J. Soc. Cosmet. Scientists Korea
Vol. 34. No. 3. September 2008. 167-173

눈의 물리적인 특성과 유사한 펄 원료 개발 및 이를 이용한 화장료 조성물 제조방법

이 윤 하† · 김 경 남 · 선 우 건* · Norbert Rick** · Antje Reichnek** · 최 영 진 · 고 승 용 · 한 상 훈 · 강 학 회 · 이 옥 섭

(주)아모레퍼시픽 기술연구원 화장품연구소, Merck Korea*, Merck KgaA**
(2008년 8월 25일 접수, 2008년 9월 22일 채택)

Development of Pearl Pigment which Has the Similar Properties of Snow in Make-up Products

Yunha Lee†, Kyung Nam Kim, Gun Sunwoo*, Norbert Rick**, Antje Reichnek**
Yeongjin Choi, Seungyong Ko, Sanghun Han, Hakhee Kang, and Oksub Lee

Amore Pacific Corporation/R&D Center, 314-1 Bora-dong, Giheng-gu, Yongin-si 449-729, Korea
*Merck Korea
**Merck KgaA
(Received August 25, 2008; Accepted September 22, 2008)

요 약: 화장품 분야에서 펄 안료는 다양하게 적용되어져 왔다. 지금까지 가장 대중적으로 사용된 펄 안료는 마이카 기재에 산화철이 코팅된 것이었지만, 최종 제품에 이와 같은 펄을 사용하게 될 경우 천연 마이카에 함유된 불순물로 인해 약간의 불투명한 노란 색상이 띄게 된다[1,2]. 본 연구는 눈과 같은 반짝임을 제공하는 펄 안료 개발에 초점을 맞췄고, 눈과 같은 효과는 펄 안료의 구조와 순도 등의 영향 때문인 것을 알게 되었다. 특히, 이번 펄 안료 개발은 유리 기재와 산화철을 코팅시켜 눈의 광학적인 값(refractive index)과 입자 크기(particle size)를 눈과 유사하게 개발하였고 이는 눈과 같이 화려한 반짝임(glittering) 효과를 구현할 수 있게 되었다. 그리고 메이크업 제품에 본 펄 안료를 적용하여 화려한 제품을 개발하게 되었다.

Abstract: Pearlescent pigments have been widely used in cosmetic applications. Up to date; the most widely used pearl effect pigment is the mica-based pigment, which uses natural mica as the substrate that is in turn coated with metal oxide interference layer. However, when natural mica is employed as a base material the final product often has a yellowish color, mainly due to the fact that natural mica contains low levels of iron as an impurity[1,2]. This study was focused on developing a pearl pigment which might have a similar sparkling effect as snow. This effect was found to be due to its structure and purity, and this concept was also applied to development of our pearl pigments. More specifically, this invented pearl effect pigments are the mixture of glass-flake and glass-flake coated metal oxides and present the optical properties of snow matrix such as refractive index and particle size, unlike only the glass-flake or glass-flake coated metal oxides to be applied in. Using base material having similar physical properties (refractive index and particle size) as snow matrix as platelet for pearl effect pigments, these invented pigments present a three-dimensional glittering effect of the snow matrix. With this invented pigments an applied; we achieved the beauty of snow crystal from makeup products containing these pigments.

Keywords: *snow, glass-flake, pearl effect, snow matrix, makeup products*

† 주 저자 (e-mail: smile265@amorepacific.com)

1. Introduction

Pearl effect pigments are developed and manufactured in a small minority of countries, especially Germany, USA, Korea, and China, and applied in cosmetics, households, ink, wallpapers, printing, plastics, and automotives to manufacture value-added products[3].

Conventional pearl effect pigments have been achieved through coating processes in which base materials such as mica, platelet alumina, and platelet silica are coated with titanium dioxide or other metal oxides[4]. The color and the effect of pearl effect pigments are established, according to the specific type, thickness, and particle size of base materials and the specific type of coating metal oxide. Among these base materials, mica is known to be easily broken into thin layered flakes.

Chemical compounded platelet silica and platelet alumina have some advantages, such as high purities and even particle size distributions[5]. In the case of platelet silica-based pigments, the interference effect is stronger than the glittering effect since silica has its own interference effect on the viewing angle[6,7]. On the other hands, the particle size of alumina-based pigments is too small to present a desirable glittering effect of the snow matrix.

The purpose of this invention was to develop pearl effect pigment to present the three-dimensional beauty of snow matrix. To solve the above-mentioned problems, a suitable base material having the similar refractive index and particle size of the snow crystal was selected to present the glittering effect of the snow matrix. Using the aggregated property of glass flake, we achieved the three-dimensional beauty of snow matrix.

2. Materials and Methods

Snow exhibits a sparkling effect due to the following factors; it is a hexagonal & bisymmetric crystal network, is transparent, and has a low refractive index[8]. These three factors were considered in the development of our new pearls with the addition of narrow particle size distribution to avoid scattering of light. Among the various substrates tested, glass-flake was shown to have the most similar properties to those of snow.

To achieve the above-mentioned purpose, this invention proposed that glass-flake and glass-flake-coated metal oxides were suitable. For glass-flake-based pearl effect pigments in this invention, the surface of glass-flake was firstly coated with silica and metal oxides such as titanium dioxide and iron oxides having the refractive index 1.3 ~ 3.0. Regarding the glass-flake, the mean particle size was 10 ~ 500 μm, the thickness was below 5 μm, and the shape was platelet. The type of glass-flake was one of A, C, or E glass. The thickness of metal oxides was 10 ~ 300 μm. In the mixture of glass-flake and glass-flake-based pearl effect pigments, the desirable ratio of glass-flake and glass-flake-based pearl effect pigments was 1 : 1 to 10 : 1.

The purpose of this invention was to develop the pearl effect pigments having the snow matrix effect with glass-flake and glass-flake-coated with metal oxides.

The snow matrix effect is, when the incident light is reflected on the surface of the aggregated snow, the reflected light presents the three dimensional glittering effect with various color shade unlike the plane glittering effect of conventional pearl effect pigments. Compared to other pearl effect pigments, glass-flake has the aggregated property. Mixture of glass-flake

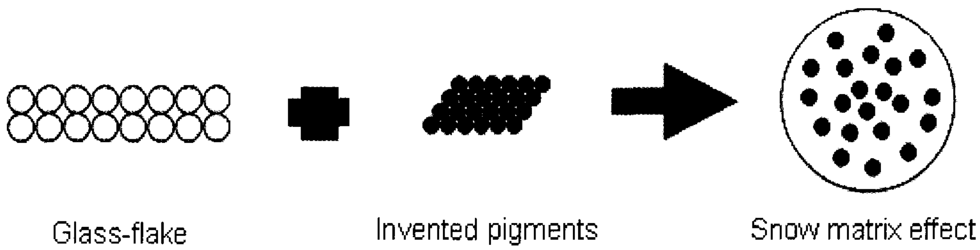

Figure 1. A simplified the illustration of the snow matrix effect of pearl pigments.

ıaving the aggregated property and glass-flake coated with metal oxides having the reflection property presents the snow matrix effect. In other words we can achieve the pearl effect pigments having the snow matrix effect.

Metal oxides having the strong reflection property were coated on the surface of glass-flake and mixed with pure glass-flake having a strong aggregating property[9]. This mixture of glass-flake and glass-flake coated with metal oxides formed an effect similar to snow matrix. The surface of this mixture reflected the incident light to various angles and presented the three-dimensional glittering effect with various color shades.

The desirable ratio of pure glass-flake and glass-flake coated with metal oxides was 1 : 1 to 10 : 1 in the mixture. With a ratio of pure glass-flake below 50 %, it was difficult to present the snow matrix effect due to weak aggregating property. With ratio of pure glass-flake was over 10 times of glass-flake coated metal oxides, the glittering effect was decreased due to weak light reflection property. In the glass-flake coated with metal oxides, silica was coated on the surface of pure glass flake; it was the protective layer and kept the safety for the skin[10].

The mean particle size of pure glass flake was 10 ~ 500 μm and more desirably 10 ~ 200 μm. The thickness of pure glass-flake was below 5 μm and more desirably below 2 μm. This material was transparent or semi-transparent to minimize the scattering of the incident light and maximize the glittering effect. The thickness of metal oxides which is coated on the base material was 10 ~ 300 μm. According to the specific type, thickness and particle size of metal oxides, light interference effects and color shades were different. To achieve various color shades, the above-mentioned thickness of metal oxides was desirable.

The types of pure glass-flake were A, C, and E, and all types were available for cosmetic use. A type of pure glass-flake is soda-lime glass, and the content of sodium is more than potassium and calcium carbonate. C type of pure glass-flake, namely chemical glass, has a strong tolerance for erosion by acid and water and contains zinc oxide and other oxides. E type of glass-flake, electronic glass, is applied in electronic industries, stable in high temperatures but easily damaged by chemicals.

2.1. Experiment 1

1) To achieve pearl effect pigments having the physical properties of the snow matrix manufactured the glass-flake coated with metal oxides. Through the milling and classification process, we used glass-flake that having the particle size 20 ~ 150 μm and the thickness below 1 μm and for the skin safety the surface of glass-flake coated with silica. And then titanium dioxide is coated on the top of glass-flake coated with silica and the thickness of coated titanium dioxide is 30 to 80 μm.

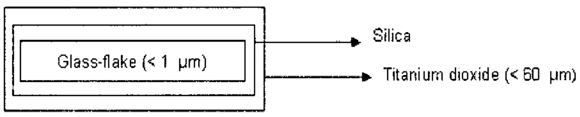

Figure 2. An illustration of invented pigments on article 1.

Figure 3. SEM picture of invented pigments on article 1.

2) Using platelet mica as base material for pearl effect pigments, and other process follow up the same procedure.

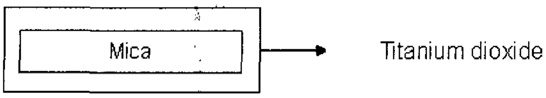

Figure 4. The illustration of invented pigments on article 2.

Figure 5. SEM picture of the invented pigments on article 2.

3) Using platelet alumina as base material for pearl effect pigments, and other process follow up the same procedure.

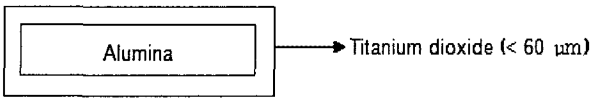

Figure 6. The illustration of invented pigments on article 3.

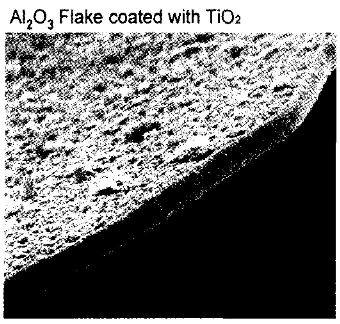

Figure 7. SEM picture of the invented pigments on article 3.

4) Using platelet alumina as base material for pearl effect pigments, and other process follow up the same procedure.

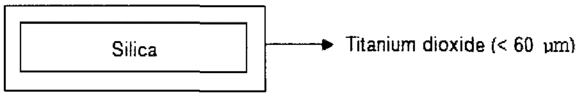

Figure 8. The illustration of invented pigments on article 4.

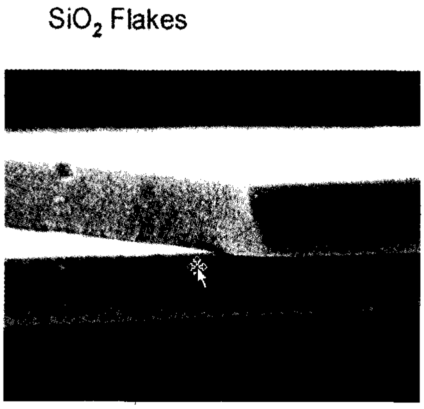

Figure 9. SEM picture of the invented pigments on article 4.

2.2. Experiment 2

Article 1, 2, 3 and 4 of Experiment 1 are mixed with pure glass-flake, analyzed which mixture presents the most suitable for snow matrix effect.

Mixed with glass-flake and glass-flake coated metal oxide, mica, and platelet alumina.

1) 80 % Glass-flake and 20 % glass-flake coated metal oxide

2) 80 % Glass-flake and 20 % mica coated metal oxide

3) 80 % Glass-flake and 20 % platelet alumina coated metal oxide

4) 80 % Glass-flake and 20 % platelet silica coated metal oxide

2.3. Experiment 3

Applied in eye shadows. Each wt% of mixture with glass-flake on Experiment 2 is applied in makeup products.

2.4. Experiment 4

Applied in lip-gloss. 5 % of mixture 1, 2, 3, and 4 were applied in makeup products, lip-gloss as the below procedure.

Table 1. Eye Shadows Used a Material of Experiment 2

	Makeup 1	Makeup 2	Makeup 3	Makeup 4
Talc	55.50	55.50	55.50	55.50
Mica	10.00	10.00	10.00	10.00
Mixture 1	30.00	-	-	-
Mixture 2	-	30.00	-	-
Mixture 3	-	-	30.00	-
Mixture 4	-	-	-	30.00
Colorants	3.00	3.00	3.00	3.00
Aluminum Stearate	1.50	1.50	1.50	1.50

Table 2. Lip-gloss Used a Material of Experiment 2

	Makeup 5	Makeup 6	Makeup 7	Makeup 8
Bees wax	4.00	4.00	4.00	4.00
Polybutene	25.00	25.00	25.00	25.00
Polyglyceryl isostearate	25.00	25.00	25.00	25.00
Glyceryl diisostearate	10.00	10.00	10.00	10.00
Diisostearymalate	26.50	26.50	26.50	26.50
Mica	3.00	3.00	3.00	3.00
Titanium dioxide	0.50	0.50	0.50	0.50
Yellow No. 5 Lake	0.30	0.30	0.30	0.30
Red No. 6 Lake	0.20	0.20	0.20	0.20
Mixture 1	5.00	-	-	-
Mixture 2	-	5.00	-	-
Mixture 3	-	-	5.00	-
Mixture 4	-	-	-	5.00
Preservatives	q.s	q.s	q.s	q.s
Perfume	q.s	q.s	q.s	q.s

1) Weigh 1 ~ 6, heat to 90 ℃ and mix using a homogenizer.
2) Weigh 7 ~ 9, add to 1) and disperse.
3) Weigh 10 ~ 15.
4) Heat to 75 ~ 85 ℃ 2), add 3) to 2) with stirring by homogenizer. Devaporize the vapor and add perfume. Package.

3. Results and Discussion

3.1. The Test Result of Experiment 1

To evaluate the presentation of the snow matrix effect, Table 3 shows the test result of article 1, 2, 3, and 4.

As above Table 3, the refractive index of platelet alumina and platelet silica is very similar to the snow crystal. But in the case of the glittering effect of platelet silica, both of titanium dioxide and silica presents the light interference effect, so the glittering effect is not maximized. In the case of platelet alumina, the glittering effect of platelet alumina is minimized under the weak light source and mica is easily broken to smaller particle sized flakes so the incident light is widely scattered to decrease the glittering effect. On the other hand glass-flake-coated titanium dioxide reflects the almost of the incident light, the glittering effect is the most suitable to develop the pearl effect pigments of snow matrix and the refractive index is similar to the

Table 3. The Test Result of Article 1, 2, 3, and 4

	1. Refractive index of base material	2. Glittering effect	3. Even particle size distribution
Article 1	◎	◎	◎
Article 2	×	○	×
Article 3	◎	×	○
Article 4	◎	○	×

1. ◎ : Very similar refractive index of base material to snow crystal.
○ : Somewhat similar refractive index of base material to snow crystal.
× : Totally different refractive index of base material to snow crystal.
2. ◎ : Very similar glittering effect to snow crystal.
○ : Somewhat similar glittering effect to snow crystal.
× : Totally different glittering effect to snow crystal.
3. ◎ : Very even particle size distribution (D50 〉 90 %).
○ : Somewhat even particle size distribution (90 % 〉 D50 〉 85 %).
× : Not even particle size distribution (85 % 〉 D50 〉 80 %).

Table 4. The Degree of the Similarity to the Glittering Effect of Snow Matrix

	Degree of the similarity to the glittering effect of snow matrix
Mixture 1	◎
Mixture 2	○
Mixture 3	×
Mixture 4	○

※ ◎ : Very similar to the glittering effect of snow matrix.
○ : Somewhat similar to the glittering effect of snow matrix.
× : Not similar to the glittering effect of snow matrix.

snow crystal, 1.3. The particle size distributions of glass-flake-coated titanium dioxide, platelet silica and alumina are very even but mica is broad due to the smaller particle sized flakes. Therefore, glass-flake-coated metal oxides is the most suitable to develop the pearl effect pigments.

3.2. The Test Result of Experiment 2

As above Table 3, the glittering effect of glass-flake coated metal oxide mixed with glass-flake presents the most similar to snow matrix. Glass-flake reflects the incident light for the glittering effect but platelet silica, platelet alumina mica are not strong for the glittering effect as much as glass-flake.

3.3. The Test Result of Experiment 3 and 4

Above makeup products were provided to 20 ~ 40 aged 30 women, and evaluate the sensory test such as safety, adhesion, feeling (bearing effect, tough and rough) and glittering effect. And evaluate each parameter from 1 to 5 and the test was 5 times followed up.

As above Table 5, Makeup 1 containing the mixture of glass-flake and glass-flake coated with metal oxide presents the strongest glittering effect. Others, safety, adhesion and feeling presented good or very good performance.

As above Table 6, Makeup 5 containing the mixture of glass-flake and glass-flake coated with metal oxide presents the most strong snow matrix effect.

The glass-flake has the hexagonal and bisymmetry crystal structure as snow. Since the incident light is reflected, refracted, and transmitted on crystals, the glittering effect occurs in the crystals without loss of light.

To produce the similar glittering effect of snow, we used the transparent glass-flake as the substrate. The glass-flake has no impurities, similar to the character of

Table 5. The Evaluation for Each Parameter

Parameter	Makeup 1	Makeup 2	Makeup 3	Makeup 4
Safety	5.0	4.5	3.8	3.4
Adhesion	4.6	4.5	4.2	4.4
Feeling	4.8	4.6	4.8	4.1
Glittering	4.5	3.8	3.5	4.0

※ 5: Very good performance.
1: Poor performance.

Table 6. The Evaluation for Each Parameter

	Snow matrix effect	Even particle size distribution
Makeup 5	4.5	4.6
Makeup 6	3.8	3.2
Makeup 7	3.6	3.5
Makeup 8	4.0	3.9

※ 5: Very good performance.
1: Poor performance.

snow, compared to the conventional substrates. Also, we were able to control light scattering by keeping the particle size distribution of these pigments to be narrow.

In addition, the refractive index of snow crystal is very low (n_d^{20} : 1.31). The glass-flake leads to an increased gloss of the interference pigments. The reason for that is a lower refractive index of glass-flake (n_d^{20} : 1.5) compared to conventional substrate (n_d^{20} : 1.6) leading to a higher refractive index gap between the substrate surface and the metal oxide coating. Low refractive index improves high reflection and refraction to lead color purity. Application of these new pearl pigments in makeup products resulted in sparkling effects similar to that of snow.

4. Conclusion

We applied the principle of why snow has the sparkling effect. This invented pearl effect pigments is the mixture of pure glass-flake and glass flake coated with metal oxide. Comparing that only glass-flake is applied in, this invented pigment presents the snow matrix effect and the physical properties such as refractive index and particle size are most similar to snow matrix effect such as glittering effect because glass-flake, the most similar to the snow crystal is used for base material of pearl effect pigments. These invented pigments are applied in makeup products to achieve the beauty of snow matrix to present the three dimension glittering effect with various color shades.

References

1. L. M. Greenstein, Pigment Handbook, John Wiley & Sons, New York (1988).
2. L. A. Basic, Optics and pearlescent pigments, *Paint Coatings Industry*, **5** (8) (1989).
3. W. J. Sullivan, P. Elliot, and D. Fleming, U.S. Patent 5753371, USA (1998).
4. F. J. Maile, G. Pfaff, and P. Reynders, Effect pigments-past, present and future, *Progress in Organic Coatings*, **54**, 150 (2005).
5. G. Pfaff and P. Reynders, Angle-dependent optical effects deriving from submicron structures of films and pigments, *Chem. Rev.*, **99**(7), 1963 (1999).
6. F. J. Maile and P. Reynders, Substrates for pearlescent pigments, *Eur. Coat. J.*, **4**, 124 (2003).
7. W. J. Marshall and H. R. Linton, US 3331699, USA (1967).
8. M. Yamamoto, Europe Patent 0723997 B1 (1996).
9. M. Suzuki, U.S. Patent 3869289; R. Schmid, Europe Patent 0940451 (1999).
10. K. Nitta, T. M. Shau, and J. Sugahara, Europe Patent 0763573 B1 (1996).