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# An X-ray crystallography of the root canal sealers.

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**Zinc oxide based (Canals) and calcium hydroxide based ( Sealapex) root canal sealers are common used in endodontic root canal filling. Many studies showed that the sealer have degradation and disolution in water. The purpose of this study was to evaluate and compare the surface structures of zinc oxide-eugenol sealer ( Canals) and calcium hydroxide based sealer (Sealapex) after mixing and immersing for a time interval. The crystal structures of sealer were analyzed by the X ray diffractometer. The results showed that within 16 weeks immersed in water, the main crystallized structure of the sealer were not changed. The author suggest that the body of the immersed sealers are stable. It will not affect the result of the endodontic treatment.**

**Key words: X ray diffraction, Root canal sealers, Endodontic treatment.**

## Introduction

The root canal sealers play an important role in sealing the root canal system. Grossman has enumerated the requirements for the ideal root canal filling materials. The filling materials should include ease of introduction, adaquate sealing both laterally and apically, impermeability to mositure, lack of shrinkage, radiopacity and bacteriostasis[1]. Kazemi et al report that a significant dimensional change and contiuned volume loss can occur in some endodontic sealers[2].

Various kinds of root canal filling material for hermetical obturation of root canal have been used in routine endodontic procedure. Several studies have been undertaken to examine its biological properties as well as to compare it with other well established sealers in terms of sealing ability[3,4]. Most routinely used root canal sealers contain zinc oxide eugenol and various additives. Sealapex is a calcium hydroxide type sealer, in use since the early 1980's. Calcium hydroxide was first introduced as a pulp capping agent and

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today occupies a prominent position as a versatile medicament for use in endodontics.

Many studies examining toxicity, solubilitiy and other physical properties(3,4,5). Sleder et al studied long term sealing ability of a calcium hydroxide sealer found that Sealapex (calcium hydroxide sealer) has a sealing ability comparable to Tuble-Seal (Zinc oxide-eugenol sealer) and can withstand long-term exposure to tissue fluid without significant leakage(6). Wu et al. study showed that after 1 year follow-up study on the leakage of four root canal sealers at different thickness, the Sealapex was more leakage than other sealers after storing in water(7).

Endodontic sealers more or less have degree solubility in water, degradation in water. Maseki et al found eugenol can release from a zinc oxide-eugenol sealer(Canals)(8). Barnett and Flax demonstrated that indeed there is a loss of Sealapex over time(9). Caicedo and von Fraunhofer found Sealapex showed a significant volumetric expansion during setting(4). It is interesting to investigate what will be happened on the sealer surface structure when the sealer are degradated in solution.

X-ray diffraction is a valuable tool for the determination of the crystallographic structure of materials. Comparison XRD data to the known standards, such as the JCPDS files, is used to identify phases and study phase changes. Miller indices, hkl integers, are assigned to XRD peaks. Miller indices describe the orientation of planes of atoms to the unite cell of a material's crystal structure(10). The shape and location of peaks can provide other useful information(11). X-ray diffraction has the potential to differentiate between the various crystallographic forms of nitinol. X-ray diffraction may not easily distinguish between two closely related structures(10,11).

The purpose of this study was to evaluate and compare the surface crystallized structures of zinc oxide-eugenol sealer (Canals) and calcium hydroxide based sealer (Sealapex) by XRD analysis after mixing and immersing for a time interval.

# Material and method

## Sample preparation

The sealer used in this study were Canals (Showa Co., Tokyo, Japan) and Sealapex (Kerr Co., Michigan, USA). The components of the material are shown in Table 1. and were mixed according to the manufacturer's directions. Aluminum-made sample holder were filled with the materials to be evaluated. Each materials were filled to three sample holders. After setting, the holder were placed in 12 cm diameter petridishes filled with deionized water. They were incubated to set in 100% humidity at 37°C. At the time intervals of 1 week, 2 weeks, 4 weeks, 8 weeks and 16 weeks the test sealers were measured by

Table 1. The approximate composition of mixed sealer.

| | | |
|---|---|---|
| Canals (Showa Co., Tokyo, Japan) | | |
| Powder | Zinc oxide | 40.00% |
| | Rosin | 30.00% |
| | Barium sulfate | 15.00% |
| | Bismuth subcarbonate | 15.00% |
| Fluid | Clove oil | 83.00% |
| | Others | 17.00% |
| Sealapes (Kerr Co. Michigan, USA) | | |
| | Calcium oxide | 24.00% |
| | Barium sulfate | 20.00% |
| | Zinc oxide | 6.00% |
| | Sub-Micron silica | 4.00% |
| | Titanium dioxide | 2.00% |
| | Zinc sterate | 1.00% |
| | Blend | 42.00% |

X ray diffractometer (Shimadzu, XD-D1, Japan, Tokyo). Before testing on X ray diffractometer the sample were dried in the air. The control group was set on room temperature.

### X ray diffraction (XRD)

According to manufacturer's instructions, X ray diffraction analyses were performed on an automated diffractometer, with scan range from 20 degree to 120 degree ($2\varphi$). The analytical methods were following the Margelos et al. method[12].

In this study, the operative condition were as follows: the X ray target is copper with 30Kv voltage and 30 mA current. The slit is 1 degree divergence slit. The scatter slit is 1 degree and receiving slit is 1 degree. The scanning with drive axis is from 1 theta to 2 theta with scanning range started at 20 and ended at 120 degrees. The scan speed is 8 degree per minute. After finishing scan, the XRD data were analyzed and identified by comparing diffraction peaks with d-spacings listed in the JCPDS files (table 2).

Table 2. The condition of the presching and matching condition on x-ray diffractometer.

| Presearch condition | |
|---|---|
| matching line | 3 [3/4] |
| B.G. intensity | 5 |
| file name | Ingoranic |
| Search range | 20-120 deg |
| **Matching condition** | |
| Matching logic | d only |
| Error window | 0.5 degree |
| Min. hit value | 0.1 |
| Line at hit value | 0.1 |

# Result

### The X ray diffraction pattern (XRDP) of Canals

Figure 1 shows the X ray diffraction patterns of Canals. The figure contains the peaks of XRDP measuring on different time interval. The peak intensity of each measurements were similar except the 16th weeks pattern.

Comparing the experimental group and control group, the main structure of the Canals sealer was the zine oxide crystallization. (Figure 2) The other crystals found in the result as comparing by JCPCD files of the computer were zinc dioxide ($ZnO_2$), tetrahyydro 6-hydroxynaphthalene ($C_{10}H_{12}O$), 4 Methoxyphenol ($C_7H_8O_2$), Barium carbonate ($BaCo_4$) and Bismuth (Bi) et al.

### The X ray diffraction pattern (XRDP) of Sealapex

Figure 3 shows the X ray diffraction pattern of Sealapex. The figure contains the peaks of XRDP on different time interval. The peak intensity of each measurements were similar except the 16th weeks pattern.

The main crystal of the Sealapex sealer was the calcium oxide (CaO). From the begining to the 8th weeks the main peak of XRDP is the calcium oxide component. In 16th weeks, there was appeared a high peak at 30 degree scanning region of XRDP. The matched component was calcium carbonate ($CaCO_3$). (figure 4) The other crystasls in Sealapex sealer as comparing by JCPCD files were Barium carbonate ($BaCO_3$), Titanium oxide ($Ti_3O_5$), Calcium lead oxide ($CaPbO_3$) and Zinc oxide (ZnO) et al.

# Discussion

The root canal sealers is soluable when it is

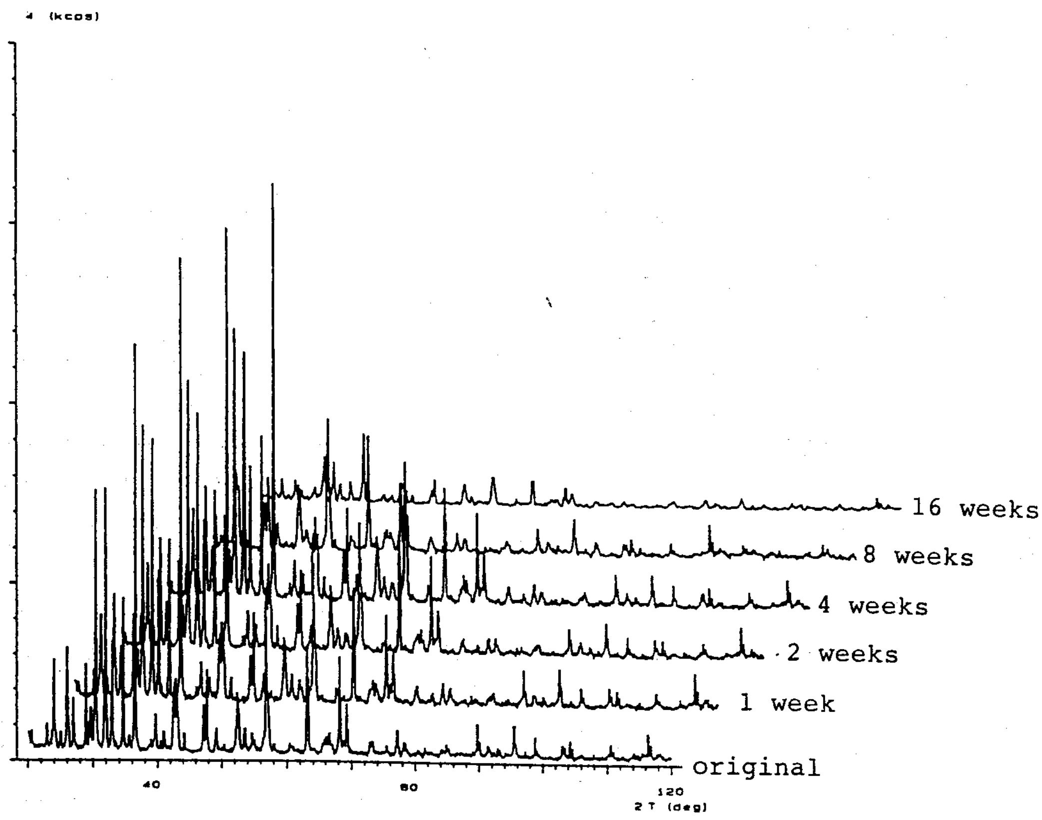


Figure 1. The XRD figure of canals sealer.

immersed in the water. The sealer placed in the deionized water for a different time interval, showed the main crystal structures of the sealer were no changed. The zinc oxide is the main structure of the Canals sealer. The calcium oxide is the main structure of the Sealapex within the 8 weeks immersion. The 16 weeks immersing result of the Sealapex shown existed the calcium carbonate crystal. It may be caused by the dioxide carbon ($CO_2$) dissolved into the deionized water. The carbonate ion combined with the calcium to form the calcium carbonate. From this point of the view, as comparing the Canals and Sealapex sealers, in vitro, the Canals surface structure is not easily dissolved dioxide carbon than the Sealapex surface structure. On the contrary, from Sleder et al study found that Sealapex statistically had no greater dissolution (based on the linear penetration) than zinc oxide eugenol sealer at both 2 and 32 weeks[(6)]. These two sealers basically are good for endodontic treatment.

Numerous studies discussed the toxicity of the sealers[(13-17)]. The toxicity may come from the sealer or from its released, such as eugenol released from the zinc oxide-eugenol sealer and formaldehyde released from the AH 26 sealer. Zinc oxide eugenol is a common used sealer.

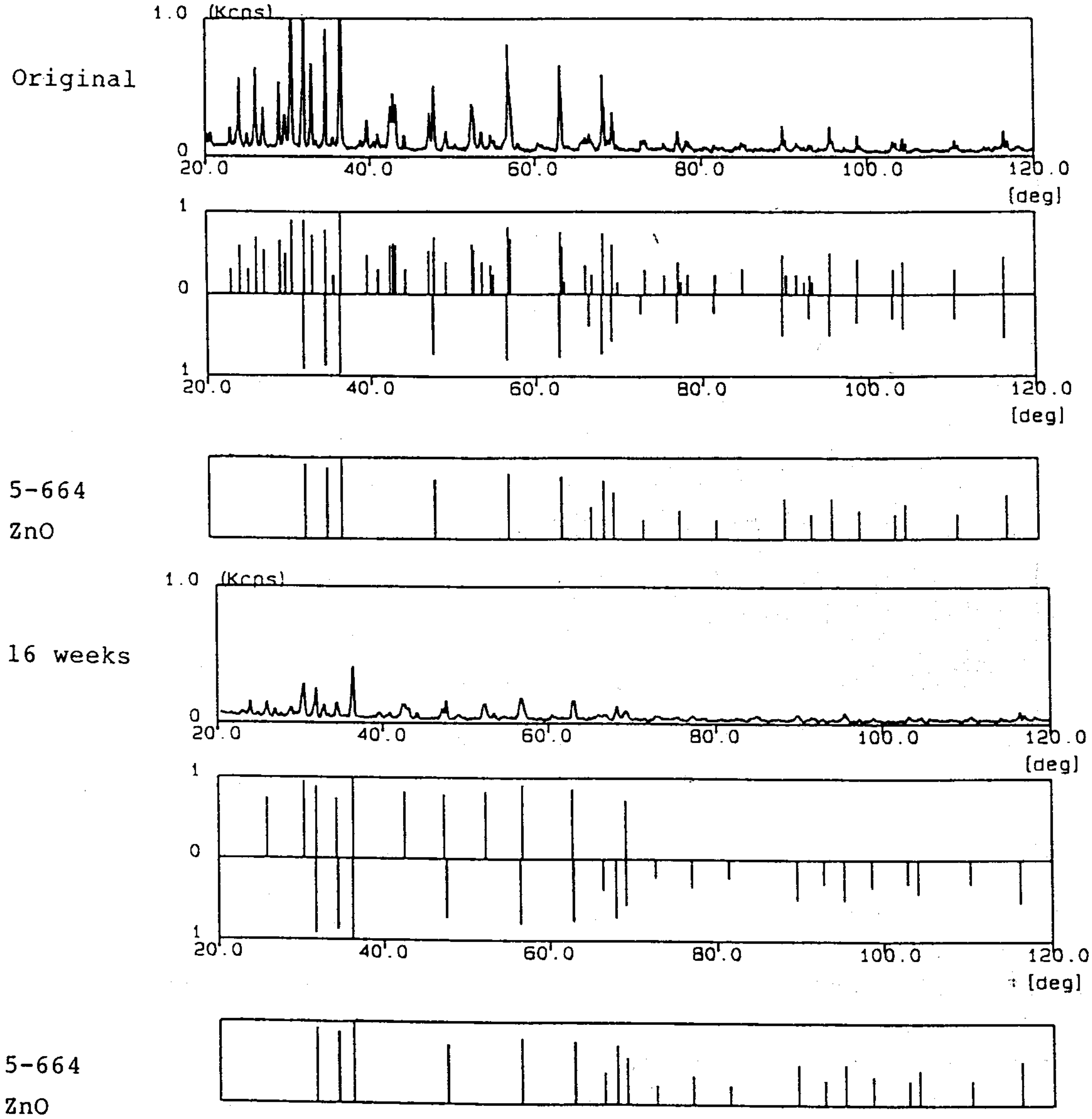


Figure 2. The matched XRD figure of Canals cement.

Free eugenol (2-methoxy-4-4 propenol phenol) is embaded within the zinc eugenolate matrix. The amount of the free eugenol released from zinc oxide-eugenol sealer is probably low. Meryon et al. reported that eugenol may be released from eugenolate when it comes into contact with free

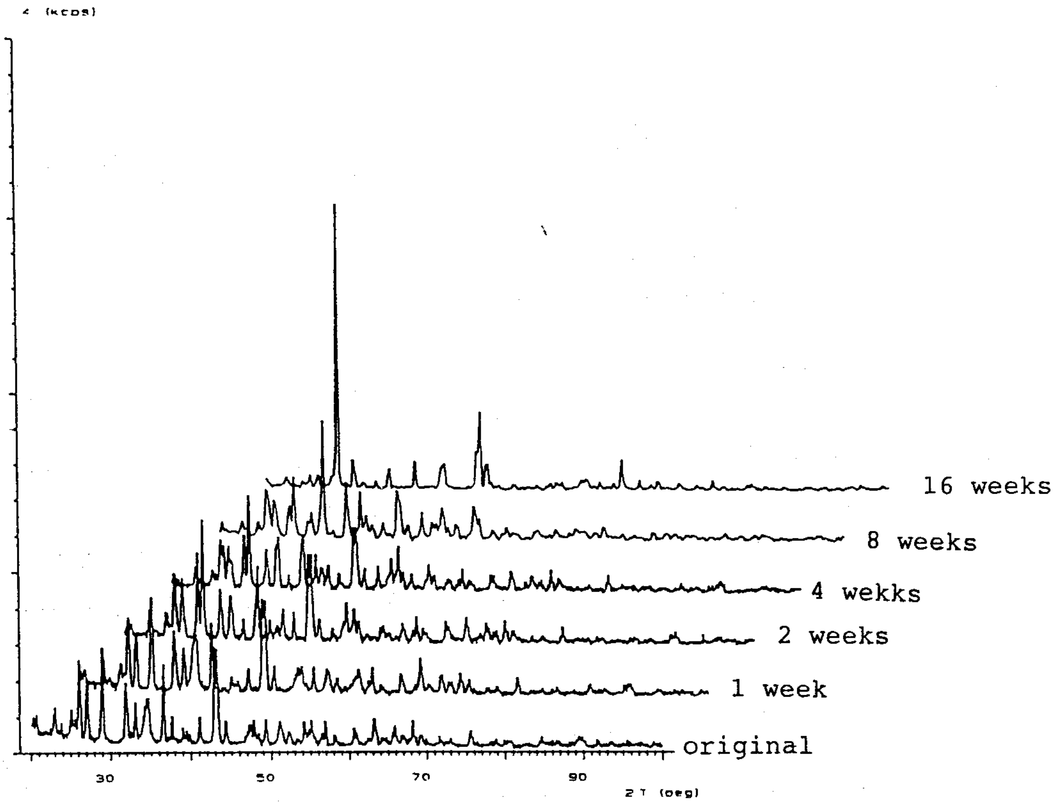


Figure 3. The XRD figure of Sealapex sealer.

water[17]. In our study there is no eugenol crystal detected in the XRD peak. There is a similar structure 4-methoxyphenol crystal that matched the Canals XRD pattern in JCPCD files. Margelos et al. found the purity of the sealer were not constant. The levels of the lead (Pb) were found significantly elevated compared to the control. Their findings indicate the need for the establishment of quality control and the development of strict specifications for the manufacturing of root canal sealers[12]. From the XRD patterns showed that there is no lead crystal on the sealer surface. It is suggested that the quality of the sealer are pure.

Fujisawa and Masuhara reported that zinc ions are released from zinc oxide-eugenol cement[18]. The zinc crystal structure is not found on the XRDP of the Canals. As above results showed that the surface crystal structures of Canals were zinc dioxide ($ZnO_2$), tetrahydro 6-hydroxynaphthalene ($C_{10}H_{12}O$), 4 Methoxyphenol ($C_7H_8O_2$), Barium carbonate ($BaCo_4$) and Bismuth (Bi). It is different from the soluable portion described by Fujisawa et al., and Maseki et al.

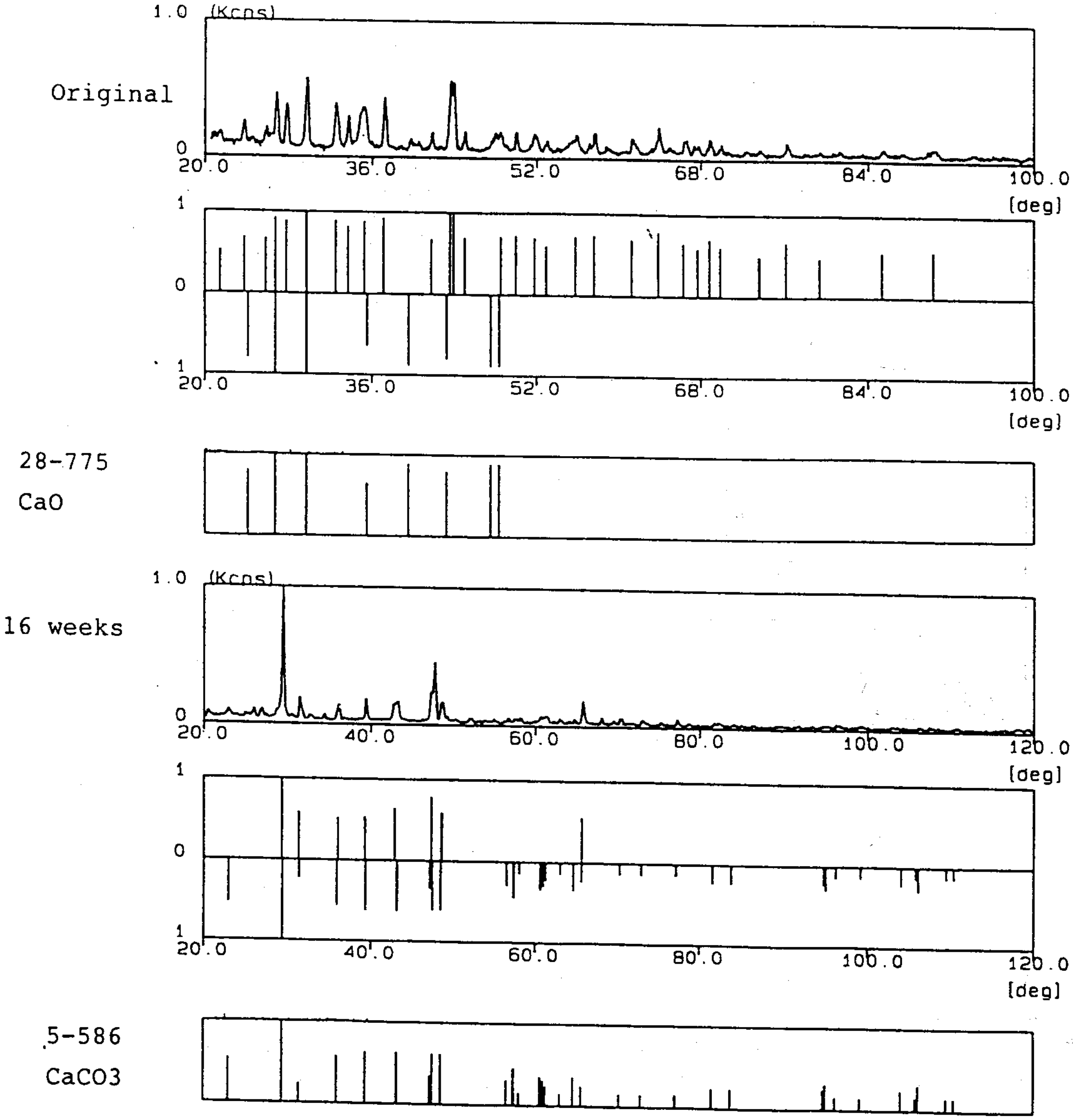


Figure 4. The matched XRD figure of Sealapex cement.

studies. The Maseki et al. have been studied on the correlation between the amount of eugenol released from zinc oxide-eugenol sealer by gas chromatograph analysis. They found that the components released from the cement were eugenol, methyl salicylic acid, benzyl alchol and others[8]. The crystal structures of the Canals, which matched by JCPCD files, were not shown as the compnents of Maseki et al. described. The discrepancy between present and above studies may be caused by the different method. The present study is focused on the setting portion of the sealer, not on the soluable portion. We found that the main crystal component of the sealer will not be changed in water. Basiclly we suggested these two sealers are stable in its character.

Sealer will degradation when it contacted with water[19]. Degradation appears to be a process following a sequence of absorption, disintegration and solution. Factors, such as cement, thickness of the cement layer, molarity, and pH of the medium, affect mostly by interaction, the degradation speed. The present study shown the main crystal component of the sealer, after degradation in deionized water, were no change. The study proved that the degradation of sealer, Canals and Sealapex, are stable within 16 weeks. Further studies should involve increasing immersed time, testing the immersed water by gas chromatograph analysis and then comparing the composition of the sealer. It is hoped that studies can be provided the structure informations of the sealer and give a full detail of the sealer which causing the cytotoxicity.

# Conclusion

From the X-ray diffraction analysis of zinc oxide-eugenol based and calcium hydroxide based sealers, the main crystal structure component of the sealers surface, such as Zinc oxide in Canals and Calcium oxide in Sealapex, are stable. It is beneficial to the endodontic treatment clinically.

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# 根管充填劑之表面結晶研究

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氧化鋅爲基底的根管充填劑與氫氧化鈣爲基底的根管充填劑乃是臨床上根管治療常用的材料。許多研究報告指出根管充填劑具有溶解性與解離性，較少有報告顯示充填劑溶解或解離後材料本身的變化。本研究的目的爲探討氧化鋅爲基底的根管充填劑與氫氧化鈣爲基底的根管充填劑經混合後於去離子水中浸泡一段時間之表面結晶結構變化。經由X光繞射分析比較不同之充填劑表面結晶結構，結果顯示經十六週之浸泡充填劑本身之結晶結構並無改變。我們認爲以氧化鋅爲基底的根管充填劑與氫氧化鈣爲基底的根管充填劑經混合後本質穩定，乃是臨床上根管治療之優良材料。

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