

A Study on Heavy Metal Materials in Cosmetic Makeup Concealers

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ABSTRACT

Background/Objective: This paper aimed to select low-priced and high priced concealer products sold in Korea to analyze the inorganic materials in these cosmetic products and to investigate whether any heavy metal materials harmful to humans are present in them.

Method: The inorganic materials and heavy metal materials in the concealer cosmetics products were observed with a scanning electron microscope and the component elements were analyzed using energy dispersion spectroscopy.

Findings: Both the low- and high-priced concealer products used for this study mainly contained silica, titanium dioxide, and iron oxide. The study found that the high-priced concealer products did not contain heavy metal materials harmful to humans but the low-priced concealer products contained the radioactive material technetium. When cosmetics containing this radioactive material are applied over a long period of time adverse health and cosmetic effects may develop.

Improvements/Applications: Not only stones and soil in nature but also metals in water may be mixed into the base materials used to manufacture cosmetics. High-purity base materials must be used to produce high-quality cosmetics and a thorough quality control process must be applied to the manufacturing process to prevent foreign materials from contaminating cosmetics products.

Keywords: concealer, cosmetics, make-up, scanning electron microscope, technetium.

Introduction

The use of colored makeup products by both males and females in Korea is continually increasing. In particular, young people are becoming more and more interested in colored makeup and routinely use makeup cosmetics^[1].

Makeup products are applied to the face every day in the course of daily living. The metal materials in cosmetic products may be absorbed into the human body through the oral cavity, the mucous membranes of eyes, and the thin skin of the face. The metals absorbed

into the human body may cause cancers and trigger toxic and chronic diseases in various parts of the body^[2-7]. The elements of colored makeup products may contain various harmful compounds such as color dyes, heavy metals^[3,8], preservatives, paraben, formaldehyde, and saturated hydrocarbons^[9].

Eight metals, including antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), mercury (Hg), nickel (Ni) and lead (Pb), are forbidden for use in cosmetic products because when these materials permeate the skin or are absorbed through the respiratory system, they may cause toxicity^[2].

Heavy metal elements, such as lead (less than 50 μ g/g), nickel (less than 30 μ g/g), arsenic (less than 10 μ g/g), mercury (less than 1 μ g/g), antimony (less than 10 μ g/g), and cadmium (less than 5 μ g/g), etc., are forbidden to be intentionally added to the base materials used in the manufacturing process of colored makeup products. All color additives used in cosmetic products

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in Korea must be approved by the Ministry of Food and Drug Safety^[10]. Particularly, metals such as nickel, cobalt, chromium, etc., are allergic antigens which can permeate through the skin of children who suffer from atopic dermatitis. Adults may develop contact dermatitis by nickel concentrations as low as 0.5ppm^[8,11].

Cosmetic products must be safe because they are used repeatedly and are directly applied to human skin. Nevertheless, there is growing concern regarding the safety of some products. Unfortunately, cosmetic products have been sold in the Korean market to which harmful heavy metals, such as antimony, were added intentionally or unintentionally.

In March 2018, Korea's Ministry of Food and Drug Safety found antimony was added over the acceptable level to the concealer products of eight cosmetics companies, including a well-known one, and took measures to suspend their sale and recall the products.

Antimony is a heavy metal and is permitted to be used in the end-product only under the acceptable level of 10µg/g according to the Korean Food and Drug Administration (KFDA) cosmetics safe standards. This heavy metal must not be added intentionally during the cosmetic manufacturing process. In cases where the material is added from the shipping materials used in the process of manufacture or storage, objective data must identify the material. When the complete removal is impossible in the process of cosmetics manufacture due to technologic limitations, the manufacturer must observe the detection limits designated in the KFDA^[10].

The concealer in colored cosmetic products is used to mask small blemishes on facial skin which cannot be masked by foundation, BB cream, etc. And it masks pigmented parts, such as acne, freckles, age spots, and dark circles, etc., in order to present the appearance of clean and bright skin. Thus, it is a functional colored cosmetic product^[12].

Concealer products are available in various forms, such as brushes, pencils, creams, liquids, and sticks, etc. Cream concealers can be applied to dark circles below the eyes by spreading it with a brush. And, the brush and stick type concealers can be applied to mask freckles or age spots.

In addition, concealers are produced in various shades and colors for different uses. Concealer that is

one tone level brighter than an individual's skin tone is recommended to mask dark areas, such as dark circles, etc. But, concealer one tone darker is better at masking dark parts, such as acne, etc., to make the bumps appear less prominent. Thus, concealer cosmetic products, which have various functions and usages, are popular among young people, too. Korean people use colored cosmetic products less than Americans and Europeans, except for lip gloss, lip balm, lipstick, eyeliner and eyebrow products^[13]. But, as the cosmetics industry develops in Korea, the use of colored cosmetic products by all age groups is increasing.

The experimental materials used in this study were the concealers which caused social problems recently in Korea due to the heavy metal materials contained in these products. The inorganic minerals and heavy metal materials added to these products were analyzed with a scanning electron microscope. Then, energy dispersive X-ray spectroscopy was utilized in order to investigate whether harmful heavy metal materials could be detected in these concealer products.

Materials and Method

Materials Preparation: Among the concealer cosmetic products sold in Korea, the researchers in this study purchased low- and high-priced stick-type concealers which almost every woman uses, including young people, and used them as the test materials. In order to analyze the heavy metal materials added to the concealers, 1g of every test material was put into a Falcon tube (50ml) and was washed three times for an hour with acetone (30ml, Merck, Germany). Next, it was washed with absolute ethanol (30ml, Merck, Germany) three times for an hour to remove the organic materials before it was precipitated.

Test Method

Scanning Electron Microscopy: In order to identify the ultrastructural characteristics of the inorganic materials added to the concealer products, each test material was deposited on a stub treated with carbon and copper tape and was allowed to air dry. Then, it was coated with platinum to a thickness of 20nm with the aid of the ion coater (IB-5 ion coater, Eiko, Japan). The coated test materials were analyzed at an accelerated voltage of 15kV with the aid of energy dispersive X-ray spectroscopy (INCA, Oxford

Ins, Great Britain). It was observed at the 15kV with the aid of the scanning electron microscope (S-4700, Hitachi, Japan).

Analyzing the Component Elements: In order to analyze the component elements of the materials which were added to the concealer products, the test materials were made in the same way as the sample for the scanning electron microscope were made. Next, the test materials were deposited on the stub where the carbon tape was attached. Then, they were coated with platinum to a thickness of 20nm with the aid of the ion coater (IB-5 ion coater, Eiko, Japan). Finally, the coated samples were analyzed at the accelerated voltage of 15kV with the aid of the energy dispersive X-ray spectroscopy (INCA, Oxford Ins, Great Britain).

Results and Discussion

First, the low-priced stick-type concealers were observed with a low-power scanning electron microscope. Globular-shaped silica was observed by low-power scanning electron microscopy. The various sizes of silica were evenly distributed from 4 μ m in diameter to 15 μ m in diameter. Flat-type material, 20 μ m in diameter was observed around the silica [Figure 1a]. Polygonal flat-type kaolin material, has a homogenous and smooth surface and its boundary is very soft. Tetragonal or octagonal kaolin is uniquely smooth and has a homogenous surface and excellent absorptivity so that it is used as a base material for medical and cosmetic products^[14,15].

Silica is an environmentally-friendly inorganic pigment which is used, not only in cosmetic products but also in paper manufacture, the textile industry, chemistry, paints, and biological preparations, etc.^[16-19]. The silica which was added to the low-priced concealers had a smooth surface and a lot of titanium dioxide particles attached to its surfaces [Figure 1b].

Talc added to the low-priced concealers was observed as a thin flat-type or as a mass composed of layers of thin plates. The thin plates were about 20 μ m in diameter [Figure 2a]. Talc has a wide surface area so that it can be applied and adhere to the skin effectively. There is neither an electric charge on the surface of talc nor any cations between the thin flats. Talc is held together by weak van der Waals forces which exists between the layers piled one over another^[20]. Because of this, the talc particles are dispersed easily, giving talc a soft, smooth touch.

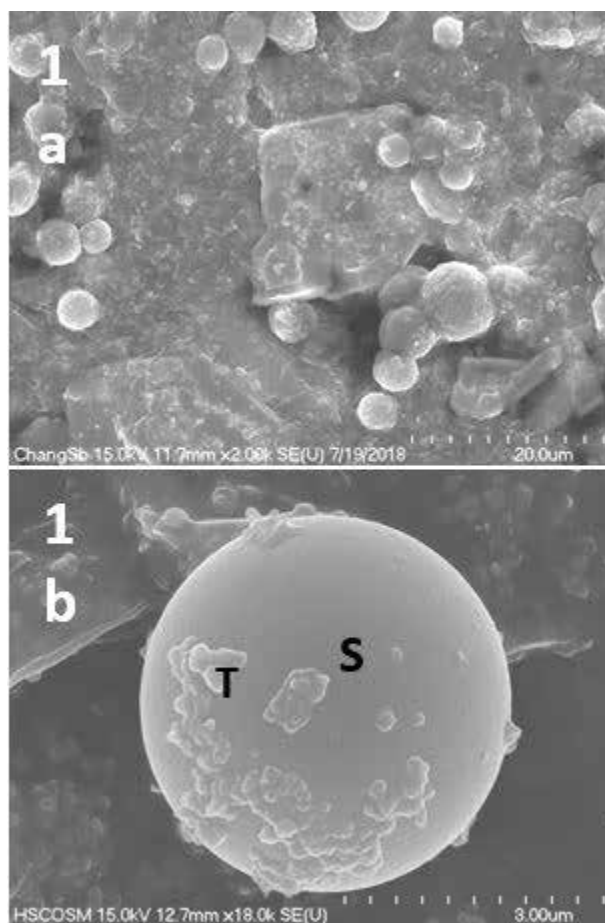


Figure 1: Scanning electron micrographs of the elements in low- priced concealer cosmetic products. a: Various sizes of silica (S) and flat-typed kaolin are observed. b: The surface of the silica appears smooth, and titanium dioxides (T) attached to the surface of the silica.

According to the image taken by the high magnification scanning electron microscope, the particles of titanium dioxide were not distributed evenly, built up a chunk, and were in cubic form with smooth surfaces. Its size measured 0.2-0.3 μ m in diameter [Figure 2b].

In this study, the component elements of low-priced concealers were analyzed with energy dispersive X-ray spectroscopy. The results demonstrated that titanium (Ti), technetium (Tc), silica (Si), iron (Fe), chloride (Cl), and aluminum (Al) were detected [Figure 3]. The component elements identified were Ti (40.4%), Si (28.51%), Tc (12.03%), Fe (6.68%), Cl (3.46%) [Figure 3].

Technetium is a radioactive material whose color is silver gray and changes slowly in wet air. Technetium, whose atomic number is 43, doesn't have a stable isotope and is generally considered to be an extinguished element in the Earth. Technetium, artificially manufactured by humans has been produced

for the last several decades^[21,22]. Technetium may exist in polluted underground water and sediments of surface water in locations near nuclear facilities^[23].

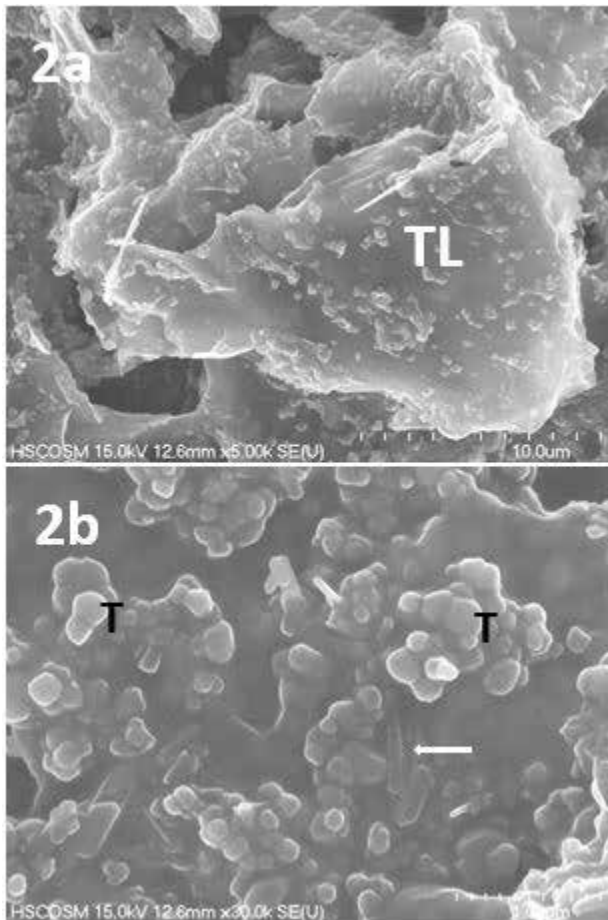


Figure 2: a: Talc (TL) in the low-priced concealers. This image was taken by the scanning electron microscope. b: The particles of titanium dioxide (T) combined into chunks. Rod shaped iron oxide (arrow) is observed between the titanium dioxide particles.

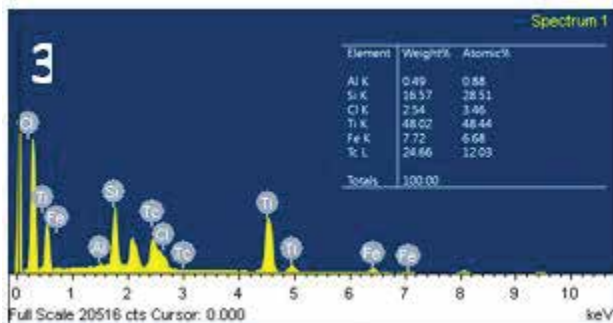


Figure 3. Analysis of low-priced cosmetics products by the energy dispersive X-ray spectroscopy showing detection of elements, such as titanium (Ti), technetium (Tc), silica (Si), iron (Fe), chloride (Cl), and aluminum (Al). Inset: Content by percentage of component elements in low-priced concealer products.

Stones and soil which exist in the natural environment, and metals which exist in water may be mixed into the base material in the process of manufacturing cosmetic products^[2]. The technetium detected in the concealers used in the study was likely added in the process of mixing the base materials or was mixed in the base materials themselves. This material is forbidden to being added during cosmetic production.

The metal materials discovered most in the personal care cosmetics include antimony, arsenic, cadmium, cobalt, chromium, mercury, nickel and lead^[24]. A lot of metals included in cosmetics from the base materials may cause many abnormal side effects, such as cancers, allergic contact dermatitis, mutations, respiratory problems, as well as development and reproductive problems^[24,25].

The high-priced stick-type concealer products were observed with the scanning electron microscope. The globular silica was evenly distributed on the surface of the test materials. Silica is a porous structure, so a lot of titanium dioxides particles were attached to the surface [Figure 4a]. Silica is used comprehensively as an additive in order to help improve the spreading and application of cosmetic products to the skin. The particulate material of silica, which has a multi-perforated nano-structure, can block UV rays and absorb sweat and sebum^[26].

The silica added to the high-priced concealers in this study was globular in shape with a multi-perforated structure and its size ranged from 3 μ m to 18 μ m in diameter.

Nano-particles of titanium dioxide were observed mostly around the silica in the high-priced test materials [Figure 4b]. The picture taken by the high-magnification scanning electron microscope showed that the cubiform titanium dioxide had a regular size and oxidized steel was observed around it. Titanium dioxide blocks UV rays, along with zinc oxide, and its size is less than 100nm. These inorganic materials of nanometer-sized units cannot permeate the skin under normal conditions. Since it stimulates skin less, it is comprehensively used as particulate material in cosmetic products^[5].

As a result of the analysis of the component elements of the high-priced stick-type concealers by energy dispersive X-ray spectroscopy elements, such as titanium, silica, and iron, were detected [Figure 5].

The content of the component elements of the high-priced concealers was Ti (77.31%), Fe (20.33%), and Si (2.36%) [Figure 5].

Besides titanium dioxide, iron oxide, and silica, no other inorganic materials were detected in the high-priced concealer cosmetics. When cosmetic products containing even the minimum amount of heavy metals are used over a long period of time, they accumulate in the human body and may cause various problems in biological systems of the human body, potentially resulting in serious health problems^[25,27]. Therefore, a thorough quality control process must be carried out in order to prevent the addition of various foreign materials to the base material of cosmetic products and to prevent contamination during the manufacturing process.

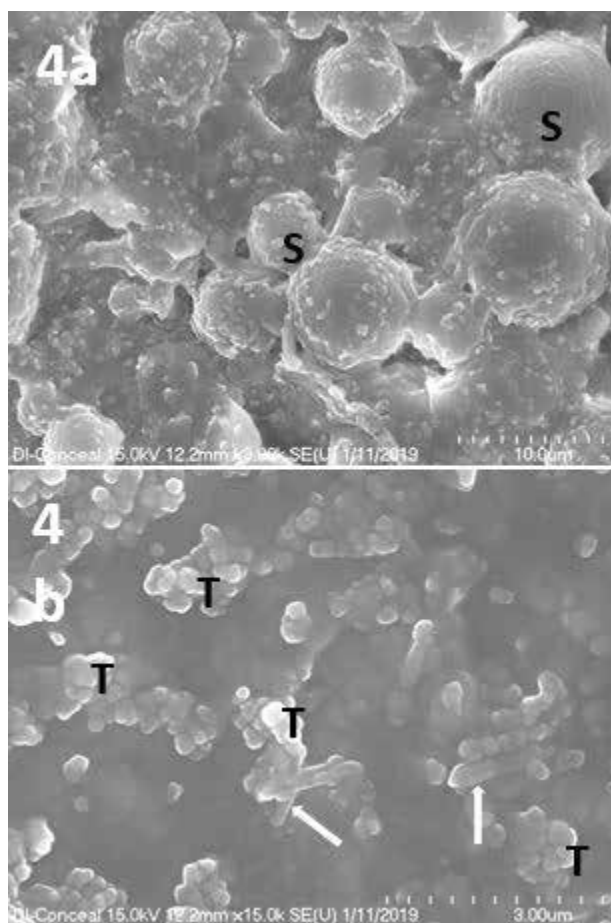


Figure 4: Component elements of low-priced concealer cosmetics taken by the low-magnification scanning electron microscope. a: Various sizes of silica (S) were observed with many titanium dioxide particles attached to its surface. b: Titanium dioxide (T) and rod shaped iron oxide (arrows) in the high-priced concealers were observed by the high-magnification scanning electron microscope.

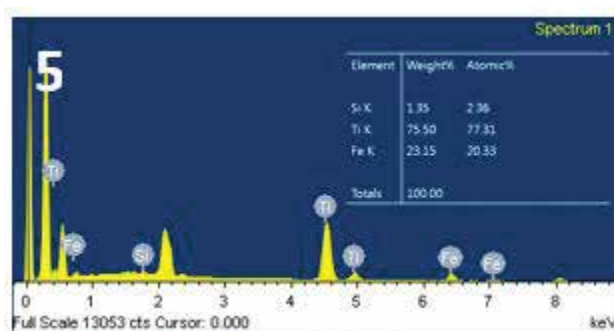


Figure 5: Energy dispersive X-ray spectroscopy of the high-priced cosmetic products detected titanium (Ti), silica (Si), and iron (Fe). Inset: The percentage content of the component elements of the high-priced concealer products.

Conclusion

This study observed the morphologic characteristics of materials added to both low-priced and high-priced concealer products using the scanning electron microscope and carried out comparative analyses of the component elements with energy dispersion spectroscopy.

The scanning electron microscopy results demonstrated that silica, titanium dioxide, rod shaped iron oxide, talc, and kaolin structures were detected in the low-priced concealer products. And scanning electron microscopy of the high-priced concealer products detected silica, titanium dioxide, and iron oxide. The energy dispersion spectroscopy analysis detected titanium, technetium, silica, iron, chloride, and aluminum in the low-priced concealer products, and titanium, silica, and iron in the high-priced concealer products.

As a result of this study, although metal materials harmful to the human body were not detected, technetium, which is characteristically a radioactive material, was detected in the low-priced concealer products. When cosmetic products containing this kind of radioactive material are used over a long period of time, they may threaten human health and cosmetic appearance. Given the fact that these kinds of cosmetic products were sold under the brand name of the well-known company in Korea, caution must be exercised in order to produce safe cosmetic products, starting from the stage of base material selection so that better cosmetic products can be distributed in the market.

Ethical Clearance: Not required

Source of Funding: This study was conducted under the 2018 Intramural Research Support Project of Hanseo University.

Conflict of Interest: Nil

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