Color stability and colorant effect on maxillofacial elastomers. Part II: Weathering effect on physical properties

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Statement of problem. The clinical life of a maxillofacial prosthesis averages about 6 months, before it needs to be refabricated. Degradation of the color and physical properties of the prosthesis are the principle reasons for replacement.
Purpose. This second part of a 3-part in vitro investigation evaluated the change in physical properties of popular colorant-elastomer combinations as a result of weather exposure.
Material and methods. Fifteen dumbbell-shaped and 15 trouser-shaped specimens were fabricated for each of the 3 elastomers (Silastic medical adhesive type A, Silastic 4-4210, and Silicone A-2186) and 6 colorant combinations (dry earth pigments, rayon fiber flocking, artist's oil paints, kaolin, liquid cosmetics, and no-colorants) for a total of 540 specimens. The 15 dumbbell-shaped and trouser-shaped specimens of each elastomer colorant combination were separated into 5 of each shape among 3 test condition groups (control, time passage, and natural weathering). Control specimens were evaluated within 1 month of fabrication. The time passage group was sealed in glass containers and kept in the dark for 6 months before testing. The natural-weathering groups were placed on the roof of the dental school for 6 months and exposed to sunlight and weathering. Evaluations of hardness and tear strength were made on trouser-shaped specimens, and evaluations of the ultimate tensile strength and percentage elongation on dumbbell-shaped specimens. Physical property data for each elastomer-colorant combination were subjected to a 1-way analysis of variance to examine effects among the test conditions. When significant differences were observed, the Student-Newman-Keuls multiple range test was performed to identify differences in elastomer-colorant combinations among each test condition at a significance level of .05.
Results. Exposure to weathering and time changes of the physical properties of many colorant-elastomer combinations indicated that properties of a clinical prosthesis can change with time.
Conclusion. The addition of colorants to the silicones altered the effects of weathering. In addition, the silicones were not as stable as previously assumed. (JProsthet Dent 1999;81:423-30.)

CLINICAL IMPLICATIONS

The clinician must keep in mind that the physical properties of the elastomers used to fabricate maxillofacial prostheses can change with time. Also, when possible, avoid colorants that contain components that can leach out or evaporate over time and exacerbate the problem of physical property changes.

Barnhart[1] introduced the use of silicone elastomers for facial prostheses in 1960. Because of the material's clinical inertness, strength, durability, and ease of manipulation, silicone elastomers have become the material of choice for maxillofacial prostheses.[2] The maxillofacial prosthodontist's primary goal is to restore the patient's appearance, improve their self-esteem, and help them lead as normal a life as possible. It is critical that the prosthesis be fabricated with optimal esthetics and physical properties and for maintenance of its properties over its service lifetime. The most common reason for refabrication of facial prostheses is degradation of color and physical properties.

Yu and Koran[3] studied permanent deterioration of 4 silicones before and after accelerated aging; however, most of these materials are no longer in popular use.[2] Yu et al[4] evaluated ultimate tensile strength, percentage elongation, shear strength, tear energy, and shore A hardness of 4 silicones after accelerated aging and found Silastic 4-4210 adhesive (Dow Corning Corp, Midland, Mich.) was the best choice of materials.

Wiens[5] evaluated changes in shore A hardness, axial stiffness, elastic modulus, strain energy, and apparent tensile strength of Silastic 4-4210 silicone after accelerated aging in a weatherometer and outdoor aging.

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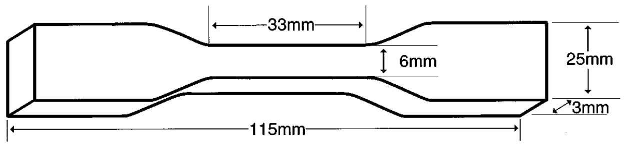

Fig. 1. ASTM No. D412 specifications for dumbbell-shaped specimens.

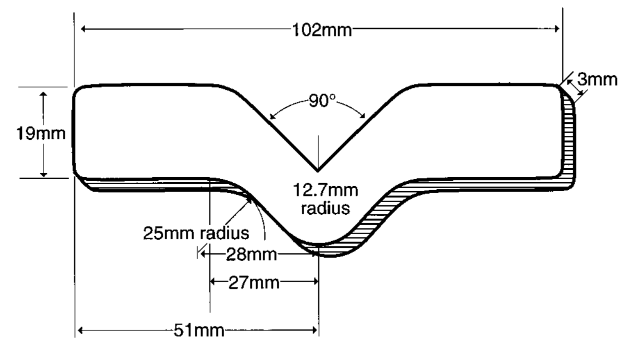

Fig. 2. ASTM No. D624 (die C) specifications for trouser-shaped specimens.

Accelerated weathering altered the properties of the elastomers faster and with greater magnitude than outdoor weathering. Haug et al[6] evaluated the effects of natural weathering, the passage of time, 2 common adhesives, 2 common cleaning agents, and cosmetics on ultimate tensile strength, percentage elongation, shore A hardness, and tear strength of 1 polyurethane (Epithane-3, Daro Products, Inc, Butler, Wis.), 3 silicones (Silastic medical adhesive type A, Silastic 44210, and Silastic 4-4515, Dow Corning Corp), and 2 newly introduced silicones (Silicone A-2186 and Silicone A-102, Factor II, Inc, Lakeside, Ariz.). The polyurethane was the most affected by the treatment groups, and Silastic medical adhesive type A was the least affected.

In 1994, Dootz et al[7] evaluated tensile strength, elongation, shore A hardness, and tear resistance of Silastic 4-4210, Silicone A-2186, and Cosmesil elastomers (Cosmedica Ltd, Cardiff, U.K.) before and after 900 hours of accelerated aging in a weatherometer. When the results of their study were compared with the results of Haug et al,[6] the use of accelerated weathering to reflect natural weathering was brought into question, because the results differed. Specifically, Dootz et al[7] reported no difference in the percentage elongation and the hardness before and after weathering of Silastic 4-4210 silicone, whereas Haug et al[6] found a significant difference.

This second part of a 3-part in vitro study examines the interactions between elastomers, colorants, and weathering as they influence properties that are related to the effective life span of these prostheses. The purpose of this second part is to evaluate the change in physical properties of popular colorant-polymer combinations as a result of time passage and exposure to weathering.

MATERIAL AND METHODS

Four commonly used intrinsic coloring agents, based on a recent survey of both the American Academy of Maxillofacial Prosthetics and the American Anaplastology Association,[8] were evaluated: dry earth pigments, rayon fiber flocking, artists' oil paints, and kaolin (Factor II) and 1 recently introduced method[9] that used a liquid facial cosmetic (Estée Lauder polished performance liquid make-up, Alabaster Beige 18-N, Estée Lauder, New York, N.Y.).

The maxillofacial elastomers evaluated were 3 of the more commonly used elastomers, based on that same survey: Silastic medical adhesive type A (Dow Corning Corp); Silastic 4-4210 (Dow Corning Corp), and Silicone A-2186 (Factor II, Inc). All elastomer-colorant combinations were evaluated for tear strength, percentage elongation, and ultimate tensile strength with a Universal testing machine (Instron Corp, Canton, Mass.). Hardness was measured with a shore type A durometer (Shore Mfg Co, Jamaica, N.Y.).

Thirty specimens of each elastomer-colorant combination were fabricated according to the American Society for Testing and Materials (ASTM) No. D412[10] (Fig. 1) and No. D624 (die C)[11] (Fig. 2) specifications in 2 improved dental stone molds (Silky-Rock, Whip-Mix Corp, Louisville, Ky.). Of the 30 specimens, 15 dumbbell-shaped (DS) specimens were used to evaluate ultimate tensile strength and percentage elongation, and 15 trouser-shaped (TS) specimens were used to measure hardness and tear strength.

A total of 540 specimens were fabricated; there were 180 of each of the 3 elastomers. For each elastomer category, there were 6 colorant categories (5 colorants and 1 with no colorant) of 30 specimens each. Within each colorant category, there were 3 test condition categories (control, natural weathering, and time passage) of 10 specimens each. Within each test condition category, there were 2 specimen shapes (DS and TS), each with 5 specimens.

Each material was handled in strict compliance with the manufacturer's instructions. To achieve maximum consistency among specimens within an elastomer colorant category, all 30 specimens were fabricated during 1 processing. For the 2-part room temperature vulcanizing system, Silastic 44210 and Silicone A-2186, 545 g of base were mixed with 55 g of catalyst to achieve the recommended ratio of 10:1. Six hundred grams of medical adhesive A (a 1-part, room-temperature vulcanizing material) was used directly from the tube. Colorants then were added in amounts to achieve concentrations similar to those found in clinical prostheses and are described in the first part of this study.[12]

The colorants were mixed with the elastomers by hand using wooden tongue blades in 5-quart paper paint pails for 5 minutes. Each mixture (both the 1- and 2-part system) was de-aired under a vacuum of at least 30 in of mercury for 20 minutes. The mixture was then placed in the stone molds, which were coated with 2 applications of tinfoil substitute (Al-Cote, Dentsply Trubyte, York, Pa.) and allowed to dry. Care was taken not to incorporate air bubbles into the mold space or mixture. The mold was then closed and clamped with a 1-inch web-type ratcheting clamp (Pony clamp, Adjustable Clamp Co, Chicago, Ill.). The molds were placed in a 100°F dry oven (Imperial II radiant heat oven, Labline Instruments, Inc, Melrose Park, Ill.) to polymerize for 16 hours. After polymerization, molds were carefully separated, specimens were removed and flash was trimmed away with a sharp scalpel. Specimens were then separated into treatment groups.

Test conditions

For the control groups, the tear strength, percentage elongation, and ultimate tensile strength of the specimens from the control groups were evaluated within 30 days after polymerization. The specimens were stored in sealed glass containers in a dark environment at ambient room temperature (72°F ± 5°F) and humidity (50% ± 10%) until tested. Control data for hardness also were measured within 30 days after polymerization and stored under the same conditions. However, these data were obtained on the same specimens that were later subjected to the test conditions of natural weathering or time passage. Collection of these data did not affect the specimen. It was believed that this technique would minimize uncontrolled variables that may have occurred if a second group of specimens were used for control measurements.

For the natural weathering groups, specimens were suspended from wooden racks by stainless steel suture material. The assembly was placed on the roof of the dental school at Indiana University for a period of 6 months. This period was selected because it is thought to be the average life span of a maxillofacial prosthesis.[6,13] At the end of the treatment period, specimens were removed and cleaned in an ultrasonic cleaner with tap water and liquid detergent for 10 minutes. Specimens were rinsed in running tap water, wiped dry, and then tested for changes in physical properties.

For the time passage group, specimens were placed in sealed glass containers and placed in a dark environment at ambient room temperature and humidity for 6 months. At the end of this period, the specimens were removed and tested. This group acted as a nonweathered control group with which the natural-weathering group could be compared, because both groups included the time variable.

Physical property testing procedures

Evaluations for hardness were made on the TS specimens. These specimens were then used for testing tear strength. The DS specimens were used to simultaneously perform tests on the ultimate tensile strength and percentage elongation tests. All tests were performed at ambient room temperature and humidity after the specimens had been held in these conditions for at least 24 hours.

Shore A hardness test

Three specimens were stacked on one another on a hard horizontal surface in random order for a total of about 9 mm to obtain the 6 mm minimal thickness required of the ASTM specification No. D-2240.[14] The shore A durometer was held in a vertical position, and the pressor foot was applied to the surface of the specimens as rapidly as possible without shock. Readings were made 1 second after firm contact was achieved. Five sites were measured per specimen (12 mm distance between each site and a 6 mm distance from edge of the specimen). The specimen at the bottom of the stack was removed, and a new specimen placed on top, and the procedure was repeated to obtain readings for that specimen. This process was repeated until all 5 specimens for that colorant/test condition group were evaluated. The mean of the 25 measurements was recorded as the hardness of that group. Because these specimens were able to serve as their own controls (were not damaged by measurement and could be measured before and after test conditions), the control data included 50 measurements, 25 from each test condition group.

Tear strength test

Tear strength is defined as the maximum force (Newtons) required to break the TS specimen, divided by the thickness of the specimen. The thickness of the specimen (at 3 mm, depending on the degree of mold closure) was measured at the intersection of the trouser leg with a vernier caliper with digital readout (Mitutoyo Digimatic CD-6, Mitutoyo Corp, Tokyo, Japan). The specimen was placed in the jaws of the universal testing machine and stretched at a rate of 500 mm/min. From these measurements, the tear strength of that specimen was calculated. The value reported for a colorant/test condition group was the mean of the values obtained from the 5 specimens of that group.

Ultimate tensile strength test

The ultimate tensile strength is defined as the force required to break the DS specimen, divided by the

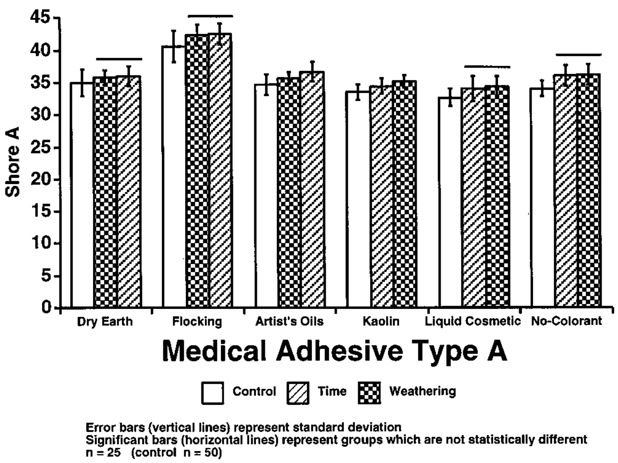

Fig. 3. Effects of weathering and time on hardness of medical adhesive A.

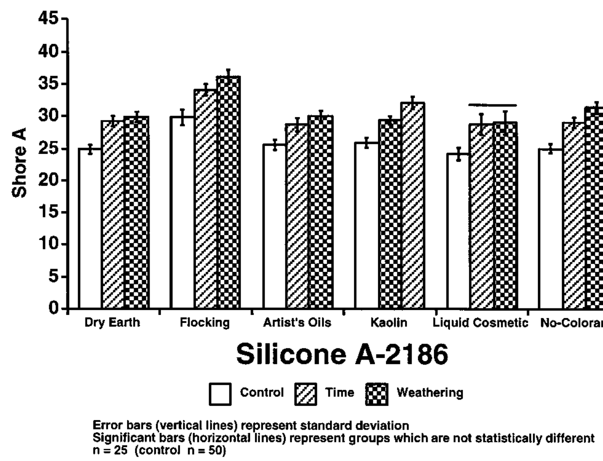

Fig. 5. Effects of weathering and time on hardness of Silicone A-2186.

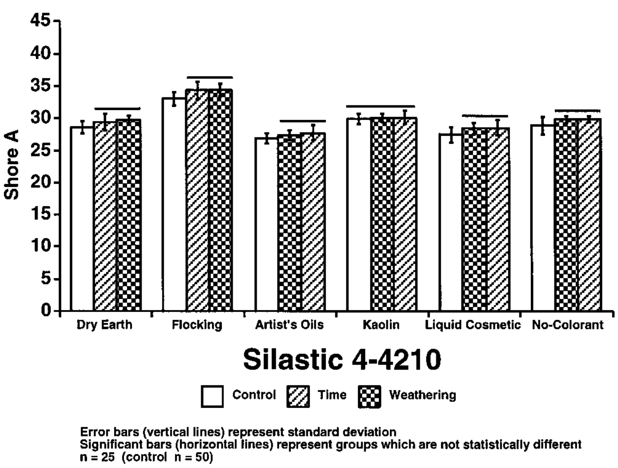

Fig. 4. Effects of weathering and time on hardness of Silastic 4-4210.

cross-sectional area (width × thickness of reduced section) of unstretched specimen. The thickness measurement (approximately 3 mm, depending on the degree of mold closure) was made at the center of the reduced section of the specimen with a vernier caliper with digital readout. The width was 6 mm (width of the mold). In keeping with ASTM D-412 specifications, the specimen was placed in the jaws of the Universal testing machine and stretched at a rate of 8.5 mm/min. The maximum load before breaking (in Newtons) was obtained, and the tensile strength of that specimen calculated. Mean tensile strength value for all specimens in that colorant/test condition group was reported as the ultimate tensile strength for that group.

Percentage elongation test

Benchmarks were placed on the DS specimen 25 mm apart before testing, and the additional distance between the benchmarks at fracture was recorded. This additional distance at fracture, divided by the original distance of the unloaded specimen, multiplied by 100, was recorded as the percentage elongation of that specimen. The mean value obtained for all specimens in the colorant/test condition group was reported as the percentage elongation for that group.

Statistical analysis

Because colorants were added as representative values, and each elastomer may have required a different concentration of a given colorant to achieve a similar clinical effect, only pairings within each elastomer were of clinical relevance. Physical property data for each elastomer-colorant combination were subjected to a 1-way analysis of variance (ANOVA) to examine effects among the test conditions (control, time passage, and weathering). When significant differences were observed, the Student-Newman-Keuls multiple range test was performed to identify differences in elastomer-colorant combinations among each test condition at a significance level of $\alpha \geq .05$. Changes from the control condition that are statistically different are described.

RESULTS

Hardness

Hardness values of medical adhesive type A with no colorant exhibited a significant increase with both time and weathering compared with control measurements, which had been made within 1 month of fabrication (Fig. 3). However, there was no significant difference between the time and the weathering groups. Thus, weathering alone did not increase the hardness, but some change inherent in the material increased the

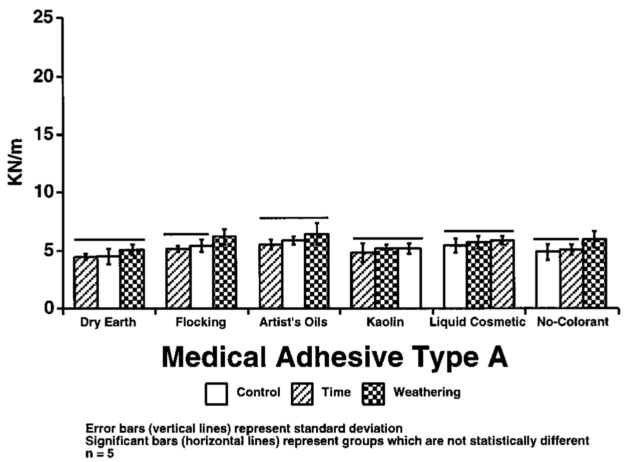

Fig. 6. Effects of weathering and time on tear strength of medical adhesive A.

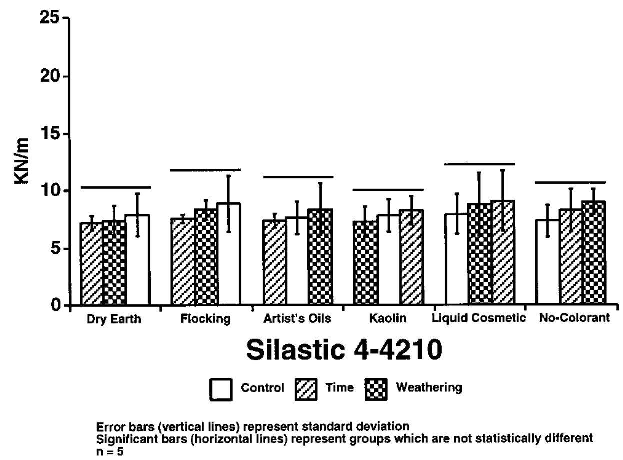

Fig. 7. Effects of weathering and time on tear strength of Silastic 4-4210.

hardness over time. With the addition of liquid cosmetic, rayon flocking, and dry earth pigments in medical adhesive type A, the same increase in hardness with both weathering and time could be seen, with no statistically significant differences between weathering and time. The addition of kaolin had a different effect on medical adhesive type A. Time statistically increased the hardness of the material, but weathering increased the hardness even further. The addition of artist's oils to medical adhesive type A had a different effect. Hardness increased with weathering, but not as much as the increase with time alone. Hardness after weathering showed a statistically significant decrease compared with time. The hardness of Silastic 4-4210 increased with time with no significant difference between time and weathering for all groups, except after the addition of kaolin, which produced no difference among the test conditions (Fig. 4).

Something quite different occurred to Silicone A-2186 elastomer, for both colored and noncolorant groups, when exposed to time and weathering (Fig. 5). Hardness increased significantly over time and then increased significantly again with weathering. The only exceptions were with the use of kaolin, which time had a greater effect than weathering, and with the use of liquid cosmetic, which produced no difference between time and weathering.

Tear strength

The result of the addition of colorant was inconclusive with regard to the effect on the tear strength of the elastomers as a function of time and weathering (Figs. 6 through 8). The only statement that can be made is that weathering increased the tear strength of the uncolored and the flocking-colored medical adhesive type A, compared with the time and control groups.

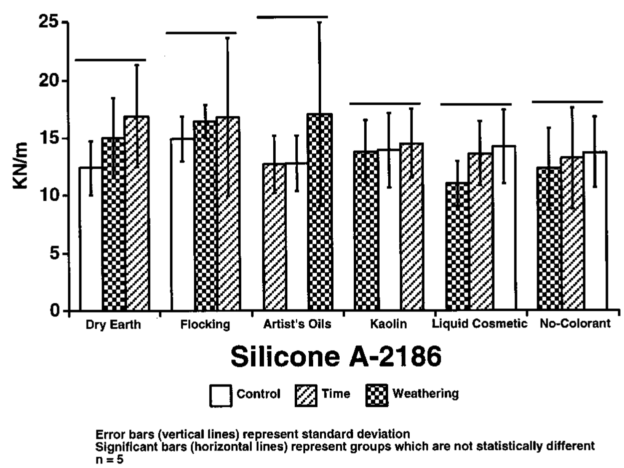

Fig. 8. Effects of weathering and time on tear strength of Silicone A2186.

Ultimate tensile strength

Ultimate tensile strength of medical adhesive type A with no colorants decreased by time and weathering, with no significant difference produced between the 2 effects (Fig. 9). With the addition of rayon flocking, weathering increased the ultimate tensile strength, but time had no effect. With liquid cosmetic, weathering decreased the tensile strength compared with the control. The addition of the remainder of the colorants did not reveal any significant differences.

For Silastic 4-4210 and Silicone A-2186 elastomers, in every case the ultimate tensile strength was decreased by both time and weathering with no statistically significant differences between the time or weathering groups (Figs. 10 and 11).

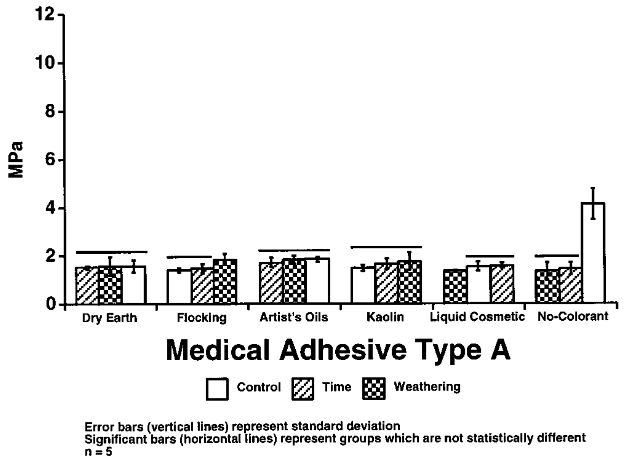

Fig. 9. Effects of weathering and time on ultimate tensile strength of medical adhesive A.

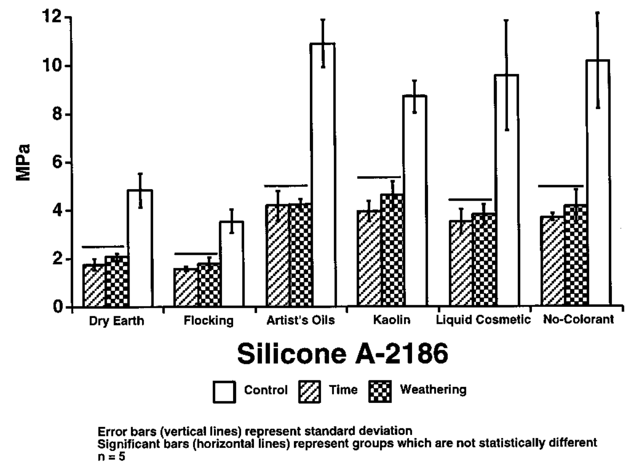

Fig. 11. Effects of weathering and time on ultimate tensile strength of Silicone A-2186.

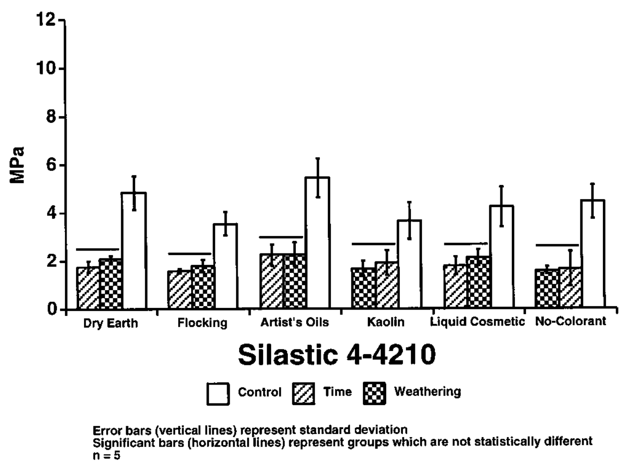

Fig. 10. Effects of weathering and time on ultimate tensile strength of Silastic 4-4210.

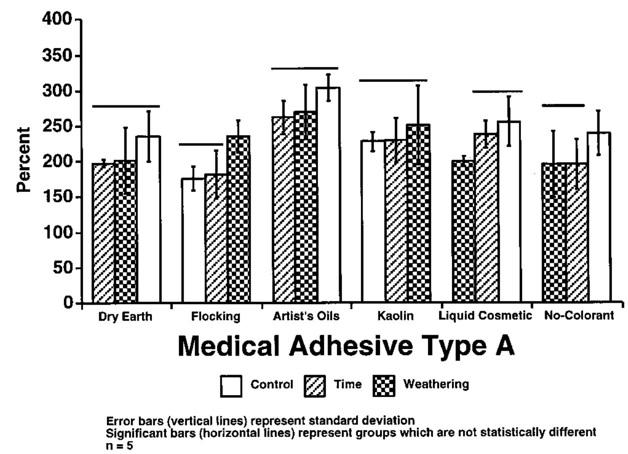

Fig. 12. Effects of weathering and time on percentage elongation of medical adhesive A.

Percentage elongation

The percentage elongation decreased for medical adhesive type A with no colorant with both weathering and time (Fig. 12). However, weathering increased the percentage elongation of the rayon-flocking colored group. Weathering decreased the percentage elongation of the liquid cosmetic colored specimens, and no difference could be determined for the remainder of the colorants. The percentage elongation of Silastic 4-4210 elastomer with no colorant was decreased by weathering, but not with time (Fig. 13). For the colorant groups, no significant differences were found.

Both weathering and time decreased the percentage elongation of Silicone A-2186 elastomer, with no colorant (Fig. 14). When either liquid cosmetic or artist's oils were added, only time decreased the percentage elongation with no effect from weathering. For the addition of the other colorants, no significant differences were demonstrated.

DISCUSSION

Most maxillofacial prostheses must be refabricated about every 6 months, because of the degradation of the color and physical properties of the prosthesis. The ideal elastomer-colorant combination should not only allow satisfactory esthetics to be achieved clinically, but should also maintain the esthetics and physical properties indefinitely, or at least until the patient's tissues have changed to a point that the fit or the prosthesis would require refabrication of the prosthesis.

Two types of colorants are available, inorganic and organic. Inorganic colorants usually are metallic oxides and, as a result of the ionic bonds, these molecules are stable. These components are commonly used in prod-

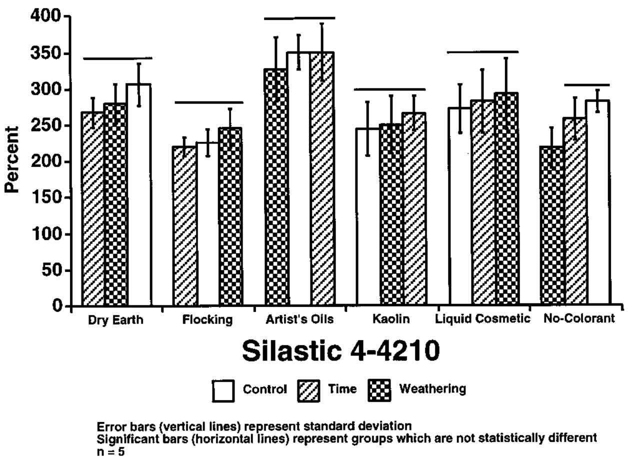

Fig. 13. Effects of weathering and time on percentage elongation of Silastic 4-4210.

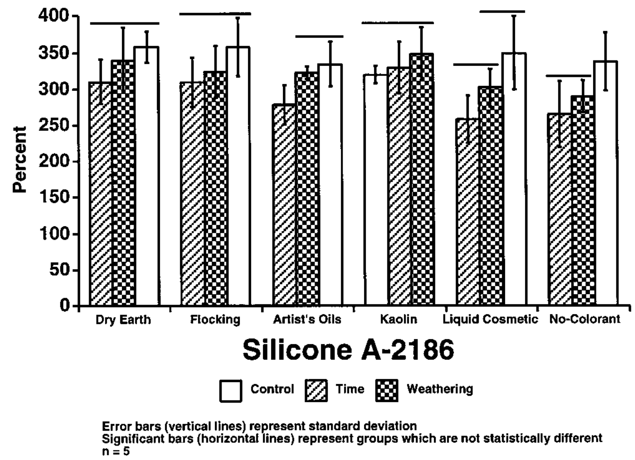

Fig. 14. Effects of weathering and time on percentage elongation of Silicone A-2186.

ucts such as paints and tend to be extremely color-stable, unless the components are washed away. Organic colorants rely on the placement of double and triple bonds to impart color to the molecule. Because these bonds tend to be relatively reactive, these colorants are less stable. A common example of organic colorant use is in textiles.

Dry earth pigments and kaolin are inorganic coloring agents. Artist's oil paints and liquid facial cosmetic most likely contain inorganic coloring agents, the difference being how they are supplied. Artist's oil paints and liquid facial cosmetic use some type of vehicle for the colorant. The vehicle allows the colorant to be handled in liquid form, but the material eventually hardens, most likely through evaporation or absorption of the vehicle. In addition, these materials can evaporate or leach out with time, changing the physical properties of the prosthesis, which was demonstrated by the data regarding the differences in physical properties among the control group and the weathering and time groups.

One unexpected outcome of this study was the elastomers physical properties were not as stable as had been assumed by the profession. Changes in physical properties occurred in colored and noncolorant specimens that had been sealed in containers and kept in the dark for 6 months. For example, the statistically significant changes in the ultimate tensile strength of Silastic 4-4210 and Silicone A-2186 elastomers were similar for both time and weathering. This indicates the effects were inherent in the elastomers and not influenced by weathering. It is possible that the changes were caused by impurities incorporated during manufacturing, by reaction products, by initiators, or by some other mechanism. Determination of the reason for these changes could lead to more stable formulations, which would grant longer clinical prosthesis life.

CONCLUSIONS

The following conclusions were drawn from this study:

1. The addition of colorants to the silicones altered the effect of weathering on the physical properties.
2. The silicones were not as stable as assumed by the profession. Physical property changes occurred in both colored and uncolored specimens, which had been sealed in containers and kept in the dark.

REFERENCES

1. Barnhart GW. A new material and technic in the art of somato-prosthesis. J Dent Res 1960;39:836-44.
2. Andres CJ, Haug SP, Munoz CA, Bernal G. Effects of environmental factors on maxillofacial elastomers: part I—literature review. J Prosthet Dent 1992;68:327-30.
3. Yu R, Koran A. Dimensional stability of elastomers for maxillofacial applications. J Dent Res 1979;58:1908-9.
4. Yu R, Koran A 3d, Craig RG. Physical properties of maxillofacial elastomers under conditions of accelerated aging. J Dent Res 1980;59:1041-7.
5. Wiens JP. A comparative study of selected elastomers subjected to accelerated and outdoor weathering. [Thesis.] Rochester: The University of Minnesota; 1980. p. 183.
6. Haug SP, Andres CJ, Munoz CA, Okamura M. Effects of environmental factors on maxillofacial elastomers: part III—physical properties. J Prosthet Dent 1992;68:644-51.
7. Dootz ER, Koran A 3d, Craig RG. Physical properties of three maxillofacial materials as a function of accelerated aging. J Prosthet Dent 1994;71:379-83.
8. Andres CJ, Haug SP, Brown DT, Bernal G. Effects of environmental factors on maxillofacial elastomers: part II—report of survey. J Prosthet Dent 1992;68:519-22.
9. Over LM. The development of an intrinsic shade guide for facial prostheses using a colorimeter with an RTV silicone. [Thesis.] Indianapolis: Indiana University School of Dentistry; 1992. p. 157.
10. American National Standards ASTM No. 412. Philadelphia: American Society for Testing and Materials; 1981. (Pt 37).
11. American National Standards ASTM No. 624. Philadelphia: American Society for Testing and Materials; 1981. (Pt 37).
12. Haug SP, Andres CJ, Moore BK. Color stability and colorant effect on maxillofacial elastomers. Part 1: colorant effect on physical properties. J Prosthet Dent 1999 (in press)

13. Haug SP, Andres CJ, Munoz CA, Bernal G. Effects of environmental factors on maxillofacial elastomers: part IV—optical properties. J Prosthet Dent 1992;68:820-3.
14. American National Standards ASTM No. 2240. Philadelphia: American Society for Testing and Materials; 1981. (Pt 37).

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Noteworthy Abstracts of the Current Literature

Physicomechanical and cytotoxic properties of room temperature vulcanizing silicone prosthetic elastomers
Polyzois GL, Pettersen AH. *Acta Odontol Scand* 1998;56: 245-8.

Purpose. This study evaluated and compared 3 silicone elastomers used to fabricate extraoral maxillofacial prostheses relative to tensile strength, modulus, percentage elongation, tear strength, hardness, color stability, and in vitro cytotoxicity.
Material and methods. Two commercially available room temperature vulcanizing (RTV) silicone elastomers (Ideal and Silskin 2000) and another new RTV silicone (Elastomil M3500) were used. Ten test specimens of each silicone elastomer were made for each specific test (tensile strength, modulus, percentage elongation, tear strength, hardness, color stability, and in vitro cytotoxicity). Specimens were handled aseptically. In vitro cytotoxicity was assessed with the agar diffusion test and mouse fibroblast cells (L929). Test procedures conformed closely to specifications established by the American Society for Testing and Materials and the International Organization for Standardization. All specimens were tested less than 1 week after vulcanization. Results were subject to ANOVA followed by Tukey's pairwise comparison test at a P=.05 level of significance.
Results. Elastosil M3500 had a better combination of high tear strength, elongation at break, and low hardness than Ideal and Silskin 2000. All 3 materials demonstrated a low cytotoxic profile.
Conclusion. The authors conclude that Elastosil M3500 warrants further attention as a maxillofacial material with clinical trials. 10 References. —*RP Renner*