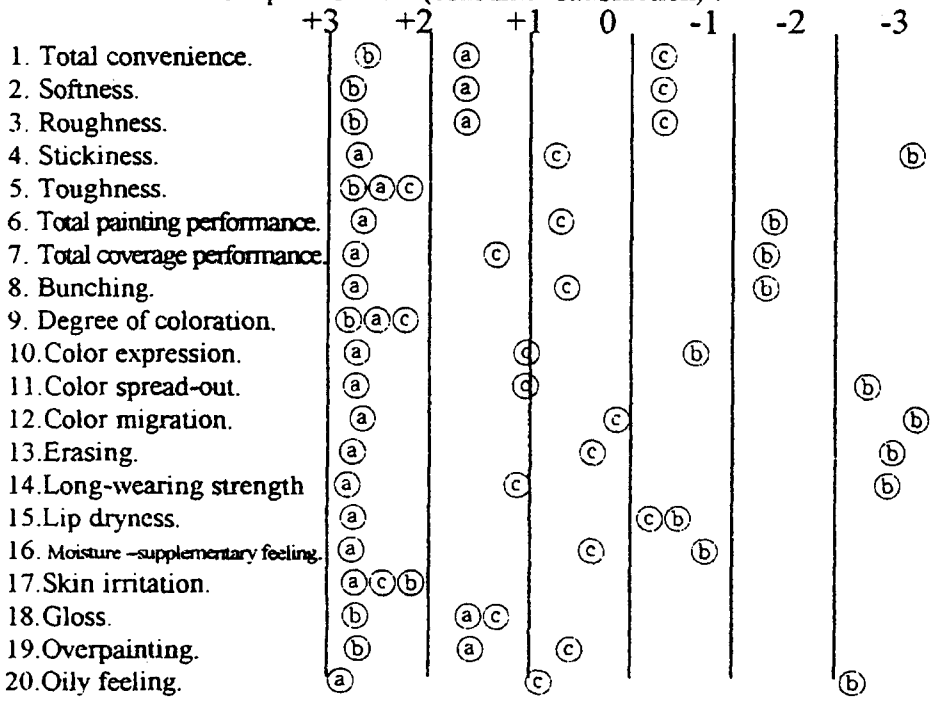
Table III. Heat stability of each type measured in 55 ℃ incubator

TYPE	ⓒ powdery type	ⓑ oily type	ⓐ The new type lipstick
Heat stability(55 ℃)	60min~80min	40min~50min	60min~80min

Table IV. L*.a*.b* measured by spectrophotometer

D65	Target ⓐ	1st color-migrated value of ⓐ type	3rd color-migrated value of ⓐ type
L*	41.88	42.35	42.59
a*	42.39	42.91	41.09
b*	22.21	22.76	21.57
⊿ E*ab	0.00	0.89	1.62
D65	Target ⓑ	1st color-migrated value of ⓑ type	3rd color-migrated value of ⓑ type
L*	40.93	42.13	43.38
a*	40.03	40.25	37.59
b*	21.21	21.02	19.97
⊿ E*ab	0.00	1.26	3.73
D65	Target ⓒ	1st color-migrated value of ⓒ type	3rd color-migrated value of ⓒ type
L*	42.12	42.39	43.91
a*	40.78	40.06	37.46
b*	21.43	20.91	20.19
⊿ E*ab	0.00	0.92	3..97

Table. V Details on questionnaire(consumer satisfaction) .



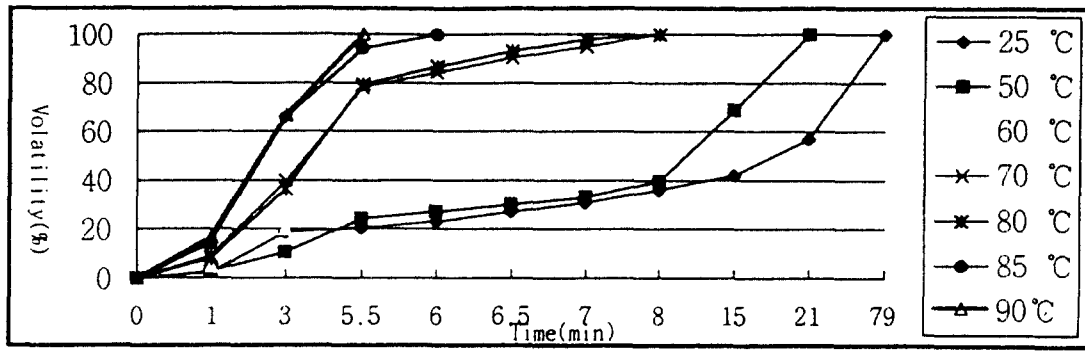


Fig. 1. Volatility test of PPIE by temperature.

Figures 2-9, see next page

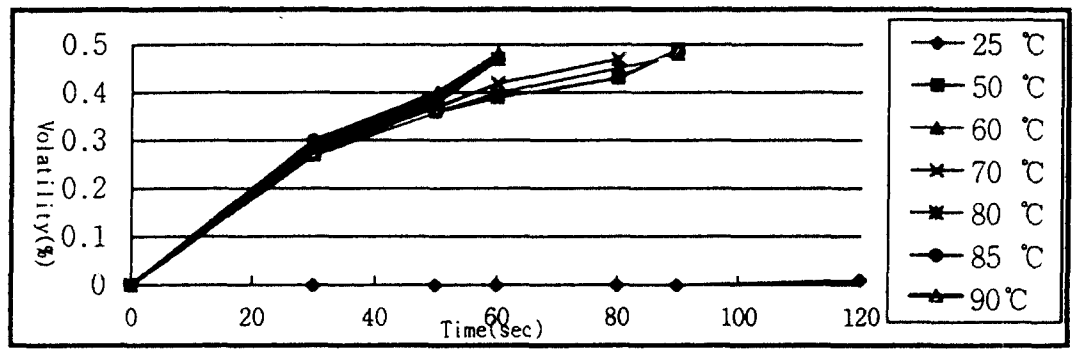


Fig .10 Volatile test of the new type lipstick by temperature

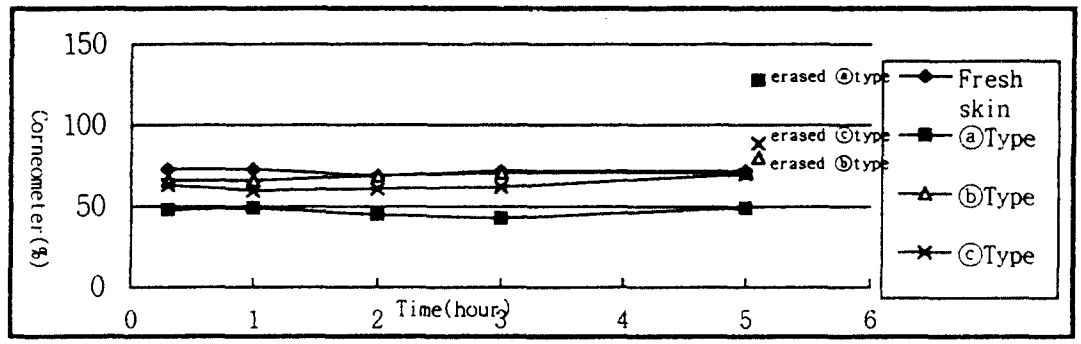


Fig .11 Moisture diffusion restraint test of each type of lipsticks.

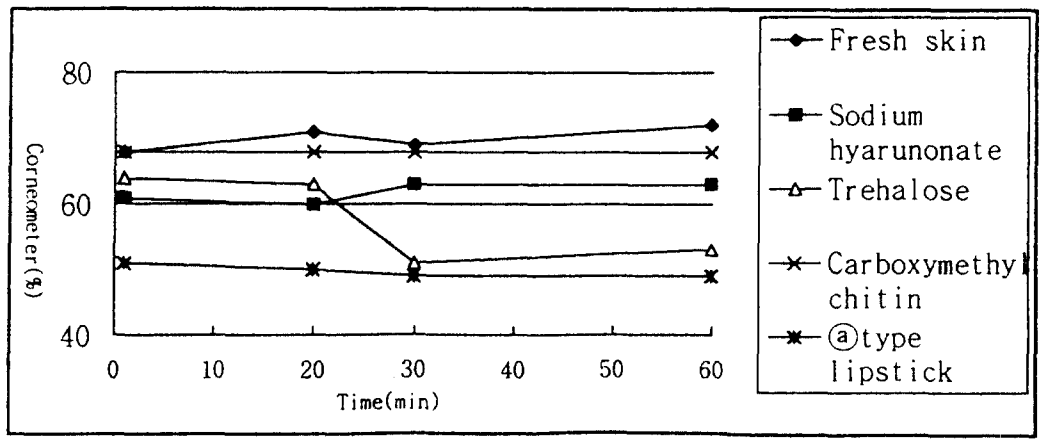


Fig. 12 Moisture diffusion restraint test to moisture -supplementary agents

Fig. 2 Image analyzing of structure obtained from process A (waxes&colors &powders)

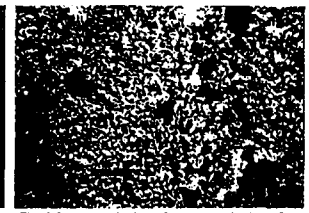


Fig. 3 Image analyzing of structure obtained from process B (waxes&colors & oil &powders)

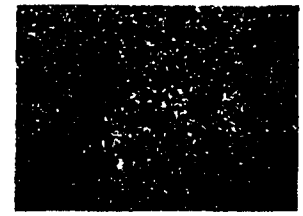


Fig. 4 Image analyzing of structure obtained from process C (waxes&colors&oil&powders&PPIE)

Fig. 5 Image analyzing of structure obtained fro processD (waxes&colors&oil&powders&PPIE)

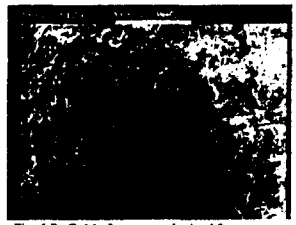


Fig. 6 S . E .M of structure obtained from process A (wax&colors &powders)

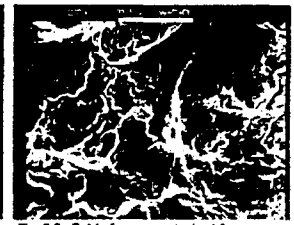


Fig. 7 S . E. M of structure obtained from process B (wax&colors & oil &powders)

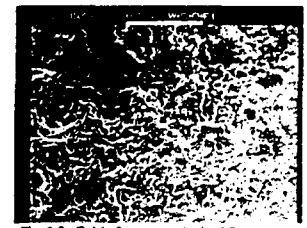


Fig. 8 S . E. M of structure obtained from process C (wax&colors&oil&powders&PPIE)

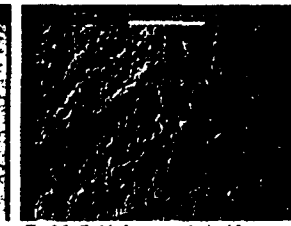


Fig. 9 S . E . M of structure obtained from processD (wax&colors&oil&powders&PPIE)

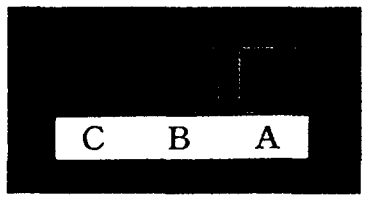


Fig. 13 the first painted state

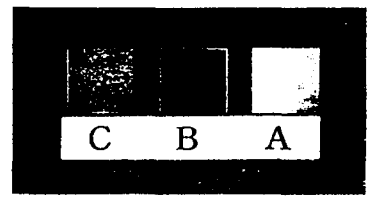


Fig. 14. the first migrated state

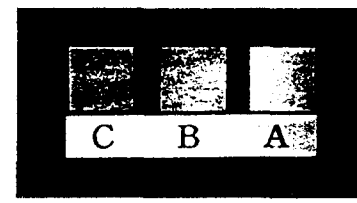


Fig. 15 the third migrated state

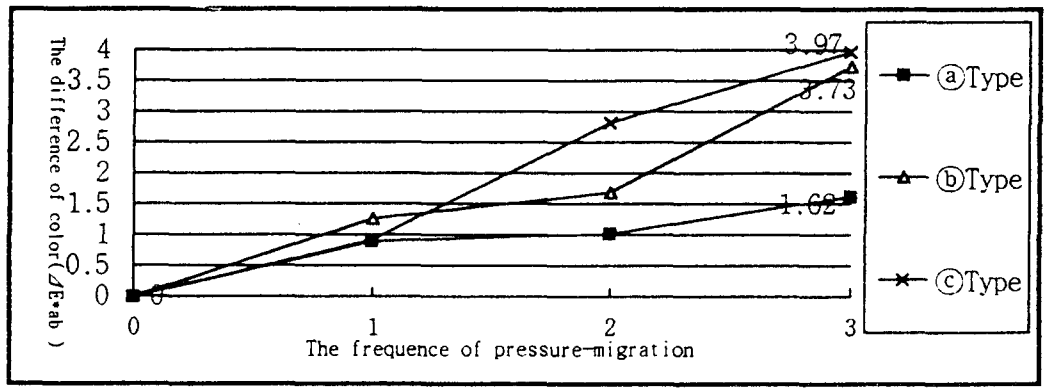


Fig. 16. Color migration by spectrophotometer
And on the above graph, each detailed datum is represented on Table .IV

Fig.17,ⓑ oily type

Fig.18.ⓒ powdery type

Fig.19 ⓐ The new type lipstick