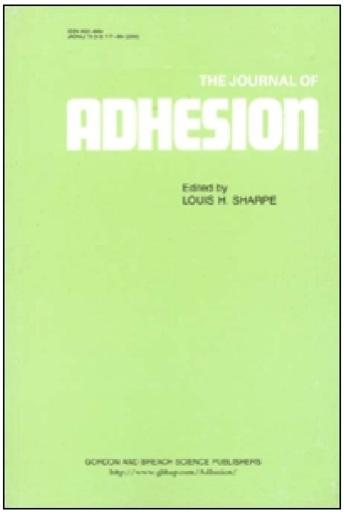

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Ferric Oxalate with Nitric Acid as a Conditioner in an Adhesive Bonding System

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Strong adhesive bonding of composite resins to dentin and enamel is obtained by conditioning the surface and applying adhesion-promoting compounds. This study examines tensile adhesive bond strengths and effects of the conditioners having various concentrations of ferric oxalate (FO) and nitric acid.

In the first part of this study, the average tensile bond strengths increased with concentrations of commercial FO as received up to about 6.8% and averaged no higher with higher concentrations. After this part of the testing had been completed, it was discovered that the FO as received contained a small amount of nitric acid. Use of solutions having from 6.8% to 20% ferric oxalate as received yielded bonds with strengths that averaged about 13 MPa psi) to dentin and 16 MPa (2,400 psi) to enamel.

In the second part of this study, the FO was stripped of the fortuitous nitric acid and, based on results from the first part of this study, solutions were made up to contain a fixed concentration of purified FO [6.8% $Fe_2(C_2O_4)_3$] and various known concentrations of nitric acid. The highest bond strengths to dentin and enamel were obtained with the purified FO solution which contained approximately 2.5% nitric acid.

KEY WORDS Adhesion; bonding agents; composite; dentin; enamel; ferric oxalate; resins.

INTRODUCTION

Unprecedented strong bonding of composite restorative materials to both dentin and enamel of human teeth has been achieved by preparing the hard tooth tissue surfaces with sequential applications of an aqueous solution of commercial ferric oxalate† (FO) (Iron III Oxalate, $Fe_2(C_2O_4)_3 \cdot 6H_2O$, Lot 040883, Alfa Products, Thiokol/Ventron Div., Danvers, MA 31116) as received; an acetone solution of a surface-active compound such as NPG (N-phenylglycine) or NTG-GMA [adduct of N(*p*-tolyl)glycine and glycidyl methacrylate]; and an acetone solution of a difunctional monomer, PMDM (adduct of hydroxyethyl methacrylate and pyromellitic dianhydride).[1,2,3,4] The concentrations of the FO in those studies had not been evaluated systematically over a wide range. The first part of the present work searches for the optimum concentration of the commercial ferric oxalate as received. The second part looks for the optimum concentration of nitric acid with purified ferric oxalate after it was discovered that the seemingly dry microcrystalline FO powder contained a small but beneficial amount of HNO_3 as received.

EXPERIMENTAL

As described previously,[1,2,5,6] recently-extracted, noncarious human molars that had been stored in distilled water at 5°C were used for testing adhesion. For dentin, the occlusal enamel of the tooth was removed by sectioning with a slowly rotating diamond blade (Isomet, Buehler, Ltd) under running water, and the circumferential enamel was removed with rotating abrasive instruments under running water. A hole was made between the roots of the teeth into the pulp chamber, and the soft pulp tissues were removed. For enamel, facets were prepared on tooth crowns to provide bonding areas with diameters of at least 3 mm. The specimens were held in a self-curing methacrylate (Formatray, Sybron Corp.) in the cupped ends of adhesion-testing cylinders.[5] Each test assembly consisted of a precision-fitting outer sleeve and two sliding cylinders. One cylinder held a tooth specimen in acrylic resin. The other cylinder had a plunger to which dental composite resin would be applied. An iris with an opening the size of the plunger determined the area of the adhesive bond to be tested. The tensile adhesion tests were conducted on flat tooth surfaces, finished with 320 grit abrasive, oriented so that the dentinal tubules or enamel rods were predominantly perpendicular to the test surfaces.

In the first aspect of this work, the various concentrations of FO were prepared with distilled water and "ferric oxalate hexahydrate" (including the small amount of HNO_3) as received from Alfa Products; all percentages were w/w, not counting the water of hydration as part of the solvent. The concentration of HNO_3 was proportional to the $Fe_2(C_2O_4)_3$ in the first aspect of this study because the solutions were all prepared from the same lot of material. The NTG-GMA (Esschem Co., Essington, PA) was recrystallized from acetone. The NPG was synthesized and recrystallized.[7] Acetone solutions containing 10% of either of

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† Certain commercial materials and equipment are identified in this paper to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or the ADA Health Foundation or that the material or equipment identified is necessarily the best available for the purpose.

these compounds were freshly prepared before each use. The PMDM (Esschem Co., Essington, PA) was recrystallized from methanol by the addition of water. Fresh 5% PMDM (w/w) acetone solutions were used in the bonding procedures.

The horizontal abraded dentin or enamel surface was covered with a drop of FO for one minute, rinsed with distilled water for 10 seconds and then blown dry. A drop of NTG-GMA or NPG solution was applied for 60 seconds, followed by a drop of acetone for 10 seconds to eliminate the unbound compound. The surface was blown with air for 10 seconds before the PMDM was applied for a minute. The surface was blown with air for 10 seconds to evaporate residual solvent. A composite (Adaptic™ Dental Restorative, Johnson & Johnson, East Windsor, NY 08520) mix was then pressed onto this treated surface with a 2.8 Kg weight for 5 seconds. The composite was allowed to polymerize 15 minutes before immersion in distilled water. Specimens were soaked in water at room temperature for 24 hours prior to testing. An equal number of tests were conducted with NPG and NTG-GMA.

To determine the effects of the HNO_3 content, the same FO powder (lot 040883) was washed four times with reagent grade acetone which removed detectable nitric acid. Solutions were then prepared with this FO at a constant 6.8 w/w % $Fe_2(C_2O_4)_3$ and with HNO_3 concentrations of 0, 0.068, 0.68, 1.85, 2.5, and 10 w/w %. These solutions were applied to dentin and enamel prior to application of NTG-GMA and PMDM.

RESULTS

The bond strengths for the various FO concentrations are shown in Figure 1. An analysis of variance showed that bond strengths for NTG-GMA compared with

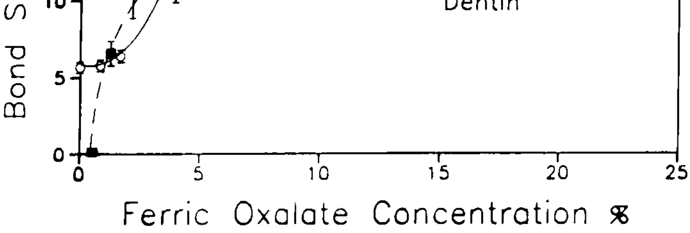

FIGURE 1 The effects of as-received ferric oxalate (FO) concentrations on adhesive bond strengths to dentin ($n = 24$) and enamel ($n = 9$). The apparent concentrations for the enamel data have been offset 0.25% to the right in the plots to improve visibility. Error bars are given as standard error of the mean.

NPG were statistically indistinguishable for each FO concentration and substrate (enamel or dentin). Therefore, their values were combined to simplify Figure 1.

The 0% FO conditioning treatment resulted in virtually no strength with enamel. With small increases in FO, the enamel strength increased sharply, reaching the same average value for dentin at about 0.85% FO; at 1.7%, the average ranked higher than with dentin. Overall, the bond strengths to enamel were only slightly higher than with dentin [$p < 0.05$].[8] This lowest average bond strength to dentin occurred at 0% FO. This may reflect the low cohesive strength of the mechanically-induced smeared surface of dentin.[6] These values are comparable with those of some contemporary proprietary dentin bonding agents.[4] The bond strengths to dentin were consistently low below 3.4% FO. An increase at 3.4% ($p < 0.01$) was observed.

The highest-ranking strengths to either dentin or enamel were obtained in the 6.8 to 20% range of FO concentrations. For either dentin or enamel, the bond strengths within the 6.8 to 20% range were not significantly different when the NTG-GMA and NPG data were combined or analyzed separately (Duncan's multiple comparison test, $p < 0.01$). The optimum concentration of the commercial "ferric oxalate hexahydrate" as received was at least 6.8%.

In the second part of this study, in which the purified FO concentration (6.8%)

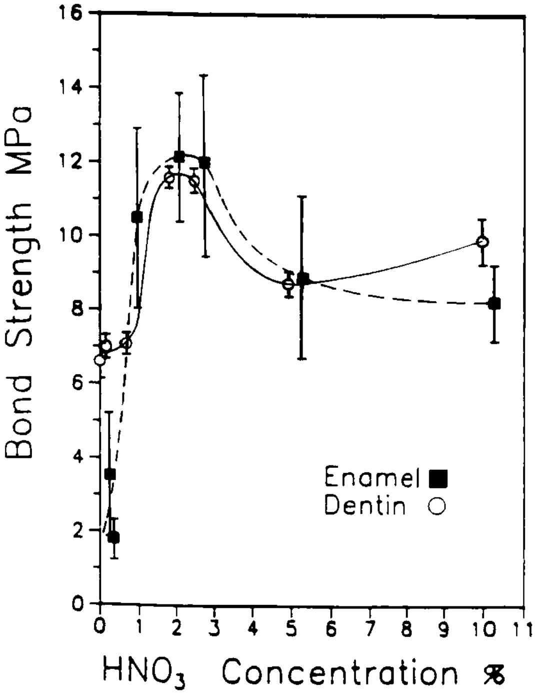

FIGURE 2 Average tensile bond strengths *vs.* nitric acid content in 6.8% purified FO solutions ($n = 15$, dentin; $n = 6$, enamel). The apparent concentrations for the enamel data have been offset 0.25% to the right in the plots to improve visibility. Error bars are given as standard error of the mean.

was held constant, the highest bond strengths were obtained with the solutions containing about 1.85 to 2.5% HNO_3. These gave about equal average bond strengths to dentin or enamel. These average bond strengths ranked higher than those resulting from the use of solutions containing the lower concentrations of 0.068 or 0.68% (the estimated range of HNO_3 in the "as received" FO in the first part of this study) or higher concentrations of HNO_3 (Figure 2).

DISCUSSION

In bonding to dentin, the low bond strength at the two lowest FO concentrations (0.85 and 1.7%) might be interpreted as insufficient acid in the commercial FO as

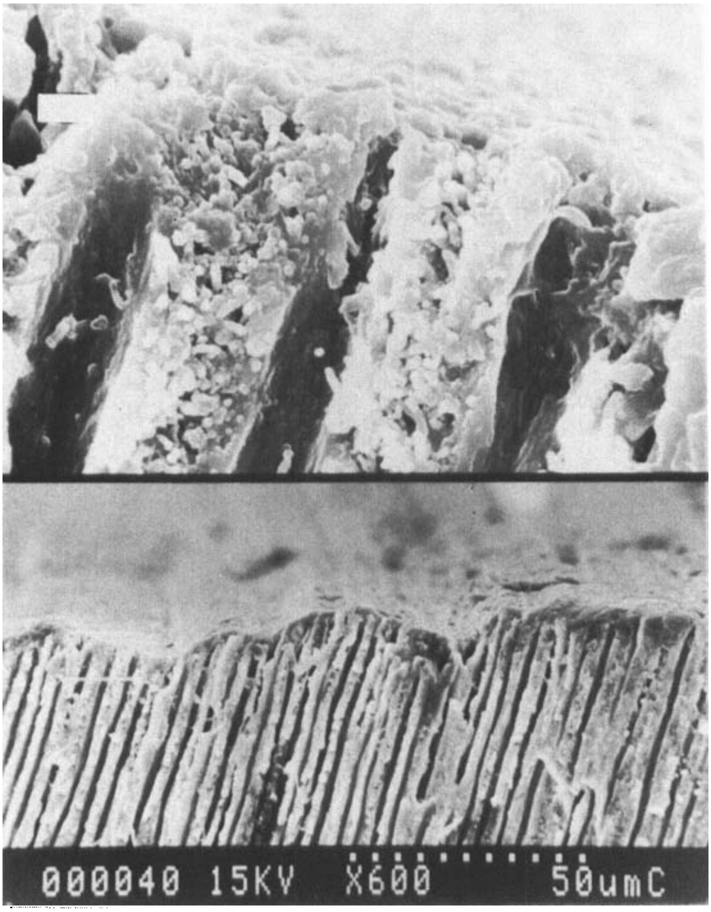

FIGURE 3 Abraded dentin treated with 3.4% as-received ferric oxalate, washed, dried, and fractured at a right angle. This solution was acidic enough to remove the smeared layer partially as shown by the serrated appearance of the edge. The field widths are 15 micrometers (upper) and 150 (lower).

received to remove the mechanically-induced smeared surface. With enamel, a certain amount of FO (acidity and capacity) apparently was required to remove smeared surface material and to develop texture (acid-etch the enamel) for any bonding. SEM observations of enamel and dentin morphologies resulting from varying concentrations of FO are shown in Figures 3, 4, 5 and 6.

In the second aspect of the study, where only the HNO_3 was varied, analysis of variance indicated that 2.5% HNO_3 was significantly ($p < 0.05$) better on dentin than the much lower or higher concentrations. Comparison at 1.85% HNO_3 concentration gave similar results. Experimental difficulties and fewer replications of enamel measurements prevented all but ranking comparisons.

Based on the present findings, a further study determines tensile bond strengths as a function of ferric oxalate concentration in 2.5 weight percent nitric acid

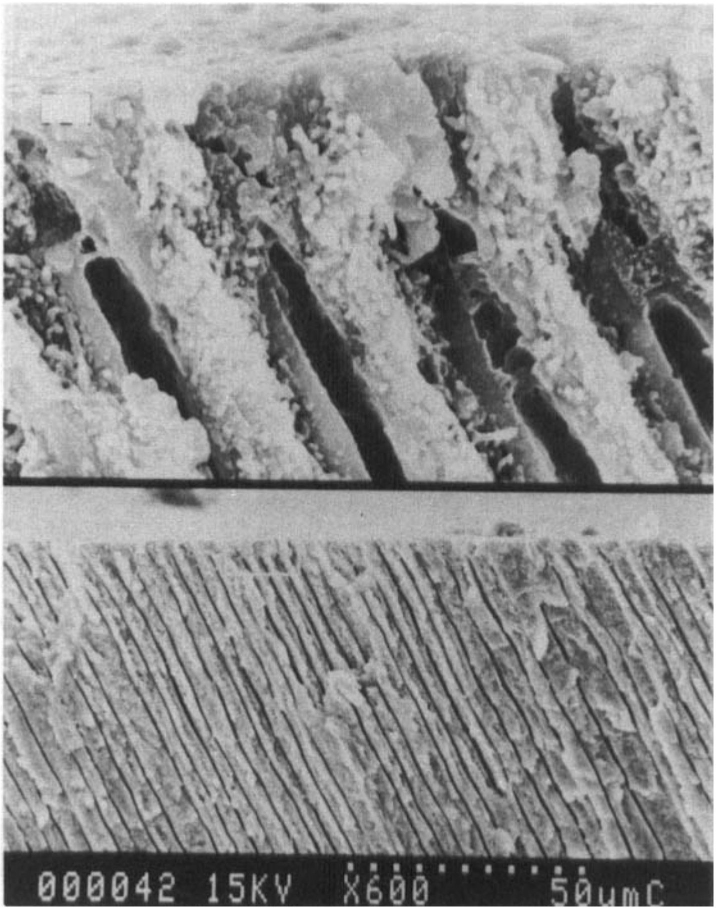

FIGURE 4 Surface treated with 20% as-received ferric oxalate appears flatter, suggesting more dentin removed. The tubular lumina are substantially obturated by material induced by the treatment at the surface. Field widths: 15 and 150 micrometers.

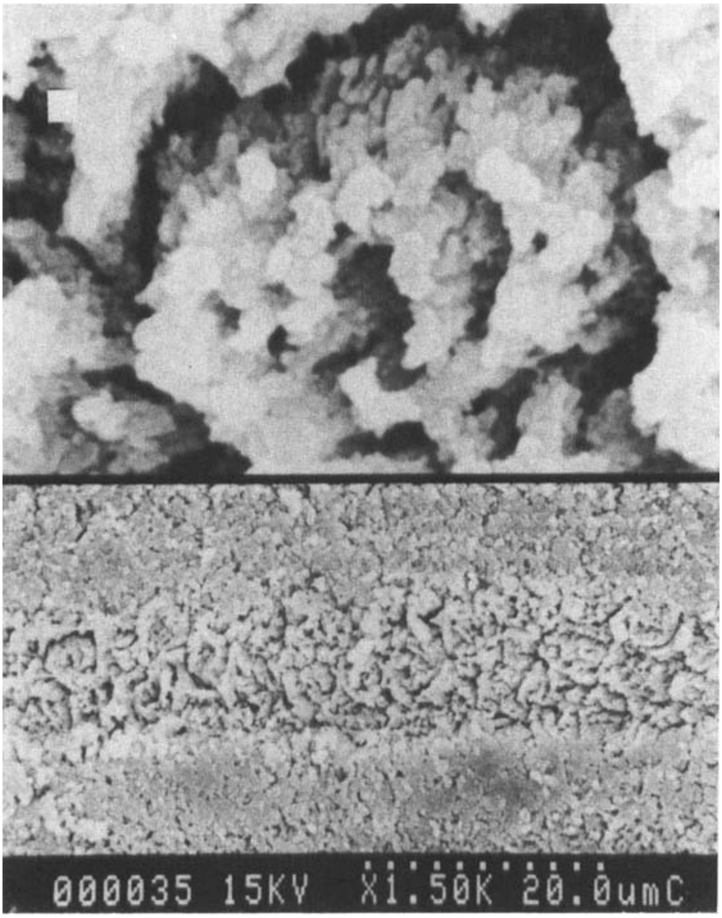

FIGURE 5 The 6.8% as-received ferric oxalate solution has removed most of the smeared enamel and has lightly etched the surface. Strong bonds were obtained, perhaps due to micromechanical interpenetration and chemical interactions with the PMDM resin. Field widths: 6 and 60 micrometers.

solution.[9] Biocompatibility studies in animals and in human teeth extracted for orthodontic reasons have evinced the safety of formulations containing 2.5% HNO_3. Higher concentrations of HNO_3 have not been tested in the oral cavity. Phosphoric and several other acids ranked somewhat less effective when compared in bonding tests of this kind.

CONCLUSIONS

Where the application of a ferric oxalate solution is desired as the initial step in this experimental bonding system, a sufficient amount of nitric acid is necessary in the solution to remove disturbed surface layers, etch enamel surfaces, and ensure

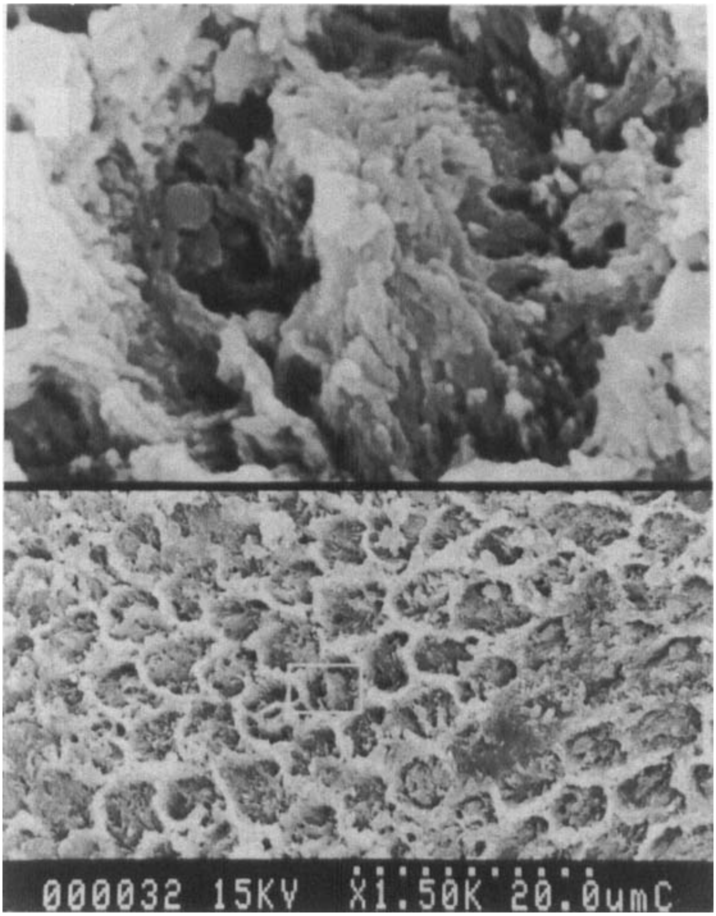

FIGURE 6 Treatment with 12.6% as-received ferric oxalate revealed enamel prisms and rod sheaths. The ridges and grooves from the surface preparation are not prominent. There is a suggestion of globular reaction products that did not wash away. Field widths: 6 and 60 micrometers.

strong adhesion with composite resins. Evidence from scanning electron microscopy, transmission electron microscopy, and other studies, most of which are not yet published, suggests that the acidic solution removes a small amount of the substrate surface, leaving roughened enamel, intertubular dentin that is superficially somewhat porous, and dentinal tubules that contain a precipitate presumably derived from interactions of ferric oxalate with dissolved dentin. The evidence to date suggests a combination of impregnation ("mechanical interlocks") and chemical interactions with these substrates.

NPG and NTG-GMA perform equally well as part of this experimental bonding system. Dentin and enamel respond to this bonding system in a relatively proportionate manner even though these two tissues are very different in structure and composition. It would not be surprising if these materials and methods could find broader applications in industry for adhesive bonding.[10]

Acknowledgment

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