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A study of the acid etch pretreatment used with the Nuva-seal" dental process

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A STUDY OF THE ACID ETCH PRETREATMENT USED WITH THE "NUVA-SEAL" DENTAL PROCESS

by

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ABSTRACT

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Nuva-Seal, a bisphenol-A-glycidyl-methacrylate polymer, is applied to the occlusal surface of teeth to prevent tooth decay. Before application of the sealant, the enamel surface is etched for one minute by a 50 per cent by weight solution of phosphoric acid containing seven per cent by weight of zinc oxide. This treatment renders the tooth surface more porous and surface active to insure a strong bond between tooth and sealant. Past studies at Union College have shown that the etching treatment removes much of the enamel from the tooth.

In the current work the amount of tooth removed by acid etching was determined gravimetrically. Seven teeth were etched <u>in vitro</u> using an etchant solution similar to that recommended for use with Nuva-Seal. The total time of etching was one minute. Measurements of the weight losses for each tooth were made after every 20 seconds of acid attack. The maximum amount of etch appears to occur between 20 and 40 seconds of acid etching.

The results of an extensive literature search are also included.

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INTRODUCTION

Pit and fissure sealants are a fairly recent development in the field of preventative dentistry. By applying these polymeric sealants to the occlusal surfaces of teeth, any irregularities in the enamel (i.e., the pits and fissures) are covered. Food debris is prevented from collecting and decaying in the pits and fissures, thereby preventing caries.

Nuva-Seal (L.D. Caulk Company, Milford, Delaware) (49) is the most widely used of the pit and fissure sealants available today. It was introduced by Michael Buonocore in 1970 (9,10) and is currently classified as "acceptable" by the American Dental Association. Nuva-Seal consists of three parts by weight of the reaction product of bisphenol A and glycidyl methacrylate and one part by weight of methyl methacrylate monomer. Two per cent by weight of benzoin methyl ether is added as an ultraviolet light sensitive catalyst. Nuva-Lite (L.D. Caulk Company, Milford, Delaware) (49) is the light source used to initiate the polymerization of the sealant. The wavelength of the radiation used is 366 nanometers and the exposure time is one minute (9).

Because a strong bond must exist between the tooth and the polymer to insure good retention of the sealant, the enamel surface is conditioned with an acid solution before application of the sealant. This etching process was first proposed by Buonocore in 1955 (8). In this initial study an 85 per cent phosphoric acid solution was applied to the tooth surface for 30 seconds. An increased adhesion, relative to untreated enamel, of acrylic drops to the tooth was found. The following five reasons were suggested for this increased bond strength: 1) the surface area of the enamel was increased, 2) the organic framework of the enamel was exposed and served as a framework about which the acrylic drop adhered, 3) a new surface was made by precipitation of certain substances to which the acrylic drop bonded, 4) the old, fully-reacted, and inert layer of enamel was removed, leaving a more reactive surface, and 5) an adsorbed layer of polar phosphate groups developed on the tooth causing strong polar bonds to form between the tooth and the acrylic drop. It was also suggested that the acid etch treatment increased the wettability of the tooth.

Today a solution of 50 per cent phosphoric acid by weight containing seven per cent by weight of zinc oxide is used as the etching solution for the Nuva-Seal treatment. It is applied to the enamel surface for one minute. During this one minute period, enamel is removed from the surface of the tooth.

The purpose of this research project is to report on the literature which has been found concerning the acid etch treatment and to present the results obtained at Union College from *in vitro* determinations of the amount of tooth lost during the etching pretreatment recommended for the application of Nuva-Seal.

LITERATURE

I. History of Pit and Fissure Sealants

Long before pit and fissure sealants were developed, dental research had been concerned with finding a successful method of reducing caries development in these areas. Various techniques were investigated before sealants were introduced.

Experimentation with various chemical compounds began in 1905 when W.D. Miller (44) tried precipitating silver nitrate into pits and fissures. Then in 1950 J. Miller (43) made six monthly applications of a copper cement to the enamel. In the same year Ast (2) attempted to seal pits and fissures with zinc ferrocyanide.

A different approach to the problem was taken by Hyatt in 1923. His "Prophylactic Odontotomy" (27) included drilling all pits and fissures and then filling them with amalgam. In 1964 Bodecker introduced "Eradication of Enamel Fissures" (5) where only drilling of these areas was recommended.

None of the above procedures were found to be practical and/or successful.

The alkyl (including methyl, ethyl, and butyl) cyanoacrylates were the first pit and fissure sealants developed. In 1966 Takeuchi et al. (65) were among the first authors to report on this type of sealant. In addition to the cyanoacrylate, methyl methacrylate polymer powder and certain metal powders were included in the sealant. No acid etch pretreatment was used and a reduction of caries was reported (11).

A year later Cueto and Buonocore (17) reported a caries reduction of 86.3 per cent with another cyanoacrylate polymer. The acid etch pretreatment was used in this study. The working time of this particular sealant was one minute.

There were other studies made using the alkyl cyanoacrylate sealants. Because these sealants are biodegradable and hydrolyze when exposed to the oral environment (11,47), they are not currently being used in commercially available sealants.

The polyurethane sealants (11,14) are usually produced from the reaction of polyhydroxy compounds with di- or polyisocyanates. Epoxylite 9070 (Lee Pharmaceuticals) is commercially available. Because of the rubbery consistency of the polymer after polymerization and the weakness of the bond between the tooth and the polymer, caries reduction is very small with these sealants. The polyurethanes are generally not used as sealants but rather as a method for the application and retention of topical fluorides.

The polymer used in Nuva-Seal, namely, the reaction product of bisphenol A and glycidyl methacrylate, was introduced by Bowen in 1962 (6). There are several variations of this Bis-GMA polymer.

In 1968 Roydhouse (14,47,58) reported a 29 per cent reduction in caries after three years using the Bis-GMA reaction product and methyl methacrylate monomer. This monomer is added because the reaction product itself is too viscous to make a suitable sealant. A benzoyl-peroxide-acrylate catalyst-accelerator system was used to polymerize the sealant. No acid etching was used.

Epoxylite 9075 (Lee Pharmaceuticals) and Concise Enamel Bond are two other sealants which are based on this polymer. Both are conventionally polymerized and self-curing.

Nuva-Seal is the most widely used of all the above mentioned sealants. Its major advantage is the fact that it has a long working time because it will not polymerize until exposed to ultraviolet radiation. Several reports of the effectiveness of Nuva-Seal in caries prevention have been made (9,10,42,56,60).

The polycarboxylates are some of the newer polymers being investigated (14). One of the major advantages of these polymers is that they require no acid etching and in fact, etching seems to reduce their bond strengths to the tooth. Their disadvantage is that they are not resistant to abrasion.

2. The Effect of Acid on Enamel

There are four basic ways in which enamel may be etched. They are 1) preferential dissolution of the prism cores of the enamel, 2) preferential dissolution of the prism peripheries, 3) formation of a pitted surface, and 4) featureless dissolution (22). The less the etch, the smaller are any of these histologic changes. Of these four ways, dissolution of the prism cores is the most common. The exact pattern of etch depends on the amount of time that the tooth is exposed to the acid and also on the particular composition and structure of the enamel (38).

After acid etching, teeth lose their luster and take on a chalky, white appearance. The condition of teeth after etching has been compared to that found in the advanced stages of the carious process (26,48).

As was suggested by Buonocore in his initial article on acid etching, the treatment has several purposes. First, it removes the organic pellicle covering the tooth (22) as well as the outer enamel surface which has reacted fully with various materials in the oral environment. The underlying layers of the tooth, which are more reactive towards bond formation with the sealant, are exposed.

Etching increases the surface area of the tooth, thereby improving adhesion. Resin tags are formed by the sealant flowing into the microspaces created in the enamel by the acid attack. These tags help the sealant to be mechanically bonded to the tooth.

Chemical and physical bonds are also formed between the sealant and tooth (23). Chemical bonding is covalent (21). Van der Waals forces and capillary action also help to increase the adhesion (13).

The increased wettability of the tooth's surface caused by acid etching adds indirectly to the strength of the bond. The more wettable the surface, the more easily the sealant flows onto the tooth and forms the above mentioned bonds (21).

Chemical wetting of the tooth and removal of the organic pellicle on the enamel occur during the first ten seconds of acid exposure. After this time mineral salts begin to be removed from the tooth (19).

Resin tags, which were mentioned above as contributing to the sealant bond strength, also help to prevent marginal leakage around the sealant and to prevent caries formation in the etched enamel after the sealant has been lost (61,69). These tags have an average length of 25 microns (24) but may be as long as 100 microns (62).

In order for the bonding between the sealant and tooth to be strong, care must be taken to completely dry the etched surface before sealant application. If water is present, the affinity of the tooth's surface for the sealant is reduced and penetration of the sealant into the microspaces is prevented (12).

The enamel surface must not be over-etched. One study showed that excessive etching may produce a surface which is too rough to allow a free flow of adhesive over the surface (57). Another study reported that excessive etching with phosphoric acid does not continue to increase the roughness of the tooth but rather dissolves the prism cores flat so that mechanical bonding is at a minimum (35).

Because the outer 20 per cent of the enamel is the hardest, and therefore the most resistant to acid attack, worn enamel surfaces decalcify first (18). If all the enamel is removed, the acid will continue to etch the dentin, or the underlying surface of the tooth. Because the dentin is porous, the acid can penetrate further in it than in enamel (28).

Neweseley (48) has proposed that the hydrogen ions of the various acids attack the phosphate and hydroxy positions of the hydroxyapatite ($Ca_5(PO_4)_3OH$), the compound of which enamel is made, and form $Ca_5(PO_4)_3^{+}$, $Ca_5(HPO_4)(PO_4)_2^{++}$, $CaHPO_4$, and $Ca(H_2PO_4)_2 \cdot H_2O$ (monocalcium phosphate monohydrate). Of these four compounds, only the monocalcium phosphate monohydrate is less soluble than the original hydroxyapatite. Several other authors have also reported the formation of monocalcium phosphate monohydrate during acid attack (15,20,54).

The amount of tooth removed during etching reaches a maximum and then decreases with time until eventually little or no more of the tooth is removed. It has been reported that 90 per cent of the enamel which had been dissolved after two days was removed after the first five minutes of acid exposure (33). Another study reported that the amount of etch increased up to one minute (53). The final level of etching is known as the "characteristic etch level". Three reasons have been suggested for the decreased solubility of teeth with time (3). First, the nature of the organic matrix of the tooth changes deeper in the enamel. It becomes increasingly more difficult for the acid to penetrate into the enamel. Second, calcium and phosphorus ions protect enamel from dissolving. As the enamel dissolves, these ions are released and help prevent further dissolution. Third, insoluble salts, such as $Ca(H_2PO_4)_2 \cdot H_2O$, form on the enamel surface and protect it from acid attack (20,54).

Several reports have been made of the depth of the acid etch (21,23,69). Wickwire et al. (70) report the following depths of enamel lost after etching with phosphoric acid: after a two minute exposure, five to ten microns were lost; after a four minute etch, five to 15 microns; and after six minutes, 20 to 30 microns.

One of the dangers of acid etching, besides leaving the tooth with virtually no natural protection against caries, is that acid may cause pulpal irritation. Two studies were made to determine if the acid could seep through the enamel and dentin into the pulp. One study showed that a solution of 50 per cent phosphoric acid did not penetrate one millimeter of dentin (35). However, another study did show pulpal irritation after acid exposure and recommended a protective lining be used to cover exposed dentin (55).

Pulpal irritation may also occur when the Bis-GMA polymer is applied to dentin. This irritation is intensified by acid etching.

3. Factors Which May Change Tooth Solubility in Acid

The amount of tooth dissolved by acid etching may vary. Various conditions of the tooth itself and changes in the etchant solution will affect enamel solubility.

The age of the tooth appears to have an effect on enamel dissolution in acid. Most authors agree that older enamel etches less than younger enamel (67,71). The reason generally given for this occurrence is that older teeth have reacted with many different substances which have made them less susceptible to acid attack. Mizuma (45) reported the only study showing increasing solubility with age which was found. However, it must be noted that this conclusion was based on a sample of only three teeth.

The differences in the effect of acid on caries-susceptible and caries-immune enamel is debatable. Volker (67) found carious enamel to be less soluble than non-carious enamel. Two other studies (31,63) show caries-susceptible enamel and caries-resistant enamel to have no differences in solubility. Mizuma (45) reported that caries-susceptible enamel is more soluble than caries-immune.

Enamel which had been previously etched for one minute by a solution of 30 per cent by weight of phosphoric acid was found to be more soluble in acetic acid than unetched enamel due to its increased porosity (61). After the etched enamel was exposed to saliva for 24 hours, it behaved as unetched enamel.

Other conditions of the enamel and their effects on enamel solubility are as follows: enamel solubility does not vary between freshly extracted teeth and teeth which have been kept (31,63), ground enamel is more soluble than intact enamel (63), lingual enamel is more soluble than buccal (63), and enamel dried in air between 110° and 115° C is more soluble than enamel dried in vacuo at the same temperature (67).

The pH of the etching solutions is an important factor in determining enamel solubility. At sufficiently high pH's no dissolution will occur. The upper limit for dissolution is not well defined. One study showed no dissolution after ten weeks at a pH of 3.8 or after 34 weeks at a pH greater than 4.0 (3). Another study found that dissolution occurred at pH's less than 5.2 (31). McClelland (39) reported that no decalcification occurred between pH 6.5 and 11.0. Part of the differences observed in the results is due to the different acids and experimental techniques used.

The pH of the etchant solution also affects the rate of enamel dissolution. The greater the hydrogen ion concentration in the solution, the faster the dissolution (39, 51,63). Leach (33) found that as the pH increases from 3.54 to 5.74 the amount of dissolution decreased.

It has also been found that at a given pH, the stronger the acid, the less enamel which is dissolved (63).

Other variations in the etchant solution which affect the enamel solubility are viscosity and the rate of stirring. The more viscous the acid solution, the less soluble the tooth (45,63). More stirring promotes more dissolution (63).

Not all acids will etch enamel to the same extent. Combining several sources, the following is a list of acids in order of increasing etching ability: sulfuric $<$ HF, acetic, EDTA $<$ citric, formic $<$ lactic $<$ malic $<$ tartaric $<$ fumaric $<$ phosphoric $<$ HCl $<$ nitric (22,34,45,48,53,59,63,66). There is a particular concentration at which maximum etching occurs for all acids. This concentration varies from acid to acid (53,54).

Different concentrations of phosphoric acid etch the tooth to different degrees with less concentrated solutions generally removing more enamel than highly concentrated solutions (54,59). The maximum depth of etching is caused by a 40 per cent solution (54). 85 per cent phosphoric acid removes only five microns of enamel, whereas a 50 per cent and ten per cent solution remove between five and 25 microns (22). The reason for the eventually decreasing etch with concentration is due to the formation of monocalcium phosphate monohydrate (15,20,54). After a certain concentration of phosphoric acid, the effect of the increasing pH is counteracted by the fact that the monocalcium phosphate monohydrate is formed faster and protects the tooth sooner against further dissolution.

McLundie et al. (41) reported that with a 30 per cent solution of phosphoric acid applied to the tooth for one minute, less etching occurred with the buffered solution than with the unbuffered. The difference in etch was very small. Silverstone (59) also found that unbuffered solutions etched slightly more than buffered.

Because teeth differ in their structure and composition, there is no single etching treatment which provides an optimum etch for all teeth. However, the following suggestions have been made. Wickwire et al. (70) suggest a four minute etching with phosphoric acid because a uniform roughness is observed. Rock (57) found the highest bond strength after a one minute etch with 30 per cent phosphoric acid. Other reports show better adhesion with longer etching times (38) and greater bond strength to bovine enamel was obtained without zinc oxide in the etching solution (7). A 20 per cent lactic acid solution has also been recommended because it is less acidic but appears to make for higher bond strengths (7).

Addition of certain compounds (such as oils and fats) and ions to the etching solution or to other substances which come in contact with the tooth can change the solubility of the enamel. The compounds or ions react, either by adsorption or exchange, with the calcium phosphate of the tooth surface to form a new compound with either higher or lower solubility than the original enamel (68). Certain salts may undergo chemical reactions with the enamel and form compounds which are deposited on the tooth's surface (33). Rae and Clegg (52) said, "any salt whose anions form an insoluble calcium salt or whose cations form insoluble phosphate salts will protect the teeth and reduce the apparent solubility of tooth enamel and calcium phosphate."

In their initial study Rae and Clegg found that barium nitrate, silver nitrate, silver fluoride, and lead nitrate showed "protective effects" on teeth immersed in lactic acid, decreasing the solubility of enamel in this acid. Manly and Bibby (37) reported on 147 substances whose effects on enamel solubility were investigated. Of the 147 substances, 74 reduced the solubility of powdered enamel in an acetate buffer of pH 4.0 after a 15 or 20 minute exposure. Generally speaking, the elements of Groups III and IV in the periodic table appeared to be the best in reducing enamel solubility. McLundie (41) found that molybdenum and selenium markedly increased the rate of enamel solubility, tin increased it only slightly, vanadium slowed down the rate, and zinc had no apparent effect of it. A table listing the abilities of various compounds to affect enamel solubility is given by Muhler and Van Huysen (46).

Both calcium and phosphate ions reduce enamel solubility because of the common ion effect (40,64). Bibby and Averill (4) found that phosphates which come in contact with the enamel reduce its solubility. If there is no direct contact, the phosphate ions show no effect. Osborn (50) reported that inorganic phosphates can reduce enamel solubility in a solution of saliva and sucrose. A 15 per cent solution of sodium monofluorophosphate will also reduce acid etching of enamel (30).

4. Remineralization and Recalcification

When teeth which have been etched are placed in an oral-like environment, they return to normal appearance. This process is called remineralization. Recalcification is the actual redepositing of an enamel-like (i.e., inorganic) material on the teeth. Many dentists, who are advocates of Nuva-Seal and acid etching, argue for the acid treatment on the basis of the occurrence of remineralization. In fact, recalcification is the pertinent process.

Remineralization is most rapid during the initial hour that the teeth are in the oral-like environment and tapers off during the next 48 hours (29). After 48 to 96 hours, the etched surface has returned to a completely normal appearance (1,32). Remineralization appears to occur faster in younger people (1).

There are three reasons why recalcification or the deposition of new enamel does not occur. First, it is possible that a part of the tooth necessary for recalcification to occur was lost during the etching (29). Second, enamel is a very organized structure and it is highly improbable that any new substance which is deposited on the tooth will be deposited in such an organized structure as the enamel. Osborn (50) states, "It is probable that irreversible damage will be done by any decalcifying process (i.e., etching) extensive enough to destroy this organized condition." Third, if recalcification does occur, the outer layers of the tooth will be recalcified first and prevent the inner layers from being affected (29,48). Lenz and Mühlemann (36) maintain that no recalcification occurs and that an organic (salivary) pellicle and no inorganic layer is deposited on the tooth.

In summary, the tooth may return to normal appearance but it does not return to the same condition that it was in before etching.

PAST RESEARCH AT UNION COLLEGE

This research was begun two years ago at Union College by Vicki Herzl (25). While several of the experimental techniques and the etchant solution used in this past work have been modified in the present work, useful information concerning the amount of tooth removed by acid etching was obtained. For more details on this work than presented here, the reader is referred to the Herzl thesis.

1. Experimental Procedure

In this *in vitro* study the teeth were etched by a 50 per cent by weight solution of phosphoric acid containing no zinc oxide for varying lengths of time. The apparatus used for etching consisted of a three milliliter rubber bulb, punctured at the tip, inverted in a 13 x 100 test tube. The tooth was inserted into the mouth of the bulb. It was believed that the positive pressure created in the test tube would prevent the acid from seeping below the mouth of the bulb and into the root area of the tooth when the apparatus was immersed in the etchant solution. Immediately after etching, the teeth were thoroughly rinsed with distilled water.

The amount of tooth lost during the etching process was determined gravimetrically. Two trials were carried out. Each trial used a different method of drying to bring the teeth to constant weight. In the first trial the teeth were placed in test tubes which were put into a 110° C oven for three hours. They were then placed in a desiccator and weighed at frequent intervals until a constant weight was obtained. Vacuum drying was used in the second trial. In this trial the teeth were placed on watch glasses in a vacuum desiccator. Three times a day the pressure was reduced to approximately one millimeter of mercury and allowed to equilibrate for one hour before the procedure was repeated. This entire process was continued until the teeth reached constant weight.

2. Results

In the first trial 20 teeth, having a mean weight of 1.1084 grams, were etched for one minute and then for an additional five minutes. After the initial minute etch, a mean weight loss of 0.086 grams with a 95 per cent confidence interval of 0.0070 to 0.0102 grams using Student's *t* distribution was reported. The per cent weight loss during this minute was 0.78 per cent. During the next five minutes of etching, the mean weight loss was 0.0139 grams with a 95 per cent confidence interval of 0.0110 to 0.0168 grams. The per cent weight loss was 1.25 per cent. The per cent weight losses were calculated from the mean weight losses omitting any outliners. One outliner was omitted in the one-minute etch and two were omitted in the six-minute etch.

The second trial consisted of 14 teeth being etched for totals of 30 seconds, one minute, and five minutes. The mean weight of the teeth before etching was 1.0321 grams. After the 30-second etch the mean weight loss was 0.0006 grams with a 95 per cent confidence interval of 0.0002 to 0.0010 grams. The per cent weight loss was 0.058 per cent. A mean weight loss of 0.0038 grams with a 95 per cent confidence interval of 0.0027 to 0.0049 grams and a per cent weight loss of 0.361 per cent was reported after the one-minute etch. After five minutes the mean weight loss was 0.0044 grams with a 95 per cent confidence interval of 0.0015 to 0.0073 grams. The per cent weight loss was 0.43 per cent. Two outliners were omitted in the 30-second averages and one tooth was eliminated after the 30-second etch.

The above results are summarized in Table #1.

In the second trial four of the teeth showed a weight increase between the one- and five-minute etches.

The mean weight loss from the teeth of younger patients was generally greater than that for older patients. The

TABLE #1: Mean Amounts of Tooth Lost During Various Periods of Acid Etching (V. Herzl, B.S. Thesis, Union College, 1976)

	Trial 1	Trial 2
Initial Weight of Tooth	1.1084 g	1.0321 g
Weight Loss After 30 Seconds	-	0.0006 g
95% Confidence Interval	-	0.0002 - 0.0010 g
Per Cent Weight Loss	-	0.058%
Weight Loss After 1 Minute	0.0086 g	0.0038 g
95% Confidence Interval	0.0070 - 0.0102 g	0.0027 - 0.0049 g
Per Cent Weight Loss	0.78%	0.361%
Weight Loss After 5 Minutes	-	0.0044 g
95% Confidence Interval	-	0.0015 - 0.0073 g
Per Cent Weight Loss	-	0.43%
Weight Loss After 6 Minutes	0.0139 g	-
95% Confidence Interval	0.0110 - 0.0168 g	-
Per Cent Weight Loss	1.25%	-

older teeth lost weight during the 30-second etch while the younger teeth did not.

3. Discussion

Drying was found to have a destructive effect on the teeth. Both methods of drying caused several of the teeth to crack and/or chip. During vacuum drying some of the teeth actually split apart. It was concluded that the observed deterioration was a result of the drying out of the teeth and not due to other inherent factors (i.e., heat) in the particular drying method. This conclusion was reached because deterioration occurred using both drying methods.

The differences in the magnitudes of the results between the two trials was most likely due to the different methods of drying. The teeth which were oven-dried were more soluble than those dried in vacuo. This find is consistent with Volker's conclusion (see p.12). Volker found that enamel dried in air between 110° and 115° C is more soluble than enamel dried in vacuo at the same temperature. It is important to note that Volker based his conclusions on the fact that both methods of drying were at the same temperature, namely, between 110° and 115° C. In this study the vacuum drying was at room temperature.

The results obtained indicate that the majority of material lost from the tooth during acid etching was removed during the initial minute of acid exposure (i.e., the etching time recommended for the Nuva-Seal pretreatment). Most of this loss occurred between the 30-second and one-minute etch. The weight loss during the first 30 seconds was very small.

The decreased weight loss with time is consistent with the idea of the formation of monocalcium phosphate monohydrate on the tooth's surface to protect it from further dissolution (see p.10). It is possible that if the four teeth which showed an increase in weight between the one-minute and five-minute etches were not thoroughly rinsed after etching, some of this compound might have remained causing the weight gain. The adsorption of polar phosphate groups onto the tooth surface (see p.2) is another possible cause for the increase.

The reported increase in acid solubility of teeth with age does not agree with the majority of the literature. Mizuma (see p.11) was the only author who reported an increase in the solubility of enamel with age.

CURRENT RESEARCH AT UNION COLLEGE

1. Experimental Procedure

The current research also involves a gravimetric determination of the amount of tooth lost during *in vitro* acid etching. The amount of tooth removed was determined from the difference between the "constant weight" of the tooth before etching and that after. The teeth were considered to be at "constant weight" when two weight measurements, one day apart, showed a change in weight of one-half a milligram or less. The Mettler H10 balance was used for all weight measurements.

After the teeth were cleaned, primarily by scraping, picking, and rubbing, they were placed in 10 milliliter beakers in a desiccator. The pressure in the desiccator was reduced using an aspirator during the first several days of drying. This procedure was discontinued because the condition of the teeth began to deteriorate. After this time the teeth were dried and brought to constant weight by placing them in the desiccator in an atmosphere of dry nitrogen.

In this study seven teeth were etched by a 50 per cent by weight solution of phosphoric acid containing seven per cent by weight zinc oxide, i.e., the etching solution used with Nuva-Seal. The pH of this solution was 1.45 (the pH meter was standardized at a pH of 4.01). While holding each tooth in a pair of hemostats, its crown was dipped into a beaker containing the etchant solution for 20 seconds. Immediately after etching, the teeth were thoroughly rinsed with distilled water. They were then dried in a stream of dry nitrogen before being returned to the desiccator and again brought to constant weight by the procedure described above. This entire process was repeated a total of three times for every tooth, making the total etching time one minute.

2. Results

The seven teeth used in this study varied in age, type of tooth, and number, if any, of fillings. Table #2 gives this information for each tooth.

Table #3 presents the weights of the teeth before and after every 20 second etching. After the 20-second etch, approximately one-third of the crown fell off of Tooth #2. The weight of this tooth after the chip fell off was used as its new "initial" weight for weight loss calculations.

The absolute weight changes and per cent weight changes

TABLE #2: Age of Teeth, Type of Teeth, and Number of Fillings

Tooth Number	Age Group	Type of Tooth	Number of Fillings
1	20 - 45 yrs.	Molar	0
2	20 - 45 yrs.	Bicuspid	1
3	20 - 45 yrs.	Molar	1
4	20 - 45 yrs.	Molar	0
5	20 - 45 yrs.	Bicuspid	1
6	20 - 45 yrs.	Molar	0
7	over 45 yrs.	Bicuspid	2

TABLE #3: Weights (in grams) of Teeth Before and After Etching

Tooth Number	Initial Weight	Weight After 20-Sec. Etch	Weight After 40-Sec. Etch	Weight After 60-Sec. Etch
1	1.4562 ± 0.0002	1.4576 ± 0.0002	1.4557 ± 0.0002	1.4532 ± 0.0002
2	1.2864 ± 0.0002	1.1541* ± 0.0002	1.1529 ± 0.0002	1.1520 ± 0.0002
3	1.9555 ± 0.0002	1.9586 ± 0.0002	1.9600 ± 0.0002	1.9590 ± 0.0002
4	1.3880 ± 0.0002	1.3855 ± 0.0002	1.3833 ± 0.0002	1.3818 ± 0.0002
5	1.4171 ± 0.0002	1.4167 ± 0.0002	1.4151 ± 0.0002	1.4146 ± 0.0002
6	1.3551 ± 0.0002	1.3541 ± 0.0002	1.3531 ± 0.0002	1.3517 ± 0.0002
7	1.4196 ± 0.0002	1.4181 ± 0.0002	1.4169 ± 0.0002	1.4165 ± 0.0002

*One-third of the crown fell off after the first etch. All future calculations are based on this weight being the "initial" weight.

after each etch are given in Table #4. Figure #1 is a plot of the per cent weight changes for each tooth versus the length of etch. Only the per cent weight changes after the 40- and 60-second etch were plotted for Tooth #2 because of the problem mentioned above.

The average per cent weight loss for each etch time was calculated using two different methods. In both calculations Tooth #2 was completely omitted because after loosing the enamel chip, part of the dentin was exposed. Therefore, this part of the dentin, as well as the remaining enamel, was being etched (see p.9). Using the Q-Test the value for the per cent weight loss after the one-minute etch for Tooth #3 was rejected. Omitting the above values, the average per cent weight losses are: 0.023 ± 0.028 grams after 20 seconds of etching, 0.10 ± 0.03 grams after 40 seconds, and 0.26 ± 0.03 grams after 60 seconds. Figure #2 is a plot of these averages. A second set of average per cent weight losses was calculated using the data from only those teeth which lost weight throughout the entire study, namely, Teeth #4 through #7. The average per cent weight losses using these data are: 0.099 ± 0.030 after 20 seconds of etching, 0.20 ± 0.03 after 40 seconds, and 0.27 ± 0.03 after one minute. These averages are plotted in Figure #3.

3. Discussion

Drying appears to have a destructive effect on teeth.

TABLE #4: Absolute (in grams) and Per Cent Weight Changes After Etching

Tooth Number	20-Second Etch		40-Second Etch		60-Second Etch	
	Absolute	Per Cent	Absolute	Per Cent	Absolute	Per Cent
1	+0.0014 ± 0.0004	+0.096 ± 0.027	-0.0005 ± 0.0004	-0.03 ± 0.03	-0.0030 ± 0.0004	-0.21 ± 0.03
2	-	-	-0.0012 ± 0.0004	-0.10 ± 0.03	-0.0021 ± 0.0004	-0.18 ± 0.03
3	+0.0031 ± 0.0004	+0.16 ± 0.02	+0.0045 ± 0.0004	+0.23 ± 0.02	+0.0035 ± 0.0004	+0.18 ± 0.02
4	-0.0025 ± 0.0004	-0.18 ± 0.03	-0.0047 ± 0.0004	-0.34 ± 0.03	-0.0062 ± 0.0004	-0.45 ± 0.03
5	-0.0004 ± 0.0004	-0.03 ± 0.03	-0.0020 ± 0.0004	-0.14 ± 0.03	-0.0025 ± 0.0004	-0.18 ± 0.03
6	-0.0010 ± 0.0004	-0.074 ± 0.030	-0.0020 ± 0.0004	-0.15 ± 0.03	-0.0034 ± 0.0004	-0.25 ± 0.03
7	-0.0015 ± 0.0004	-0.11 ± 0.03	-0.0027 ± 0.0004	-0.19 ± 0.03	-0.0031 ± 0.0004	-0.22 ± 0.03

FIGURE #1: Plot of Etch Time Versus Per Cent Weight Change of Teeth

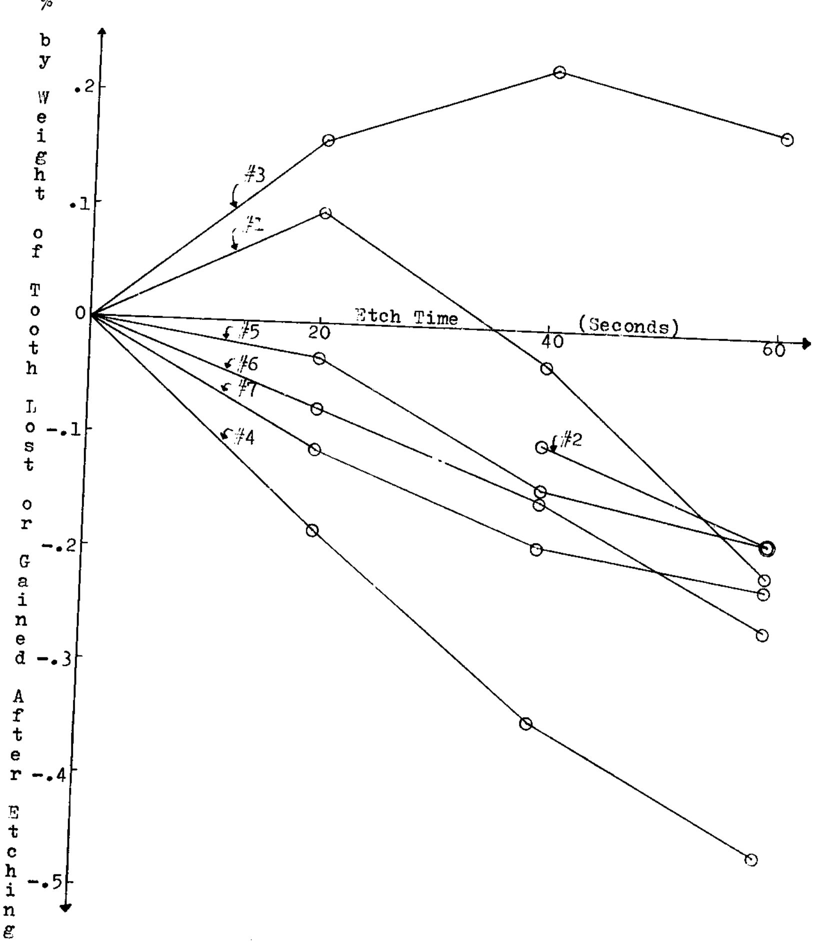


FIGURE #2: Plot of Etch Time Versus Average Per Cent Weight Loss (I)

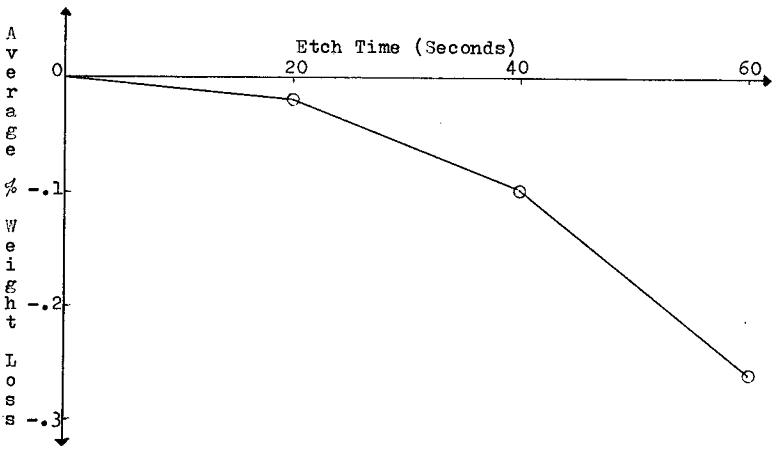
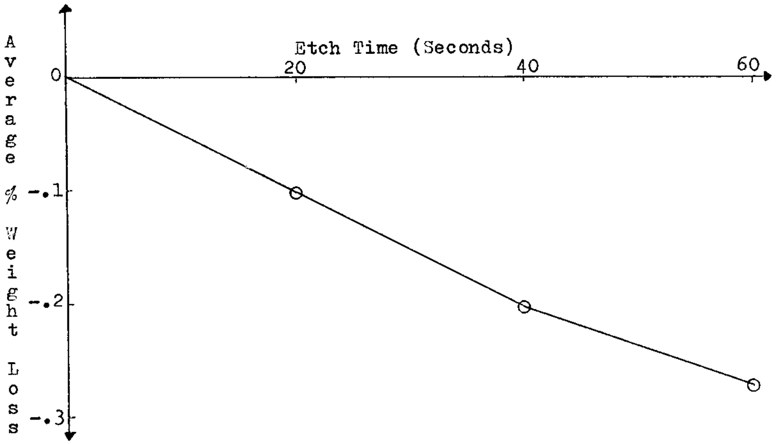


FIGURE #3: Plot of Etch Time Versus Average Per Cent Weight Loss (II)



Almost all of the teeth lost small chips of enamel sometime during vacuum drying. Vacuum drying also caused what appeared to be the enamel of one tooth, not reported with these results, to "lift" off the remainder of the tooth. This loosened material could be easily chipped off the sides of the tooth with a scalpel using very little pressure. The loss of one-third of the crown from Tooth #2 occurred after the tooth had been vacuum dried. Even after vacuum drying was discontinued, pieces of enamel still fell off some of the teeth. However, the deterioration was not as extensive as during vacuum drying. It is therefore concluded that while all three different methods of drying used for the work at Union College cause some damage to teeth, drying in a desiccator in a nitrogen atmosphere is the least destructive.

In order to approximate the etching conditions used as a pretreatment for Nuva-Seal as closely as possible, the zinc oxide buffer was included in the etchant solution. In past work it had been omitted. The literature reports a difference in the amount of etch obtained with and without buffer in the etchant solution (see p.14). Because of this difference, the present results can only be compared with the past data on a qualitative level.

Because the composition of the crown's enamel is different from that of the root, care must be taken during *in vitro* etching to assure that no acid comes in contact with the root. The rubber bulb and test tube technique used in the past work for etching was found to allow acid to seep into the root area. This leakage was discovered by immersing the entire etching apparatus into a solution of methyl violet. The violet color not only covered the crown but extended into parts of the root.

The precise amount of tooth lost during acid etching is a function of the size, more specifically the surface area, of each tooth. Therefore per cent weight losses, and not absolute weight losses, are the results which are comparable between teeth.

It should be noted that straight lines were used to connect the data points for the three etching times in the three plots. These lines are not intended to indicate a steady rate of etching during each period. In actuality there should probably be some curvature to all of these lines.

Teeth #1 and #3 showed weight increases after acid etching. It is believed that these increases were not due to an uptake of a solid inorganic material but rather to the uptake of water during the time the teeth were immersed in the acid solution. Tooth #3 was exceptionally large and this may account for its large uptake of water. Other than this difference, there were no other major variations in these two teeth from the others.

Because of the sample size used in this study, no conclusive statements concerning the amount of tooth removed during etching can be made. However, some interesting trends are apparent.

Figure #1 shows that the first 20 seconds of acid etching removed only a relatively small amount of enamel from most of the teeth. Any organic material which might have remained on the teeth after cleaning would have been removed during this time. During the next 20 seconds, the rate of tooth removal either remained about the same (Teeth #4,6,7) or increased (Teeth #1,5). The slopes of all the lines between the 20- and 40-second etches, except for Tooth #3, are approximately equal, indicating the rate of dissolution during this period was about equal for all five teeth. During the next 20 seconds, the amount of etching began to taper off for some of the teeth (Teeth #4,5,7), while for others the rate of etching continued at an accelerated rate (Teeth #1,6). This difference in behavior was most likely due to the fact that the composition of all teeth is not the same. Five of the seven teeth clustered about a per cent weight loss of about 0.2 per cent after one minute of etching.

Not enough data are available to made any conclusive statements concerning correlations between the amount of tooth removed by etching and the age of the patient, type of tooth, or number of fillings.

Figure #2 shows an increasing average per cent weight loss with time. However, it must be remembered that the averages plotted for the 20- and 40-second etches included individual per cent weight increases which raised the average value. No such increasing values were included in the calculations for the 60-second etch. Figure #3 shows a steady loss of tooth material up to 40 seconds. After this time the rate of etching began to decrease.

Both this study and the past work done at Union College indicate that tooth material is removed during etching. Most of the loss appears to occur during the first minute of acid exposure, and more specifically between the 20- and 40-second exposures. No conclusive quantitative data concerning the exact amount of tooth lost during this treatment can be reported at this time.

SUGGESTIONS FOR FURTHER STUDY

Many questions still remain concerning acid etching. There is much literature available which qualitatively discusses the etching treatment. However, quantitative results are few. Until these quantitative results are found, it is difficult to determine if the advantages of acid etching outweigh the disadvantage, namely, the loss of much, if not all, of the enamel from the tooth.

The next step in laboratory work should be to continue the research started for this paper in order to obtain enough data for a statistically significant study. The amount of tooth lost should be measured gravimetrically and/or by determining the calcium ion concentration in the etching solution (assuming the only source of these ions is the dissolved tooth) using a calcium ion selective electrode. The total time of etching should be increased to two minutes. No vacuum drying should be used since it appears to cause more damage to the teeth than drying them in a desiccator alone. It may also prove advantageous to store the teeth in water, rather than in alcohol as was done for this study, for one day before beginning the drying procedure. If the weight increase reported in the present work was due to water uptake, this occurrence might be eliminated by storage of the teeth in water.

After determining the amount of etch caused by the 50 per cent phosphoric acid - seven per cent zinc oxide solution, changes in the etchant solution should be made to determine their effects on the amount of tooth removed by the acid attack. Based on the literature reported in Chapter II, some suggestions for these changes are 1) the addition of calcium phosphate, and possibly other compounds, to the acid solution (see pp. 15,16), 2) the use of various concentrations of phosphoric acid (see pp. 13,14), and 3) the addition and subtraction of different amounts of zinc oxide to the etchant solution (see p.14). Because the pH of all the solutions mentioned above will be slightly different, the effect of pH on tooth solubility in acid can be investigated.

Another interesting study would be to examine the amounts of tooth removed by different acids (see p.13).

Through all this work the differences in the solubility of teeth from various age groups should be examined.

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