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Morphological effects produced, *in vitro*, by ferric oxalate treatment of enamel surfaces. A preliminary SEM study.

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SUMMARY

The morphological changes produced, in vitro, by application of ferric oxalate on enamel surfaces were examined by scanning electron microscopy. Exposure of human enamel surfaces to ferric oxalate (5.3% w/w aqueous solution or added to phosphoric or citric acid) resulted in cleaned, activated enamel surfaces and a mild etching which increased surface roughness and porosity. Deposition of crystal formations occured in approximately 50% of the examined areas. Crystals bond firmly to the porous underlying surfaces and resist washing with 5, 10 or 20 ml of distilled water.

KEY WORDS:
Enamel, Morphology, SEM, Ferric Oxalate.

RÉSUMÉ

L'aspect morphologique de surfaces d'émail soit poncées soit abrasées à la pointe diamantée a été observé, en microscopie électronique à balayage, après les traitements suivants:
1) Application d'oxalate ferrique en solution aqueuse (5,3% en poids);
2) oxalate ferrique ajouté à une solution d'acide phosphorique titrant 2 mol/l;
3) oxalate ferrique ajouté à une solution d'acide citrique titrant 10% en poids.
Les témoins ont été traités avec des solutions d'acide phosphorique ou citrique de concentrations identiques. Le traitement à l'oxalate ferrique, pendant 1 ou 2 minutes, produit les effets suivants:
- **nettoyage et activation des surfaces,**
- **un léger «etching» avec augmentation de la porosité et de la rugosité des surfaces traitées; l'atteinte de l'émail se produit surtout au niveau des cristallites,**
- **sur la moitié des échantillons apparaissent des cristaux. Ces cristaux semblent adhérer assez fortement à la surface sous-jacente car ils sont encore présents après un rinçage avec des quantités d'eau distillée de 5, 10 ou 20 ml. Ils résistent également à un séjour de 25 mn dans des bains d'acétone de concentrations croissantes.**

MOTS CLÉS:
Email, Morphologie, MEB, Oxalate ferrique.

INTRODUCTION

Various composite materials are now available commercially. Such materials have physical properties which make them ideal for use as dental restoratives. However, a problem exists in effecting adequate bonding of such materials to enamel and dentin in such a manner as to make the restoration virtually permanent. From the extensive investigations of Bowen (1965, 1973, 1978, 1980, 1985, 1986) it would appear that improved bonding is obtained if, before attaching the restorative materials, the tooth surfaces are conditioned with solutions of a ferric salt. It is argued that Fe^{3+} ions form complexes with the tooth tissues and restorative materials in rather the same way as «mordanting» ions will forme a «lake» between a material (e.g. wool, cotton) and a dyestuff, helping to «fix» the dye in the material.

Mordanting agents examined were: ferric chlorides (Bowen, 1978; Bowen et al., 1978; Gills and Bowen, 1979; Bowen, 1980; Jedrychowski et al., 1981; Clarkson et al., 1984). Ferric oxalate (F.O.) as a «cleanser/mordant» (Bowen et al., 1982a; 1982b; Bowen and Cobb, 1983; Bowen, 1985). Bowen and Misra (1986) concluded that the sequential use of ferric oxalate ($Fe_2(C_2O_4)_3.6\ H_2O$, NTG-GMA (the adduct of N (p-tolyl) glycine and glycidyl methacrylate) and PMDM (the addition reaction product of pyromellitic dianhydride and 2-hydroxyethyl methacrylate) yielded strong adhesive bonding of composites to both dentin and enamel. Bowen and Misra (1986) attempted to reduce the number of steps in the procedure by combining the «cleanser-mordanting» step with the application of the coupling agent (NTG-GMA or the NPG-GMA).

With teeth, material may attach to enamel by means of chemisorption or physical absorption; in either case the strength of the attachment will be a function of the chemical and physical characteristics of the tooth surface. It is the latter with which we are concerned here, especially the roughness and increased surface area of a tooth after conditioning with ferric salts, and we have attempted to assess this by means of scanning electron microscopy.

MATERIALS AND METHODS

The ferric compound we have used is ferric oxalate which in a 5.3% w/w aqueous solution has a pH of 1.3. Therefore, it is necessary to distinguish the effects produced by a low pH from those resulting from reaction of the tooth with ferric and oxalate ions. We have therefore compared enamel surfaces conditioned in each of 5 ways:

Controls: a. phosphoric acid 2 mol/l (approximately 16.3%), pH 0.65,
b. citric acid 10% w/w, pH 1.27.

Experimental: a. ferric oxalate solution

The solution was prepared by dissolving iron (III) anhydrous oxalate $Fe_2(C_2O_4)_3$ (Ventron GMBH D 7500 Karlsruhe 1, purity certified) in distilled water at a concentration of about 5.3% w/w. After the oxalate had slowly dissolved the solution was filtered, giving a clear yellow color. The ferric oxalate solution was kept in an amber dropper bottle at room temperature.

b. ferric oxalate in phosphoric acid,
c. ferric oxalate in citric acid.

Material preparation:

Most of the enamel surface (214/253) were cleaned with a suspension of flour of pumice with a rotary cup for about 60 s., rinsed with water and air-sprayed about 10 s., blown free of apparent water.

Other surfaces (39) were mechanically lightly milled at high speed for 10 s. The milling was performed with a fine grain, flame-type pointed diamond bur (Ref. 221/014 F Horico, Germany) under water coolant.

Chemical treatment of enamel surfaces: Fig. 1, 2 and 3.

The surfaces were wetted with an excess of the test solution for either 1 or 2 min. then rinsed with distilled water and blown relatively dry with air for about 10 s.

Rinsing step: Fig. 4.

Various parameters were investigated in this study:

a. the quantity of water used during the rinsing times: different amounts of distilled water were used, respectively 5, 10 or 20 ml;

b. the specimens were soaked for 5 min. (for each bath) in acetone by gradual and increasing concentrations.

Preparation for SEM observations:

The specimens were dehydrated and vacuum-coated a 20 nm layer of gold. The surfaces were examined in a scanning electron microscope JEOL JSM 35 C, usually operated at 15 kV.

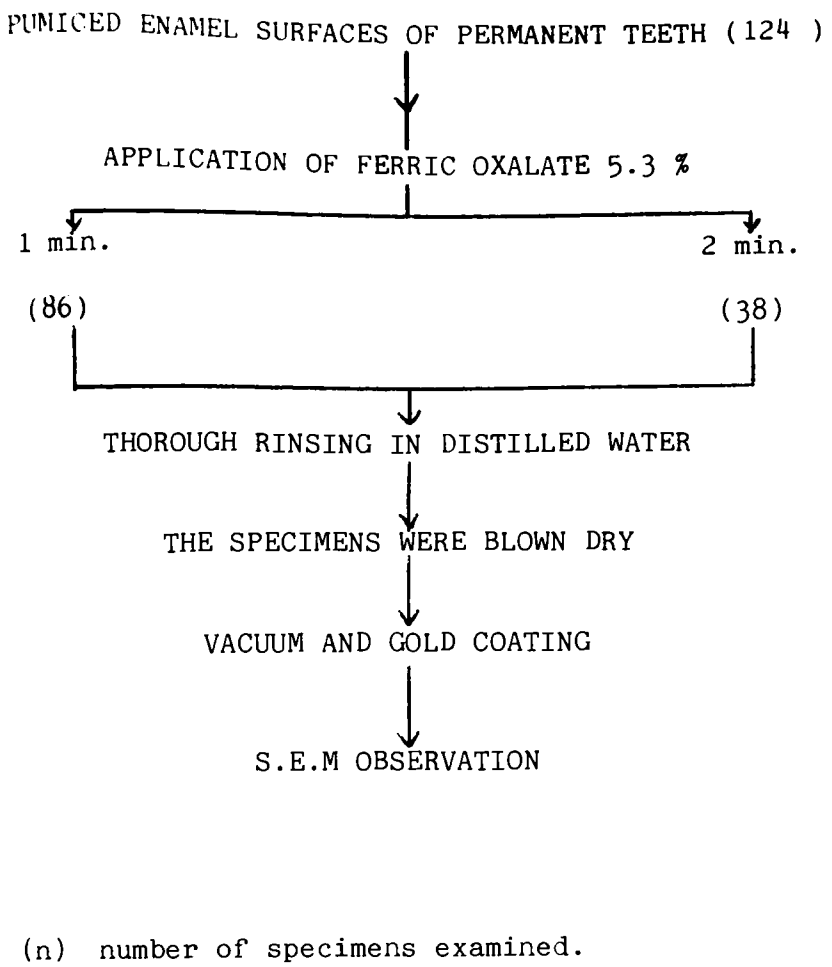

Fig. 1 - Diagram of experimental procedure.
Fig. 1 - Diagramme représentant les méthodes expérimentales utilisées.

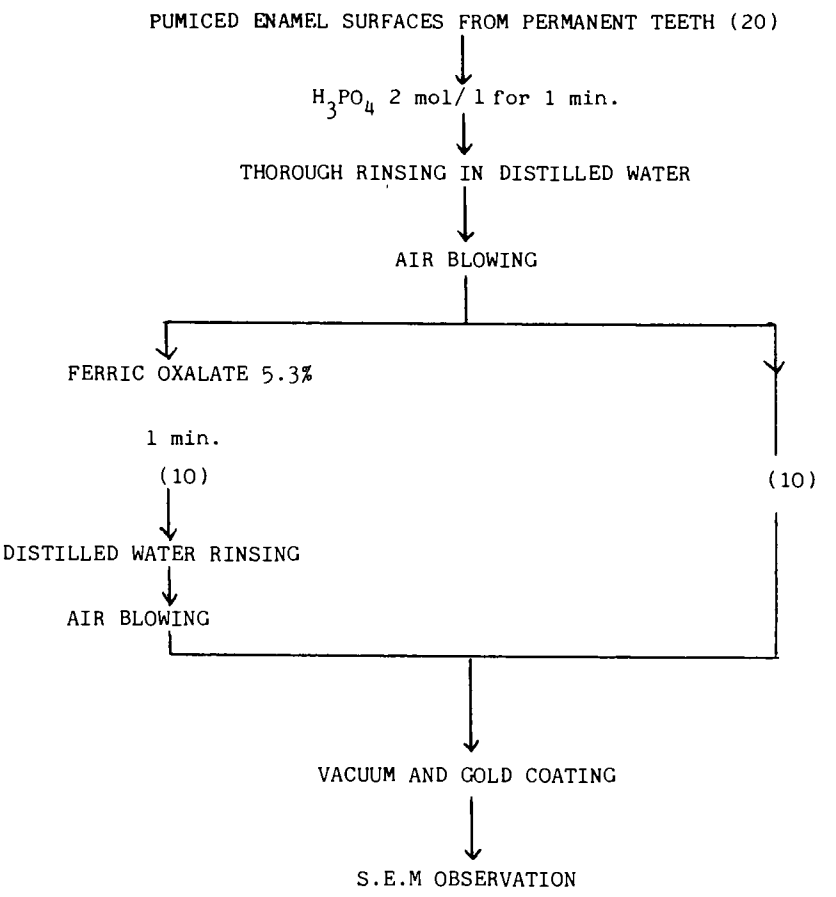

Fig. 3 - Diagram of experimental procedure. Successive etching and mordanting steps.
Fig. 3 - Traitement de surfaces d'émail poncées, par:
a. H_3PO_4 2 mol/l, 1 minute,
b. puis F.O. 5.3 %
parallèlement à des échantillons témoins.

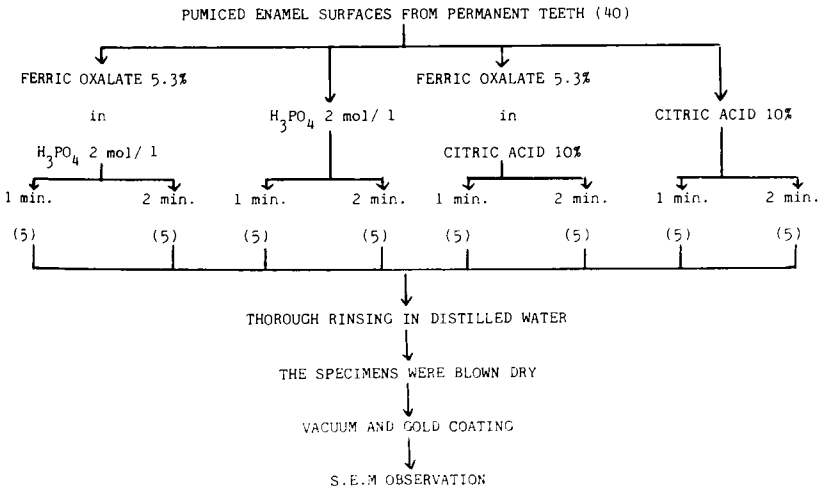

Fig. 2 - Diagram of experimental procedure. Combined etching and mordanting steps.
Fig. 2 - Traitement de surfaces d'émail poncées par:
– 2 solutions expérimentales: F.O. + H_3PO_4
F.O. + acide citrique
– 2 solutions témoins: H_3PO_4 et acide citrique, aux mêmes concentrations.

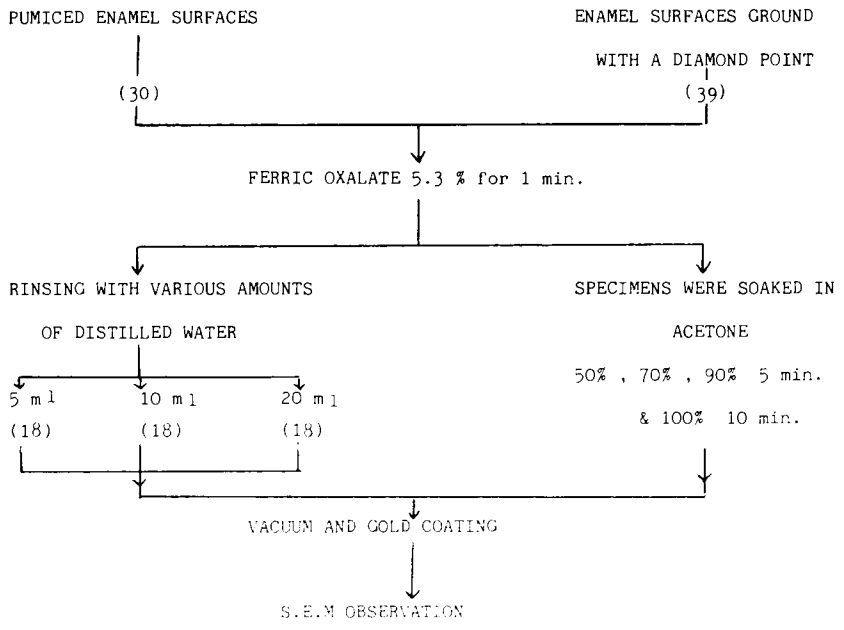

Fig. 4 - Diagram of experimental procedure.
Solubility of deposits left on the enamel after mordanting.
Various forms of rinsing tested.
Fig. 4 - Diverses modalités de rinçage ou de dissolution dans l'acétone visant à tester la solubilité des cristaux obtenus après traitement à l'oxalate ferrique des surfaces d'émail.

RESULTS

A. Controls:

In a precedent study (Rodde, 1989) we showed that neither citric acid nor medium concentrations of phosphoric acid were very efficient on pumiced surfaces. In fact, etching pattern type 1 (according to Silverstone's classification with hollowing of prism centers) or type 2 (e.g. preferential dissolution of prism periphery) were only present in areas where the superficial aprismatic layer had been previously destroyed by physiological attrition during mastication or mechanically during pumicing. Surfaces conditioned with such acids reached only the second score in Sheykholeslam and Buonocore scale (e.g. SEM evaluation of the retentive capacity of etched enamel surfaces).

B. Enamel surfaces conditioned with ferric oxalate:

It is not necessary to separate samples treated with F.O. for either 1 or 2 min. because we observed no noticeable differences between these two groups.

– 5.3 w/w aqueous F.O. solution:

The attack of enamel surfaces was light with little surface roughness and porosity. F.O. by its own chemical action produced the crazing of the enamel's surfaces into many pieces. Some fragments were eliminated. It seems that, from the surface, by successive thin layers (the thickness of which was about 2 or 3 μm) the enamel was peeling off (Fig. 5 and 6).

In abraded areas, sometimes F.O. gave, as the response to acid-etching, regular patterns due to preferential dissolution of the prism's core (Fig. 7 and 8) but, generally, the attack of enamel's surfaces by F.O. was characterized by:

1. The attack at the cristallite level:

Prism structure was no more distinguishable, the treated surfaces appeared bristled, with innumerable spines (Fig. 9 and 10). For each surface morphological aspects were specially heterogeneous: islands of apparently unaltered enamel were seen admist areas of great changes.

2. Surface coating and crystal deposits:

On approximately half of the examined surfaces (70 about 142 areas for which photographs were taken) we observed crystal precipitations. Viewing by SEM does not reveal the chemical composition of these precipitates. From their morphological appearance they may be:

Fig. 5 - Area of the buccal surface of an upper right canine, from a middle-age man. The enamel surface had been pumiced then ferric oxalate was applied for 2 min. The attack of enamel was only slight. Superficial thin enamel's layers were completely disrupted. Remnants which look like bundles of crystallites are scattered out. It seems that the outer part of enamel was «peeling off». ⊢——⊣ = 10 μm.

Fig. 5 - Portion d'une face vestibulaire d'une canine supérieure (dent extraite chez un adulte). Application d'oxalate ferrique, pendant 2 mn. L'atteinte de l'émail est légère. La couche la plus superficielle est complètement désorganisée. Il persiste des résidus de cette couche superficielle sous forme de groupes de cristaux. ⊢——⊣ *= 10 μm.*

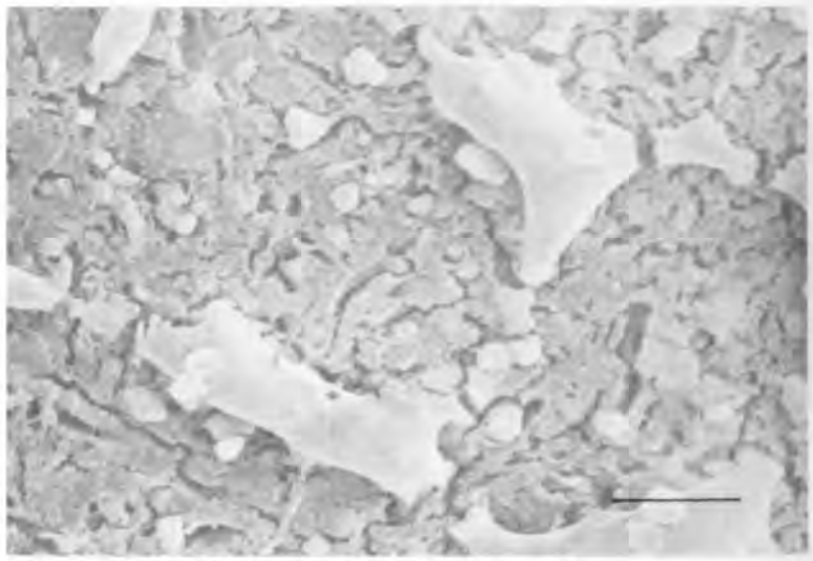

Fig. 6 - Pumiced enamel surface from a left third upper molar of a young man. The sample had been treated by ferric oxalate for 1 min. and soaked in acetone for 25 min. Islands of apparently unaltered enamel were laying on a rough and porous partly demineralized subsurface enamel. They may be remnants of the aprismatic enamel layer.
We can see some high calcium material similar to rice-like structures found on dentin. ⊢——⊣ = 5 μm.

Fig. 6 - Surface d'émail ayant appartenu à la 3e molaire d'un adulte jeune. Application d'oxalate ferrique, pendant 1 minute, sur surface poncée. Il reste de petites portions d'émail relativement inaltérées, reposant sur une couche sous jacente poreuse, partiellement déminéralisée. On peut voir des cristaux en forme de grains de riz.
⊢——⊣ *= 5 μm.*

Fig. 7 - Pumiced surface from a young first right premolar treated by ferric oxalate for 1 min. and then rinsed with 20 ml of distilled water. Exceptionally the enamel surface resembles the usual acid-etch pattern 1 with a preferential dissolution of the prism's core. We can see that a 20 ml water-rinsing is efficient to eliminate all the debris. ⊢——⊣ = 5 μm.

Fig. 7 - Email provenant d'une prémolaire prélevée chez un jeune patient. La surface simplement poncée a été traitée à l'oxalate ferrique pendant 1 mn. puis rincée avec 20 ml d'eau distillée. Cette surface présente un type 1 «d'etching». Le mordançage est, pour cet échantillon aussi efficace que celui obtenu pour des concentrations en H_3PO_4 de 37 ou 50%. Il faut signaler que ce résultat est exceptionnel par rapport au nombre d'échantillons traités. Le rinçage, effectué ici avec 20 ml d'eau distillée paraît efficace, tous les débris ont été éliminés. ⊢——⊣ = 5 μm.

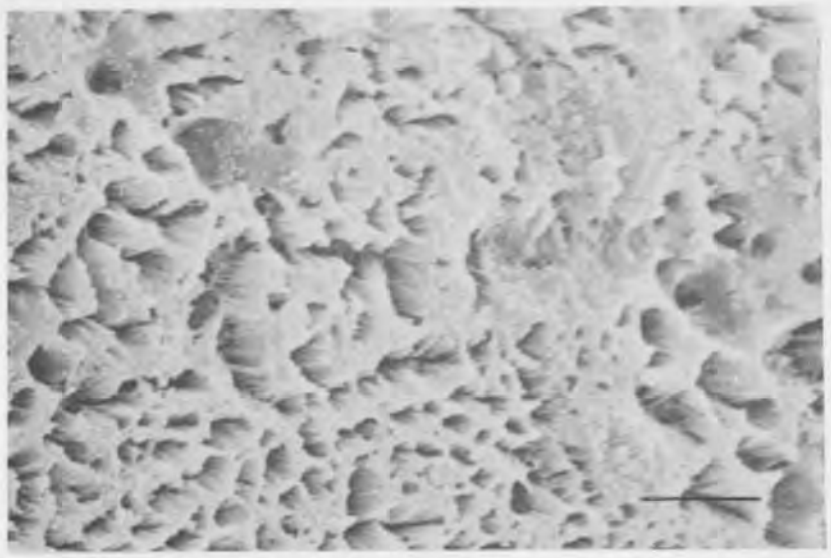

Fig. 9 - Pumiced surface from the buccal surface of a lower right first incisor of a middle-age woman. The sample had been treated by ferric oxalate for 2 min. F.O. had produced some microporosity. This surface seems able to produce some capacity of mechanical retention. ⊢——⊣ = 5 μm.

Fig. 9 - Surface d'émail poncée (face vestibulaire d'une incisive inférieure ayant appartenu à une femme d'âge moyen). Traitement à l'oxalate ferrique, 2 mn. Les microporosités ne sont pas associées à la structure prismatique. La surface apparaît néanmoins rétentive.

⊢——⊣ = 5 μm.

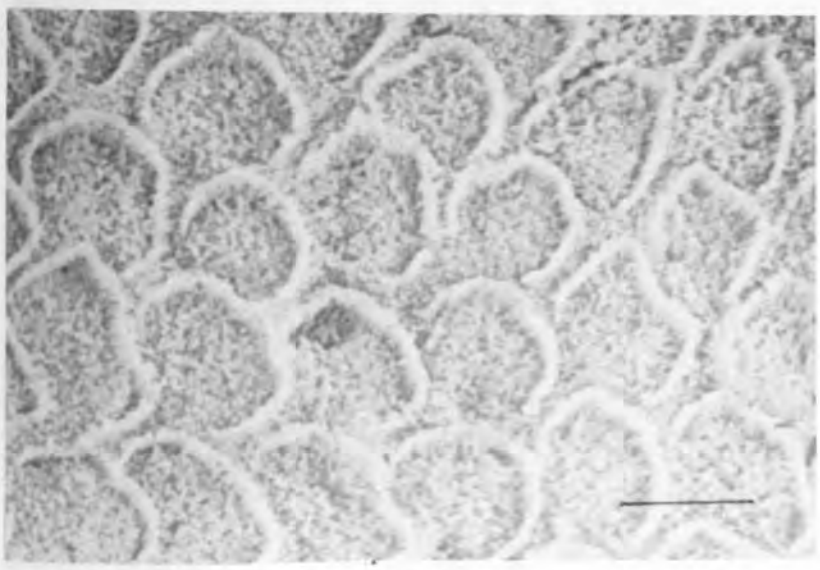

Fig. 8 - Area of the buccal surface of a left lower lateral incisor from a middle-age woman. The enamel had been pumiced, then treated by ferric oxalate for 1 min. and soaked in acetone baths. Attack of enamel was noticeable both at the prism and the crystallite levels. This enamel surface seems very clean and chemically activated. ⊢——⊣ = 5 μm.

Fig. 8 - Portion d'une face vestibulaire d'une incisive inférieure ayant appartenu à une femme d'âge moyen. La surface d'émail poncée a été traitée à l'oxalate ferrique pendant 1 mn. L'échantillon a été rincé dans des bains d'acétone. L'attaque de l'émail s'est effectuée aussi bien au niveau des prismes (type 1) que des cristallites. ⊢——⊣ = 5 μm.

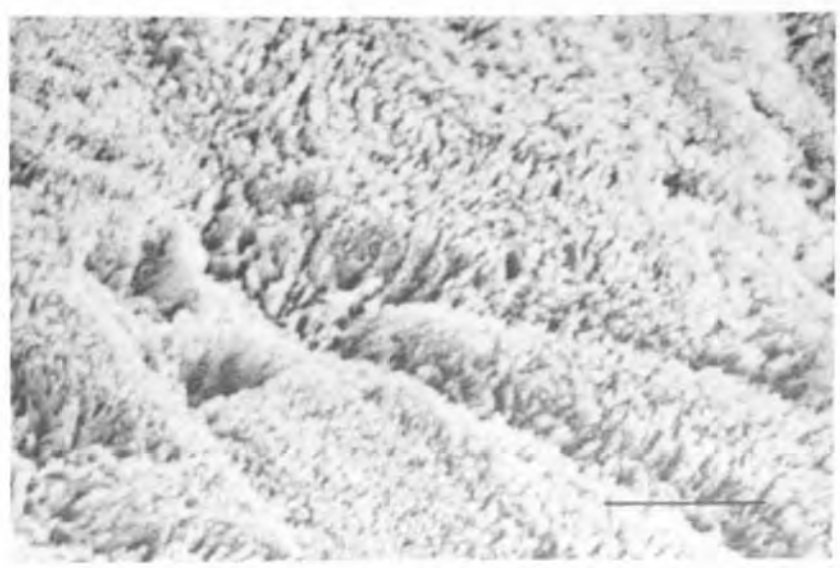

Fig. 10 - Pumiced surface from a right first upper incisor of an adult woman which had been treated with ferric oxalate for 1 min. The outlined crystallites got a bristled surface with innumerable spindles which seem able to produce some mechanical retention. ⊢——⊣ = 5 μm.

Fig. 10 - Surface poncée (incisive centrale supérieure ayant appartenu à une jeune adulte) traitée pendant 1 mn à l'oxalate ferrique. L'attaque de l'émail au niveau des cristallites produit une surface hérissée d'une multitude de petites aiguilles. ⊢——⊣ = 5 μm.

a. remnants of the aprismatic layer which has been destroyed by F.O. treatement (Fig. 11). The main part of the superficial enamel has been dissolved and eliminated during the rinsing step;

b. reprecipitation of dissolved materials under a different crystalline form. These crystals resemble:

– globular deposits scattered on the enamel surface or corpuscules tending to clump together (Fig. 12).

– needle-shaped crystals laying on a porous enamel, the structure of which was completely disrupted (Fig. 13),

– or, also, elliptical, clearly delineated crystals (Fig. 14). These crystals seem denser than the partly demineralized enamel structure to which they adhere. Besides these clearly apparent crystals different solubility tests (presented Fig. 4) allow to disclose the presence of a microscopic deposit (invisible by scanning electron microscopy) which is spread on the entire enamel surfaces. After soaking for 25 min. in acetone the surfaces appeared cleaner (Fig. 8).

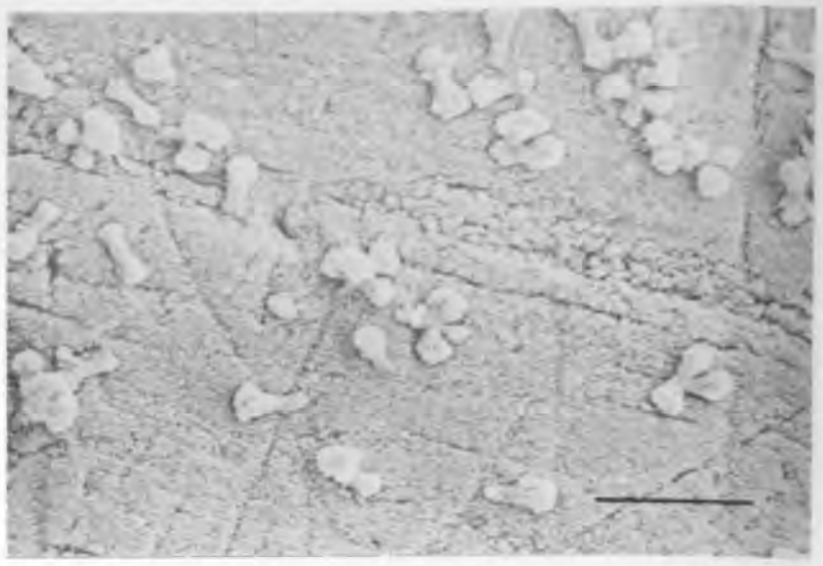

Fig. 11 - Area of the distal face of a first right upper molar from a young woman. The enamel sample had been pumiced, then treated by ferric oxalate for 1 min. A thin superficial enamel layer had been dissolved. Some structures which look like «bundles of cauliflower» were present at the enamel surface.

⊢——⊣ = 10 μm.

Fig. 11 - Portion d'une surface distale d'une 1e molaire (adulte jeune). Après ponçage, la surface a été traitée à l'oxalate ferrique, 1 mn. Ce traitement a entraîné la dissolution d'une fine couche d'émail superficiel. On peut observer un certain nombre de cristallisations en forme de choux-fleur. ⊢——⊣ *= 10 μm.*

– F.O. added to phosphoric or citric acid:

The addition of either phosphoric acid (2 mol/l) or citric acid (10% w/w) to F.O. did not enhance significatively roughness and microporosity of the enamel surfaces. But the simultaneous or successive use of acid and F.O. seems to produce:

a. a significant damage in the subsurface: under an apparently sound layer, sometimes only cracked, the combined acid solutions had penetrated deeper and disrupted the structure in the subjacent enamel (Fig. 15);

b. an increase in the crystal formation.

3. Crystal solubility:

For few years it has been claimed that crystal formation might be a better alternative to acid-etching to gain retention especially for enamel pretreatment in bracket bonding. But, a further dissolution in saliva can lead to marginal leakage and impair the quality of esthetic restorations. So, we have to test the solubility of the crystal formations obtained after F.O. conditioning. After the specimens were rinsed with either 5, 10 or 20 ml of distilled water or soaked in acetone for 25 min. crystals were still present.

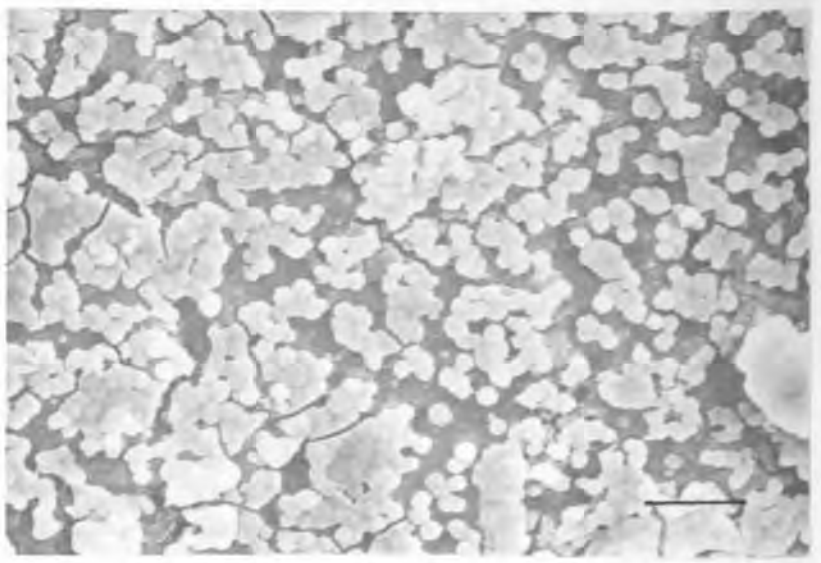

Fig. 12 - Pumiced enamel surface treated by F.O. for 1 min. The superficial enamel layer had been broken into many pieces. The dissolved mineral salts had got globules which can be isolated or which tended to clump together. ⊢——⊣ = 5 μm.

Fig. 12 - Surface d'émail poncée traitée à l'oxalate ferrique, 1 mn. La couche la plus superficielle de l'émail est éclatée en nombreux fragments. On peut observer de nombreuses cristallisations globulaires isolées ou par petits groupes. ⊢——⊣ *= 5 μm.*

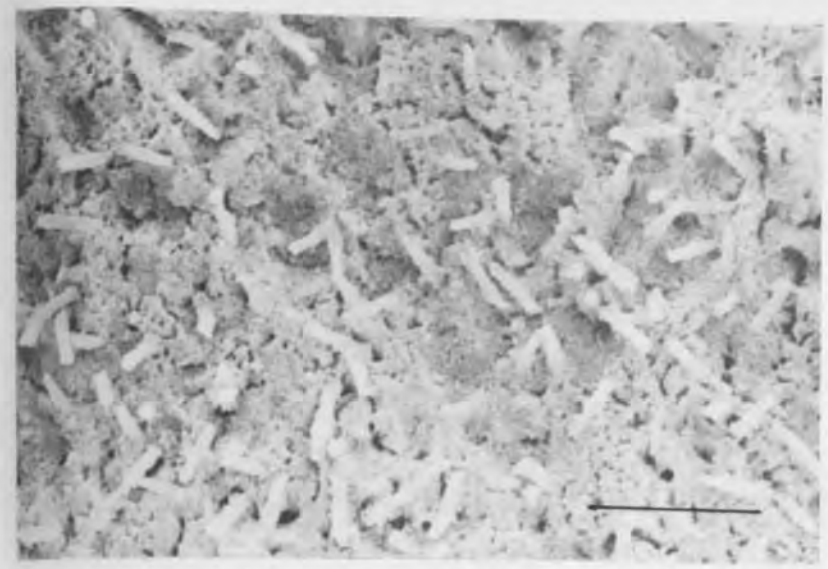

Fig. 13 - Buccal surface of a first upper right molar from a young man. This area was situated at the middle third of the crown. A 2 min. F.O. treatment had produced a partial demineralization of subsurface enamel. We can see needle-shaped crystals lying on a porous enamel. ⊢——⊣ = 10 μm.

Fig. 13 - Surface vestibulaire d'une 1e molaire (adulte jeune). Portion d'émail située au tiers moyen de la couronne. Le traitement à l'oxalate ferrique, 2 mn, a produit une déminéralisation de l'émail en subsurface. Présence de nombreux cristaux en forme d'aiguilles reposant sur une surface poreuse. ⊢——⊣ *= 10 μm.*

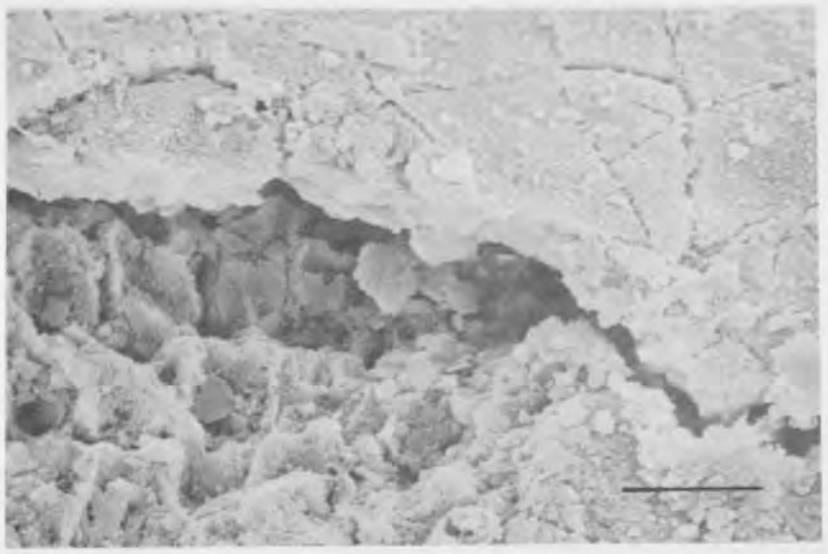

Fig. 15 - Under an apparently intact enamel's layer the acid solution had diffused and vigourously attacked the subsurface enamel. F.O. 2 min. on a pumiced enamel surface from the vestibular face of an upper right lateral incisor of a middle-age man.

⊢——⊣ = 10 μm.

Fig. 15 - Sous une couche d'émail relativement peu altérée, la solution acide a diffusé en subsurface. L'émail sous jacent est fortement atteint. F.O. 2 mn; surface poncée ayant appartenu à une surface vestibulaire d'une incisive latérale supérieure (adulte d'âge moyen).

⊢——⊣ *= 10 μm.*

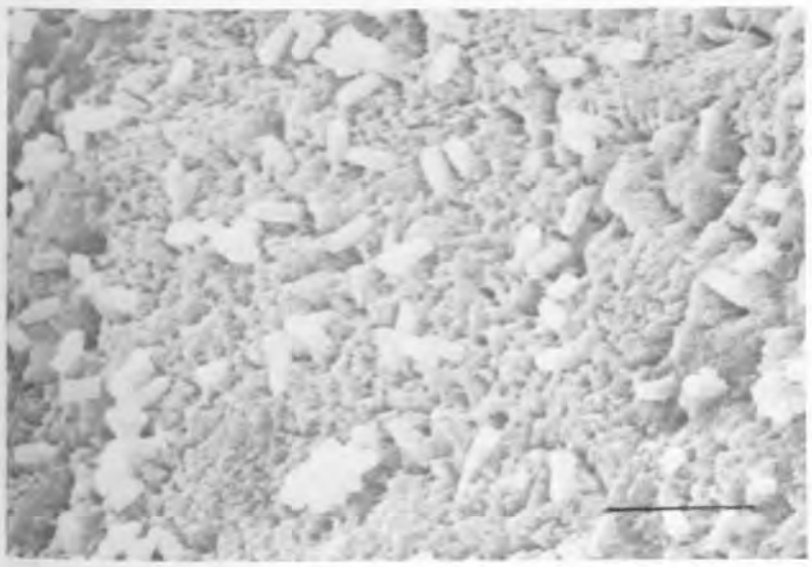

Fig. 14 - Area of a vestibular face of a left lower canine from an adult woman. The pumiced surface was treated by the combination of citric acid 10% w/w and ferric oxalate for 1 min. The superficial enamel's layer had been destroyed leaving a porous subsurface enamel on which were scattered dense, clearly delineated elliptical crystals. These crystals look like calcium precipitates described by some authors. ⊢——⊣ = 5 μm.

Fig. 14 - Face vestibulaire d'une canine inférieure (adulte jeune). La surface a été poncée puis traitée, pendant 1 mn, avec un mélange d'acide citrique et d'oxalate ferrique. La couche la plus superficielle de l'émail a été détruite faisant apparaître une surface rugueuse sur laquelle sont disposés de nombreux cristaux, très denses, de forme elliptique. ⊢——⊣ *= 5 μm.*

DISCUSSION

Ferric oxalate has been tested for two different uses: 1. Conditioning of pumiced enamel surfaces before brackets bonding in orthodontics and 2. to clean and enhance the roughness of instrumented tooth surfaces before composite restorations.

On pumiced surfaces neither acid etching nor ferric oxalate were 100% efficient in terms of prism hollowing. As far as SEM can tell us F.O. seems more able that citric or phosphoric acid to enhance the microporosity of enamel surfaces by two means:

a. creation of very numerous microscopic spindles by exposure of enamel cristallites and b. formation of crystals. This cristal formation may be of some interest after Smith and Catz (1973), Maijer and Smith (1977), Smith et al. (1980), Artun and Bergland (1984), Mac Phee et al. (1985), Maijer and Smith (1986) and Read et al. (1986) shown that such crystals may be considered as an efficient auxiliary retention.

In our study crystals were not dissolved by water or acetone. Oxalate crystals were considered as practically insoluble after the studies conducted by Greenhill and Pashley (1981), Bowen et al., (1982) and Pashley and Galloway, (1985).

Bowen (1985) saids that the effects on enamel, as observed by SEM, resemble that produced by etching with phosphoric acid solutions. Unfortunately, no micrograph was produced, nor was the concentration of H_2PO_4 known.

We observed that F.O. may produce a typical type 1 etching pattern on pumiced surfaces, but in our sample this preferential loss of prism's core occurs occasionaly. On abraded surfaces F.O. sometimes produces a typical etching pattern but, more often, the attack appears at the crystallite level.

Bowen (1978) observed that the surfaces treated with F.O. appear clean, without superficial debris. This is also the case in our study.

Although the ferric oxalate solution was colored, none of the treated surfaces had shown any change of its colour. This observation was also noticed by Bowen in its paper published in 1978.

Ferric oxalate has not yet acquired a commercial success in France but we think that further studies have to be continued. Ferric oxalate is less dangerous for the dentin that acid etchants and it appears as an attractive product because it can be used either on dentin and enamel.

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