The study of solid-solid separation phenomena of crystal wax components on the oil, wax and pigment system

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1 Introduction

The phenomenon of the extracted solid powders on the surface of cosmetic pencil formed with oil-wax-pigment mixture is called as bloom. To avoid it, the various researches have been carried out [1-4]. The bloom does not injure an original property of goods, but deteriorates a value of goods because it makes their appearance rotten in white. That is a kind of separation phenomenon of liquid-liquid or solid-liquid which is caused by the difference of density, temperature, humidity, sunlight, and the infection by a microbe. It is caused by not only these phase separations in short term, but also the separation of solid components in long, which has a discord due to the low compatibility. But there are few studies on the solid-solid separation, except for works by cosmetic companies and foods ones, since these phenomena's unfavorable sides are not considered seriously. Matchda Haru et. al. found that stearic acid was the bloom making material through the study on the bloom formation by an additional high quality carboxy acid in oil-wax-pigment mixture. It was reported that the bloom was reduced by using an oil being able to solve more stearic acid and was completely constrained by using sugar ester. On the other hand, food makers have utilized sorbitan-type surfactant in order to avoid the bloom, which makes goods appearance rotten in white as it is infected by microbe.

In this study, it was found that the bloom was caused by the crystallized carboxy acid with 12-18 carbons and the separation on the goods surface was prohibited by selective non-catalyzer esterification with a high quality alcohol.

2. Basis research

2-1. Properties of solid-wax-phase materials

Eyebrow pencil mainly consists of wax-phase materials, which affect on its availability and stability and surface bloom with various property of wax. Therefore study on wax-phase source material is important in this system having the structure of oil-wax-pigment mixture. Classifications and structures of various wax-phase materials are shown in Table 1.

These wax-phase raw materials commonly include Carbon's chain and their states vary with a length a bonding type of its chain. The orthogonal Hydrocarbon exists as a gas-phase up to 4 carbons, liquid-one from 5 to 17, and solid-one in more than 18. [5] Its chemical properties largely depend on the functional group attached to carbon chains and Acid (R-COOH) and Alcohol (R-OH) groups lead to solid-phase in more than around 12-14 carbons. But, Hydrocarbon with the branched structure chain not straight one does even exist as liquid-phase over 18 carbons. The unsaturated carbon including double bond in their chains largely change physical or chemical properties.

Originally, a wax indicates a solid-phase Ester, but generally includes solid-ones of all Alcohol, Acid, Ester and Oil. Table 2 shows the melting points and the hardness of available solid-phase Acid, Alcohol, Oil and wax. Alcohol and Acid groups have a low melting point and a hard crystal type, while Hydrocarbon oil has a high melting point. Other natural waxes and Esters group have wide ranges of melting point and hardness.

2-2. Usage of oil/wax

The role of oil/wax is very important in a pencil prescription. Oil plays a role in wax being painted on the skin and controls its hardness. Ester oil is widely used, but has a problem that it makes easily a overflow on a skin surface when being overmixed. In order to prevent from this, mineral oil can be used but not available for common use because of the fault of low solubility with free acid, of promoting a bloom generation.

Steric Acid, Japan wax and Ceresin wax which are used as a solid-phase wax have an inherent property so

that their combinations are very useful on being balanced. When Steric Acid (Emersol-132), a crystal Acid, is used alone, it is not expected to be uniformly dispersed because it has very high hardness and causes to be a flaking on the three roll surface when dispersing colors. Japan wax has a advantage to be cut without core's braking or fracturing in the wood type goods, but must be used as a mixture with something hard because it has a low melting point and a low hardness. Ceresin in Hydrocarbon group does not make a bloom and has a high melting point, but not spread on a skin surface at all on being used alone. Other waxes in the Ester group does not have a special property but overall satisfied these items. PE wax is considered as a substitute material of Stearic Acid, but not used yet.

In this study, softisan-142 and Ceraply-50 which was found out as source materials in generating bloom are excluded. Emersol-132, a crystal Acid is used with below 7%. Solid-phase Alcohol, 6%, Ester wax,cutina-CP, 7.5% is used. Process esterfication is derived by using Ceresin-7475, a Hydrocarbon wax. Candelilla wax 5% is used to intensify a hardness and to prevent from being sticky.

Oil phase materials which don't effect on performance and concept materials with small content are not used. IPP 1% as a oil phase is used. Also, Butyl Paraben and B.H.T are used as an antiseptic and an antioxidant, respectively

2-3. Bloom generating and its principles

Bloom is white powder on the surface, which is separated from solid-gas interfaced region by environmental conditions. They is generated by Acid's contraction and water-absorption of near wax in the oil/wax-pigment mixture. [2] Many of studies on bloom generating have been performed. [1-4]

Reference [2] reported that Stearic Acid was a cause component for generating bloom and oil with a high solution degree into Stearic Acid used to restrain bloom. And it was reported Sugar Ester was valid in prevent from generating bloom. [3] While these studies in the foods industry using oil and carboxy aicd as main raw materials were performed and it was found out that using multi-alcohol, a surfactant could restrain the bloom. [1] This surface extraction of Acid can be identified directly by microscope and SEM. Fig.1 shows bloom generating on the surface magnified by 1000. The white parts is bloom extracted on the interface and its generating rate is accelerated with time passing.

In order to find out substance arising bloom, the aging observation from 2 months to 1 year for each test samples with various components is carried out. As results, it is found out main materials causing bloom are Emersol-132, Softisan 142 and Ceraphyl 50. Analysis on each component is as follows. Emersol-132 is Fatty Acid with C16:C18=55:45, Softisan-142 is Hydrogenated Coco-Glyceride water-added with Coconut oil, and Cerapyl-50 is an ester mixture with Myristic Alcohol and Lactic Acid. All of three materials are able to include Fatty Acid.

3. Experiment

3-1. Test samples

The samples to be examined are mixture of oils and waxes, which is melted up to 80~85°C in water bath and pigments are added. And then they are uniformly mixed with 3-roll mill and stored in the stainless steel container, 15mm x 60mm x 3mm, in relative humidity, 50% and constant temperature.

For investigating an effect of heat treatment, core ϕ 2mm is made from the mixture ingot and then treated in 48ûC during 30 minutes.

3-2. Analysis of gas chromatography

Gas chromatography of each sample is preprocessed and resolved into ethyl ether is analyzed with the Gas Chromatography Model 5890 series-II (Hewlett Packard). The column used is 0V-1 (25m) and conditions are set with injection temperature 330ûC, detector temperature 340°C, oven temperature 320°C. The range of temperature is 100-320°C, and heating rate is 6ûC min.

3-3. Observation of bloom on surface

Bloom generated on surface is observed with both of eyes and SEM (JSM-840A, JEOL Co.)

4. Results and considerations

4-1. Identification of materials causing bloom

In order to analyze components in bloom, bloom sample scratched by small volume is resolved into ethyl ether. Fig.2 shows a result of gas chromatography analysis. Materials causing bloom is determined as C10-14 Acid, unlike the previous report that materials causing bloom is C18 Stearic Acid. As shown in Fig. 2, three materials include components less than 16 carbons, which are deduced to be C10-14 Acid from chemical composition. Also, it is found from these results that the 1st material generating bloom is the crystal Acid with a little carbons and the long chain carboxy acid delays to generate bloom.

4-2. Restriction from generating bloom by esterification

In the previous chapter, solid-phase carboxy Acid as a raw material and free carboxy Acid as impurities are the key materials causing bloom. These carboxy Acid should is substituted by other material or impurities be eliminated in advanced. For the purpose of solving these problems, high quality-carboxy acid, the raw material of cosmetics is used in this study. As a result, crystal carboxy acid is esterificated without catalyst and bloom is prevented. Ester and water are created from this reaction which is described as equation (1).

$$R - COOH + R' - OH \longleftrightarrow R\text{-}COOR' + H_2O \quad (1)$$

This reaction is reversible. To proceed the reaction positively, strong acid is used as catalyst or one of reactants is used exceedingly or water created from the reaction is removed. [5] But in case using strong acid as catalyst, retrieval of catalyst is too difficult. If catalyst remains in the product, this strong acid may cause a secondary effect. Therefore, catalyst is not used in this study and crystal carboxy is esterificated with high quality-alcohol at 85°C for 30 minute. To make sure that the reaction proceeds, acid value of reactant and resultant is measured by acid quantitative analysis. Comparing the acid values before and after the reaction, it is certificated that the reaction proceeds. Fig. 3 is the 1000 times magnified SEM photograph for the surfaces of various kinds of experiments. These products are manufactured at same condition and these are stored in constant temperature place at 25±1°C, relative humidity 50% for 2 months. From this result, there are big difference between previous surface and the surfaces using Cetyl Alcohol and Stearyl Alcohol. Comparing the whiteness degree of surfaces, bloom does not exist in the surface using Alcohol.

5. Conclusions

As results of study on the phenomenon of crystal solid-phase wax being separated in oil-wax-pigment mixture system, it is found out that these phenomenon, bloom, is to change surface white as the low crystal carboxy Acid moves to the stable solid-gas interface with time. Growth of bloom by crystal carboxy Acid on the surface can be observed with SEM. In order to prevent from generating bloom, crystal carboxy Acid which finds out to be a cause component of bloom could be replaced by the high quality alcohol with the non-catalyzer esterification in 85°C.

References

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高級脂肪酸配合 Bloom 現象,58[2],64-72

3. Oil wax- 色材混合表面, 固體分離現象
高級脂肪, Hydro genated castor oil Bloom 現象

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處理溫度, Bloom 關係

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Table 1. Structure of solid wax-phase materials

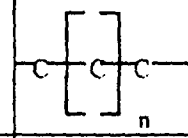
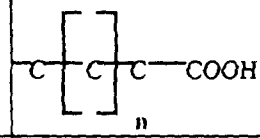
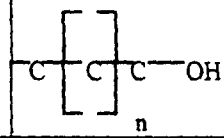
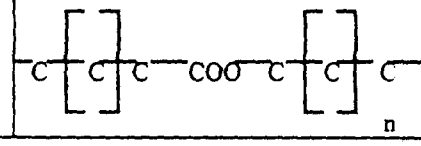
Classifications	Struture	CTFA name	Trade name
Hydrocarbon		Paraffin	Ceresin, Multi wax Ozokerite
Acid		Stearic Acid(C-18)	Emersol-132 Cutina-Fs45
Alcohol		Cetostearyl Alcohol (C-16:18)	Lanette-0
Ester wax		Cetyl Palmitate	Cutina- CP

Table 2. Comparison with property of solid-phase wax materials

	Materials	Melting point *°C	Hardness	Organic/Inorganic
I	Paraffin Wax	56.3	0.38	520/0
	Multi Wax	57.2	0.39	800-1000/0
	Ceresin-810	72.1	1.44	580-740/0
	Ozokerite	78.7	1.14	580-740/0
	Ceresin-920	81.5	3.00	580-740/0
	Ceresin-7425	88.5	1.54	580-740/0
II	Softisan-142	43	0.22	
	Sugar Ester-AIOE	46.3	3.00	
	Cutina-CP	48.9	0.53	
	Japan Wax	52.2	0.90	1020/180
	Lanolin Wax	55	0.06	
	Arlacel-165	56.3	2.08	
	GMS-105	57.3	1.66	
	Beeswax	63.2	0.82	920/60
	Candellila Wax	68	3.00	1140/60
	Castor Wax MP80	80.5	0.66	
	Carnauba Wax	82.5	3.00	
III	Cetyl Alcohol	48.2	1.49	
	Dehydag-0	50.7	1.26	
	Stearyl Alcohol	54. 1	2.78	
IV	Silicone Wax	53.9	0.32	
	Stearic Acid	55.5	1.82	360/150
	Carbowax-6000	62	3.00	
	LMW PE WAX	83.1	1.75	(40/0)n

* Hardness measuring : pressured 6m/m by Fudoh Rheometer Sp. #31 after 24 hours in 30ûC reservoir
I : Hydrocarbon group
II : Ester/Triglyceride/Natural
III : Alcohol group
IV : Others (Acid/Silicon etc.)

Fig.1 SEM photograph for bloom on the eyebrow pencil (x 1000)

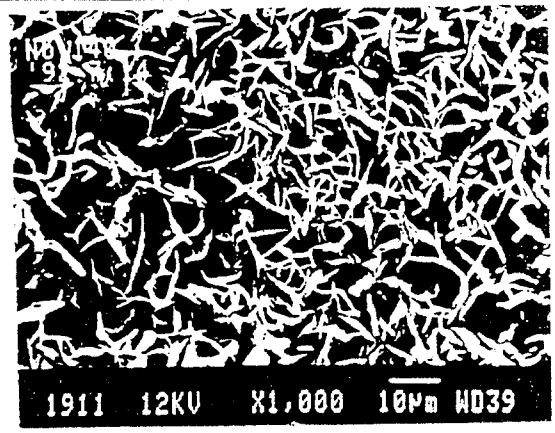


Fig. 2 Gas chromatography chart for some waxy materials

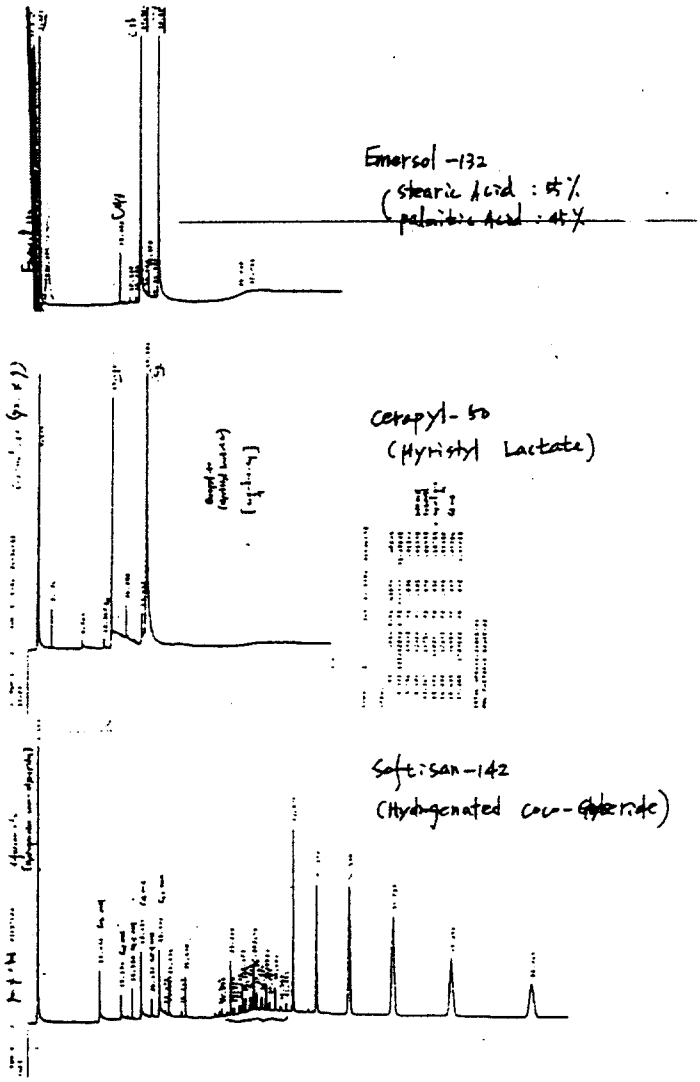
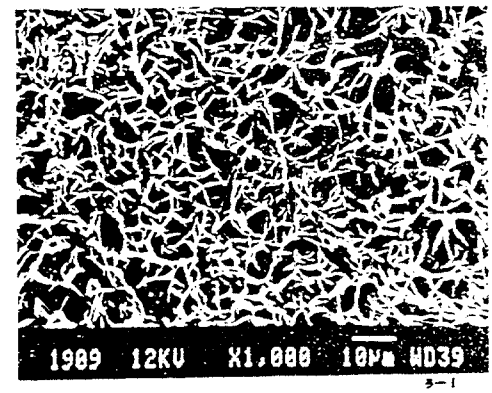
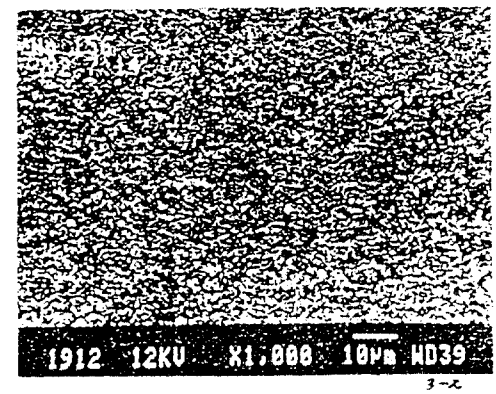


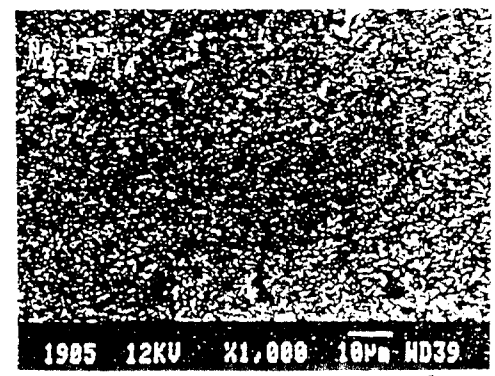
Fig. 3 SEM Photograph for the Surfaces of Various Kinds of Experiments.
3-1) product with Bloom
3-2) product with Bloom + Cetyl Alcohol
3-3) product with Bloom + Stearyl Alcohol



3-1



3-2



3-3