

Aug. 7, 1973

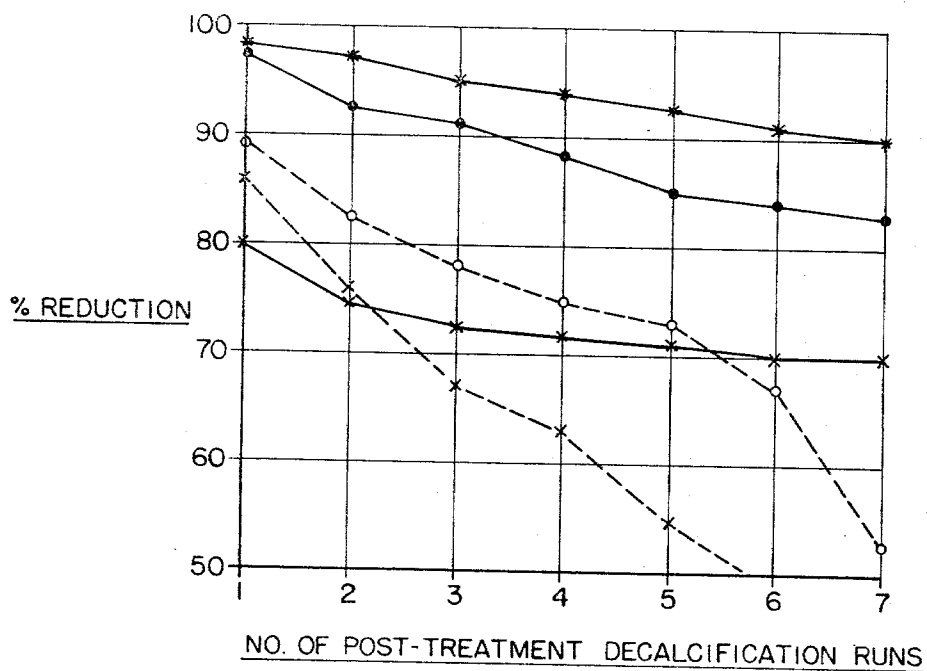
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3,751,568

METHOD OF COATING TEETH WITH A DURABLE GLAZE

Filed June 18, 1971

TOPICAL EFFECTS OF TiF_4 AND YbCl_3
ON ENAMEL SOLUBILITY REDUCTION



— $\text{TiF}_4 + \text{YbCl}_3$ ACIDULATED

●—● $\text{TiF}_4 + \text{YbCl}_3$

○---○ $\text{YbCl}_3 + \text{TiF}_4$

x--x YbCl_3 ACIDULATED

— TiF_4

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3,751,568

METHOD OF COATING TEETH WITH A DURABLE GLAZE

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Filed June 18, 1971, Ser. No. 154,360

Int. Cl. A61k 7/16

U.S. Cl. 424-131

14 Claims

ABSTRACT OF THE DISCLOSURE

Ytterbium chloride and acidified solutions thereof are applied topically to teeth either preceding or following the topical application of titanium tetrafluoride to increase the resistance thereof to dental caries. The acidified solution of ytterbium chloride, certain organic acids, such as formic acid, acetic acid and the like and their salts, and certain inorganic acids, such as, hydrochloric acid, form an aesthetically pleasing, durable fluoride glaze on the tooth surface when applied topically either following or preceding the topical application of titanium tetrafluoride.

BACKGROUND OF THE INVENTION

This invention relates to a method for the reduction of dental caries, and more particularly to a method of treating teeth by the topical application of a specified class of chemical agents.

Several chemical compounds have been reported for effectively reducing the solubility of tooth enamel and thereby reducing the incidence of dental caries. Among these compounds the fluorides, such as those disclosed by Norris et al. in U.S. 2,946,725, and especially stannous fluoride, are the best known. Tucker et al. in U.S. 3,175,951 also discloses treating teeth with certain fluoride-indium ion agents including an acidic aqueous solution of titanium tetrafluoride alone and in combination with indium chloride to reduce phosphate release from enamel surfaces. Other agents, such as dysprosium chloride and ceric nitrate have been topically applied to teeth by Manly and Bibby in J.D. Res. 28, 160 (1949). However, these agents and treatment methods are not characterized by extended durability, nor do they contribute extensively to the aesthetic appearance of the teeth to which they are topically applied.

OBJECTS OF THE INVENTION

Accordingly, it is an object of this invention to provide a method of coating teeth with chemical agents which impart a durable glaze to the tooth surface.

It is another object of this invention to provide a method of coating teeth with a durable glaze which enhances the aesthetic appearance of the teeth.

It is still another object of this invention to provide a method of coating teeth with chemical agents for caries prophylaxis wherein certain combinations of said chemical agents impart an aesthetically-pleasing, durable glaze on the surface of the teeth.

Other objects and advantages of this invention will become apparent from the following detailed description taken in connection with the accompanying drawings.

SUMMARY OF THE INVENTION

We have found that the application of titanium tetrafluoride on a tooth surface either followed by or preceded by treating said tooth surface with certain organic carboxylic acids, such as acetic acid and formic acid and the like and salts thereof, or certain inorganic acids such as hydrochloric acid and the like, produces unexpectedly

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a durable, aesthetically pleasing fluoride glaze on the tooth. We have also found unexpectedly that ytterbium chloride and acidulated ytterbium chloride applied topically to teeth either preceding or following the topical application of titanium tetrafluoride increases the resistance of the enamel to the incidence of dental caries, and that the acidulated ytterbium chloride also forms a durable, aesthetically pleasing fluoride glaze on the enamel of the teeth when applied before or after the topical application of titanium tetrafluoride. In the formation of the durable, aesthetically pleasing fluoride glaze on teeth by the topical application of titanium tetrafluoride it is critical that the titanium tetrafluoride be applied to the surface of the tooth prior to or following the application of the acidulated ytterbium chloride, the acids or the salts of the acids.

A durable glaze is defined as a long-lasting coating on the surface of the tooth which coating is capable of withstanding repeated exposure to acids and other substances normally having a corrosive or damaging effect on teeth and substances topically applied thereto. The coating is transparent and produces a smooth, glossy, lustrous finish on the surface of the tooth.

BRIEF DESCRIPTION OF THE DRAWING

The figure is a graphic representation of the topical effects of titanium tetrafluoride and ytterbium chloride on enamel solubility reduction.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred form of this invention which provides an aesthetically pleasing glaze on the tooth's surface and thereby provides improved reduction of enamel solubility, comprises the topical application of titanium tetrafluoride on the tooth surface followed by or preceded by the application of carboxylic acids such as certain monocarboxylic and dicarboxylic acids and derivatives thereof on the surface of the tooth. The titanium tetrafluoride and the organic acids or their salts are preferably applied to the tooth surface in the form of dilute aqueous solutions.

Examples of the monocarboxylic acids and salts and derivatives thereof suitable for use in coating the tooth surface with a durable, aesthetically pleasing fluoride glaze in accordance with this invention are formic acid, acetic acid, propionic acid, and trichloroacetic acid and the sodium, potassium and aluminum and magnesium salts thereof.

Examples of dicarboxylic acids and salts and derivatives thereof are glutaric acid, oxalic acid, malonic acid, maleic acid and the sodium, potassium, aluminum and magnesium salts thereof. Another carboxylic acid found useful in the present invention is citric acid. By carboxylic acids we mean the organic monocarboxylic and polycarboxylic acids containing at least one -COOH group. The salts of the carboxylic acid as used herein are the sodium, potassium, aluminum, and magnesium salts, such as, sodium citrate, sodium oxalate, magnesium citrate, sodium acetate, aluminum acetate and the like. All of these organic acids and their salts are capable of forming the protective, aesthetically pleasing glaze upon the tooth surface when they are applied either before or after at least one topical application of titanium tetrafluoride.

Although other fluoride compounds such as stannous fluoride, zirconium tetrafluoride, and sodium fluoride have been found useful in the reduction of enamel solubility, these fluorides do not produce the durable glaze of the present invention.

The durable glaze coating resulting from the treatment of the tooth surface with titanium tetrafluoride followed

by or preceding the application of the organic acids of this invention observed during the course of enamel solubility tests, appear on the tooth surface as a glassy coating which upon close examination reflected the colors of the spectrum from the surface. The glaze was produced on human teeth as well as on bovine enamel surfaces. The method of this invention also produces whiter enamel surfaces.

The pH of the titanium tetrafluoride solution used in the topical application must be less than 6.0 in order to produce the durable fluoride glaze of the present invention, and it is preferred that the pH of the titanium tetrafluoride solution be approximately 1.5 to 3.0. The pH of the organic acids or the salts thereof which may be in the form of a buffer should also have a pH of 8.0 or lower in order to produce the durable, aesthetically pleasing glaze of the present invention. In the preferred form of this invention the pH of the organic acid or its salt is approximately 2 to 5.

The titanium tetrafluoride solution is generally applied at a concentration of 0.05 to 1.0 percent (by weight) and may be applied in the form of an aqueous solution having a concentration as high as 2.0%. Although titanium tetrafluoride having higher concentrations may be applied to the tooth surface, additional reduction of solubility is not achieved thereby. The topical application of the titanium tetrafluoride may be from one-half minute to fifteen minutes and preferably for two to five minutes, depending upon the concentration of the titanium tetrafluoride used for the topical application.

The organic acids and the derivatives and salts thereof which may be in the form of a buffer, may be applied to the tooth surface at a concentration of 0.1 mole to 3.0 moles and preferably from about 0.1 mole to 1.0 mole. The topical application of the organic acid such as acetic acid, or the salts thereof such as the sodium formate, may be applied to the tooth surface from one-half minute to fifteen minutes and preferably for two to five minutes, depending upon the concentration of the acid or the salt.

Other adjuvants may be added in admixture with the titanium tetrafluoride and the organic acid or the salts or derivatives thereof, or may be added in steps preceding or following the application of the titanium tetrafluoride or the organic acids or salts thereof, as long as such adjuvants do not interfere with the coating of the tooth surface with the durable fluoride glaze of the present invention. It is considered within the scope of the present invention to apply combinations of the organic acids to the tooth surface either before or after or both before and after at least one topical application of titanium tetrafluoride.

In another embodiment of our invention we have found that there is improved reduction of enamel solubility and the formation of an aesthetically pleasing glaze on the tooth surface when certain inorganic acids are applied to the tooth surface either following or preceding the topical application of titanium tetrafluoride. The titanium tetrafluoride is topically applied at concentrations and pH as described above. Examples of the inorganic acids which are useful in this embodiment, are diluted hydrochloric, phosphoric, molybdic and sulfuric acids. The inorganic acids may be applied to the tooth surface in the form of an aqueous solution at a pH of about 1.0 to about 6.5 and at a concentration of 0.05 to 10%. Other adjuvants which do not inhibit or reduce the glaze, may also be used with the titanium tetrafluoride and inorganic acids.

In another embodiment of our invention we have found that the topical application of ytterbium chloride to the surface of a tooth reduces enamel solubility when used in conjunction with at least one topical application of titanium tetrafluoride. We have also found that the durability increases greatly when the ytterbium chloride is acidulated. When acidulated ytterbium chloride is topically applied to the tooth surface, the enamel solubility reducing effects not only increase but also persist through a

greater number of decalcifications. Acidulated ytterbium chloride is ytterbium chloride which has been made more acidic by the addition of an acid, for example, acetic acid, hydrochloric acid and the like.

It is believed that the enamel solubility reducing effect of ytterbium chloride is primarily due to ytterbic hydroxide formation. These hydroxides may be bound with the enamel apatite crystal in the tooth. Some of the replaced OH^- , which might be present in the fluid of the inter-crystallite spaces, may combine with the Yb^{+3} or Yb^{+2} to form insoluble ytterbic hydroxide, resulting in an increase in the density of the enamel, which in turn, may prevent the diffusion of acid into the enamel.

The acidulated ytterbium chloride forms a durable, aesthetically pleasing fluoride glaze coating on the surface of the tooth when applied in conjunction with titanium tetrafluoride. The topical application of the titanium tetrafluoride followed by or preceded by or preceded by and followed by the topical application of the acidulated ytterbium chloride produces a glassy coating which is defined herein as a glaze, said glaze having a relatively long-lasting effect when compared to treatment with titanium tetrafluoride alone. The titanium tetrafluoride is applied to the surface of the tooth as described previously. The acidulated ytterbium chloride is applied to the surface of the tooth in the form of an aqueous solution for a period of 0.5 to 15 minutes and preferably for two to five minutes depending upon the concentration of the ytterbium chloride. Acidulated ytterbium chloride may be applied at a concentration of about 0.5% (by weight) to about 3.0% by weight. The effectiveness of the acidulated ytterbium chloride levels off at about 3.0% and concentrations higher than 3.0% produce solubility reductions which are no better than those produced from 3.0% acidulated ytterbium chloride. Although application of the acidulated ytterbium chloride and the titanium tetrafluoride, in the reverse order, that is, acidulated ytterbium chloride followed by titanium tetrafluoride, produces reduced enamel solubility and forms a glaze on the surface of the tooth, the durability of the glaze and the solubility reductions are not as persistent as those obtained by the application of the titanium tetrafluoride followed by the topical application of the acidulated ytterbium chloride on the tooth surface.

Ytterbium chloride may be acidulated by the addition of any of the inorganic acids such as hydrochloric acid, sulfuric acid or nitric acid or it may be acidulated by an organic acid such as acetic acid. The pH of the acidulated ytterbium chloride may be from 2.0 to 6.0 and is preferably about 2.6 to 3.5. The pH of the ytterbium chloride (non-acidulated) at a concentration of 1.5 percent by weight in an aqueous solution is 5.35 and may be applied to the surface of the tooth at a pH of less than 6.0.

Although the results reported herein are in the form of measurements which determine enamel solubility, the results may be construed in terms of incidence of dental caries by one skilled in the art due to the fact that enamel solubility is directly related to the incidence of dental caries. The resistance of the enamel to solution in acid tends to lower the incidence of dental caries. Accordingly, enamel solubility reductions as reported herein are deemed an indication of the effectiveness of our invention in the prevention of caries.

It is to be understood that the fluoride process of this invention wherein a durable, aesthetically pleasing glaze is coated on the tooth, comprises at least one titanium tetrafluoride topical application and at least one topical application of at least one organic acid, a salt thereof, an organic acid buffer, an inorganic acid or acidulated ytterbium chloride or combinations thereof. It is within the scope of the present invention to provide a three, four or multi-step process by applying various of the agents of this invention in successive steps. The agents of this invention may be applied either before or after or, before and after the topical application of titanium tetrafluoride.

Although the length of time of any particular process step, that is, the length of time for the topical application of an agent in a single step, is generally within 0.5 to 15 minutes, the actual length of time for topical application is dependent upon the concentration of the chemical agent applied, and also varies as to the particular agent. The length of time for topical applications may also be made dependent upon the desired thickness or aesthetic properties of the glaze produced thereby. Enamel solubility reduction, as well as glaze, may be increased by increased time of exposure to or topical application of the chemical agents of this invention.

Generally the pH of the agents of this invention which are topically applied to teeth, are acidic in nature and have a pH from 1.0 to 6.0. However, we have found that certain near neutral buffers and salts of the monocarboxylic acids produce a durable, aesthetically pleasing glaze when applied in conjunction with titanium tetrafluoride, and accordingly, the pH of the chemical agents may also be as high as 8.5 and still produce a suitable glaze. Such buffer solutions as acetic acid-sodium acetate, acetic acid-aluminum acetate and the like, have been found useful in the present invention, and accordingly, buffer as used herein means the solution of a weak acid and the salt of that acid.

EXAMPLES

Enamel solubilities for the present invention were conducted in accordance with a method described as the window technique. Adult bovine incisor teeth were used in making enamel blocks. The teeth were obtained from local abattoirs and were stored in a freezer. Only adult bovine teeth with clean, smooth labial surfaces, free from internal stains, caries, cracks or fissures were used. The roots were cut off at the neck near the cemento-enamel junction and the pulp chambers were cleaned. The crowns were sectioned mesio-distally into labial and lingual halves by means of a thin sectioning machine under running water. The labial halves were then ground with a plaster grinding machine under running water into roughly circular blocks of approximately one centimeter in diameter. The blocks were stored in distilled water in a refrigerator.

The inner or dentinal surfaces of the blocks were roughened by means of a bar under water spray and dried. Three inch long plastic rods, one quarter inch in diameter, were fixed to the inner surfaces of the blocks by a cold-curing acrylic resin. The rods were placed as centrally as possible and at right angles to the enamel surfaces of the blocks.

Windows were made on the individual blocks prior to use. The enamel surfaces were smoothened with sandpaper discs followed by rubber-cup pumicing. This was done in order to remove extraneous material, including coronal cementum, as well as to eliminate irregularities on the enamel surfaces. The blocks were thoroughly washed with distilled water and dried. Circular pieces of masking tape were cut with a paper punch using the same punch for every window. One of these paper discs was fixed on each of the prepared enamel surfaces. The surrounding portions of the enamel blocks were then carefully coated with nail varnish to give a uniform thin, bubble-free layer. After the varnish was thoroughly dried the circular pieces of the tape were carefully removed without chipping the varnish margins. The exposed enamel windows were then examined carefully for any flaws in the margins. Any windows with loose coatings or chipped margins were discarded. This technique made it possible to expose the same area of the enamel surface in all experiments thereby giving more comparable results between experimental runs.

Solubility measurements were made by measuring enamel dissolution resulting from the spinning of the window enamel blocks in an acid medium. All tests were conducted at a constant temperature of 37° C. The test

block was completely submerged in an acid solution, and the submerged block was attached to a motor by means of the plastic rod and rotated at a speed of 3450 r.p.m. The acid (generally acetic acid) solution was analyzed for phosphorous in order to determine the enamel dissolution. The percent enamel solubility reduction is expressed as

$$\frac{B-C}{B \times 100}$$

where B is the amount of phosphorous determined before the treatment and C is the amount of phosphorous determined after the treatment. Aliquots from different experiments were taken at random and were analyzed for both calcium and phosphorous content. Calcium-phosphorous ratios (Ca/P) in all the samples were found to be fairly close to the normal value of 2.15. Therefore, for the sake of convenience and time only phosphorous contents of the aliquots were used as the base lines in determining enamel dissolution.

To test the effects of applying agents topically to the tooth surface in a manner resembling that used in a clinical treatment, windows were prepared as above and given two pretreatment decalcification runs (A and B) in an acid buffer, such as acetic acid at pH 4.0. After washing in water the windows were dried and the test solutions were applied topically with cotton swabs, rubbing gently on the enamel surfaces. Repeated applications of the solution were made by using the same cotton swabs. Generally, two or five minute applications of the test solutions were made. The excess solution was blotted off with tissue and the window was washed in distilled water. A post-treatment decalcification run (C) was then carried out as described above in the acid buffer solution.

The durability or lasting protective effects of the various agents against enamel decalcification by acids was determined by running successive post-treatment decalcification runs. Generally, seven successive post-treatment decalcification runs were carried out on each tooth surface. In some cases, several windows were prepared on a single tooth, and each window was exposed to series of runs before the other windows were exposed to a series of similar tests. The multiple window technique provides identical enamel surfaces for testing in accordance with this invention.

Phosphorous was determined by a spectrophotometric technique as described on page 1626 of Volume 27 of Analytical Chemistry (1955). This technique involves the development of a yellow molybdovanadophosphoric acid complex which is then read spectrophotometrically.

The following examples illustrate more clearly the principles and practice of the present invention to those skilled in the art.

EXAMPLE I

A window was prepared on a bovine incisor according to the procedure set forth above. A 1.0% aqueous solution of titanium tetrafluoride having a pH of 1.65 was topically applied to the surface of the tooth in the area of the window. Seven successive post-treatment decalcification runs were conducted following a single topical treatment of the enamel surface with titanium tetrafluoride alone for two minutes. The enamel solubility was based upon the amount of phosphorous dissolved before and after the topical application of the titanium tetrafluoride. The results are set forth in Table I below and in the graph set forth in the figure.

EXAMPLE II

Ytterbium chloride ($\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$) in a 1.5% by weight aqueous solution having a pH of 5.35 was applied to the

exposed window of a bovine incisor as described above, and the enamel solubility reduction was determined in seven successive post-treatment decalcification runs following a five minute topical treatment with ytterbium chloride. The results based upon the amount of phosphorous dissolved before and after the treatment with ytterbium chloride are shown in Table I below. Although ytterbium chloride has an enamel solubility reducing effect, it can be seen that it does not exert a prolonged protective effect and therefore, does not have the durable characteristics of the other agents described by our invention. Negative values for runs 5-7 indicate that decalcification is greater than if no ytterbium chloride had been used at all.

EXAMPLE III

The pH of a 1.5% by weight aqueous solution of ytterbium chloride was adjusted to 3.5 with dilute hydrochloric acid. This acidulated ytterbium chloride was applied to the surface of a bovine incisor in the area of the window prepared in accordance with the procedure set forth above. The enamel solubility reduction was determined for seven successive post-treatment decalcification runs following a five minute topical treatment with the acidulated ytterbium chloride. The enamel solubility was based upon the amount of phosphorous dissolved before and after the treatment. The results of this example are set forth in Table I below and in the graph set forth in the figure. An analysis of the data shows that the acidulated ytterbium chloride was not only more effective than non-acidulated ytterbium chloride in reducing enamel solubility, but that it also exerted a more prolonged protective effect.

effect in the sixth and seventh post-treatment decalcification runs.

EXAMPLE V

Titanium tetrafluoride and ytterbium chloride were applied under the conditions and concentrations set forth in Example IV except the sequence of the order of the application of the agents was reversed. The enamel solubility reduction, based on the amount of phosphorous dissolved before and after the treatment, in seven successive post-treatment decalcification runs wherein titanium tetrafluoride was topically applied for two minutes and ytterbium chloride was topically applied for three minutes is given in Table I below and in the graph in the figure. When compared with the enamel solubility reduction produced by titanium tetrafluoride alone, the titanium tetrafluoride-ytterbium chloride treatment shows substan-

EXAMPLE VI

Titanium tetrafluoride (1.0%, pH 1.65) was applied to the surface of the bovine incisor at the area of the window and was followed by the application of a 1.5% aqueous solution of ytterbium chloride as in Example V with the exception that the ytterbium chloride was acidulated with dilute hydrochloric acid to a pH of 3.5 as disclosed in Example III. The enamel solubility reduction based upon the amount of phosphorous dissolved before and after the treatment was determined for seven successive post treatment decalcification runs. The results are set forth in Table I below and in the graph set forth in the figure. The tooth surface was not washed between applications of the agents. Significantly higher enamel solubility reduction and prolonged effectiveness were obtained.

TABLE I.—ENAMEL SOLUBILITY REDUCTION IN SEVEN SUCCESSIVE POST-TREATMENT DECALCIFICATION RUNS

Agent	Application time (minutes)	Percent solubility reductions						
		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
TiF ₄ (Ex. I)	2	80	75	73	72	71	70	70
YbCl ₃ (Ex. II)	5	54	40	15	0	-5	-9	-15
Acidulated YbCl ₃ (Ex. III)	5	86	76	67	63	54	45	39
YbCl ₃ and TiF ₄ (Ex. IV)	3, 2	89	83	78	75	73	67	53
TiF ₄ and YbCl ₃ (Ex. V)	2, 3	97	93	91	88	85	84	83
TiF and acidulated YbCl ₃ (Ex. VI)	2, 3	98	97	95	94	93	91	90

¹ A distinctive aesthetically-pleasing glaze was obtained on the tooth surface in Example VI.

EXAMPLE IV

A window prepared on a bovine incisor according to the procedure set forth above was treated with a 1.5% aqueous solution of ytterbium chloride having a pH of 5.35. A 1.0% by weight aqueous solution of titanium tetrafluoride having a pH of 1.65 was applied to the tooth surface in the area of the window following treatment with ytterbium chloride. The enamel solubility reduction was determined for seven successive post-treatment decalcification runs. The ytterbium chloride was applied to the tooth surface for three minutes, and the titanium tetrafluoride was applied to the tooth surface for two minutes. The enamel solubility reduction for the seven successive post-treatment decalcification runs is shown in Table I below and in the figure. An examination of the graph set forth in the figure indicates a substantial loss of protective

EXAMPLE VII

Tests were conducted on the effect of enamel solubility and glaze relationship for titanium tetrafluoride and various acids, buffers and salts. These are set forth in Table II below. The glaze studies were conducted on both bovine and human incisors. The enamel solubilities were conducted essentially as described above by using the window technique with the exception that the acid solution was stirred and the tooth was in a fixed position as opposed to the rotation of the tooth in Examples I-VI above. The time of exposure and concentration of the reagents is set forth in Table II below. In Table II the agent first designated was applied first followed by topical application of the second-named agent. Five successive solubility reduction runs were conducted in the first and second set of tests. The glaze determination was made by visible inspection of the surface of the tooth following treatment thereof.

TABLE II.—ENAMEL SOLUBILITY AND GLAZE RELATIONSHIP

Agents ¹	Conc. (percent by wt.)	Time of exposure (minutes)	Glaze ²	Percent solubility reduction in acetic acid				
				Run 1	Run 2	Run 3	Run 4	Run 5
TiF ₄ (1.65).....	1	5	+++	89	83	79	77	76
Acetic acid (4.0).....	0.1M	5						
HCl (2.0).....	8	2	+++	91	83	78	75	71
TiF ₄ (1.65).....	1	2						
TiF ₄ (1.65).....	1	5	+++					
HCl (2.0).....	8	5						
TiF ₄ (1.65).....	1	5	+++					
Formic acid (4.0).....	0.1M	5						
TiF ₄ (1.65).....	1	5	0					
TiF ₄ (1.65).....	1	5						
Lactic acid (4.0).....	0.1M	5	0					
YbCl ₃ (5.35).....	1.5	5						
YbCl ₃ acidulated (3.5).....	1.5	5	0					
TiF ₄ (1.65).....	1	5						
Aluminum acetate buffer (4.3).....	1	2	+++					
TiF ₄ (1.65).....	1	3						
Sodium acetate buffer (7.45).....	2	5	+++					
TiF ₄ (1.65).....	1	5						
YbCl ₃ acidulated acetic acid (3.5).....	1.5	2	++					
TiF ₄ (1.65).....	1	2						
YbCl ₃ acidulated acetic acid (2.65).....	1.5	3	+++					
TiF ₄ (1.65).....	1	2						
YbCl ₃ acidulated with HCl (3.5).....	1.5	3	+++					
TiF ₄ (1.65).....	1	5						
Propionic acid (4.1).....	0.1M	5	++++					
TiF ₄ (1.65).....	1	5						
Glutaric acid (4.0).....	0.1M	5	++++					
TiF ₄ (1.65).....	1	5						
Citric acid (3.95).....	0.1M	5	+++					
TiF ₄ (1.65).....	1	5						
Trichloroacetic acid (4.0).....	0.1M	5	+++					
TiF ₄ (1.65).....	1	5						
Sulfuric acid (3.85).....	0.1M	5	+++					
TiF ₄ (1.65).....	1	5						
Sodium citrate (8.35).....	1	5	+++					
TiF ₄ (1.65).....	1	5						
Sodium oxalate (7.15).....	1	5	+++					
TiF ₄ (1.65).....	1	5						
Oxalic acid (4.15).....	0.1M	5	++					
TiF ₄ (1.65).....	1	5						
HNO ₃ (4.45).....	0.1M	5	++					
TiF ₄ (1.65).....	1	5						
H ₂ PO ₄ (4.7).....	0.1M	5	++					
TiF ₄ (1.65).....	1	5						
Molybdic acid (5.35).....	0.1M	5	++					
TiF ₄ (1.65).....	1	5						
Magnesium citrate (5.2).....	1.0	5	++					
TiF ₄ (1.65).....	1	5						
Malonic (3.85).....	0.1M	5	+					
TiF ₄ (1.65).....	1	5						
Maleic (4.1).....	0.1M	5	+					
TiF ₄ (1.65).....	1	5						
Glutamic acid (3.85).....	0.1M	5	0					
TiF ₄ (1.65).....	1	5						
Perchloric acid (4.6).....	0.1M	5	0					

¹ Numbers in parenthesis after each agent represent the pH of the solution used in the topical application.

² An excellent glaze on the tooth surface is designated by +++. A good glaze on the tooth surface is designated by ++. A fair glaze is designated by +. Slight glaze is designated by +. No glaze is designated by 0.

An analysis of Table II indicates that several organic acids such as acetic acid, formic acid, propionic acid, glutaric acid, citric acid, trichloroacetic acid and certain salts thereof, such as sodium acetate, produce a good or excellent fluoride glaze when topically applied to teeth which are also treated with titanium tetrafluoride. Tooth surfaces treated with titanium tetrafluoride and acetic acid and tooth surfaces coated with titanium tetrafluoride and hydrochloric acid demonstrated acceptable solubility reductions. Titanium tetrafluoride alone and titanium tetrafluoride in conjunction with lactic acid, glutamic acid and perchloric acid do not produce a glaze on the tooth surface. Ytterbium chloride used alone or acidulated does not produce a glaze, but when used in conjunction with titanium tetrafluoride, acidulated ytterbium chloride produces a good-excellent glaze on the tooth surface, depending upon the pH. Other acids and salts shown in Table II demonstrate good or slight fluoride glazes on the tooth surface when used with titanium tetrafluoride application.

When glazed teeth were compared with non-glazed teeth, it was also observed that the enamel on the glazed teeth was whiter in appearance, and light shining upon

the surface of the glazed tooth appeared to separate faintly into the colors of the spectrum. The enhanced whiteness, appearance of the colors of the spectrum and the glaze produced an aesthetically pleasing effect on the tooth surface.

The percent enamel solubility reduction for seven successive post-treatment decalcification runs of the 2 minute topical application of titanium tetrafluoride alone (from Example I) and the percent enamel solubility reduction of the 2 minute topical application of titanium tetrafluoride followed by a 3 minute topical application of acidulated ytterbium chloride (from Example VI) can be compared in the graph of the figure. The effects of the topical treatments of the titanium tetrafluoride and acidulated ytterbium chloride are superior to titanium tetrafluoride alone.

The above examples are not meant to limit the scope of the invention or the applications to which this invention may be directed. It is to be understood that although the invention has been described with specific reference to particular embodiments thereof it is not to be so limited, since changes and alterations therein may be made which are in the full intended scope of the invention as defined by the appended claims.

We claim:

1. A method of forming an aesthetically pleasing durable glaze on a tooth surface for improving the resistance of said surface to dental caries comprising topically applying in separate steps to said tooth surface for a sufficient time to produce the desired glaze titanium tetrafluoride having a concentration of at least about 0.05% (by weight) and at least one carboxylic acid selected from the group consisting of formic acid, acetic acid, trichloroacetic acid, propionic acid, oxalic acid, malonic acid, glutaric acid, citric acid and maleic acid and the sodium, aluminum, potassium and magnesium salts thereof, said carboxylic acid having a concentration of about 0.1 mole to about 3.0 moles.

2. A method in accordance with claim 1 wherein said titanium tetrafluoride is applied at concentrations from about 0.05% to about 2.0% (by weight).

3. A method in accordance with claim 1 wherein titanium tetrafluoride and said carboxylic acid are each applied to the tooth surface for about 0.5 minute to about 15 minutes.

4. A method of forming an aesthetically pleasing, durable fluoride glaze on a tooth surface for improving the resistance of said surface to dental caries comprising topically applying in separate steps to said tooth surface for a sufficient time to produce the desired glaze titanium tetrafluoride having a concentration of at least about 0.05% (by weight) and at least one inorganic acid selected from the group consisting of hydrochloric acid, phosphoric acid, sulfuric acid and molybdic acid, said inorganic acid having a concentration of about 0.05% to about 10.0% (by weight).

5. A method in accordance with claim 4 wherein said titanium tetrafluoride is applied at concentrations from about 0.05% to about 2.0% (by weight).

6. A method in accordance with claim 4 wherein titanium tetrafluoride and said inorganic acid are each applied to the tooth surface for about 0.5 minute to about 15 minutes.

7. A method of forming an aesthetically pleasing, durable fluoride glaze on a tooth surface for improving the resistance of said surface to dental caries, comprising topically applying in separate steps to said tooth surface for a sufficient time to produce the desired glaze titanium tetrafluoride having a concentration of at least about 0.05% (by weight) and acidulated ytterbium chloride having a concentration of at least about 0.5% (by weight).

8. A method in accordance with claim 7 wherein said titanium tetrafluoride is applied at concentrations of about 0.05% to about 2.0% (by weight) and acidulated ytterbium chloride is applied at concentrations of about 0.5% to about 3.0%.

9. A method in accordance with claim 7 wherein said titanium tetrafluoride and said acidulated ytterbium chloride are each applied to the tooth surface for about 0.5 to about 15 minutes.

10. A method of reducing the solubility of tooth enamel to improve the resistance of the tooth surface to dental caries comprising topically applying to said surface for at least about 0.5 minute a compound selected from the group consisting of ytterbium chloride and acidulated ytterbium chloride, said compound having a concentration of at least about 0.5% (by weight).

11. A method in accordance with claim 10 wherein the concentration of the ytterbium chloride and acidulated ytterbium chloride is from about 0.5% to about 3.0%.

12. A method in accordance with claim 10 wherein said ytterbium chloride and acidulated ytterbium chloride are applied to the tooth surface for about 0.5 to about 15 minutes.

13. A method of forming an aesthetically pleasing, durable fluoride glaze on a tooth surface for reducing the enamel solubility thereof and thereby improving the resistance of said surface to dental caries comprising topically applying in separate steps to said tooth surface for a sufficient time to produce the desired glaze about 0.05% to about 2.0% (by weight) aqueous titanium tetrafluoride solution and at least one glazing agent selected from the group consisting of formic acid, acetic acid, trichloroacetic acid, propionic acid, oxalic acid, malonic acid, glutaric acid, citric acid, maleic acid, and the sodium, aluminum, potassium and magnesium salts thereof, hydrochloric acid, phosphoric acid, sulfuric acid, molybdic acid and acidulated ytterbium chloride; said formic acid, acetic acid, trichloroacetic acid, propionic acid, oxalic acid, malonic acid, glutaric acid, citric acid, maleic acid and the sodium, aluminum, potassium and magnesium salts thereof applied at concentrations of about 0.1 mole to about 3.0 moles at a pH of about 1.0 to about 8.5; said hydrochloric acid, phosphoric acid, sulfuric acid and molybdic acid applied at concentrations of about 0.05% to about 10% (by weight) at a pH of about 1.0 to about 6.5 and said acidulated ytterbium chloride applied at a concentration of about 0.5% to about 3.0% (by weight) at a pH of about 2.0 to about 6.0.

14. A method in accordance with claim 13 wherein titanium tetrafluoride and said glazing agent are each applied to the tooth surface for about 0.5 minute to about 15 minutes.

No references cited.

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U.S. Cl. X.R.

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