OBSERVATION OF THE SWEATING IN LIPSTICK BY SCANNING ELECTRON MICROSCOPY

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SUMMARY

In this study, the relationship between wax matrix in lipstick and sweating was investigated by observing the change of size and shape of wax matrix with sweating by Scanning Electron Microscopy (SEM). For observation by SEM, a lipstick sample was frozen in liquid nitrogen, then the oil in the lipstick was extracted out in cold isopropanol (-70°C) for 1-3days. After isopropanol was evaporated, the sample was sputtered with gold, and examined by SEM. When examined the sweated sample by SEM, the change of wax matrix underneath the surface from fine, uniform structure to coarse, nonuniform structure was observed, which was resulted from the caking of surrounding wax matrix. That is, the oil underneath the surface was migrated to the surface of lipstick with sweating, consequently the wax matrix at that region was rearranged into the coarse matrix. In case of flamed lipstick, sweating was delayed and the wax matrix was much coarser than that of unflamed one. Its larger wax matrix at surface region was good for including oil. The effect of molding temperature on sweating was also studied. As the molding temperature was increased, sweating was greatly reduced and the size of wax matrix was increased.

It was also found that sweating was influenced with the compatibility of wax and oil. A formula consisting of wax and oil which have good compatibility has a tendency of reduced sweating and increased size of wax matrix. When pigment was added to wax and oil, sweating was increased because of weakening of the binding force between wax and oil. It was also found that sweating was influenced with the passage of time by observing a thick membrane of wax on surface of lipstick after a month from molding. In case of some lipsticks, the size of wax matrix was altered to bigger or smaller.

In conclusion, the structure of wax matrix at the surface region of lipstick was changed with the process of flaming, molding temperature, compatibility of wax and oil, addition of pigment, and the passage of time. In most cases, as the size of wax matrix was increased, sweating was reduced and delayed.

INTRODUCTION

Sweating is a phenomenon of the oil excretion on the surface of a lipstick, which is usually observed after a large temperature fluctuation, and is regarded by consumers as unattractive. Dweck(1) explained that the wax lattice modifies with increasing temperature and the wax/oil equilibrium is altered so that the oil is not held by the lattice, and the oil begins to migrate to the surface of the stick. And he also insisted that all the theory relating to sweating must be understood in relation to a poor formula, and the better the formula the higher the percentage of oil that can be included. Matsuda et al.(2) reported that the oil in wax/oil matrix was excluded with increasing temperature by expansion of volume through a channel within a lipstick. They explained sweating by polarizing microscopy, or model diagram. Matsuda et al.(3) tried to observe the wax matrix by cryo-SEM, but by this method it could not be observed without changing of its original structure.

In general, lipstick contains abundance of oil, so that it is difficult to observe the wax matrix of lipstick by SEM. Moreover, the boundary between wax and oil is not clear, even if it is made possible to observe. But in this study, the wax matrix of lipstick was observed precisely without changing its original structure by SEM using a new preparation method. This method was based on the oil substitution with isopropanol after fixation of wax matrix by freezing. At first, we examined the change of wax matrix at the surface region of lipstick after sweating. And then, the relationship between wax matrix and sweating was investigated according to the factors which have effect on sweating. The factors considered in this study were the process of flaming, molding temperature, compatibility of wax and oil, addition of pigment, and the passage of time.

EXPERIMENTAL

Molding method of lipsticks

Lipsticks were prepared by mixing and melting oil and waxes at 80°C, followed by molding at the ambient temperature. The ratio of oil and wax in lipstick was 80 : 20 and that of it in pigment added lipstick was 75 : 20 : 5(pigment). Castor oil and castor wax used in this experiment were purchased from Itoh oil Co.. Candellila and ceresin were obtained from Kahl & Co and Nikko Rica Co. respectively. Isopropanol was in guaranteed reagent grade, and purchased from Baxter Healthcare Co. and bees wax was obtained from Croda Co.. And four kinds of pigments were used, D&C red #7, D&C red #36, I.O.Red, and TiO_2. D&C red #7 and D&C red #36, which were Ca lake and Al lake respectively, were purchased from Sun chemical, and Warner & Jenkinson respectively. And I.O.Red and TiO_2 were purchased from Sun chemical.

In order to observe the wax matrix of lipstick by SEM, every sample was treated by the method mentioned below after a day from molding except for lipsticks to examine with the passage of time. Sweating was tested at room temperature and also at 45°C after a day from molding.

Scanning Electron Microscopy

In this study, wax matrix in lipstick was observed by the freeze substitution method (5,6) with some modifications. Sample preparation for SEM was as follows ; A sample taken at surface area of lipstick was cut into small pieces(about 2 x 2 x 1mm) and put on aluminum foil mesh and rapidly frozen by submerging in liquid nitrogen (-196갚C). The frozen sample was fractured with tweezers to obtain a fresh surface, and then quickly transferred into previously cooled isopropanol (-70°C) in 5ml glass vial. The oil was slowly substituted with isopropanol over a period of 1-3 days in the deep freezer (-70°C). The temperature of the isopropanol solution was then allowed to rise gradually to room temperature for 2-4hr. The sample was washed with fresh isopropanol and dried in the air. And then sample was sputtered with gold and examined by SEM. The SEM used for this study was a JEOL JSM 840A.

RESULT AND DISCUSSION

Observation of wax matrix at the surface region of lipstick after sweating

In usual, the wax matrix at the surface region was hyperfine structure and the size of the matrix was gradually increased with depth up to some extent(about 0.5-1.5mm from the surface), but no longer increased in the deeper region.(4) It was resulted from difference of cooling rate from surface to core of lipstick in molder. The surface of stick experiences sudden cooling in the initial contact of the mass with the mold to give a hyperfine crystal structure. With depth, the cooling rate was gradually decreased up to some extent and the size of wax matrix was increased, and at the deeper region, the cooling rate was the same, so the wax matrix had the same size. Fig. 1 shows the wax matrix at surface region of lipstick consisting of 10% candellila, 10% ceresin and 80% castor oil. As shown in fig. 1(a) and (b), the change of wax matrix underneath the surface from fine, uniform structure to coarse, nonuniform structure was observed, which was resulted from the caking of surrounding wax network. Also, the better sweating in lipstick, the more changes in wax matrix was observed. But the change of wax matrix with sweating could be observed only underneath the surface, and the wax matrix at the deeper region was not changed. Therefore, it would seem that the oil underneath the surface migrates to the surface of the stick with sweating, consequently the wax matrix at that region is rearranged into a coarse matrix.

Effect of flaming

In case of flamed stick consisting of the same composition as above, sweating was delayed. As shown in fig. 1(d), the size of the wax matrix of flamed stick was much bigger than that of unflamed one. The top surface of the stick is rapidly melted by the process of flaming, so that the wax/oil matrix at flamed region was rearranged into bigger structure because of slow cooling in the atmosphere. It was assumed that this bigger wax matrix was more profitable for including oil, and this result was also found in the study of sweating with the effect of molding temperature. However, when the lipstick was flamed excessively, sweating was increased in spite of increase of the size of wax matrix. This means that sweating is not related with only size of wax matrix. And in case of a flamed lipstick, the change of wax matrix after sweating was not found remarkably.

Effect of molding temperature

In order to observe the effect of molding temperature on sweating, lipsticks were molded at -15°C, ambient temp. and 50°C. Lipstick consisting of 15% candellila, 5% ceresin and 80% castor oil was molded in a molder preserved at -15°C, ambient temp., and 50°C more than 1 hr. The lipstick molded at -15°C sweated at once after separated from molder, and the lipstick molded at ambient temp. also sweated a little after several hours. But sweating was delayed exceedingly in the lipstick molded at 50°C.

As shown in fig. 2, the wax matrix at the surface region of lipstick molded at -15°C had fine structure, whereas the lipstick molded at 50°C had larger wax matrix than those of -15°C, and ambient temperature. As the molding temperature increased, the size of wax matrix was increased and the growing rate of the size with depth was increased(4). As mentioned above, these were caused by the difference of the cooling rate of lipstick in molder. That is, the wax matrix of lipstick molded at -15°C had fine structure due to rapid cooling, whereas lipstick molded at 50°C had large structure due to slow cooling. Therefore, as the molding temperature increased, the size of wax matrix increased, and sweating was greatly reduced.

Effect of compatibility of wax and oil

According to the kinds of wax and oil, the size and shape of wax matrix of lipstick was different characteristically.(4) It was assumed that the compatibility of wax and oil was responsible to that appearance. When wax and oil in a lipstick had bad compatibility, the lipstick sweated better. The relationship between sweating and compatibility was investigated for some waxes with castor oil. In fig. 3(a), (b), and fig. 1(a), the size of wax matrix was compared with three lipsticks of which the ratios of candellila and ceresin were 15:5, 5:15 and 10:10. The castor oil is made up of ester, and ceresin is made up of hydrocarbons. And candellila consists of 29% ester, 45% fatty acids, and others. Concerning of compatibility, it was expected that the candellila gave more stable formula with castor oil and sweated less than ceresin. Practically, as the content of candellila was increased, sweating was delayed and the size of wax matrix was increased. Castor wax consisting of ester was also used for experiments. In fig. 3 (c) and (d), lipsticks consisting of 15% candellila and 5% castor wax and 15% ceresin and 5% castor wax were compared. And lipstick only containing bees wax (e) was also examined. Bees wax was made up of 70% ester. As shown in fig. 3, the wax matrix of lipstick (c) was coarser than lipstick (a) and (d). The size of wax matrix of lipstick (e) was the biggest, and sweating was reduced in lipstick (c) and (e). In case of lipstick (b) and (d), the wax matrix underneath the surface was changed to coarse structure with sweating. Therefore, sweating was influenced by the compatibility of wax and oil, and the better compatibility the wax and oil had, the less sweating observed.

Effect of pigments

In order to determine the effects of pigments on sweating, four kinds of pigment were tested, which were D&C red #7, D&C red #36, I.O.Red and TiO_2. Lipstick consisting of 10% candellila, 10% ceresin, 75% castor oil, and 5% pigment was used for experiments. Pigments were prepared by 25% base in castor oil and were treated with three roll mill in three times. Pigment added lipsticks sweated largely at once after separating from molder. Matsuda et al.(3) reported that when pigment was added in wax matrix, sweating was increased because of weakening the binding force between wax and oil.

As shown in fig. 4, the wax matrix of lipstick(a) added with D&C red #7, an organic pigment, was more fine than that of lipstick in fig. 1(a). And in case of lipstick(b) added with D&C red #36, which is also an organic pigment, the size of wax matrix was similar with that of lipstick in fig. 1(a) but the pigment was caked in wax matrix. Consequently the size of wax matrix at surface region was smaller. Whereas the lipsticks added with inorganic pigment, which were I.O.Red(c) and TiO_2(d), had wax matrix bigger than that of fig. 1(a). However these lipsticks also sweated largely nevertheless the large size of wax matrix. It means that sweating is not related only with size of wax matrix, and this result is the same as the case of excessively flamed lipstick.

Effect of the passage of time

With the passage of time, it was also observed that the oil excluded on surface of lipstick returned to the lipstick, and sweated to surface again. And the amount of sweating was various during this process. In some lipsticks sweating was not observed.

Fig. 5 (a) shows the wax matrix of lipstick consisting of 15% candellila, 5% ceresin, and 80% castor oil after a month from molding. Compared with the lipstick (in fig. 2 b) after a day, the size of wax matrix was slightly decreased all over surface region and sweating was increased after a month. On the other hand, the size of wax matrix of the lipstick(c) consisting of 15% candellila, 5% castor wax, and 80% castor oil was slightly increased in comparison with lipstick (b) after a day.

And practically, sweating was hardly found in this lipstick. However wax matrix of all lipsticks was not changed after the passage of time. An interesting fact was observed in most of lipsticks that the thick membrane of wax was formed at surface of lipstick after the passage of time. As a result of this, it could be concluded that wax matrix was changed with the passage of time and was related with sweating.

CONCLUSION

Observations by Scanning Electron Microscopy showed that there was a change of wax matrix underneath the surface of lipstick from fine, uniform structure to coarse, nonuniform structure after sweating. The relationship between wax matrix and sweating was investigated with the factors having an effect on sweating, which were the process of flaming, molding temperature, compatibility of wax and oil, addition of pigment, and the passage of time. It was found out that the structure of wax matrix at the surface region of lipstick was affected by these factors. In most cases, as the size of wax matrix was increased, sweating was reduced. However, it could not forecast the extent of sweating with the size of wax matrix, because sweating was not related only the size of wax matrix. But in view of the results so far achieved, sweating was influenced from and related closely with wax matrix.

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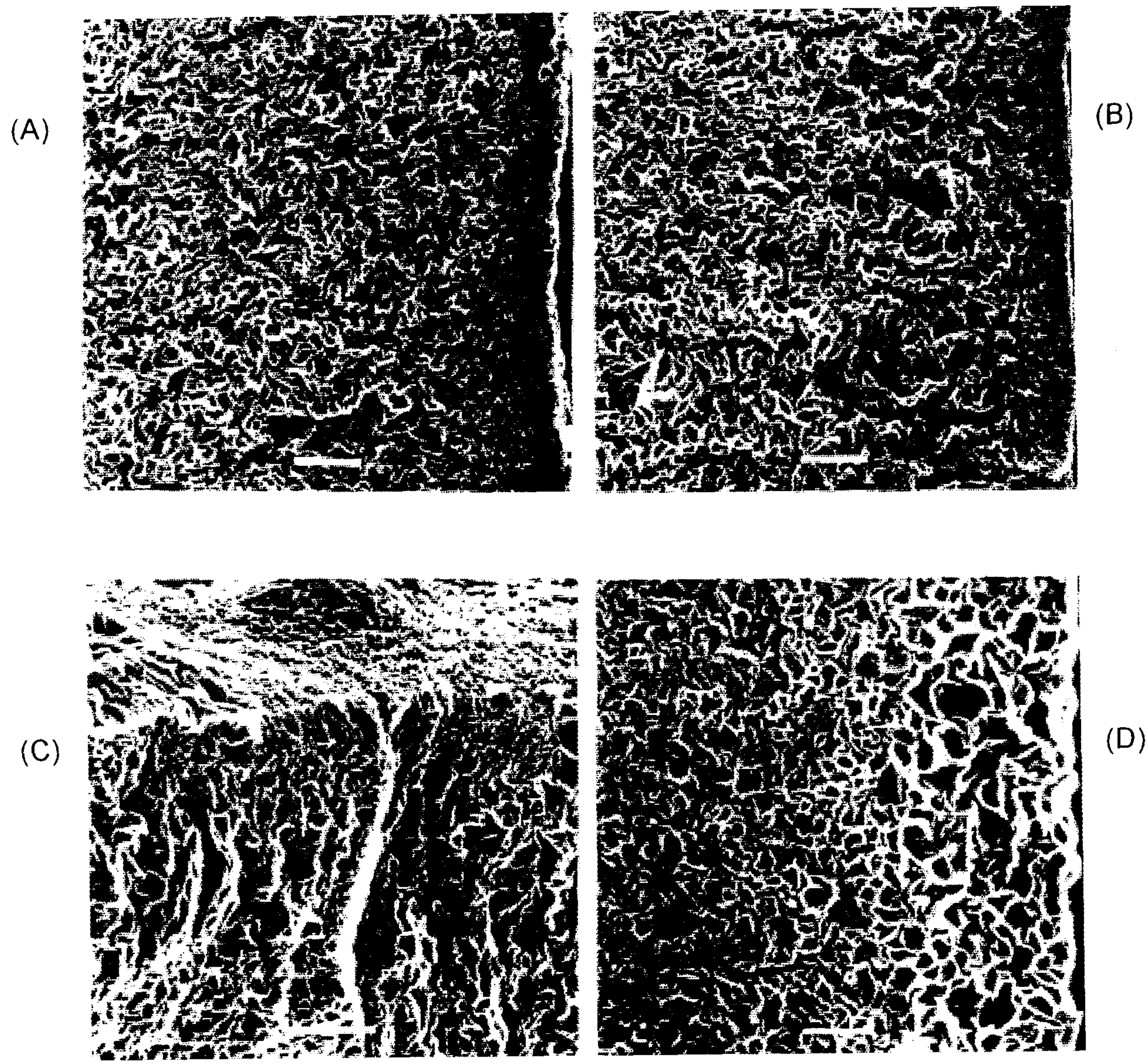

Fig. 1 Scanning Electron Microphotographs of wax matrix at the surface region of lipsticks.

Lipsticks were composed of 10% candellila, 10% ceresine, and 80% castor oil. (bar = 10(μm) In pictures a, b, and d, the right-hand side is the surface region. But in picture c, the top side is the surface region of lipstick.

(a) Unflamed lipstick before sweating (x 1000)
(b) Unflamed lipstick after sweating (x 1000)
(c) Unflamed lipstick after sweating (x 1300)
(d) Flamed lipstick before sweating (x 1000)

(A)

(B)

(C)

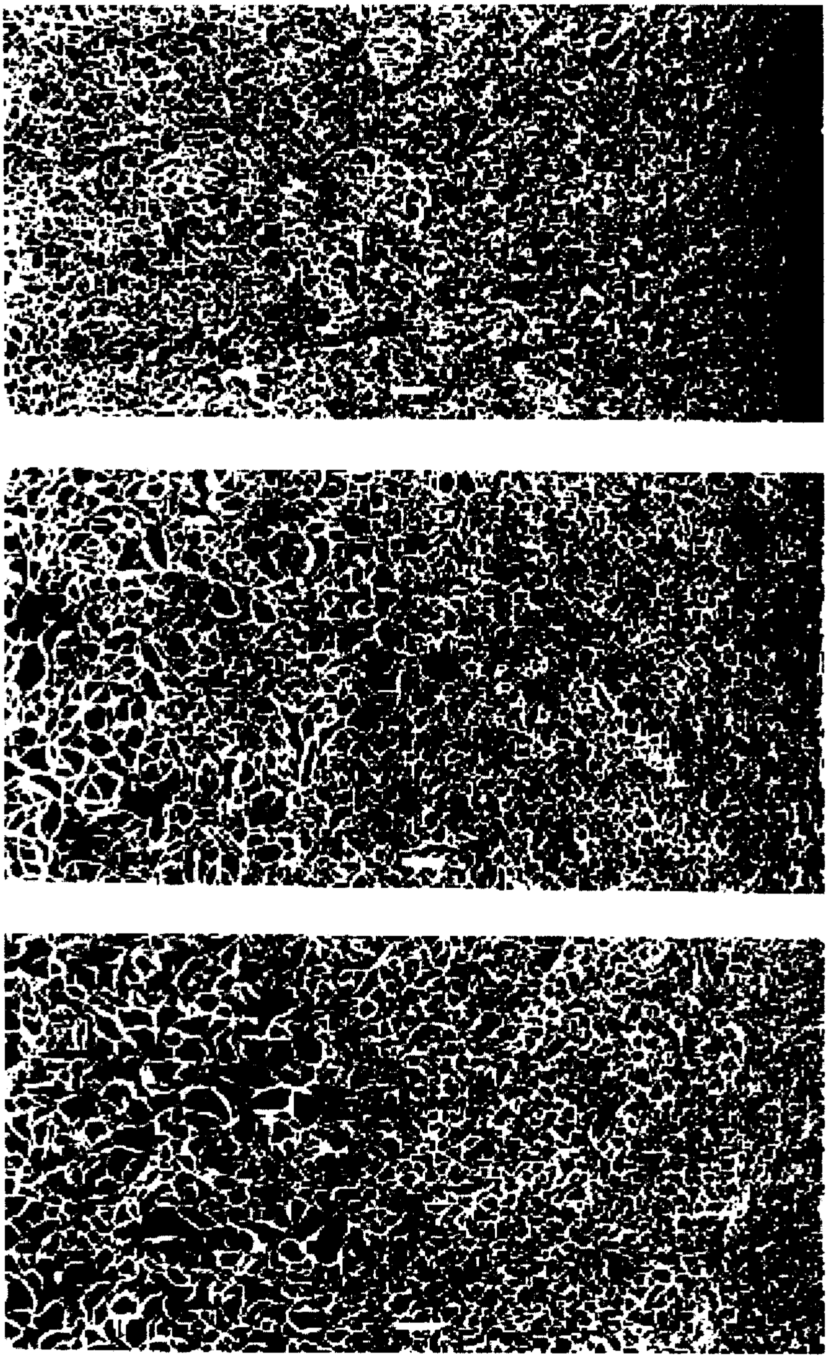

Fig. 2 The wax matrix at the surface region of lipsticks molded at -15캜, ambient temp. and 50 캜. Lipsticks were composed of 15% candellila, 5% ceresin and 80% castor oil.(bar = 10μm) The right-hand side is the surface region.

(a) Lipstick molded at -15캜 (x 500)

(b) Lipstick molded at ambient temp. (x 500)

(c) Lipstick molded at 50캜 (x 500)

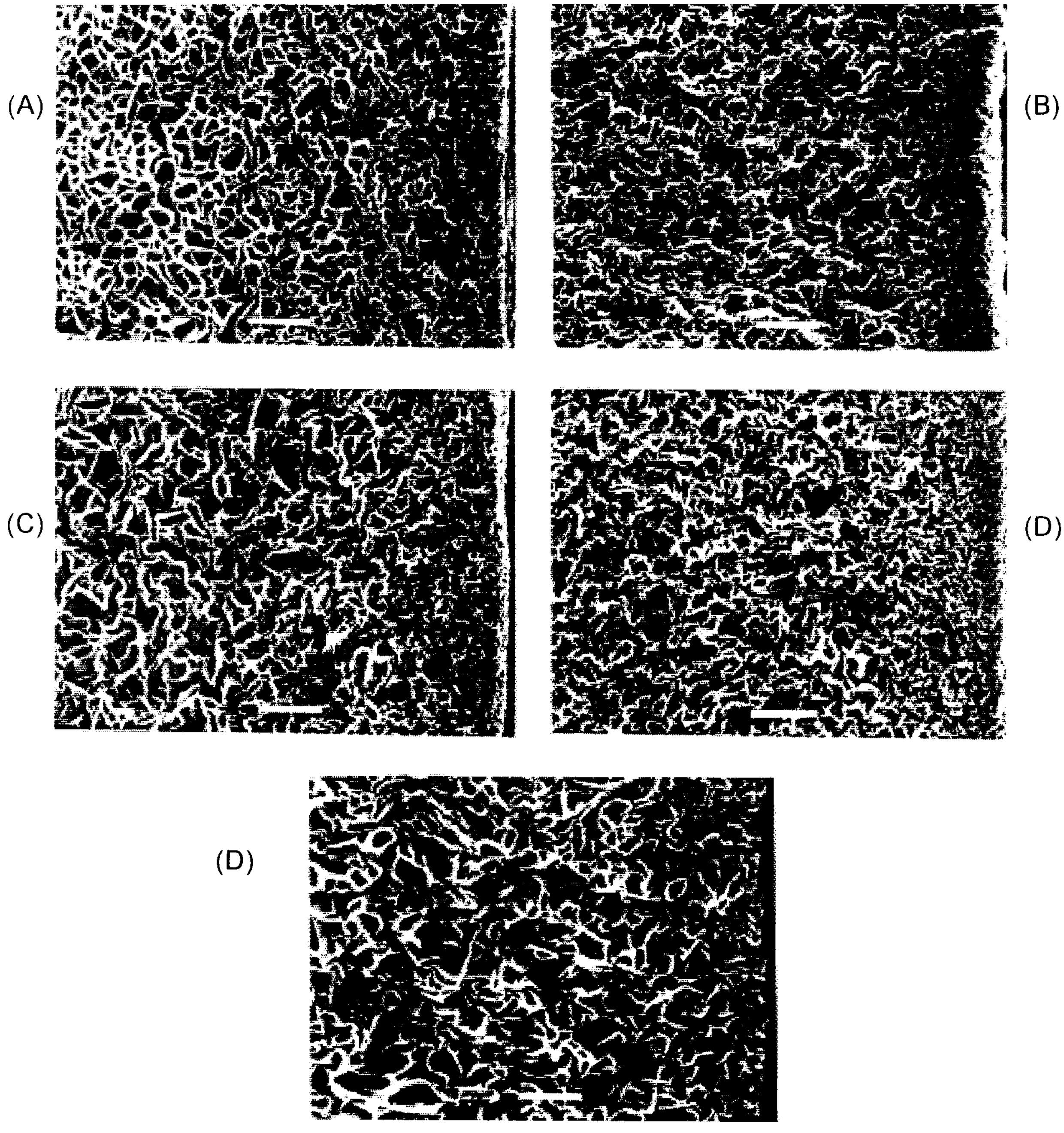

Fig. 3 The wax matrix at the surface region of lipsticks consisting of various waxes and castor oil. (bar = 10(μm) The right-hand side is the surface region.

(a) Lipstick consisting of 15% candellila, 5% ceresin, and 80% castor oil (x1000)
(b) Lipstick consisting of 5% candellila, 15% ceresin, and 80% castor oil (x1000)
(c) Lipstick consisting of 15% candellila, 5% castor wax, and 80% castor oil (x1000)
(d) Lipstick consisting of 15% ceresin, 5% castor wax, and 80% castor oil (x1000)
(e) Lipstick consisting of 20% bees wax and 80% castor oil (x1000)

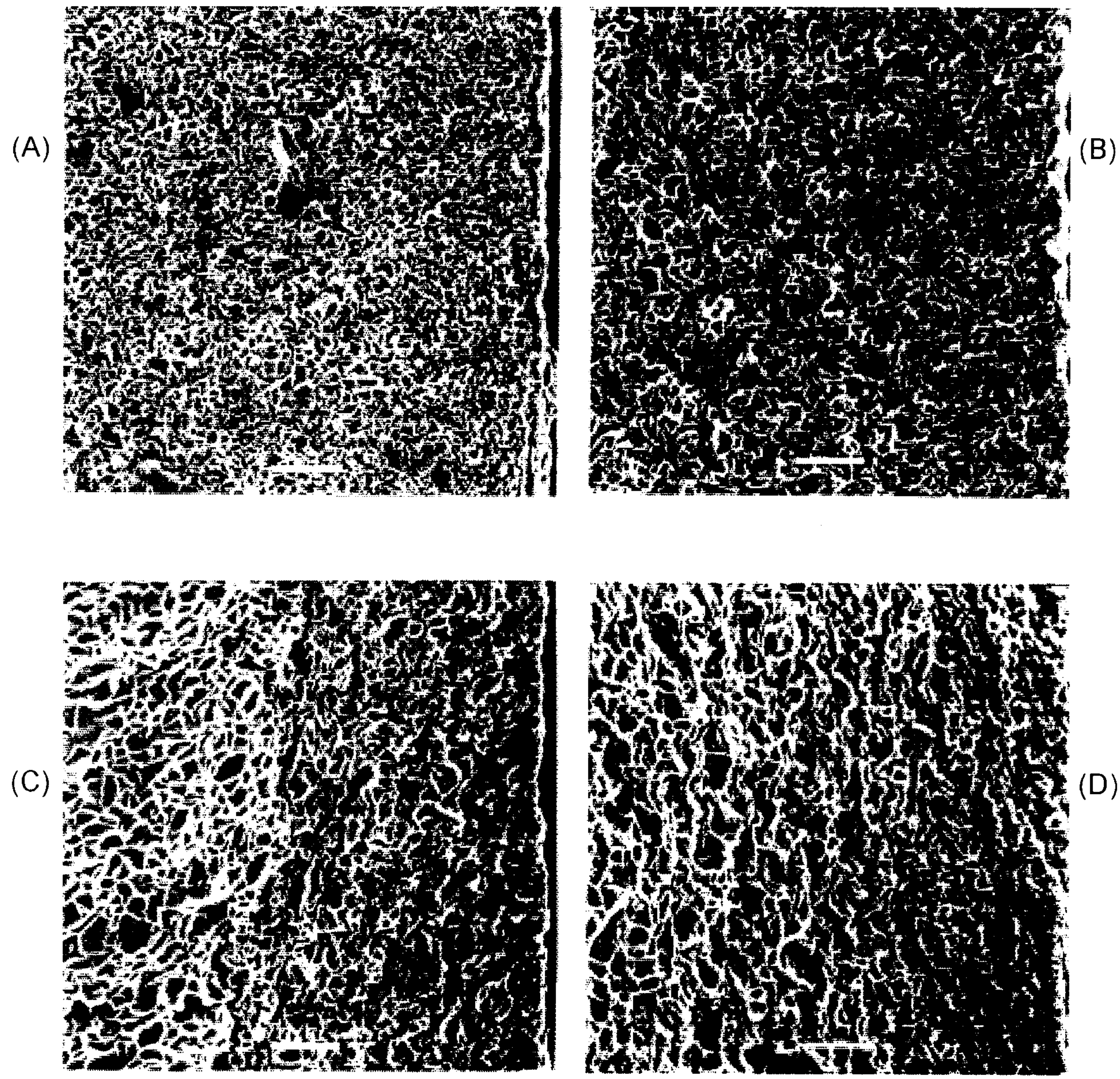

Fig. 4 The wax matrix at the surface region of lipsticks added various pigments. Lipsticks were composed of 10% candellila, 10% ceresin, 75% castor oil, and 5% pigment. (bar = 10(μm) The right-hand side is the surface region.

(a) Lipstick added D & C red #7 Ca lake (x1000)
(b) Lipstick added D & C red #36 Al lake (x1000)
(c) Lipstick added I.O.Red (x1000)
(d) Lipstick added TiO_2 (x1000)

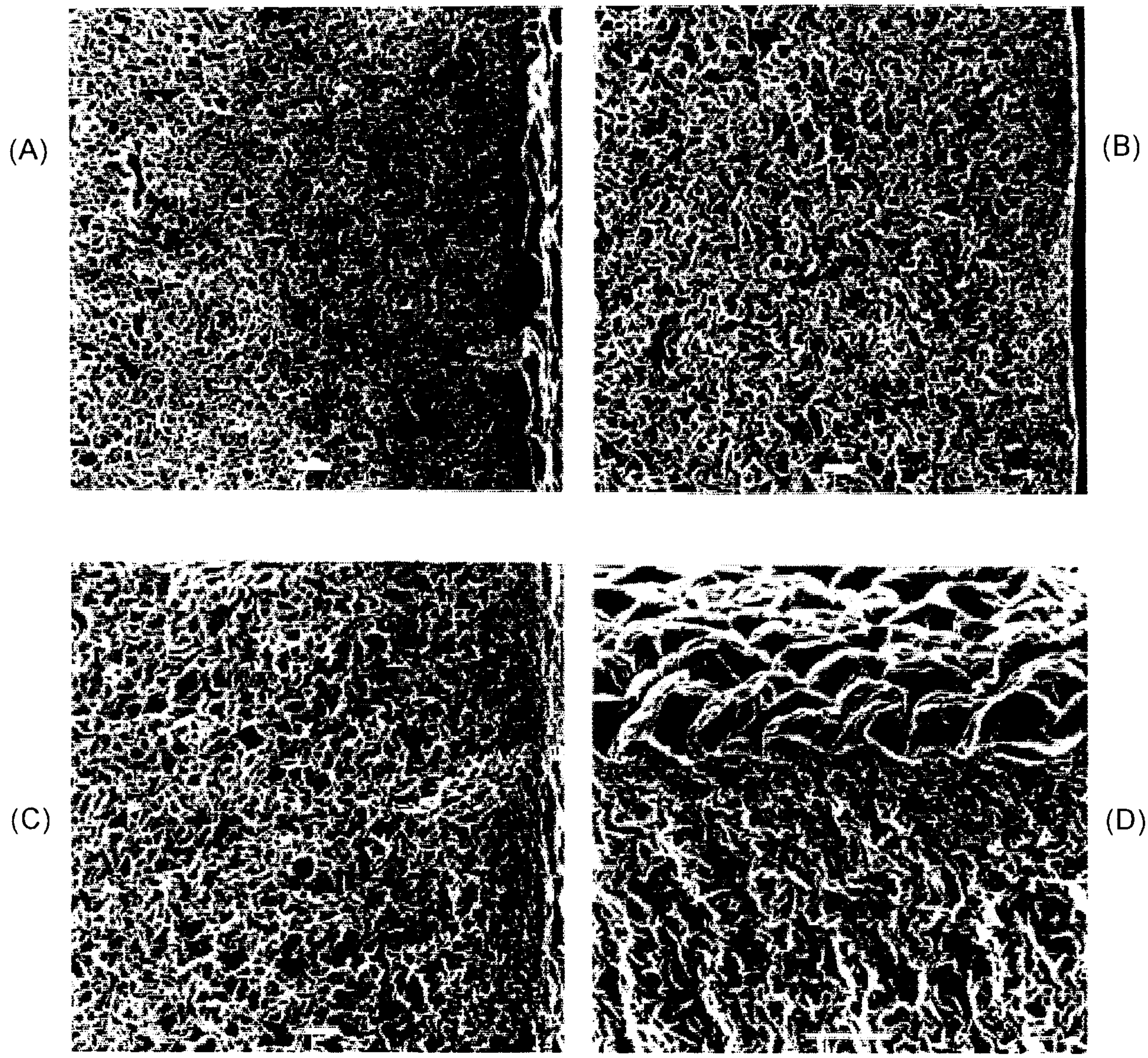

Fig. 5 The wax matrix at the surface region of lipsticks after the passage of time. (bar = 10(μm) In pictures a, b, and c, the right-hand side is the surface region. But in picture d, the top side is the surface region of lipstick.

(a)Lipstick consisting of 15% candellila, 5% ceresin, and 80% castor oil after a month from molding (x500)
(b)Lipstick consisting of 15% candellila, 5% castor wax, and 80% castor oil after a day from molding (x500)
(c)Lipstick consisting of 15% candellila, 5% castor wax, and 80% castor oil after a month from molding (x500)
(d)Lipstick consisting of 10% candellila, 10% ceresin, and 80% castor oil after a month from molding (x1300)