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# A caries prophylactic study on artificial lesions in bovine tooth enamel coated with cyanoacrylate adhesives containing fluoride compounds

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Enamel lesions produced by a buffered solution have been examined, by means of a polarized-light microscope, for abrased bovine tooth enamel coated with methyl-α-cyanoacrylates containing six kinds of fluoride compounds. The "white-spot" lesion of the demineralization area was found for all bovine tooth enamels, such as a control specimen coated with only methyl-α-cyanoacrylate without a fluoride compound and those with cyanoacrylates containing fluoride compounds, but both polarizing microscopy and the calcium solubility showed a difference in the demineralization area and in the amount of dissolved calcium among the bovine tooth enamels. Of the cyanoacrylates investigated, three cyanoacrylates containing NaF, $SnF_2$ and $ZnF_2$ as the fluoride compound were effective in the formation of a thin demineralization area which reduced "white-spot" lesion.

## 1. Introduction

In general, fluoride plays a role in reducing caries by a mechanism by which tooth enamel inhibits the dissolution of calcium and this reduces the demineralization [1, 2]. Fluoride decreases the rate of dissolution of calcium and the mineral of human dental roots, because fluoride is absorbed to the hydroxyapatite in human enamels [3–5]. The reduction in dissolution is also related to both the acid concentration and the pH of the buffer solution to form artificial "white-spot" caries lesions [5, 6]. By using enamel treated with $SnF_2$, SnCl and NaF, the dissolution of human tooth enamel is inhibited for both sound enamel and enamel with incipient caries-like lesions [7]. Topical fluoride applications were performed widely for the prevention of dental caries, and it is considered that the effectiveness may depend on the ability of the applications to deposit fluoride on the surface enamel [8]. However, application was not attempted using alkyl cyanoacrylates, because previous studies had been carried out for enamel treated with the above solutions without using an alkyl-α-cyanoacrylate.

The purpose of this study was to clarify the difference of the solubility of calcium and fluoride among bovine tooth enamels coated with methyl-α-cyanoacrylates containing different fluoride compounds, and to examine the "white-spot" demineralization lesions on the abrased enamel surface of bovine tooth by a polarized-light microscope.

## 2. Materials and methods

According to previous studies [10, 11] a methyl-α-cyanoacrylate adhesive was selected (Taoka Chemical Co., Osaka, Japan), which contained 10 wt % of fluoride compounds such as $BiF_3$, KF, $Na_2FPO_4$, NaF, $SnF_2$ and $ZnF_2$. The surface of 3-year-old bovine tooth enamel was coated manually with each methyl-α-cyanoacrylate. The experiments were carried out as indicated in Table I. The immersion conditions (for 1 week and 1 month at 37° C in distilled water) were similar to those in [11]. In bovine tooth surface coated with the cyanoacrylate the measurement of calcium and fluoride in distilled water (20 ml) was made for three pieces of bovine teeth for each experiment according to the procedure in [11]; that is, the mean values were calculated by a calibration method. The calibration curves for calcium and fluoride are therefore not given here. Their curves are shown in [11] for a solution of pH 6. A control specimen was coated with a methyl-α-cyanoacrylate adhesive without a fluoride compound. After immersion in distilled water, the brushing abrasion test was done $10^5$ times in distilled water as follows: brushing abrasion test

TABLE I Procedures for caries test. Before the caries test the bovine tooth was immersed in distilled water for 1 week and 1 month at 37° C, and the brushing abrasive test was done $10^5$ times for all specimens

| |
|---|
| Immersion (distilled water; 20 ml) |
| (1 week and 1 month at 37° C) |
| ↓ |
| Brushing test |
| ($10^5$ times) |
| ↓ |
| Caries (pH 5.5) |
| ("white-spots" caries, 20 ml |
| for 1 week at 37° C) |



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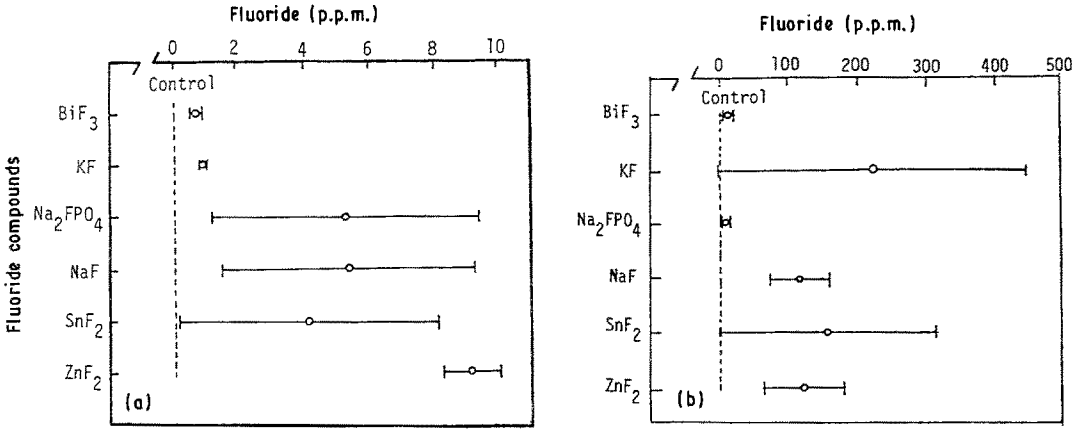


*Figure 1* Amount of fluoride solubility contained in distilled water (1 ml) for specimens coated with cyanoacrylates: six kinds of fluoride compounds; $BiF_3$, KF, $Na_2FPO_4$, NaF, $SnF_2$ and $ZnF_2$ (control; bovine enamel coated with methyl-α-cyanoacrylate without a fluoride compound). (a) After 1 week and (b) after 1 month of immersion in distilled water.

machine (Fukuda Co., Osaka, Japan) and brushing (Perio H; Sunstar, Kyoto, Japan). The brushing speed was 60 times per minute, and the surface of bovine tooth enamel was placed in a water bath in the brushing machine to keep the surface covered with distilled water. The caries test to obtain artificial "white-spot" was done in buffered acetic acid of pH 5.5, which was tried initially by one of the authors in the present study [12]. (The ratio of 0.1 M acetic acid to 0.1 M sodium acetate was 1/5, and "white-spot" treatment was done for 1 week at 37° C by using the solution. Before the treatment the coated film with the cyanoacrylate was removed manually.)

After the procedure indicated in Table I, polarizing microscopy was carried out for a very thin foil, the specimen being cut to 100 μm thickness from the bovine tooth enamel immersed in the buffered acetic acid (low-speed cutting machine; Beuhler Co., Chicago, USA). The foil, which was polished carefully by an abrasive paper # 1200, was examined to determine whether the demineralization area due to the formation of artificial "white-spot" occurred inside bovine tooth enamel.

## 3. Results

The fluoride concentration in distilled water (1 ml) after 1 week and 1 month of immersion was determined for each methyl-α-cyanoacrylate containing six different types of fluoride compounds in Figs 1a and b, along with the average value and standard deviation. Both figures demonstrated a significantly large difference in fluoride concentration, and the value became large for specimens coated with cyanoacrylates containing KF, $Na_2FPO_4$, NaF, $SnF_2$ and $ZnF_2$ compared with the control specimen without fluoride compound. Individual value variations were observed with a large standard deviation when a large amount of fluoride was released.

The calcium and fluoride contents for the control specimen and the specimens with cyanoacrylates having six kinds of fluoride compounds are shown in Figs 2 and 3. In this case the "white-spot" treatment was done after a $10^5$ times brushing test. For the bovine tooth enamels brushed after 1 week of immersion (distilled water), the release of calcium in the buffered solution was inhibited, except for the cyanoacrylate containing a KF fluoride compound,

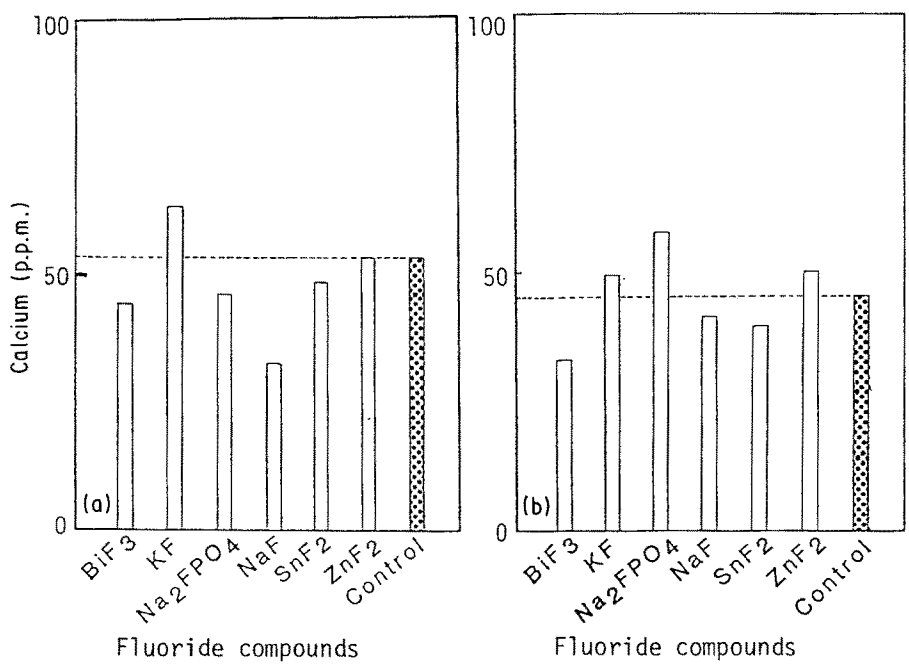


*Figure 2* Calcium solubility. (a) After 1 week and (b) after 1 month of immersion.

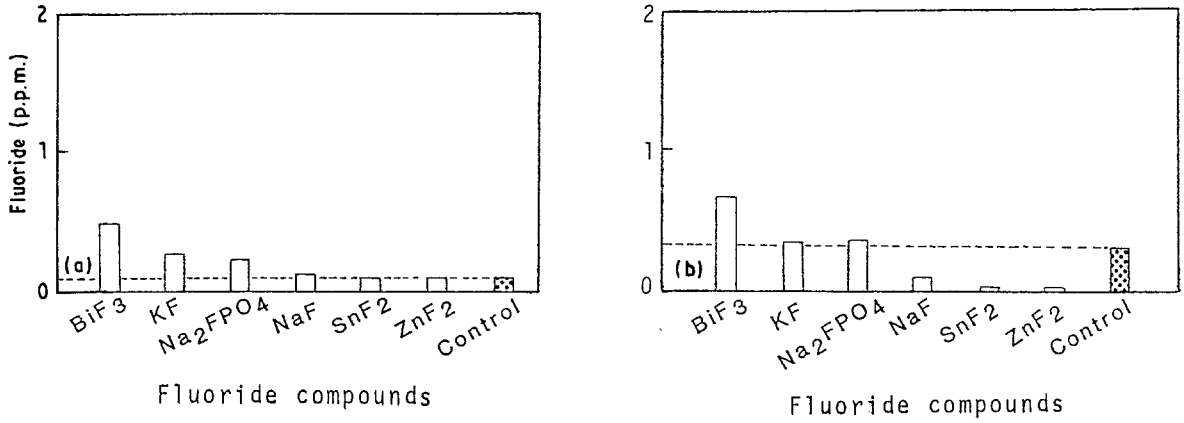


*Figure 3* Fluoride content when immersed in a buffered solution after immersion for both immersion times. (a) 1 week and (b) 1 month in distilled water.

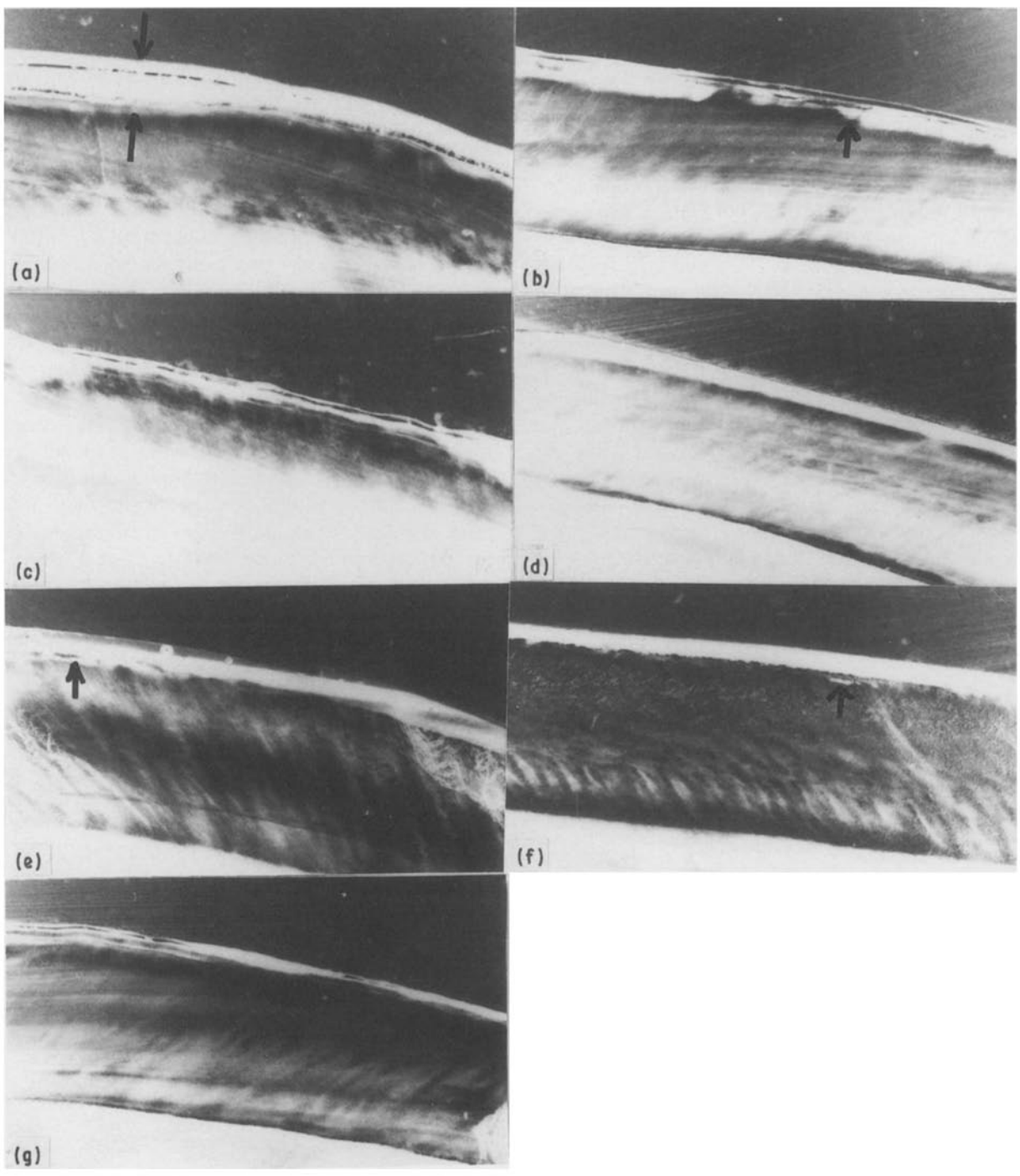


*Figure 4* Micrographs of "white-spot" demineralization lesions in bovine enamels after immersion in the buffered solution (as a pretreatment, the immersion time in distilled water was 1 month). Magnification × 100. (a) Control, (b) $BiF_3$, (c) KF (d) $Na_2FPO_4$, (e) NaF, (f) $SnF_2$ and (g) $ZnF_2$.

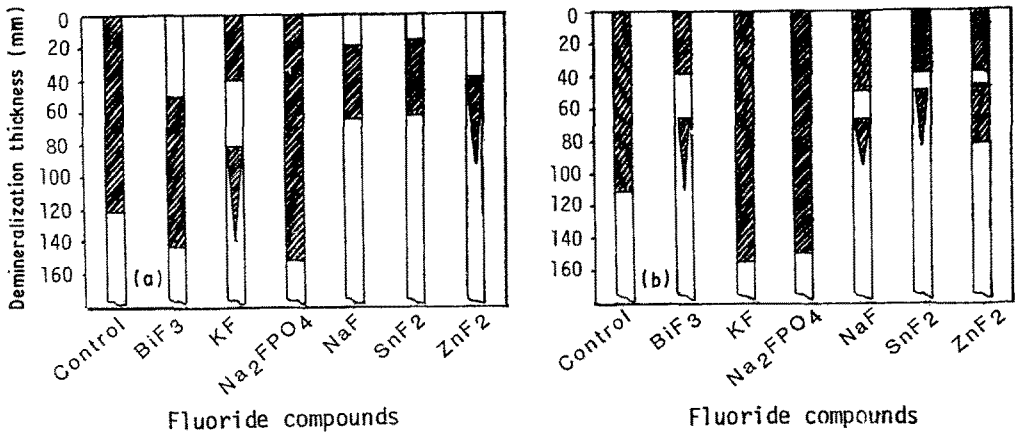


*Figure 5* The average width of "white-spot" demineralization lesions after immersing the coated specimens in the buffered solution, which were pretreated for (a) 1 week and (b) 1 month in distilled water.

compared with control bovine tooth enamel coated with the cyanoacrylate having no fluoride compound. However, three types of fluoride compounds ($BiF_3$, NaF and $SnF_2$) inhibited the dissolution of calcium. At the same measurement the fluoride content in Figs 2a and b was very low compared with each control specimen after the treatment at 1 week and 1 month of immersion.

Micrographs of artificial lesions are shown in Figs 4a to g. Fig. 4a shows a thick demineralization area for a control bovine enamel; Fig. 4b a band-like demineralization area at the outermost enamel surface and a partially demineralized image for a $BiF_3$-containing methyl-α-cyanoacrylate; Fig. 4c the partially demineralized outermost enamel surface for a KF-containing one; Fig. 4d, the demineralization over the enamel surface for a $Na_2FPO_4$-containing one; Figs 4e, f and g show the thin demineralized area for NaF-, $SnF_2$- and $ZnF_2$-containing ones. Thus, the average thickness of the demineralization area due to calcium release is shown in Figs 5a (1 week of immersion in distilled water) and b (1 month) for three pieces of thin foil obtained from the coated specimen. The average depth of the demineralized area was large (about 100 μm) for a control specimen, and also KF- and $Na_2FPO_4$-containing cyanoacrylate adhesives. The value was small (about 40 μm) for the specimens coated with $SnF_2$- and $ZnF_2$-containing cyanoacrylates (Fig. 5b).

## 4. Discussion

Fluoride decreased bovine tooth enamel solubility [2], and had little inhibitory effect above a pH of 5 [2, 9]. The effect of fluoride compounds on *in vitro* demineralization was different among them as shown in Figs 2 and 3, depending on the immersion time in distilled water before treatment with a buffered solution. In using each cyanoacrylate containing $BiF_3$, NaF and $SnF_2$ as a fluoride compound, the amount of decalcification was reduced even though the pretreatment in distilled water before a white-spot caries experiment was carried out for 1 month at 37° C (Table I). On the contrary, the fluoride content was low for all cyanoacrylates investigated, at below 1 p.p.m. (Figs 3a and b). These comparisons with the calcium and fluoride contents in six kinds of cyanoacrylates with different fluoride compounds (Figs 2 and 3) suggest that there was a difference among the micrographs from polarized-light microscopy (Figs 4a to g). These artificial carious lesions, such as "white-spot", were produced by exposing bovine tooth enamel to a buffer solution of pH 5, because they formed in the solution of pH range 4.0 to 5.5 for bovine tooth enamel [13–15].

For the control specimen, a lesion of demineralization with large width was observed (Fig. 4a), and the micrograph shows that there was a different formation of demineralization than with the others. The demineralized portion at the outermost surface was observed for the cyanoacrylate including KF as a fluoride compound, and the sound tooth enamel existed partially (Fig. 4c). From this observation the dissolution of calcium may be irregular for this cyanoacrylate (Fig. 5a). In Fig. 4d ($Na_2FPO_4$-containing cyanoacrylate), a demineralization area of thick width was found over the outermost bovine tooth enamel. On the contrary, a thin area of demineralization was found for NaF-, $SnF_2$- and $ZnF_2$-containing cyanoacrylates (Figs 4e, f and g). In this area of demineralization the relative resistance of the surface enamel to dissolution is considered to be large, because the width of the demineralization area corresponds to the decalcification area, which means the region attacked by the buffered solution. It is deduced that a periodic variation appears in the structure or composition of the bovine tooth enamel investigated. As a result the calcium content in a buffered "white-spot" solution was reduced, showing the thinness of the demineralization area in the enamel. For a $BiF_3$-containing cyanoacrylate a sound surface of bovine tooth enamel was formed partially, and thus the calcium content was small. Particularly for NaF-, $SnF_2$- and $ZnF_2$-containing cyanoacrylates, a thin area of demineralization was found pronouncedly compared with the others.

In conclusion, this study clarified the role of fluoride compounds contained in a methyl-α-cyanoacrylate applied to a fissure sealant in the dental field. It seems that the fluoride compounds NaF, $SnF_2$ and $ZnF_2$ which are partly solved in distilled water are useful in the reduction of the decalcification in bovine tooth, but there is no evidence from the present experiment that the fluoride compounds are available directly to

human teeth. It is rather suggested that the "white-spot" lesions produced by a buffered solution (pH 5.5) are controlled by the kinds of fluoride compounds in the alkyl methyl cyanoacrylate.

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