Study and Application of the New Stick Make Up Product Using Clay Minerals as Binder & Buffer.

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ABSTRACT

The new stick make-up product was studied by using a gel, which is a viscous complex formed with clay minerals, vitamins A and E and fluorinated liquid polymer with a 1500 molecular weight. The gel cannot be obtained with any random combination of clay minerals and the ingredients described above. It takes the sequential manufacturing method as follows to get this kind of gel. Firstly, clay minerals and liquid polymers have to be pre-mixed in order to saturate the liquid polymers with the clay minerals. Then the on-processed gel has to be finely crystallized. The clay minerals, which are the core elements for this gel, were used as a function of Binder & Buffer and liquid polymer was mixed together for the deterioration of the surface tension of each component and to form a functional film in the gel. This liquid polymer was combined with clay minerals because it is not miscible with most oils and solvents. Waxes have a function of keeping a solid status in the stick. We reduced the usage of waxes by putting clay minerals as buffer in the proportion of 0.5:1 with oil phase. Ceramide takes care of the skin when used regularly and maintains the skin's moisture. Vitamins A and E contribute to preventing skin aging by the activation of skin cells. We could get the stable viscous gel, which has about 80% oil phase using clay minerals and liquid polymer. The crystalline structures of gel were surface-chemically-analyzed using SEM and Image Analyzer and were thermodynamically analyzed using DSC. Surface tension test and softness were done by Rheometer. In the end, these characteristics were verified by consumer panel tests in Seoul, Daegeon and Pusan in Korea and Hokkaido, Osaka and Miyazaki in Japan with correlation to the climate.

INTRODUCTION

Clay minerals give a lot of functionality in cosmetics as extended pigments more than anything else, these clay minerals have been used widely in Base Make-up area like foundation. Recently these clay minerals is used for Skin care product as well, like Astringent containing powder, Sun screen cream with a type of W/O, T-zone sebum control cream and Body shower cologne with mica powder. The first part of this study reported clay minerals provide the special functions in a mixture of liquid polymer with 1500 molecular weight, waxes-oils phase and vitamins. In this experiment, we used Perfluoropolymethylisopropyl Ether(PPIE) which is hydophilic, lipophilic, liquid polymer for the purpose of decreasing the interface tension of ingredients and forming the functional film in viscous clay mineral gel. Used liquid polymer that is immiscible with general solvents or oils was sprayed to clay minerals and was adsorbed together physically to make the powder base. Based on this powders base, we made a success to fabricate the complex viscous clay mineral gel(CVCG) through the process of sequential bonding and giving flexibility after we put this powders base into waxes-oils phase and vitamins. In general performances of lipsticks rely on the base materials like waxes, oils and pigments. Some resin or polymers used as additives. In case of clay minerals, mica has been primarily used within a range of 2-3 % as a quality improver. But it is difficult to find applications or trials using clay minerals as core materials of product. We stabilized PPIE to the complex gel using clay minerals as a network binder. We reduced the usage ratio of waxes by putting clay minerals as buffer in the portion of 0.5:1 with total oil phase. We could get the stable CVCG, which has about 80% oil phase using clay minerals and liquid polymer. The crystalline structures of gel were surface-chemically-analyzed using SEM and were thermodynamically analyzed using DSC. Interface tension test of PPIE and softness were done by Rheometer.

Secondly, we applied CVCG to lipsticks and then, its characteristics were verified by consumer panel test in Seoul, Daegeon and Pusan in Korea and Hokkaido, Osaka and Miyazaki in Japan with correlation to the climate.

MATERIAL AND METHODS

Behavior of clay minerals in oil base

We measured the behavior of each clay mineral in oil base. The measurement items are

miscibility and dispersion of clay mineral in oil base. We considered 8 kinds of clay minerals like Table 1 and oils are generally used in market. Behaviors of each clay mineral carried out by adding each 0.5g clay mineral to 20gs oil base. Clay minerals were acquired by ourselves (goods ordered by us)

Type of Clay Minerals	Each Clay Mineral of 0.5g
Talc A	Talc
Talc B	Talc/Squalane/Methyl polysiloxane
Talc C	Talc/Diethanol amine salt of perfluoro alkyl phosphate
Sericite A	Sericite/Squalane/Methyl polysiloxane
Sericite B	Sericite/Methicone/Titanium dioxide/Boron nitride I
Sericite C	Sericite/Methicone/Titanium dioxide/Boron nitride II
Mica A	Mica/Bismuth oxychloride/Titanium hydroxide/Bismuth
Mica B	Mica/Titanium dioxide/Stannic oxide
Composition of Oil Base 20g	
Lanolin	7. 6g
Squalane	5. 6g
Jojoba oil	6. 8g

Table 1: Ingredients of Clay minerals & Oil Base

Behavior of clay minerals in oil phase

It's very important whether each clay mineral is miscible with oil phase or not. The things, which are miscible and dispersible with oil phase, can be used as base materials. The measurement items are miscibility, appearance and spread condition. For experiment 8 kinds of clay minerals like Table 1 and oil phase components like Table 2 were used. Behaviors of each clay mineral carried out by adding each 0.5g clay mineral to 20gs oil phase.

Component	*Portion (%)*
Carnauba	0. 61g
Ceresin wax	2. 25g
Ozokerite Wax	0. 62g
Bees wax	0. 66g
Lanolin	5. 96g
Squalane	4. 37g
Jojoba oil	5. 53g

Table 2: Ingredients of Oil Phase 20g

Behavior of clay minerals in a liquid polymer PPIE

We measured the behavior of each clay mineral in a PPIE for its composition ratio. The measurement items are degree of oil absorption and degree of separation in accordance to over time. Behaviors of each clay mineral carried out by adding each 1.0g clay mineral to 20gs PPIE. PPIE obtained from Ausimont.

Preparation of powder base

We used PPIE to reduce the interface tension between each ingredient and power complex using its homophobicity. We also used it to form a functional film in a gel. PPIE can't be applied using general mrthod because it has hydophobicity and lipophobicity. So we used clay mineral as a network binder. PPIE was sprayed during the mixing of powders. And we aged it for 24hr at a room temperature for complete powder base. Component formula was described at Table 3. We defined the structure of powder complex and powder base using Sem(Thosiba Ik 637k).

Clay mineral	*Portion(%)*
Talc A	4.0
Talc B	2.0
Talc C	0.5
Sericite A	3.2
Sericite B	1.3
Sericite C	2.0
Mica A	1.0
Mica B	4.0
PPIE	

Table 3: Formula of Powder Base

Experiments on the reducing interface tension of liquid polymer PPIE

We measured degree of interface tension decrease of PPIE. PPIE has homophobicity especially in times of mixing. For this experiment we prepared the formula shown Table 4. The rheological analysis was carried out by results of strength and max.g with Sun Rheometer cr-200.

Component	*10% sample*	*6% sample*	*2%sample*
Waxes	18.89 %	18.89 %	18.89 %
Oils	50.80 %	50.80 %	50.80 %
Powders	20.00%	20.0 %	20.0 %
PPIE	10 .00%	6.00 %	2.00 %

Table 4: Formula for Surface tension test of PPIE

Complex viscous clay mineral gel CVCG

CVCG is not made by simple mixture between powder base described above and total oil phase components. The farther details are as follows.

1) Put the manufactured powder base into oil phase for 1st irregular CVCG.
2) To make it stabilized, it micro crystallized through specially designed device. The reason is that powder base and PPIE can be separated by increased entropy in an oil phase of high temperature. Micro crystallization process can be recombining them.

In this experiment, we prepared stabilized CVCG by using 20% powders base and 80 % oil phase. Table 5 showed formula of CVCG. To define CVCG, we used the oil component as a control and used Sem(Shimazu alpha 25a) to analyze the structure of CVCG on the basis of surface-chemically and used Dsc(Dupont co.) to elucidate the crystal structure thermodynamically. The rheological analysis was carried out by results of strength and max.g with Sun Rheometer cr-200.

CVCG	*Portion(%)*
Powder Base	20.0
Carnauba wax	2.32
Ceresin wax	8.48
Ozokerite wax	2.38
Bees wax	2.78
Lanolin	22.43
Squalane	16.76
Jojoba oil	20.41
Preservatives	0.18
B.H.T	0.26
Ceramide ls3728	0.50
Tocopheryl acetate	3.00
Rethinol palmitate	0.50

Table 5: Formula of CVCG

Make-up cosmetics of CVCG

We applied CVCG to lipstick like Table 6. We used the color stick not containing CVCG as a control and defined the difference of structure between CVCG stick make up product containing 35 % CVCG and control using Ccd camera(Thosiba lk 637k) and Image analyzer(Bummi Image top). And we measured the degree of color difference using Spectrophotometer(Minolta co.). The sample specimen was prepared as below 1) sprayed 0.2g sample on white sponge. 2) snapped shot 5 times. 3) measured it 5 times and averaged for L*,a*,b*. And then, calculated the difference color using following ecuation. $\Delta E^*ab = [(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2}$

where L* and a* represent Brightness and the direction of Red-Green and b*

represents the direction of Yellow-Blue.

Ingredients	*Control*	*CVCG Lipstick*
Oil Phase	35.00	
Clagel 20		35.00
Carnauba wax	1.03	1.03
Ceresin wax	4.93	4.93
Ozokerite wax	3.46	3.46
Rosin	2.13	2.13
Jojoba oil	12.39	12.39
Squalane	11.30	11.30
Lanolin oil	19.90	19.90
D&C Yellow 6	1.60	1.60
D&C Red 6	0.90	0.90
D&C Red 7	6.10	6.10
D&C Red 21	0.33	0.33
Iron oxide black	0.10	0.10
Preservatives	0.20	0.20
Rose hips oil	0.20	0.20
r- Orizanol	0.20	0.20
Fragrance	0.23	0.23

Table 7. Formulas of the CVCG Make up Stick Product & Control

Consumer Panel Test of CVCG lipstick

Consumer Panel Test on CLAGEL 20 lipstick prepared according to table VI was asked a favor to students who are in Beauty Schools in Seoul, Deajeon and Pusan in Korea and Hokkaido, Osaka and Miyazaki in Japan. We adopted simple method for questionnaire about consumer panel test as following. We converted each individual preference into numerical value after users used control and CVCG lipstick. The major content of questions was about the feeling of use about the samples, especially the powdery feeling.

RESULTS

Behavior of each clay mineral in oil base

All the clay minerals were almost dispersed in oil base as figure 1 when they were immediately stirred after input. After one day, Talc C and Sericite A were completely separated, but the others were dispersed in order of Sericite B, Sericite C, Mica B, Mica

A and Talc B. From this results, we found that above separated powders can't be bound solely with oils when the complex viscous gel is prepared, but this powders should be dispersed into oil phase.

Before

After 24hr

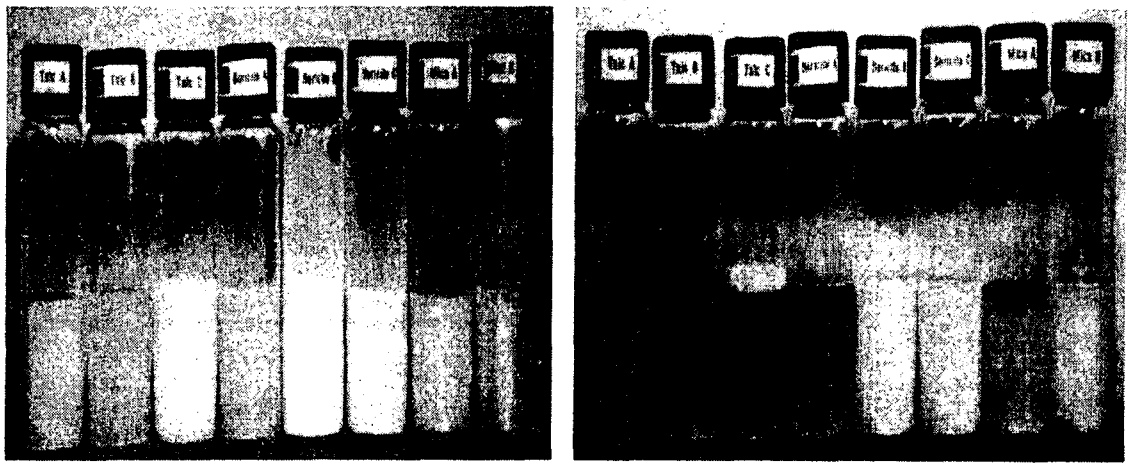


Fig 1:Behavior of each clay mineral in oil base.

Behavior of each clay mineral in oil phase

The behavior of each clay mineral in oil phase was found out such as figure 2. Talc A, B, Sericite A are miscible with oil phase and the appearances are transparent.

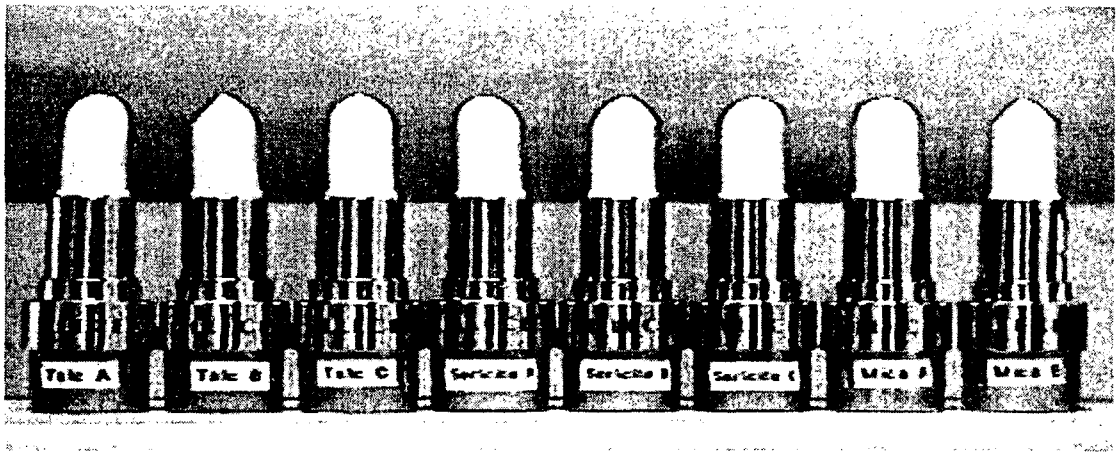


Fig 2:Behavior of each clay mineral in oil phase.

Applied states on a glass plate were also transparent. Sericite B, C, mica A and B showed good dispersion properties. The appearances of them were opaque and applied states on glass plate were also not clear. But Talc C was difficult to disperse and miscibility with oils was not good. From the results, we could obtain an important conclusion. Powders that have both good miscibility with oil phase and ability to bind to PPIE. or Powders that have both good ability to be dispersed in oil phase and ability to bind to PPIE could be applied to good binder and buffer. These powders could give a change over essential physical properties of final products.

Behavior of clay minerals in liquid polymer PPIE

We estimated the correlation between each powder and liquid polymer, PPIE in this experiment. PPIE should be adsorbed physically to powders in order to apply to manufacture because PPIE don't be easily mixed with oil components. We observed whether the mixture was separated as time goes by after stirring the mixture with the ratio of 1 % of clay mineral and 20 % of PPIE. Then we obtained the results such as figure 3. From the results, all the powders were not separated up to 30 minutes and the extent of separation of each powder was in order of Mica B> Mica A,Talc A> Sericite B.

Before

After 24hr

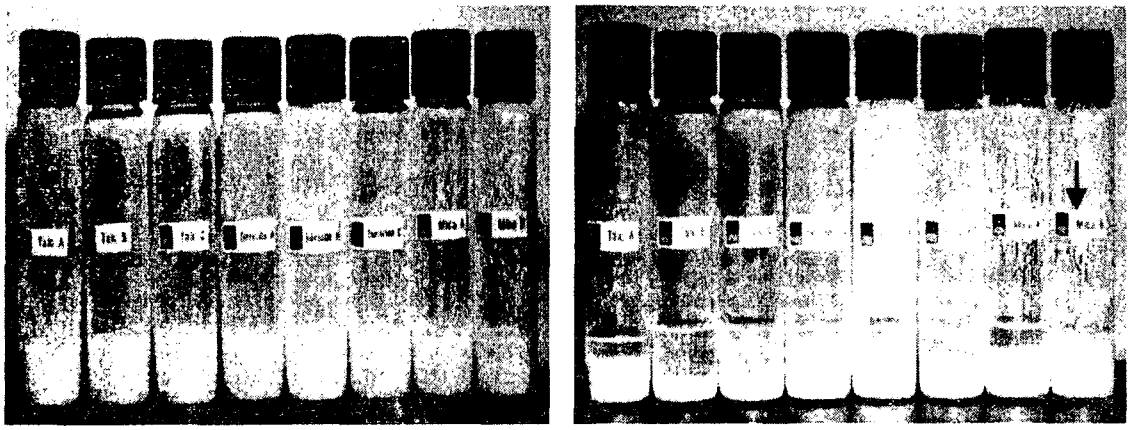


Fig.3:Behavior of clay minerals in liquid polymer PPIE

Preparation of powder base

PPIE was spread with stirring the mixture of each powder in order to adsorb each other. And then powder base was prepared by ripening at room temperature after 24 hours. Figure 4 shows the SEM(x 500) of powder complex and powder base adsorbed with

Before

After 24hr

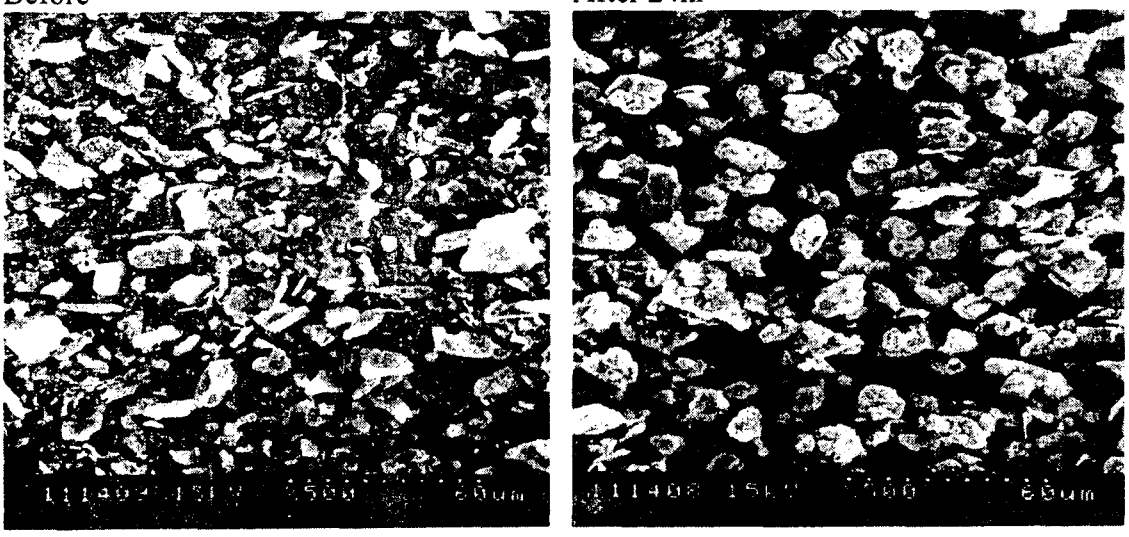


Fig. 4: SEM of Powder complex & Powder base

PPIE. We can know that each powder in powder complex is dispersed irregularly, but PPIE in powder base is stable adsorbed according to SEM.

Experiments on the reducing interface tension of liquid polymer PPIE

We could know that liquid polymer reduces the interface tension among wax, oil and powder. It has an effect to reduce the production of foam from results. Table VII shows

	10% sample	6% sample	2% sample
Di.mm	5.98	5.96	6.65
Max.g	360	395	412
Strength	353	387.3	404

Table 7:I Strength & Max. g of Each sample

Where, Di.mm=Distance to Max Point, Max.g=Max Weight ,

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

the results measured with rheometer. As a result, the strength and hardness became low with increase of amount of liquid polymer

Complex viscous clay mineral gel CVCG

Surface chemical analysis to CVCG structure.

We went through the following 3 steps to make CVCG. Fig 5 is 1000 times magnified photo by Sem for oil phase. It shoes very smooth and oily band. Fig 6 is 1000 times magnified for first irregular CVCG. It shows the structure containing oil phase and powder base. There is a powder base stuck in the oil phase.

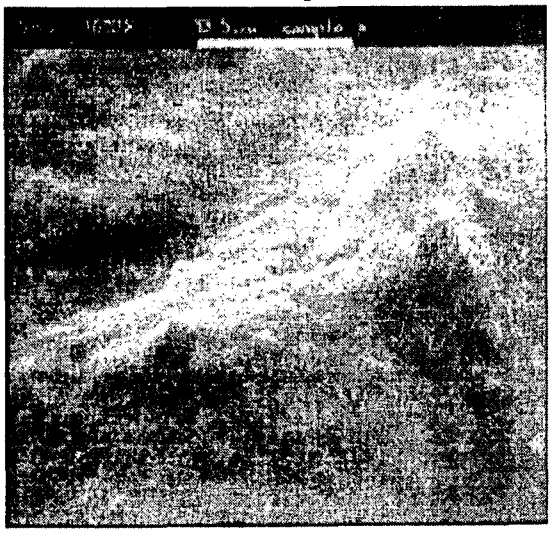


Fig.5: Sem of Oil phase

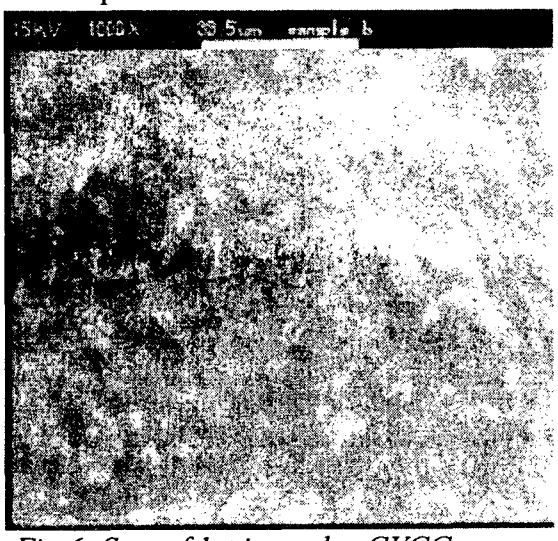


Fig 6: Sem of 1st irregular CVCG

Fig 7 shows the results of micro crystallization of 1st irregular complex viscous gel. This is more complicated than oil phase, but it show very smooth. Fig 8 shows the other part

Fig 7: Sem of CVCG

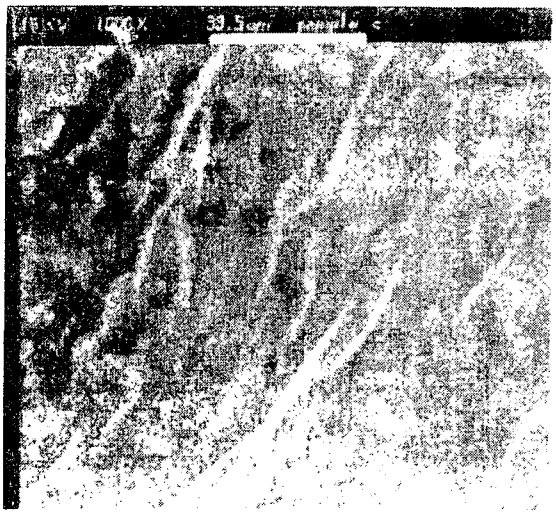
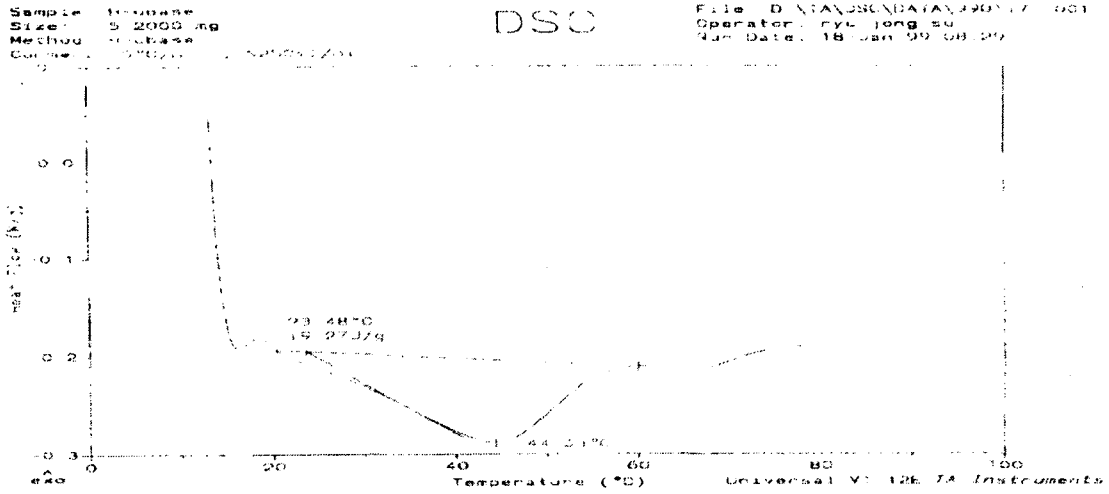


Fig 8: Sem of other part of CVCG

of micro crystallization photograph. This is also very smooth and stably crystalized compared with the 1st irregular gel.

Thermodynamic analysis on CVCG structure.

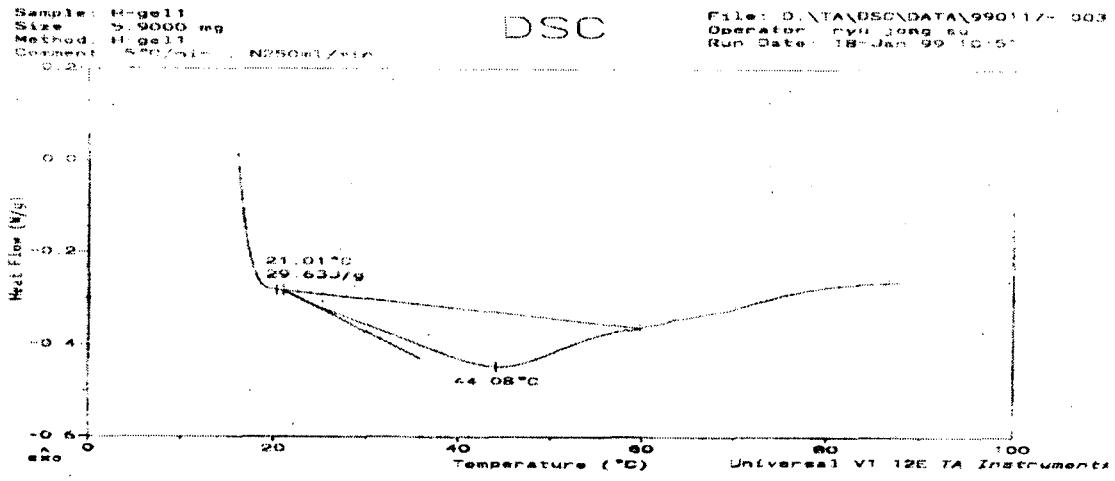
We measured and analyzed the heat variation, increasing the temperature from 0℃ to 150℃ and keeping the heat 5℃/min, using Dsc. Graph 1 is for oil phase and Graph 2 is for 1st irregular CVCG and Graph 3 is for CVCG heat variation. Judged from heat



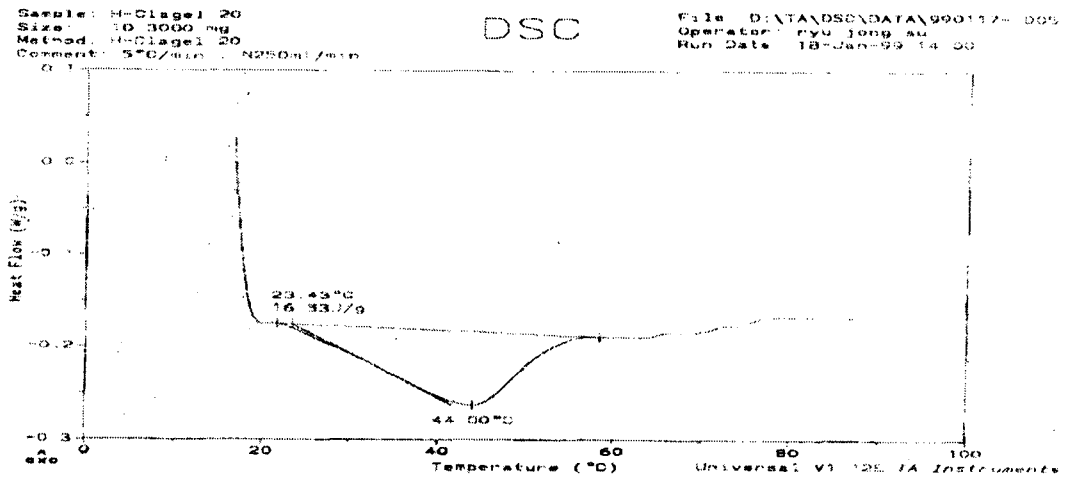
Graph 1: Dsc graph of oil phase

peaks on the graph, they followed the endothermic reaction. And the area difference between a start of endothermic reaction and a end of endothermic reaction means the variation of internal energy for phase change and this variation amount is a transition heat. Table 8 shows the transition heat of each sample. Looking at the measured

transition heat, oil phase and CVCG represented the similar transition heat, while 1st irregular did over 10J



Graph 2: Dsc graph of 1st CVCG



Graph 3: Dsc graph of CVCG

This means that 1st irregular CVCG is very heterogeneous among 3 samples while oil phase and CVCG 20 were homogeneous. We can see the regular crystal by micro crys

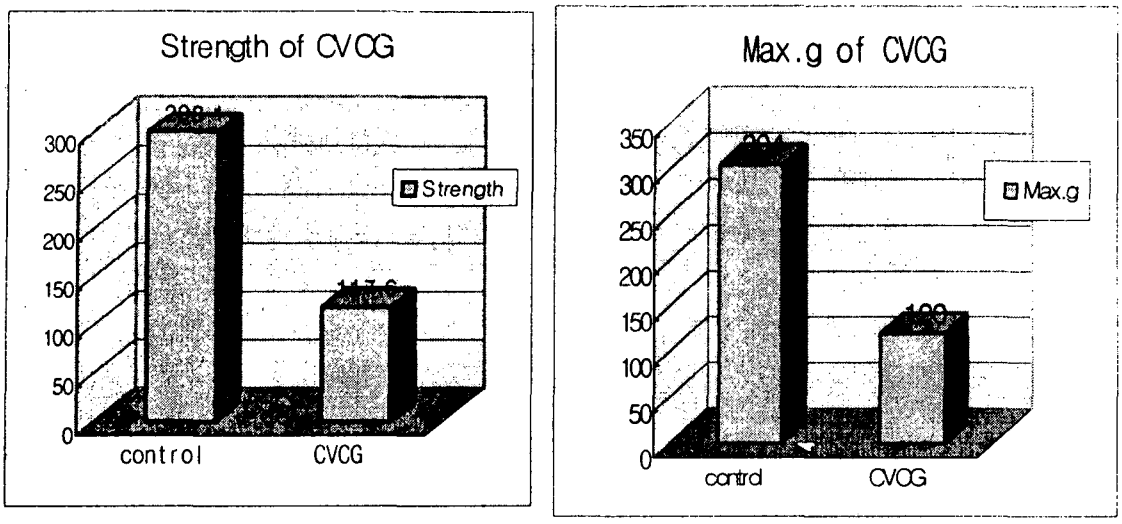
	Oil phase	1st CVCG	CVCG
Transition heat(J/g)	19.27	29.63	16.53

Table 8: Transition Heat of each sample

-talization the 1st irregular CVCG.

Physical property of CVCG

Graph 4 shows the physical property of CVCG using Rheometer with a control of oil phase. According to measurement, CVCG showed lower than control in all testing items



Graph 4. Strengh & Max.g of Clagel 20

It showed 2.5 times lower strength and 1.5 times lower max.g. based on this result, CVCG is much softer than control.

Make-up cosmetics of CVCG

Image analysis of CVCG lipstick

We analyzed the structure of CVCG lipstick and oil phase stick using Ccd camera and Image analyzer. Fig 9 is 200 times magnified photograph of each crystal using microscope. We can see the difference of structure. CVCG lipstick is more complex than control. And crystal is linked by clay minerals, oil phase and color pigments.

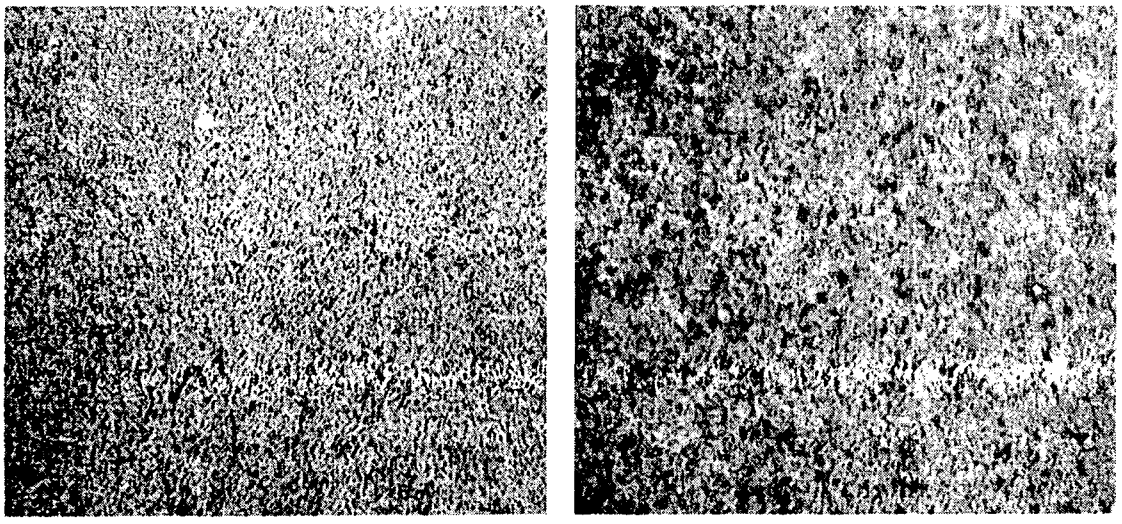


Fig.9: Microscope Analyzing of each sample

Fig 10 is a 75 times magnified photograph by investigating the light for both lipsticks using Ccd camera. As shown in the picture, CVCG lipstick was reflecting the light much more than oils phase lipstick.

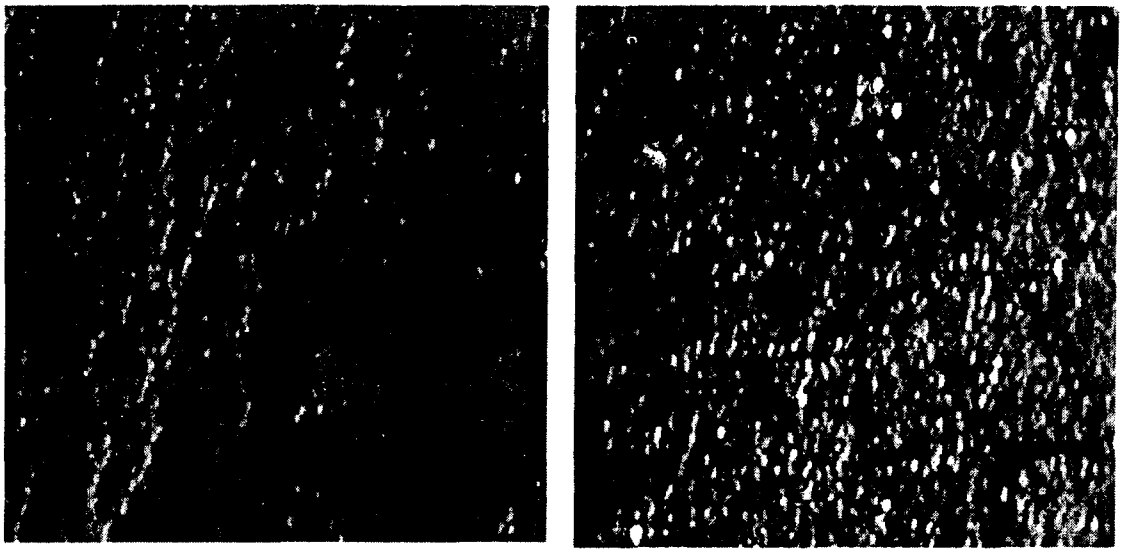


Fig 10 Image Analyzing of each sample

The surface sharpness is almost the same.

Measurement of color difference by Spectrophotometer

Table 9 shows the data of L*, a*, b* of both lipstick using spectrophotometer. Based on

	Control	CVCG lipstick
L*	35.57	35.02
a*	46.57	42.10
b*	23.55	18.19

Table VX. Data of each sample by Spectrophotometer

CVCG, the color difference is calculated as 7.03 and oil phase lipstick is more red and yellow.

Consumer Panel Test of CVCG lipstick

In this test we could find that consumers prefer the gloss type and natural type regardless of region and climate. And they feel dry on their lips very often. As shown in Table 10 consumers never feel that CVCG lipstick is powdery and superior except for some questions.

	Control	C V C G	Both
1. Oily feeling	12.50	81.25	6.25
2. luster feeling	6.67	93.33	0.00
3. Painting performance	12.50	81.25	6.25
4. Using feeling	33.33	46.67	20.00
5. Good spreading	6.67	80.00	13.33
6. Adherence	37.50	56.25	6.25
7. Moisture	25.00	62.50	12.50

8. Gloss feeling	15.38	69.23	15.38
9. Lip dryness	75.00	6.25	18.75
10. Overpainting	42.86	35.71	21.43
11. Long wearing	31.25	56.25	12.50
12. Erasing	50.00	50.00	
13. Color expression	40.00	40.00	20.00
14. Color migration	46.67	20.00	33.33

Table 10: Degree of choice rate to questionnaire

CONCLUSION

In this experiment we defined to manufacture CVCG by bonding and microcrystalizing the oil components based on clay minerals. To manufacture CVCG, we bonded the clay minerals and liquid polymer in advance and identified this powder base using Sem. Structures of oil phase, 1st irregular complex viscous gel and CVCG also identified using Sem. We defined the homogeneous structure CVCG crystal using Dsc. In existing manufacturing method of lipstick, clay mineral has been little used for improving the fit and convenience as one of additives. But in this study we used the powder base as a base material for lipstick. That is to say, some clay minerals were used for Buffer; others, which are miscible, bondable and dispersible with oily components and PPIE, were used for Binder. The application of CVCG in Make-up product will be limitless and according to mixture of each ingredient it will be possible to manufacture the various physical property of CVCG for new type of product in near time.

REFERENCE

1) Fukuji Suzuki, "Research of clay mineral pigments in cosmetics" 16, Fragrance Journal, 1994.