Color Stability of White Mineral Trioxide Aggregate in Contact with Hypochlorite Solution

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Abstract

Introduction: One of the uses of white mineral trioxide aggregate (MTA) is as an apical barrier in immature teeth. Although this treatment has been reported to have high success rates, a number of cases of discoloration have been noted. The aim of this research was to investigate the color stability of white MTA in contact with various solutions used in endodontics. Methods: The change in color of white MTA after immersion in water, sodium hypochlorite, or hydrogen peroxide was assessed by viewing the color change on digital photographs and also by using a spectrophotometer. White MTA, white Portland cement, and bismuth oxide were assessed. The changes in the material after immersion in the different solutions were assessed by X-ray diffraction analysis and Fourier transform infrared spectroscopy. Results: Immersion of white MTA and bismuth oxide in sodium hypochlorite resulted in the formation of a dark brown discoloration. This change was not observed in Portland cement. X-ray diffraction analysis and Fourier transform infrared analysis displayed the reduction of sodium hypochlorite in contact with bismuth oxide and MTA to sodium chloride. Conclusions: Contact of white MTA and other bismuth-containing materials with sodium hypochlorite solution should be avoided. (J Endod 2014;40:436–440)

Key Words

Bismuth oxide, characterization, color stability, dental material, radiopacifier, root-end filling materials

Mineral trioxide aggregate (MTA) is composed of a mixture of Portland cement and bismuth oxide (1). MTA was introduced for use as a root-end filling material and for repair of root perforations. However, it is currently used for a variety of applications including pulp capping, apexification procedures, as a dressing over pulpoto- mies, and many other endodontic procedures (2). Initially only gray MTA was available; however, because of potential discoloration effect of gray MTA, white MTA has been introduced into endodontic treatment for the same purposes. No difference was observed in the outcome of treatment (3) and biocompatibility (4) of the different variants of MTA. White MTA (MTA Branco; Angelus, Londrina, Brazil) has been used to seal root perforations where the gray version (MTA Angelus) had been reported to cause discoloration of the marginal gingiva (5).

Tooth discoloration has been reported with the use of both gray and white MTA (MTA Angelus). In fact, both types of MTA induced significant decreases in L*, a*, and b* values (Commission Internationale de l’Eclairage), with the color change being greater with gray MTA. Gray MTA led to clinically perceptible crown discoloration after 1 month, whereas the total color change caused by white MTA exceeded the perceptible threshold for the human eye after 3 months. This suggests that the application of gray MTA in the aesthetic zone should be avoided, whereas white MTA should be used with caution when filling pulp chambers with the materials (6). Crown discoloration has been reported when MTA was used as a dressing for molar pulpoto- mies instead of calcium hydroxide (7), as an apical barrier after initial calcium hydroxide therapy (MTA Angelus) (8), for apexification procedures of replanted teeth (ProRoot MTA) (9), for treatment of fractured teeth (10), for treatment of root resorption (MTA Angelus) (11), and for revascularization of immature necrotic permanent teeth (12).

Attempts at removal of MTA from the root canal revealed a change in color of the MTA (13). After the removal of MTA from the tooth where it was placed as a dressing, a significant color change was observed in the tooth crown, which was further improved with internal bleaching (14). Application of dentin bonding agent before placement of MTA may prevent tooth discoloration (15).

The recommendations by clinicians to date have been to use MTA cautiously in the aesthetic zone. The aim of this research was to investigate the color stability of white MTA in contact with various solutions used in endodontics.

Materials and Methods

Materials used in this study included Portland cement (PC) (CEM 1, 52.5 N; Lafarge Cement, Birmingham, UK), ProRoot MTA (Dentsply Tulsa Dental, Johnson City, TN; lot number 09001920), and bismuth oxide (Sigma Aldrich, St Louis, MO). The cements were mixed at a liquid-to-powder ratio of 0.30.

The cements were cured for 24 hours at 37°C and 100% humidity, after which the cements and bismuth oxide powder were immersed in different solutions for 24 hours:

1. Water
2. Sodium hypochlorite solution (Milton; Laboratoire Rivadis, Louzy, France)
3. Hydrogen peroxide (Bells Sons & Co Ltd, Southport, UK)

The cements and bismuth oxide powder were then dried and tested.

Assessment of Color Stability

Cylindrical specimens 10 mm in diameter and 2 mm high were prepared for MTA and Portland cement by curing in the molds for 24 hours at 100% humidity and 37°C.

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The color of the specimens was assessed by using a spectrophotometer (Minolta CM-50Bi; Minolta Co Ltd, Osaka, Japan). The Commission Internationale de l’Éclairage system was used to calculate the difference in color. The value of the luminance (L) and the coordinates of the chromatic component (a and b) were measured before and after immersion in different solutions. Color photographs of the specimens

**Figure 1.** Photographs of bismuth oxide powder, ProRoot MTA, and Portland cement before and after immersion in the different solutions.

**Figure 2.** Color change recorded by spectrophotometer for the different test materials after immersion in different solutions.
Assessment of Color Stability

Statistical Analysis

Characterization of Materials

were also captured by using a digital camera. The color difference of the specimens before and after immersion in the different solutions (\(\Delta E\)) was calculated by using the following formula:

\[
\Delta E = \sqrt{\left(\frac{L}{L_0}\right)^2 + \left(\frac{a}{a_0}\right)^2 + \left(\frac{b}{b_0}\right)^2}
\]

**Characterization of Materials**

After immersion in the different solutions and drying of specimens, the cements were crushed by using a mortar and pestle, and the resultant powders were assessed by using x-ray diffraction (XRD) analysis and also by Fourier transform infrared (FT-IR) spectroscopy.

Phase analysis was carried out by using XRD. The diffractometer (Bruker D8 Advance; Bruker Corp, Billerica, MA) used Cu K\(\alpha\) radiation at 40 mA and 45 kV. The cement pastes were crushed by using a mortar and pestle before testing. Samples were presented in powder form, and the detector was rotated between 16\(^\circ\) and 44\(^\circ\). A step of 0.02\(^\circ\) 2\(\theta\) and a step time of 1 second were used. The sample holder was spun at 15 rpm. Phase identification was accomplished by use of search-match software that used ICDD database (International Center for Diffraction Data, Newtown Square, PA).

Infrared spectra of the ground powders were obtained by mixing with KBr (2 mg powder/300 mg KBr) and analyzed with an FT-IR spectrometer (Shimadzu IRAffinity-1; Shimadzu Corp, Kyoto, Japan).

**Statistical Analysis**

The data were evaluated by using SPSS software (PASW Statistics 18; SPSS Inc, Chicago, IL). Parametric tests were performed as K-S tests on the results indicated that the data were normally distributed. Analysis of variance with \(P = .05\) and Tukey post hoc test were used to perform multiple comparison tests.

**Results**

### Assessment of Color Stability

The digital images of materials taken before and after immersion in the different solutions are shown in Figure 1. The values for the change in color of the bismuth oxide, MTA, and Portland cement samples before and after immersion in the different solutions are shown in Figure 2. The bismuth oxide retained its yellow color after being immersed in water and hydrogen peroxide, followed by drying. When placed in contact with sodium hypochlorite solution, the bismuth oxide turned black. A white precipitate was visible over the bismuth oxide after immersion in sodium hypochlorite (Fig. 3).

The MTA samples were darker than Portland cement. This was evident from the results of assessment of color change, where for each different solution tested, the MTA samples were darker than the corresponding Portland cement \((P < .001)\). Placement of MTA in solution resulted in a darker color \((P < .001)\). The Portland cement samples were unaffected \((P = 1)\). The bismuth oxide exhibited a change in color when immersed in both sodium hypochlorite and hydrogen peroxide solutions, whereas immersion in hydrogen peroxide led to a darker yellow immersion in sodium hypochlorite resultant in black discoloration of the bismuth oxide \((P = 1)\).

**Characterization of Materials**

The results of XRD analysis and FT-IR spectroscopy are shown in Figure 4. Bismuth oxide (ICDD: 41-1449) exhibited typical peaks at 26.926\(^\circ\), 27.37\(^\circ\), 27.991\(^\circ\), 33.04\(^\circ\), and 33.242\(^\circ\) 2\(\theta\), with the strongest peak at 27.37\(^\circ\) 2\(\theta\) in the XRD plots (Fig. 4A). These peaks were consistent regardless of the immersing solution. Immersion in sodium hypochlorite solution resulted in an additional peak at 31.694\(^\circ\) 2\(\theta\). This peak was matched with sodium chloride (ICDD: 77-2064). The only change noted in the FT-IR spectrum of bismuth oxide after immersion in sodium hypochlorite solution was an increase in peak intensity in the 3400 cm\(^{-1}\) region. In this region, symmetric and asymmetric stretching vibrations of O-H bonds are usually present (Fig. 4B).

MTA exhibited similar peaks to bismuth oxide. In addition, MTA also exhibited minor peaks for tricalcium silicate (ICDD: 86-0402) at 29.348\(^\circ\), 32.187\(^\circ\), 32.501\(^\circ\), and 34.346\(^\circ\) 2\(\theta\), together with a peak at 18.004\(^\circ\) 2\(\theta\), which was typical of Portlandite (calcium hydroxide, ICDD: 44-1481). The Portlandite peak was not present when MTA was immersed in sodium hypochlorite solution. An additional peak was also visible at 31.694\(^\circ\) 2\(\theta\). This peak was matched with sodium chloride (ICDD: 77-2064) (Fig. 4C). The Portland cement exhibited peaks for tricalcium silicate (ICDD: 86-0402) at 29.348\(^\circ\), 32.187\(^\circ\), 32.501\(^\circ\), and 34.346\(^\circ\) 2\(\theta\) and Portlandite (calcium hydroxide, ICDD: 44-1481) at 18.004\(^\circ\) 2\(\theta\). The peak intensity did not change after immersion in the various solutions. Only the peak intensity of Portlandite at 18.004\(^\circ\) 2\(\theta\) was reduced after immersion of Portland cement in sodium hypochlorite solution (Fig. 4C1). The FT-IR spectrographs of MTA and Portland cement did not change when the test materials were immersed in the different solutions (Fig. 4B2 and C2).

**Discussion**

A number of cases of crown discoloration have been reported when white MTA was used to fill the pulp chambers of immature teeth \((6–12)\). A change in color of MTA was reported in the depths of the material when MTA removal from the canal was attempted \((13)\).
In the current study, a spectrophotometer was used to measure the amount of light that was absorbed by the test materials. The instrument operates by passing a beam of light through a sample and measuring the intensity of light reaching a detector. Changes in the reflectance properties of the material imply changes in both the visually perceived color and the instrumentally measured color parameters, the lightness value ($L^*$), $a^*$, and $b^*$. The location of a color in the CIELAB color space is defined by using a 3-dimensional Cartesian coordinate system. $L^*$ indicates how light or dark a color is. The $a^*$ and $b^*$ values indicate the location on the green (−)–red (+) and blue (−)–yellow (+) axes, respectively.

Crown discoloration has been reported with the use of a number of endodontic materials, notably sealers with AH 26 and Kerr Pulp Canal Sealer, causing progressive discoloration during a period of 12 months (16). Most of the root canal sealers used for root canal obturation cause tooth discoloration, with Riebler’s paste being reported to cause the most severe discoloration (17). It has been suggested that if aesthetics are important, sealers such as AH 26 should be avoided, and an alternative material should be used (18). Materials used in endodontics may stain teeth; therefore, the choice of material should not rely solely on biological and functional criteria but also take aesthetic considerations into account. In the current study, Crown discoloration has been reported with the use of a number of endodontic materials, notably sealers with AH 26 and Kerr Pulp Canal Sealer, causing progressive discoloration during a period of 12 months (16). Most of the root canal sealers used for root canal obturation cause tooth discoloration, with Riebler’s paste being reported to cause the most severe discoloration (17). It has been suggested that if aesthetics are important, sealers such as AH 26 should be avoided, and an alternative material should be used (18). Materials used in endodontics may stain teeth; therefore, the choice of material should not rely solely on biological and functional criteria but also take aesthetic considerations into account. In the current study,
MTA and Portland cement did not exhibit the same changes when exposed to different solutions. This is in contrast to a previous study reporting no statistically significant difference between Portland cement and MTA that were placed in contact with bovine dentin for 12 months (19). Blood contamination was shown to exacerbate the change in color (19, 20). In both studies (19, 20) all the tooth specimens were washed with sodium hypochlorite solution before obturation with the different test materials.

The current study evaluated the effect that routine solutions used in endodontics have on white MTA. The hydrogen peroxide did not seem to affect the test materials. An investigation of the effect of bleaching agents on the microstructure of MTA exhibited deterioration in the MTA surface after exposure to hydrogen peroxide. The elemental distribution was affected, with a decrease in calcium and an increase in silicon shown (21). No discoloration of MTA was demonstrated in the current study; however, the effect on MTA microstructure of contact with solutions used routinely in endodontics should be investigated. The sodium hypochlorite solution that is used in every endodontic case being treated caused a change in color in both white MTA and bismuth oxide, which forms part of MTA. Contact of bismuth-containing substances with sodium hypochlorite led to a dark brown, nearly black discoloration. The sodium hypochlorite solution was reduced to sodium chloride. This was evident from the white precipitate formed on the bismuth oxide. XRD analysis of this precipitate showed definite peaks for sodium chloride. Thus, a reaction is occurring, with the sodium hypochlorite losing oxygen.

The bismuth oxide did not exhibit any evident chemical changes as observed in the FT-IR and XRD analysis. The change in color could indicate a change from oxide to bismuth metal, which is black in color. Bismuth gives similar peaks to bismuth oxide in XRD analysis. Other methods are thus suggested to verify the change from bismuth oxide to bismuth. If the oxide is converted to a metal, oxygen is lost to the environment. Thus in both reactions, oxygen gas is liberated in a confined space within the tooth. The clinical implications of this chemical reaction should be investigated. Another hypothesis put forward to explain the change in color would be the further oxidation of bismuth oxide that can cause destabilization of the oxide, with reaction of carbon dioxide in the air leading to the formation of bismuth carbonate. Bismuth carbonate is light sensitive (22). A recent investigation in the color stability of white MTA showed distinctive light sensitivity of the white MTA in oxygen-free environments (23). In addition, it was reported that the combination of light and anaerobic conditions (similar to those in clinical situations) results in differences in color of ProRoot WMTA, Angelus WMTA, and Portland cement with bismuth oxide during a period of 5 days. Only Biodentine and Portland cement demonstrated color stability (24). From the current study and the recent investigations on color stability of various tricalcium silicate cement–based materials, it is very clear that the bismuth oxide is being affected by light and oxygen, thus producing a black precipitate. Additional investigations on the exact mechanism leading to these changes are necessary.

Conclusions

Contact of white MTA and other bismuth-containing compounds with sodium hypochlorite should be avoided because this leads to reaction of the bismuth oxide and formation of dark brown precipitate, which can discolor the tooth.