COMPARATIVE EVALUATION OF COLOR STABILITY OF MAXILLOFACIAL SILICONE ELASTOMER INCORPORATED WITH NANO PARTICLE PIGMENT AND OPACIFIER BY VISUAL AND SPECTROPHOTOMETRIC ANALYSIS
–AN *IN VITRO* STUDY

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LIST OF ABBREVIATIONS

Sr. No.	Abbreviations	Full Form
1	RTV	Room temperature vulcanizing
2	HTV	Heat vulcanizing
3	PVC	Polyvinyl chloride
4	UV	Ultraviolet
5	^{0}C	Degree celsius
6	ΔE	Difference in color
7	CIELAB	Commission International d'Eclairage L*a*b* color space
8	ASTM	American Society for Testing and Materials
9	Ti	Titanium
10	W/m^2	Watts per square Meter
11	%	Percentage
12	LP	light protecting
13	TW	titanium white
14	SW	silicone intrinsic white
15	kJ/m^2	Kilojoule/square meter
16	BCC	basal cell carcinoma
17	Zn	Zinc
18	ISO	International Organization for Standardization
19	Pvt. Ltd	Private limited
20	gms	Grams
21	ml	Milliliter
22	mm	Millimeter
23	P value	Probability of happening of an event
24	SD	Standard Deviation
25	psi	Pounds per square inch
26	Pty. Ltd	Proprietary limited
27	mins	Minutes
28	DPI	Dental Products of India

Introduction

‘We restore repair and make whole those parts of the face which nature has given but fortune has taken away, not so much that they may delight the eye, but that they may buoy up the spirit and help the mind of the afflicted’

-Gapsare Tapliacozi

There is not a more severely handicapped person than the patients with gross facial disfigurement. Since facial expressions and appearance are important in a humans social and personal life, facial abnormalities due to trauma, cancer or congenital defect can decrease ones self-esteem and self-confidence. [1]

Maxillofacial Prosthodontics is defined as that branch of prosthodontics concerned with the restoration and/or replacement of the stomatognathic & craniofacial structures with prosthesis that may or may not be removed on a regular or elective basis.[2]

Maxillofacial prosthetic treatment is not at all substitute for plastic and reconstructive surgery, in certain circumstances it may be an alternative. Maxillofacial prosthesis provides a nonsurgical treatment for patients who are not good candidate for plastic surgery intervention because of advanced age, poor health, very large deformity or poor blood supply due to radiation. Moreover, prosthetic treatment is advised when anatomical structures of head and neck are not replaceable by living tissue, when recurrence is likely, when radiotherapy is administered or when fragment of fractured bones are severely displaced.[3]

The fabrication of an extraoral facial prosthesis is as much an art as it is a science. The form, coloration, and texture of the prosthesis must be as indiscernible as possible with the surrounding natural tissues. The prosthesis must duplicate the missing facial features so precisely that the patient can appear in society without fear of attracting unwanted attention.[4]

Following World War II, an era of specialization among health care professionals ensued. As a sub-specialty area of the recognized dental specialty prosthodontics, maxillofacial prosthetics has become an essential patient-care link between dentistry and surgery.[5]

Considering the psychosocial pressures for facially disfigured patients, there is an increasing need to improve material in use and to synthesize new elastomers specifically for use as a facial prosthetic material. There is no ideal facial prosthetic material, although there have been improvements in the last few decades, and silicone rubbers have established the current state-of-art material. Silicone elastomers are the material of choice because of their chemical inertness, strength, durability, and ease of manipulation. [6,7]

Color is the most important parameter used by the patients in the evaluation of facial prostheses.[8] Color change is one of the needs of substitution, which unfortunately occurs in a short period of time. The major source of color in human skin are specialized melanin-bearing organelles, the melanosomes present within the epidermis. Gross human skin color derives from the visual impact of the sum of the melanin pigmentation of the numerous epidermal melanin units.[9]

The deterioration is mainly caused by environmental exposure to ultraviolet (UV) light, air pollution and changes in humidity and temperature.[10]

The ability to withstand color change when exposed to sunlight over an extended period is one of the most desirable performance characteristic of an ideal facial prosthetic elastomer. The discoloration of a facial prosthesis is due to the intrinsic or extrinsic coloration as a result of external environmental factors and is related to the intrinsic color stability of elastomers and colorant, or loss of external coloration on the prosthesis. Regardless of the type of elastomer used in the fabrication of facial prosthesis, its service life is usually 6 months to 2 years, with an average time of 10 to 12 months.[11]

Finished facial prostheses rest on living human skin for long period and may absorb perspiration and sebum. These absorbed species may cause degradative changes in the elastomer structure, resulting in ultimate deterioration of the prosthesis.[12] However, this important issue has been addressed in relatively few published articles.

Many studies have been conducted to evaluate the effect of extraoral aging conditions, outdoor weathering, skin secretions, artificial aging, disinfection solutions and dark storage on the mechanical properties of maxillofacial silicone elastomers. However, only few studies are available regarding the effect of extraoral aging on color stability of these maxillofacial silicone elastomers.

For maintenance of esthetics, the color stability of the prosthesis is critical. Hence, we evaluated color stability by a visual method as well as spectrophotometric analysis.

Hence, this current in vitro study is intended to evaluate and compare the color variation of commonly used maxillofacial silicone elastomer with nano particle pigments (extrinsic pigments) and opacifier used for fabrication of maxillofacial prosthesis after subjecting them to human and environmental aging conditions like, outdoor weathering, skin secretions. A Ultra Violet reflection spectrophotometer and visual method will be used to evaluate the color stability of these materials.

The null hypothesis was that ‘there is no significant difference in the color stability of tested maxillofacial elastomer with and without addition of pigment and opacifier, exposed to environmental and human aging conditions.’

The alternate hypothesis was there is significant ‘difference in the color stability of tested maxillofacial silicone with and without addition of pigment and opacifier, exposed to environmental and human aging conditions.’

Primary research question was ‘Does addition of opacifier and nano particle pigment increase the color stability of maxillofacial silicone elastomer when exposed to environmental and human aging condition?’

Aim and Objectives

This study was aimed to evaluate and compare color stability of maxillofacial silicone elastomer incorporated with nano particle pigment and opacifier subjected to three types of human and environmental aging conditions by visual and spectrophotometric evaluation.

The objectives of the study were as follows:

1. To evaluate color stability of maxillofacial silicone elastomer incorporated with nano particle pigment and opacifier by subjecting it to three types of human and environmental aging conditions.
2. To compare the color variation of maxillofacial silicone material by visual and Ultra Violet spectrophotometric analysis.

Review of Literature

This review of literature provides an insight into the evolution of different materials, which are used for fabricating the maxillofacial prosthesis with special emphasis on their color stability under different circumstances. There has been a great improvement in properties and life like effect of the materials which were used in the ancient era to the present time.

Earliest forms of facial prostheses were constructed of wood, ivory, waxes, and metals.

In 1945 Clarke[13] described techniques for fabricating prostheses from latex rubber, glycerine-gelatin formulations, and electroplated metals.

In 1960 Barnhart[14] was the first to use silicone elastomers for an external prosthesis and since then it had become the material of choice because of their chemical inertness, strength, durability, and ease of manipulation.

Silicone is chemically known as polydimethylsiloxane.It is a combination of organic and inorganic compounds. Based on method of vulcanization, silicones are further divided into two basic types.[15]

a. Room temperature vulcanizing (RTV) silicone
b. Heat vulcanizing (HTV) silicone

The facial prosthesis is intended to replicate the form of natural skin. For that color matching with adjacent skin can be successfully achieved by adding different pigments. Pigments are classified into 2 groups i) organic ii) inorganic.[16]

In 1969 Cantor R, Webber RL, Stroud L, Ryge G[17] suggested that by using spectrophotometric analysis, the development of isomerically matched facial materials with skin appeared to be possible.

To obtain more lifelike natural appearance to the prostheses, they can be stained either intrinsically or extrinsically.

In 1969 Joseph E Ouellette[18] developed spray technique for coloring and tinting silicone elastomer RTV 399 extraoral maxillofacial prostheses. This method provides a simplified, effective process for realistically coloring silicone prostheses. Earlier pigments and a catalyst were brushed on extraoral maxillofacial silicone prosthesis; however, this method made it exceedingly difficult to obtain a realistic distribution of pigments and it was time-consuming. In order to overcome these difficulties, a spray technique was developed for coloring the prostheses.

In 1972 Sweeney AB, Fischer TE, Castleberry DJ, Cowperthwaite GF [19] for the first time used an accelerated aging chamber for evaluation of the color stability of maxillofacial materials. A weatherometer or weathering chamber used in the study was a device where specimens can be exposed to conditions similar to outdoor atmosphere, radiation, temperature, and humidity. Differences could be measured with a colorimeter by comparison of exposed and no exposed specimens. The authors recommended 2000 hours of exposure to evaluate maxillofacial materials.

Maxillofacial prosthesis always faces challenge of retention as it covers a large surface area, and the weight of the prosthesis increases with increase in surface area. Providing a retention to a heavy prosthesis is very difficult.

In 1976 Firtell DN, Donneau ML, Anderson CR [20]to overcome this problem of weight, invented the technique of combining materials to obtain a light-weight prosthesis by mixing RTV silicone foam with conventional RTV silicone rubber. The conventional silicone used in this study was white, and adding foam produced a beige color. The samples were made without pigment; then, red, yellow and blue pigments were added. Samples were exposed to natural and artificial light for one year and subjectively compared to identical samples stored in the dark. The amount of weight reduction appeared was adequate. However, the strength of its elastomers decreased along with a decreased weight**.**

The primary objective of maxillofacial prosthetics is the restoration of form and function of a missing or defective part so that the individual's psychological trauma can be relieved and reinstatement in society can be facilitated. To fulfill this goal prosthodontist should be aware of patient's psychology, expectation and their problem related to the prosthesis.

In 1978 R.M Jani and N.G Schaaf[21] evaluated patient reaction by a survey on facial prosthesis that were provided to the patients in the past 7 year, so that they can focus their attention on the deficiencies and try to prepare more acceptable prosthesis**.** Out of 143, 76 patients who responded, 38 patients were wearing their prosthesis and 38 patients were not wearing their prostheses. Reasons cited by the patient for not wearing their prosthesis, included lack of retention, additional surgery, discomfort, and irritation. Most of the prosthesis were prepared in silicone rubber with color characterization accomplished by the tattooing method. More than 69% of the prosthesis were remade within a year because of rapid changes in the defect, prosthesis material, or prosthesis color. The study revealed the need for improvement in materials, adhesive techniques, and the psychological orientation of the patient.

One of the major criteria of successful maxillofacial prosthetic materials iscolor stability and the greatest challenge faced by maxillofacial prosthodontist was to reproduce the patient's exact skin color and provide adequate esthetics. To reach this objective, professionals must use materials with easy characterization and that maintain color over a long period of time. Abundant researches were conducted to increase the color stability.

In 1978 Craig RG, Koran A, Yu R, Spencer J [22] tested the color stability of a non-pigmented polyvinyl chloride (Prototype III.), a polyurethane (Epithane), and 4 silicones (Silastic 382, Silastic 399, Silastic 44210, Silastic 4451). Before and after accelerated aging, all materials were evaluated with a spectrophotometer. The samples were placed in a weathering chamber with a 2500-W xenon light source. All silicone elastomers showed good color stability, although Silastic 44210 elastomer appeared to have the best overall properties. The authors concluded that the color stability of pigments and the stain resistance of the elastomers may be partly responsible for the color degradation experienced in clinical situations.

Ultraviolet radiation is one of the major reasons for color instability in the maxillofacial prosthesis. To increase the life of prosthesis it should be able to resist the ultraviolet radiation.

In 1978 Chu CC, Fischer TE[23] evaluated the effects of 11 additive UV light absorbers and one antioxidant in non-pigmented polyurethane elastomers (Calthane ND2300, Cal Polymer). By using a twin-lamp carbon arc weathering chamber as the UV source, they found that the UV light absorbers made from the benzotriazole or amine group were most effective in reducing visible yellowing of the elastomer.

In 1979 Koran A, Yu R, Powers JM, Craig RG [24] performed one investigation to understand the mechanisms of color degradation in a clinical environment. They tested 11 dry mineral earth pigments with Silastic 44210 material. The colors were vaguely identified as white, yellow, dark buff, medium brown, light brown, red-brown, black, red, blue, light orange, and orange-yellow. Before and after accelerated aging from a 2500-W xenon light source, all materials were evaluated with a spectrophotometer. Very small changes in color were detected, but this finding did not adequately explain the degree of color degradation that is seen clinically.

Color stability of the maxillofacial prostheses is dependenton the stain resistance of the base elastomers since these appliances are frequently exposed to stains in a service environment.

In 1979 Koran A, Power JM, Lepeak PJ, Craig RG[25] performed a study on non-pigmented and pigmented materials to determine resistance to external staining with tea, lipstick, and disclosing solution. Materials tested included two RTV silicones, Silastic 44210 and Silastic 382; one high temperature-vulcanized (HTV) silicone, 4-4515; and a PVC material. According to the study, tea produced the least color change; lipstick and disclosing solution produced the greatest change. Silastic 44210 was the most resistant to tea and disclosing solution, but showed. The greatest color change from lipstick. PVC was the least resistant to staining, while all silicones displayed good stain resistance.

In 1980 Craig RG, Koran A, Yu R[26] reviewed the development of maxillofacial materials in the 70s concluding that based on existing knowledge, RTV silicone polymers of the addition type (MDX 4-4210) offers optimum overall properties for maxillofacial application.

In 1981 Chen MS, Udagama A, Drane JB[27] evaluated 138 patients’ reactions to their facial prosthesis with main aim of formulating a guideline for improving prosthetic techniques and materials for a dentist, dental laboratory technicians, and manufactures. A two-part, multiple-choice questionnaire consisting of 42 questions was mailed to each patient. Part I included the patient’s history. Part II requested patients’ opinions regarding their present prostheses. The following criteria were used for patient acceptance or rejection: (1) comfort, (2) color, (3) good fit, (4) softness, (5) easy to clean, (6) esthetics, (7) cost, (8) adhesive quality, (9) no sores resulting, and (10) easy to remove.73patients answered the questionnaire, 50 men, and 23 women. The result of the study suggested that current materials and techniques used for fabricating facial prostheses have several limitations. The patients indicated that long-lasting and esthetics prosthesis, which will not change color, are preferred. Adhesives, which will be effective on surgerized and/or irritated tissues, without causing damage to the prosthesis, need further research.

Porosity and density of the silicone polymers are a major concern to the clinician. A porous prosthetic material may absorb tissue fluids and saliva provides a pathway for microbial invasion.

In 1983 Keith Kent et al [28] in order to minimize the porosity by proper handling, reviewed the chemical components of the four silicone rubber polymers. Method of controlling the porosity and density of both the one component semi-solid pre-polymer and the two-component fluid pre-polymer system were evaluated.The variables examined were (1) one-component versus two-component systems, (2) deairing the prepolymer liquid components, (3) method of packing, (4) temperature of the materials during storage and handling,(5) method of heat application to initiate or accelerate the polymerization, (6) investing the mold with or without a flask, and (7) using a wet or dry investment during heat application, and the need for investment of the mold within the confines of a closed flask. It was concluded that porosity of the medical- grade silicone rubber polymers may be totally prevented, or accurately controlled, by proper handling technique**.**

In 1983 Mischal D Hanson, Barry Shipman[29]for the first time incorporated cosmetic material into transparent silicone prior to curing, so that patient would get benefited from the use of cosmetics on their remaining facial tissue that corresponds to the cosmetics used in coloring their prostheses. For that, they used inert premixed basic mineral earth pigments. These inert pigments can be added directly to the silicone elastomer MDX4-4210. They found that the use of a combination of premixed cosmetic earth pigments in facial prosthesis- coloring techniques provides an efficient and predictable method of fabricating skin colored prosthesis. In addition, the system is easy to reproduce because of its simplicity. The use of cosmetic pigments is economical; it eliminates the need for a large supply of premixed stock silicone colors and reduces the possible waste of MDX4-4210**.**

In 1984 Turner GE, Fischer TE, Castleberry DJ, Lemon JE[30] compared the colorstability of isophorone polyurethane with spectrophotometric as well as visual analysis. Four color systems were evaluated: artist's oil pigments, dry earth pigments, kaolin modified with dry earth pigments, and Daro skin pigments (produced for use with Epithane-3.) Isophorone polyurethane with no color added served as the control. Visual and spectrophotometric observations revealed no statistically significant differences for any of the color systems before or after aging.

In 1986 McLaren[31] described a dry pigment as a finely divided colored substance that, when mixed or ground in a liquid vehicle, does not dissolve but remains dispersed in the liquid. Dyes are colored substances that dissolve and give their color effects to materials by staining. The chemical pureness of a pigment varies.

In 1991 Mayer[32] mentioned in his literature that the nomenclature of pigments can be confusing. A single color can be known by many names or 2 entirely different colors can be known by the same name. Titanium white can be known as titanium dioxide, anatase, or rutile. A system of color names is needed to eliminate the confusion of the various color names that appear in research. He also reported that the fading of a pigment or **dye on e**xposure to daylight is not the disappearance of the substance itself into thin air, but is actually the result of a chemical change. The UV wavelengths in the light react with the pigment or trigger a reaction, sometimes with the combination of air and or moisture. The pigments change to a colorless or less highly colored compound.

In 1992 Haug S, Andres C, Munoz C, Bernal G[33] evaluated the effects of the environmental treatments on the optical properties (color change and optical density) of the six elastomers-two recently introduced RTV silicones (A-2186 and A-102,), and four popular elastomers, one polyurethane (Epithane-3), one high temperature-vulcanizing silicone (Silastic 4-4515.) and two RTV silicones (Silastic Medical Adhesive, type A, and Silastic 4-4210), were subjected to the following seven environmental variables: natural weathering; normal aging; two types of adhesives; two types of cleaning agents; and cosmetics. Optical density and color changes were evaluated. They concluded that the currently used silicones Silastic 4-4210 and Silastic 4-4515, Medical Adhesive type A material, and polyurethane all showed more changes in color and optical density than the newly introduced silicone A-102 material.

In 1992 Andres CJ, P Haug SP Brown DT, Bernal G[34] In their review concluded that RTV silicone was most commonly used.Silicone as a class of materials are transparent to UV radiation and are highly permeable to moisture vapor and many gases versus organic elastomers. Any pigment that is sensitive to this type of exposure would degrade regardless of whether they were incorporated into the silicone or applied to the exterior surface.

Weathering chamber was used by many researchers to understand the mechanism of color degradation of the maxillofacial material. However, it is also important to evaluate the color degradation mechanism under environmental conditions.

In 1995 Beatty M, Mahanna G, Dick K, Jia W [35] evaluated the effect of individual environmental variables on maxillofacial elastomer instead of weathering chamber. They studied the two types of ultraviolet light as a separate variable and measured its effect on color changes occurring in an elastomer(A-2186) that was tinted with five dry pigments(Titanium white,Cadmium yellow medium,Marsviolet,Cosmetic red Cosmetic yellow ochres) for color changes(Δ E). The elastomer, pigments, and pigmented elastomers were subjected to each ultraviolet light source for 400, 600, and 1800 hours, and Δ E color shifts were determined. They concluded that, 1.Cosmetic red and cadmium yellow pigments underwent a significant color change after 400 hours of exposure to ultraviolet light.2. Mars violet and cosmetic yellow ochre pigments remained color stable after 1800 hours of ultraviolet lightexposure.3. A-2186 elastomer underwent detectable color change when stored in darkness up to 45 days. At least 600 hours of exposure to ultraviolet light was necessary before additional color changes were sufficient to be visually detected.4. Certain color stable pigments appeared to reduce the elastomer's sensitivity to ultraviolet light. However, color stability of the pigment itself did not guarantee its effectiveness in reducing elastomer sensitivity to ultraviolet light.

Color deterioration is mainly caused by environmental exposure to ultraviolet(UV) light, air pollution and changes in humidity. So to improve the color stability of prosthesis under such condition In **1995 Lemon J, Chambers M, Jacobsen M, Powers J**[36] evaluated the efficacy of an ultraviolet light absorber UV 5411 at 3 different concentrations 0.1%, 0.25% on the color stability of a pigmented facial elastomer (MDX4-4210 and type A medical adhesive). Samples were weathered artificially and outdoors at an exposure level of radiant energy of 150 - 450 $Kj/m^{2.}$ The samples changed color slightly but perceptibly. Artificial aging caused a greater change than outdoor aging. The ultraviolet light absorber UV-5411 did not protect the samples from color changes.

The clinical intrinsic coloration of maxillofacial prostheses often involves the addition of different pigments and opacifier in an attempt to make the translucency of the base elastomer approximate that of the patient’s skin, followed by the addition of other colorants to reach the desired shade. This empirical trial and method relies on the operator's experience and visual ability and can be affected by the illumination used for the shade matching.

In 1995 Johnston [37] established a translucency parameter by collecting optical scattering and absorption coefficients and applying the Kubelka- Munk reflectance theory. The actual procedure involved measuring the colored medical- grade silicone samples, which were placed on an ideal dark backing and an ideal white backing. A significant difference was noted among the translucency parameters of the colorant.

In 1998 Over L, Andres C, Moore B, Goodacre C, Munoz C[38] determined whether CIE L*a*b* color measurements of white facial skin could be correlated to those of silicone shade samples that visually matched the skin,and correlation in color measurements could be achieved between the silicone shade samples and duplicated silicone samples made using a shade-guide color formula. They found a good correlation between the patient's colorimeter measurements and the silicone samples, with the b* color dimension the most reproducible, followed by the L* and then a*. Silicone samples at 6, 8**,** and 10 mm matched the patient the best, and this study showed that silicone samples can be duplicated successfully if a good patient-silicone match is obtained. Rayon flocking fibers and liquid makeup is effective at matching facial prostheses and can be used to develop a simple shade guide for patient application.

In 1999 Gregory L. Plyzois[11] mentioned in his literature that, the inherent color stability of non-pigmented elastomer is a contributing variable to the overall color stability of a facial prosthesis experienced in clinical situations. For this reason, studies related to discoloration of non-pigmented facial elastomers after exposure to sunlight, air pollution, ambient temperature, and humidity for extended periods are fundamental to understand the reasons for failure in a service environment. So, he conducted a study on the color stability of 3 non- pigmented silicone elastomers (Silskin 2000, Elastosil M3500, Ideal) exposed to outdoor weathering for 1 year. A tristimulus colorimeter was used to evaluate the color difference (ΔE*) of the silicone elastomer every 2 months. He concluded that outdoor exposure of silicone facial elastomers for 1 year resulted in visually detectable color differences. Duration of exposure and silicone elastomer were significant factors that affected color stability. Silskin 200 was significantly less color stable than Elastosil M3500 and Ideal, which were not statistically significantly different from each other.

In 1999 Haug S, Andres C, Moore B[39] evaluated the color stability of commonly used colorant-elastomer combinations as a result of exposure to weathering. In which they used 3 elastomers (adhesive type A, Silastic 4-4210, Silicone A 2186) and 6 colorants. They evaluated the color stability of these elastomers under control, time passage, and natural weathering. They noted the change in color in many of the colorant elastomer combination. Also, acolor change occurred not only to the colored but also to uncolored materials over time without exposure to weathering and concluded that colorants tended to protect the silicone by blocking light radiation to the elastomer.

The finished prosthesis may absorb perspiration and sebum from the underlying living human skin, these secretions may alter the properties of the maxillofacialelastomer.

Polyzois G, Tarantili P, Frangou M, Andreopoulos[12] **in 2000** investigated the influence of synthetic perspiration and sebum on the physio-mechanical properties like tensile strength and modulus, elongation, tear strength, hardness, weight, and color change of a maxillofacial silicone (epsil Silicone prosthetic elastomer) after 6 months period of immersion at 37^0C.They found improved mechanical properties for specimens immersed in acidic perspiration. Some weight increase was observed for the specimens immersed into the aqueous solution, whereas for those immersed in sebum, weight loss was recorded, probably because of extraction of some compounds. In this latter case, the color change was lower than that corresponding to simulated perspiration.

In 2001 Gary J, Huget E, Powell L[40] followed the ASTM methods to determine whether predictable color changes occurred for 3 ASTM approved pigments (Burnt sienna, Hansa yellow, Alizarin red.) when each was blended singly with the specific maxillofacial elastomer (A2186), with the use of accelerated weathering in 2 locations.Odd-numbered groups were assigned to a test site in Miami, Fla, whereas the even numbered groups went to Phoenix, Ariz. Specimens weathered in Miami and Phoenix received sunlight exposures of 1305.7 MJ/m^2 and 1310.2 MJ/m^2, respectively, over time. They found that mean color changes that occurred in Arizona were larger than those produced in Florida. This study provided the valid baseline for future research.

Opacifiers are color stable, the addition of opacifier increases the life of the prosthesis. However, opacifiers have different levels of opacity that may affect the color stability of maxillofacial elastomers in different ways.

In 2002 Kiat-amnuay S, Lemon J, Powers J.[41] investigated the effect of opacifiers used at varying concentrations on the color stability of pigmented silicone A-2186 maxillofacial elastomer. They found that Mixing dry earth cosmetic pigments with opacifiers did not protect silicone A-2186 from color degradation over time, especially in the case of red pigment. The group in which pigments were mixed with

10% Artskin white had the smallest color changes over time, followed by, in order, the groups in which pigments were mixed with 10% dry pigment titanium white, 10% kaolin powder calcined, and 5% Georgia kaolin. Red pigment had a significant effect on all opacifiers, especially.

In 2004 Tran N, Scarbecz M, Gary J.[42] continued the study of John J Gary et al by incorporating the mixture of the Ultraviolet light absorber (UVA)-Tinuvin 213 and hindered amine light stabilizer(HALS)- Tinuvin 213 to the maxillofacial silicone (A-2186). As UVA absorbs the harmful radiation and does not lead to photosensitization and HALS is an effective and efficient stabilizer for polymers as a free radicle scavenger. As both the stabilizer operated by different mechanisms, a synergistic performance enhancement was also observed when used together in some applications. Burnt sienna, Hansa yellow, Alizarin red pigments were used in this study color was evaluated in the same manner as a previous study. They concluded that in specimen group with the additives (UVA and HALS) color change decreased significantly in burnt sienna and hansa yellow. Additives did not affect color changes in alizarin red group.

In 2005 Kiat-amnuay S, Johnston D, Powers J, Jacob R[43] evaluated the color stability of pigmented(dry earth pigments) A-2186 silicone maxillofacial elastomer with 10% by volume of titanium white dry earth opacifier before and after exposure to microwave energy over simulated 1.5 years period of microwave sterilization. They found lack of color stability of red dry earth pigmented A-2186 silicone maxillofacial elastomers was clinically significant after 12-month exposure to microwave energy as compared with yellow, burnt sienna and opacified A-2186 dry earth pigments.

In 2006, Sudarat Kiat-amnuay et al[44] after evaluating the effect of opacifier on color stability of maxillofacial elastomer A2186 in 2002 at different concentration authors evaluated the color stability of MDX4-4210 as over the past 3 decades, the effect of either pigments or opacifiers on the color stability of MDX4-4210 medical adhesive type A, or the combination of these elastomers has been investigated; however, no study was identified that the interactions of both pigments and different opacifiers on the color stability of the combination of MDX4-4210/medical adhesive type A. Authors measured the interactions of all oil pigments plus dry earth opacifier at 5%,10% and 15% by volume in stabilizing the color of MDX4-3210/ type A silicone elastomers before and after artificial aging. It was concluded that all 3 concentrations, oil pigments mixed with opacifier helped protect the MDX4-4210/ type A silicone elastomers from color degradation over time. Dry pigment Ti white remained the most color stable over time, followed by the pigments mixed with Kaolin calcined, Georgia kaolin, Artskin white, and Ti white artist's oil color.

Although it is proved that silicone elastomers are color stable, but these materials too, are not ideal and discoloration in these materials is due to ultraviolet light. So to reduce the discoloration due to UV radiation.

In 2008 Eleni P, Katsavou I, Krokida M, Polyzois G[45] conducted a study to evaluate the effect of different pigmentation and irradiation duration on color stability of four silicone elastomers after artificial weathering. The materials used included four different pigmented industrially synthesized RTV silicones (Epsil Europe 1, Epsil Europe 2, Epsil Europe 3, Epsil Africa 3). The materials chosen in this study were representative silicone prosthetics that are widely used in the last decade in maxillofacial prostheses. Artificial weathering was performed in a weatherometer of total radiant energy 1.35 W/m^2 (UVA – UVB). The samples were exposed in eight different periods (8, 24, 48, 72, 96, 120, 144, 168 hours).Significant differences observed in the color between the control and irradiated samples. Artificially weathering caused significant eye detectable color change in Epsil Europe 2, and Epsil Europe3. Color change was acceptable in Epsil Europe 1 and Epsil Africa 3.

Metamerism is a frequently observed problem with color matching for facial prostheses. Computerized color formulation systems offer the ability to control the degree of metamerism. To predict the colorants required for a particular skin color, spectrophotometry, colorimetry, and color formulation provided a solution.In literature, less has been reported on color matching for the African- Canadian population.

In 2008 Coward T, Seelaus R, Li S[46] investigated the effectiveness of spectrophotometry and a computerized color formulation system to predict formulas for coloring mixing silicone elastomer to match the skin color of African- Canadian people. He concluded that spectrophotometry and computerized color formulation provide a foundation in the color matching procedure for facial prostheses that offer objectively to an otherwise subjective task.

The major source of color in human skin are specialized melanin-bearing organelles, the melanosomes present within the epidermis. Gross human skin color derives from the visual impact of the sum of the melanin pigmentation of the numerous epidermal melanin units.Melanin occurs in two types: 1) black to brown eumelanin and 2) yellow to reddish pheolmelanin.It has been concluded that the melanosome distribution in keratinocytes of Asian skin is intermediate between light Caucasian and dark African. Hence, yellowish brown is the predominant color for Indian skin.

There were many studies explaining the different techniques of color reproduction but the literature was scanty with respect to the studies concerning silicone color matching that of Indian skin.

In 2008 Guttal SS, Patil NP, Nadiger RK, Kulkarni R[9] performed a study to develop a simplified silicone shade guide which matches the Indian skin color. This guide will help the prosthodontist to obtain a good intrinsic shade and minimize extrinsic coloration for Indian patients. Hence, authorsdescribed the use of powder color to develop a simplified silicone shade guide to aid in the fabrication of silicone facial prostheses for Indian patients. Ten powder pigments were used to fabricate the silicone samples with thickness variations of 1,2,4 and 6mm were fabricated. Four evaluators to check the agreement of color match did a visual assessment of the samples. This study showed that the samples of dark skin tone matched the skin tone well and showed a statistically good agreement. To further test the validity of these shade guides, facial silicone veneers were fabricated for three patients having light, medium and dark complexion. The color matching showed satisfactory result & this shade will help clinicians to obtain a good intrinsic shade and minimize extrinsic coloration.

In 2009 Paravina R, Majkic G, del Mar Perez M, Kiat-amnuay S.[47] evaluated the perceptibility and acceptability threshold for both skin type, as they may alsodiffer accordingto the skin type. They fabricated 15 pairs of light specimens (mimicking white, Asian, and Hispanic skin) and 15 pairs of dark specimens (mimicking African-

American skin) using skin-colored maxillofacial silicone elastomers(MDX4-4210), combined with opacifiers (titanium white artists' white color) and pigments (oil pigments). Color differences were calculated using CIELAB and CIEDE2000 formulae. After calculating the model parameters, receiver operating characteristics (ROC) curves and area under the ROC curve (AUC) were analyzed. They concluded that both main effects of threshold type (perceptibility and acceptability) and primary color (light and dark) on 50:50 % color difference thresholds of colored maxillofacial elastomers were found significant for both color difference formulae used (CILAB, CIEDE 2000.) In addition, a significant interaction between the two main effects was found, indicating a stronger effect of skin type on acceptability than perceptibility thresholds.

In 2009 Mancuso D, Goiato M, Santos D[48] evaluated the color stability of two types of silicones, out of which one was routinely used RTV Silicone (Silastic MDX4-4210) and other was an acetic silicone developed for industrial use (Silastic 732) For an intrinsic pigmentation of the silicones, three systems of coloring were used: Cosmetic, ceramic and iron oxide. The specimens were submitted to an accelerated system of aging for Readings were carried out initially and after periods corresponding to 163, 351, 692 and 1,000 hours of aging, using a reflection spectrophotometer. They found that during spectrophotometric analysis, both Silastic 732 and MDX4-4210 presented color instability during the different periods of time analyzed. The materials without the incorporation of pigments presented similar color alteration values and did not differ statistically. The cosmetic powder used in this study was the pigment that most altered the color of the test specimens.

Duration of replacement of prosthesis varies according to the material, environmental condition, and location of the prosthesis. However, prostheses should be replaced in a maximum period of one year, due to the color alteration detected by reflection spectrophotometry.

In 2009 Mancuso D, Goiato M, Dekon S, Gennari-Filho H[49] evaluated and compared the color stability of pigmented (make-up, ceramic, iron oxide) and non-pigmented two different silicone, medical and industrial (Silastic MDX4-4210, Silastic 732 RTV)after accelerated aging by a visual method. They concluded that both silicones, behaved similarly, they can, therefore, be indicated for use in maxillofacial prosthesis. The time factor of aging influenced negatively and independently of pigmentation, or lack of it, and of silicones and no group had visually noticeable alteration in any of the accelerated aging time independently of the addition or not of pigments.

A-2000 (Factor II Inc., Lakeside, AR) is a platinum silicone elastomer that was introduced in 2000. It is the first generation of a 1:1 mixture silicone. Till date, no research study has evaluated the color stability of silicone A-2000 maxillofacial elastomer despite the wide clinical use of the material.

In2009 Kiat-amnuay S, Beerbower M, Powers J, Paravina R[50] evaluated the color stability of silicone A- 2000 maxillofacial elastomer when mixed with silicone pigments and different concentrations of opacifiers and aging-dependent differences in color. They concluded that Silicone pigments mixed with 10% and 15% Artskin white and titanium white dry pigment opacifiers protected silicone A-2000 from color degradation over time. Yellow silicone pigment significantly affected the color stability of all opacifiers, especially silicone pigment white and calcined kaolin.

In 2010 Hu X, Johnston W, Seghi R [51] performed a study to check the accuracy of 5 digital instruments to measure the color of maxillofacial prosthesis material. They studied the hypothesis that a non- contact measuring system and 4 contact color-measuring instruments perform comparably in accuracy and precision on measurements of pigmented maxillofacial elastomer specimens having human skin colors. Measurement comparisons in accuracy on opaque standard color patches were made in Phase I. in Phase II, the system with the best accuracy was used as the reference instrument, and comparison in accuracy and precision on elastomer specimen were made. The CIDE2000 color difference formula was used. They concluded that the contact measuring systems perform differently in accuracy, possibly due to edge loss and other factors, but performed comparably in precision with the non- contact measuring instrument. This non-contact system is recommended for color measurement of maxillofacial prosthetic materials.

In 2010 Hatamleh M and Watts D[52] conducted a study to investigate the color stability of pigmented (intrinsic rose pink shade P409) and non- pigmented maxillofacial silicone elastomer (Techsil S25) exposed to different human and environmental aging conditions. (dark storage, sebum solution storage, acidic perspiration storage, light aging, natural outdoor weathering, silicone cleaning solution, and mixed conditioning of sebum storage and light aging. Conditioning periods were 6 months (group 1,2,3, 5), 360 hours (groups 4,7), and 30 hours (group 6). They noticed inherent color instability of non-pigmented facial silicone elastomers primarily contributes to the color degradation of extraoral facial prostheses. Sebaceous skin secretions along with daylight radiation cause the greatest perceivable color change to the silicone and pigments used in this study.

In 2010 Montgomery PC, Kiat-Amnuay S[53] conducted a survey on currently used materials for fabrication of extraoral maxillofacial prostheses in North America, Europe, Asia and Australia. The purpose of this survey was to review the extraoral maxillofacial materials currently used as well as the advantages and disadvantages of the materials in the fabrication of facial prostheses. They found that the views of 43 (16%) respondent indicated that the majority surveyed was using room temperature-vulcanized (RTV) silicone products. Silicone pigments for intrinsic and silicone pastes for extrinsic coloring were favored over artist’s oil colors and dry earth pigments. The polymerization process and/ or curing times and temperatures for the same silicone material varied between users. The top five advantages of most often used materials were good esthetics, ease of coloring. Easy manipulation, thin margins possible and adhesive compatibility. The top five disadvantages were discoloration over time, technique sensitive, lack of reparability, extrinsic colors peel/fade, and lack of longevity. Nontoxic/ non- allergic materials with high edge strength and color stability were the most important features when choosing a maxillofacial prosthetic material/ technique.

In 2010 dos Santos D, Goiato M, Moreno A, Pesqueira A, Haddad M [54] performed a study to evaluate the influence of two pigments (ceramic powder and oil paint) and one opacifier (barium sulfate) on the color stability of MDX4 4210 facial silicon submitted to accelerated aging. The evaluations of chromatic alteration through visual analysis and reflection spectrophotometry were carried out initially and after 252, 504,and 1008 hours aging. They concluded that opacifier protects facial silicones against color degradation, and oil paint is a stable pigment even without addition of opacifier

In 2011 Goiato M et al [55] evaluated the color stability of MDX4-4210 maxillofacial elastomer with opacifier (barium sulfate, titanium dioxide)addition submitted to chemical disinfection and accelerated aging. Disinfectant agents used were efferent tablets, neutral soap, or 4% chlorhexidine gluconate. Disinfection was conducted three times a week for 2 months. Afterward, the specimens were submitted to different periods of accelerated aging. Color evaluation was carried out over 60 days (disinfection period) and after 252,504, and 1008 hours of accelerated aging, using a reflection spectrophotometer. They concluded -1. Chlorhexidine showed the greatest color alteration. 2. Accelerated aging affected the color stability of all groups. 3. The barium sulfate opacifier was more stable in all periods.

In 2011 FilieÌ Haddad M et al [8] evaluated the color stability of maxillofacial silicone with nanoparticle pigment and opacifier submitted to disinfection and artificial weathering as literature was scarce about the interrelation of opacifier addition to facial silicones, mainly when the material is submitted to the process of chemical disinfection and artificial aging. The purpose of this study was to evaluate the color stability of a maxillofacial elastomer with the addition of a nanoparticle pigment and/or an opacifier submitted to chemical disinfection and artificial aging. Specimens were disinfected with effervescent tablets, neutral soap, or 4% chlorhexidine gluconate. Disinfection was done three times a week during two months. Afterward, specimens were submitted to different periods of artificial aging. The color evaluation was initially done, after 60 days (disinfection period) and after 252, 504, and 1008 h of artificial aging with aid of a reflection spectrophotometer. They observed that color changes occurred in all experimental periods, for all studied associations. The association between ceramic nanoparticles and BaSO4 opacifier was the most stable condition in relation to color maintenance, without considering disinfection and the aging period. All deltaE values obtained in the present study, independent of the disinfectant and of the period of artificial aging, were considered clinically acceptable.

In 2013 Kantola R, Lassila L, Tolvanen M, Valittu P[56] observed that silicone elastomers were used to fabricate external maxillofacial prostheses and are colored to match the adjacent facial skin. But, in cold winter weather, in certain individuals, the color of the skin changes toward red, which leads to a color difference between the prostheses and the surrounding tissue. Color changing leuco dyes are used in textiles, paints, to warn of icy conditions, and on radiators, engine parts, and fire doors to warn of overheating. They are usually colored in the cool state and the color transforms to translucent when the temperature rises. The typical range of color-change temperatures can be as low as -10°C to as high as +70°C.they have to be microencapsulated before use as it protects the core coloring agent from the environment. It also enhanced stability, color, and temperature control. The authors identified no previous studies evaluating the use of thermochromic pigment in a silicone elastomer. Hence they investigated the color stability of maxillofacial silicone elastomer, colored with a thermochromic, color changing pigment. Disc-shaped maxillofacial silicone specimens were prepared and divided into 3 groups; a conventionally colored group, one group additionally colored with 0.2 wt % thermochromic pigments, and one group with 0.6 wt% thermochromic pigment. Half of the surface of each specimen was covered with an aluminum foil. All of the specimens were exposed to UV radiation in 6-hour cycle over 46 days. In between the UV exposures, half of the specimens were stored in darkness, at room temperature, and the other half was stored in an incubator, at a humidity of 97% and temperature of +37^{0}C.They concluded that the specimen containing thermochromic pigment was very sensitive to UV radiation, and the thermochromic pigment is not suitable as such, to be used in maxillofacial prostheses.

In 2013 Han Y, Powers J, Kiat-amnuay S[57] studied about few investigations concerning the addition of an inorganic UV mineral based protecting agent to pigmented silicone elastomers. The UV mineral-based protecting agent (LP), a commercial cosmetic UV light blocking powder used in present study, has a sun protection factor (SPF) of 30. The SPF describes the effectiveness of sunscreen and the higher the SPF the more UV light shielding. Authors conducted a study to compare the effect of UV mineral-based light protecting agent (LP) on the color stability of pigmented maxillofacial silicone elastomer DX-4210/ type A after artificial aging to 2 widely used opacifiers. Three different types of opacifiers (LP, titanium white dry pigments [TW], or silicone intrinsic white [SW]) were added to silicone MDX-4210/type A at 3 concentration (5%, 10%,or 15%) and subsequently combined with each of 5 colors (no pigments [control], red, blue, yellow, or mixed pigments). Artists' oil pigment was used with LP and TW, while intrinsic silicone pigment was used to color SW. Before and after energy exposure of 450 kJ/m^2, they concluded that all 3 opacifiers at all concentrations protected pigmented silicone

MDX4-4210 type A from color degradation. The LP group showed the smallest color changes.

An important fact that should be considered during the prosthetic rehabilitation of patients with cancer after resection for basal cell carcinoma [BCC] and other photo-induced skin cancer is recurrence due to UV radiation. Short-wavelength UV-B radiation is suspected to be a greater risk factor in the development of BCC than long-wavelength UV-A radiation.

In 2014 Bangera B, Guttal S[58] evaluated the degree of ultraviolet protection after incorporating varying concentrations of nano-oxides in Cosmesil M511 medical grade silicone elastomer. Nanosized oxides of Zn and Ti were added in various concentrations (0.5%, 1.0%, 1.5%, 2.0%, and 2.5% by weight) to a silicone elastomer. They concluded that as compared to Ti nano-oxides (2% to 2.5%), Zn nano-oxides in lesser concentrations provided more significant and consistent ultraviolet protection in Cosmesil M511 elastomer.

In 2015 Kheur M, Sethi T, Coward T, Patel N.[59] mentioned that the color of silicone elastomer following polymerization in molds made of gypsum products was slightly different from the color that was matched in the presence of the patient before the silicone was packed. Hence, they compared and evaluated the change in color of silicone elastomer (M 511) packed in three commonly used investing materials – (Dental stone-white, Dental stone-green, Die stone); coated with three different separating media (Alginate based medium, Soap solution, and Resin-based die hardening material). In this study die stone showed the maximum color change. Among the separating media, die hardner showed the least color change. The best combination of an investing material and separating media as per this investigation is a dental stone (green) and alginate-based separating media.

Various studies on maxillofacial silicone elastomers investigated the effect of outdoor weathering on their properties. But there has been no report regarding the effect of an exceptionally hot and humid climate on the degradation of maxillofacial silicone polymers.

In 2015 Al-Harbi F, Ayad N, Saber M, ArRejaie A, Morgano S[60] performed a study to compare the effect of weathering in a hot and humid climate on the tear strength, tensile strength, modulus of elasticity, elongation percentage, and color of 3 maxillofacial materials (Techsil S25, A-2186, MED-4210). They concluded that outdoor weathering in a hot and humid climate adversely affected the properties of silicone elastomers. The heat-polymerized TechSil S25 elastomer showed better mechanical durability and color stability compared with the room-temperature polymerized A-2186 and MED-4210 materials. TechSil S25 showed the greater values of tear and tensile strengths and elongation of specimens exposed to outdoor weathering conditions. It also showed the least amount of color change among the pigmented specimens exposed to outdoor weathering.

In 2015 Akash R, Guttal S[61] evaluated the effect of incorporation of two compositions of nano-oxides (Titanium dioxide, zinc oxide) on color stability of intrinsically colored maxillofacial silicone elastomer (M511) subjected to outdoor weathering. They found that incorporation of nano-oxides improved the color stability of Cosmesil M511 silicone elastomer and also acted as an opacifier. ZnOincorporated Cosmesil M511 specimens showed minimal or no color change and proved to be most color stable after being subjected to outdoor weathering.

In 2017 Mehta S, Nandeeshwar D [62] conducted a study to evaluate and compare the color variations between M511 maxillofacial Rubber and Z004 Platinum silicone Rubber after subjecting them to extra oral aging conditions like outdoor weathering, acidic perspiration sebum, neutral soap and disinfectant. They concluded that visually perceptible and clinically unacceptable color change can occur when exposed to various extraoral aging conditions except for neutral soap solution immersion. Clinically both material would yield more or less same results, with unacceptable norms in terms of color stability under extra oral aging conditions.

Materials and Method

The present study was carried out in Dental College and Research Centre. Attempts were made to standardize the procedures throughout the study to minimize the effect of variable factors on the observations and the final result.

For convenience and clarity of description, materials and methods has been

subdivided into the following headings:

I. Materials & Armamentarium

II. Methodology

I. MATERIALS AND ARMAMENTARIUM

1. A-2186 Room temperature vulcanized silicone [Factor II, Arizona, USA]
2. Barium Sulphate [HiMedia Labratories Pvt.Ltd]
3. Titanium dioxide [Nano Labs, Jharkhand, India]
4. Addition silicone impression material (putty) [Kerr Australia Pty. Ltd]
5. Dental stone [Neelkanth Healthcare Pvt.Ltd India].
6. Cold mold seal [Dental Products of India,The Bombay Burmah Ltd.,Mumbai]
7. Distilled water
8. Simulated acidic Perspiration: Simulated acidic perspiration (pH 5.5) was prepared [12,51] as follow:

   I.L-Histidine monohydrochloride monohydrate (Chemical International, Mumbai) – 0.5gms

   II. Sodium chloride (Chemical International, Mumbai) – 5gms

   III. Sodium dihydrogen orthophosphate dehydrate (Chemical International, Mumbai) – 2.2gms.

   Above ingredients were mixed with per liter of distilled water.
9. Simulated sebum solution: Simulated sebum solution was prepared [63]as follow:

   I. 10% Palmitic acid (Chemical International, Mumbai) (wt%)

   II. 2% Glycerine Tripalmitate (Chemical International, Mumbai) (wt%)

   III. 88% Linoleic acid (Chemical International, Mumbai) (wt%).

Armamentarium used for the study

1. Custom fabricated stainless steel die having a disc shaped depression of 30mm diameter and 6mm depth.[8]
2. Rubber bowl
3. Vacuum Mixer
4. Camel hair brush
5. Bard Parker knife
6. Scissor
7. Flask with clamp
8. Bench press unit
9. Hot air oven
10. Silicone finishing burs
11. Pre- weighted plastic container
12. Weighing scale
13. Glass plate
14. Glass beaker
15. Stainless steel container
16. Spectrophotometer - SpectraScan 5100 UV Visible spectrophotometer
17. White metallic plaque

II. METHODOLOGY

1) Die preparation

A precise stainless steel die measuring 30 mm in diameter and 6 mm in thickness was customized.[8] The stainless steel die was used as an initial mould for the duplication of the diameter and the thickness of die achieved by using putty consistency addition silicone elastomeric impression material. The addition silicone elastomeric impression material was manipulated according to the manufacturer’s instructions and was inserted into the stainless steel die and was compressed with the help of a glass plate until there was a positive contact between the glass plate and the stainless steel die.

The disc samples were then trimmed with a sharp Bard Parker knife and were finished. These putty samples were then invested in a flask to make mould for fabrication of the proposed maxillofacial silicone samples. The investing was done with a type III dental stone [4] and the disc shaped samples were widely placed with even spacing between them. The investment method that was followed was a two pour method with the application of a separating media (cold mold seal) between the first and the second pour. After the stone was set, the putty samples were peeled off the mould leaving behind accurate and sharp disc shaped depressions each measuring 30 mm in diameter and 6mm in thickness. The mould was cleaned for any residual fragments of putty or any other impurities.[62]

2) Preparation of the samples

a) Preparation of clear silicone samples- Control group

- A- 2186room temperature vulcanized silicone is available in two parts
- Part A and part B were mixed in 10:1 ratio.
- The mechanical mixing under vacuum was done. The vacuum mixing was carried out at 28 inches Hg for 10 minutes.[28]
- The prepared mould was thoroughly cleaned and dried. Cold mold seal was used as a separating media and was applied evenly over the surface of the mold with the help of a small paint brush and allowed to dry.
- The mixed silicone was then loaded into a syringe and injected into the mould and the flask was closed under pressure using bench press (3.5 psi). The mould was then kept in hot air oven at 100^0 C for initial curing and then kept at room temperature for 24 hours for complete curing.
- After deflasking, samples were removed and inspected for surface irregularities, contaminants and internal defects. The flash and excess silicone was cut with a pair of sharp scissors. Any undesirable nodules were trimmed off using a sharp Bard Parker blade. The finishing of the samples were done using silicone finishing burs (coarse and fine). The samples were then thoroughly washed under running water and were cleaned in an ultrasonic cleaner with distilled water for a period of 15 minutes.

b) Preparation of experimental samples

i) Samples containing titanium dioxide

- A- 2186 room temperature vulcanized silicone is available in two parts.
- Part A and part B were mixed in 10:1 ratio.
- Titanium dioxide nano particle was added 0.2% by weight. [8]
- The mechanical mixing under vacuum was done. The vacuum mixing was carried out at 28 inches Hg for 10 minutes. [28]
- The prepared mould was thoroughly cleaned and dried. As per the manufacturer’s instructions, a cold mold seal was used as a separating media and was applied evenly over the surface of the mold with the help of a small paint brush and allowed to dry.
- The mixed silicone was then loaded into a syringe and injected into the mould and the flask was closed under pressure using bench press (3.5 psi). The mould was then kept in hot air oven at 100^0 C for initial curing and then kept at room temperature for 24 hours for complete curing.
- After deflasking, specimens were removed and inspected for surface irregularities, contaminants and internal defects. The flash and excess silicone was cut with a sharp scissors. Any undesirable nodules were trimmed off using a sharp Bard Parker blade. The finishing of the specimens were done using silicone finishing burs (coarse and fine). The samples were then thoroughly washed under running water and were cleaned in an ultrasonic cleaner with distilled water for a period of 15 minutes.

ii) Samples containing barium sulphate

- A- 2186 room temperature vulcanized silicone is available in two parts.
- Part A and part B were mixed in 10:1 ratio 23-25^{0}C.
- Barium sulphate was added 0.2% by weight [8]
- The mechanical mixing under vacuum was done. The vacuum mixing was carried out at 28 inches Hg for 10 minutes. [28]
- The prepared mould was thoroughly cleaned and dried. As per the manufacturer's instructions, cold mold seal was used as a separating media and was applied evenly over the surface of the mould with the help of a small paint brush and allowed to dry.
- The mixed silicone was then loaded into a syringe and injected into the mould and the flask was closed under pressure using bench press (3.5 psi). The mould was then kept in hot air oven at 100^0 C for initial curing and then kept at room temperature for 24 hours for complete curing.
- After deflasking, samples were removed and inspected for surface irregularities, contaminants and internal defects. The flash and excess silicone was cut with a sharp scissors. Any undesirable nodules were trimmed off using a sharp Bard Parker blade. The finishing of the samples were done using silicone finishing burs (coarse and fine). The samples were then thoroughly washed under running water and were cleaned in an ultrasonic cleaner with distilled water for a period of 15 minutes.

3. Distribution of samples:

93 samples were divided into 1 control and 2 experimental groups.

A total of 62 experimental (titanium dioxide and barium sulphate) and 31 control samples were fabricated.

Group A- Control group (Untreated)	No pigment	30 Samples +1 (Stored in closed box)*
Group B- TiO_2 (Experimental group)	samples containing titanium dioxide	30 Samples +1 (Stored in closed box)*
Group C ($BaSO_4$) (Experimental group)	samples containing barium sulphate	30 Samples +1 (Stored in closed box)*
Total		93 Samples

- * 2 experimental (titanium dioxide and barium sulphate) and 1 control (untreated) samples were made, which were stored in a closed box in a well ventilated area, for later analysis by visual method of comparison.[49,54]
- The three main groups were further divided into four sub groups containing ten samples in each sub group for testing color stability under human and environmental aging conditions and one subgroup having one sample which was kept in closed box and later used for visual analysis.

Control/untreated (Group A)		**Titanium dioxide (Group B)**		**Barium sulphate (Group C)**		**Exposure Duration**
Storage condition	Sample size	Storage condition	Sample size	Storage condition	Sample size	
1.Outdoor weathering (A_1)	10	1.Outdoor weathering (B_1)	10	1.Outdoor weathering (C_1)	10	6 months
2.Acidic perspiration (A_2)	10	2.Acidic perspiration (B_2)	10	2.Acidic perspiration (C_2)	10	6 months
3.Sebum Solution (A_3)	10	3.Sebum solution (B_3)	10	3.Sebum solution (C_3)	10	6 months
4. Closed box (A_4)	1	4. Closed box (B_4)	1	4 Closed box (C_4)	1	6 months
Total	**31**		**31**		**31**	

One control and two experimental groups

Sub-Groups	**Storage condition**	**Total Sample size**
A_1 B_1 and C_1	Subjecting to outdoor weathering	30
A_2 , B_2 and C_2	Subjecting to simulated sebum solution	30
$A_{3,}$ $B_{3,}$ andC_3	Subjecting to acidic perspiration	30
A_4, $B_{4,}$ andC_4	Stored in closed box	3
Total		93

Among the samples made, 93 best samples were selected as test samples. Each sample was labeled specifying the group and the sub group. For example, the samples belonging to the Group A and sub group 1 were marked as A_1-1, A_1-2, A_1-3, A_1-4, A_1-5, A_1-6, A_1-7, A_1-8, A_1-9, A_1-10 for the ease of identification. Likewise for both groups specific sampling labeling was done.

4) Measurement of color value of the samples prior to different human and environmental aging condition: (Base-line readings)

After finishing, all the samples from each group were dried and then each sample of silicone was subjected to color measurement, using a UV reflection spectrophotometer before subjecting them to various human and environmental aging conditions. The color measurement was done by assessing the direction of arrow which indicated the surface of sample exposed to environment and the same surface was tested. The most common method to describe color is the CIE (Commission International d'Eclairage) $L^* a^* b^*$The "L" axis is known as brightness and extends from 0 (black) to 100 (perfect white). The coordinate "a" represents the amount of red (positive values) and of green (negative values), while the coordinate "b" represents the amount of yellow (positive values) and of blue (negative values).[8,11] This system calculates the value of ΔE (color change), between two readings, by means of the formula:

- $$\Delta E = \sqrt{[\Delta L^*]^2 + [\Delta a^*]^2 + [\Delta b^*]^2}$$

The recorded values of $L^* a^* b^*$ were entered in a spreadsheet program (Microsoft Excel)

5) Exposing the samples to human and environmental aging conditions:

1. Sub group A_1, B_1 and C1– Subjected to outdoor weathering:

Atmospheric environmental exposure of samples was conformed to American Society for Testing and materials (ASTM) Designation G7-83[64] and was exposed according to the ASTM E782.[7] The samples were placed on exposure rack of plywood backed. The assembly was subjected to outdoor weathering by placing on the roof of dental institute from February 2017 to August 2017 for a period of 6 months. During the exposure to the environment, the samples were uncovered. The exposure rack was adjusted to an angle close to perpendicular to the direct beam of solar radiation, approximately 5 degrees from the horizontal to avoid standing water and maximize the amount of sunlight on the specimens.[11] This ensured the exposure of samples to sunlight, air pollution, ambient temperature, and humidity.

The samples were subjected to outdoor weathering for 8 hours from the month of February to August (6 months) to ensure the exposure of samples to all the three Indian climatic conditions (seasons).

2. Sub group A_2, B_2 and C_2– Subjected to acidic perspiration:

The samples were immersed in simulated acidic perspiration for duration of 6 months. Simulated acidic perspiration (pH 5.5) was prepared according to International Organization for Standardization (ISO) specification 105-E04:87, Part E04: Color fastness to perspiration, as described above. The simulated acidic perspiration was freshly repeated after the first three months.[12,51]

3. Sub group A_3, B_3 and C_3 – Subjected to simulated sebum solution:

The samples were immersed in simulated sebum solution for a period of 6 months. Simulated sebum solution was prepared as described by Mohite et al [63] as mentioned above. The simulated sebum solution was freshly repeated after the first three months.[12,51]

4. Sub group A_4, B_4, and C_4 -Stored in closed box

One sample from each subgroup was not submitted to any human or environmental condition. These samples were stored in a closed box in a well-ventilated area, without the interference of direct or indirect light, for later analysis by a visual method of comparison. This analysis was carried out with the samples that were submitted to the human and environmental aging conditions and the sampl that did not go through this process.[49,54]

6) Measurement of color value of the samples after exposing to different human and environmental condition:

Color measurement was done by following two methods:

I. Spectrophotometric analysis

II. Visual analysis

I.) Spectrophotometric analysis –

Samples were cleaned for 10 mins in distilled water in an ultrasonic cleaner, wiped dry and tested. Testing of samples was done as same manner using spectrophotometer. This system calculates the value of ΔE (color change), between two readings, by means of the formula:

- $$\Delta E = \sqrt{[\Delta L^*]^2 + [\Delta a^*]^2 + [\Delta b^*]^2}$$

The recorded values of L^* a^* b^* were entered in a spreadsheet program (Microsoft Excel)

II. Visual analysis

Samples were visually compared following their exposure to environmental and different human aging conditions, with samples that did not go through this aging process. Visual analysis was done by 2 color-normal observers - dental professionals whose color vision was tested in the department of ophthalmology. Samples from each group were placed in pairs with the sample stored in closed box, side by side, on the top of a white metallic plaque at a distance of 30 cm and were analyzed. For the evaluation of this method, scores varying from -5 to +5 were used: [49,54]

-5	Extremely dark
-4	Very dark
-3	Dark
-2	fairly dark
-1	Slightly darker
0	Stored in closed box
+1	Slightly clearer
+2	Fairly clear
+3	Clear
+4	Very clear
+5	Extremely clear

Results were recorded according to the scores. The visual reading was carried out among sample of the same group and not among the different groups. [47,49]

The observations for all the study samples were recorded, tabulated and the data was subjected to statistical analysis.

PLATE I

MATERIALS

Fig. 1 : Silicone Elastomer A 2186

Fig.2 : Addition Silicone

Fig. 3 : Separating medium and Dental Stone

Fig. 4 : Chemicals used

Fig. 5 : Barium sulphate

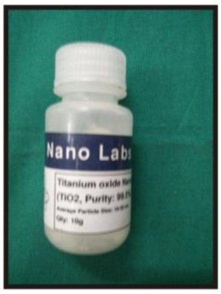

Fig. 6 : Titanium Dioxide

PLATE II

ARMAMENTARIUM

Fig. 7 : Digital weighing balance

Fig. 8 : Varsity flask

Fig. 9 : Hydraulic press

Fig. 10 : Ultrasonic cleaner

Fig. 11 : Hot air oven

Fig. 12 : Vacuum mixer

Fig. 13 : Spectrophotometer

PLATE III

ARMAMENTARIUM AND METHODOLOGY

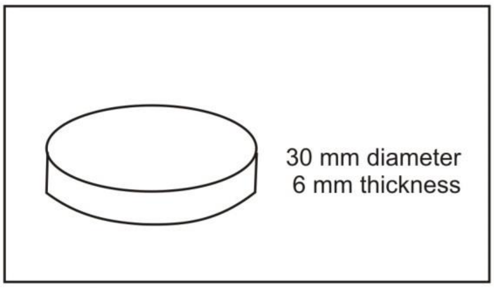

Fig. 14 : Schematic representation of stainless steel die

Fig. 15 : Stainless steel Die, putty sample, Dental stone mold

Fig. 16 : Stainless steel container

Fig. 17 : Rubber bowl, straight spatula, glass plate, camel hair brush bard parker knife, scissors, syringe, silicone finishing bur, pre-weighted plastic container

Fig. 18 : Glass Beaker

Fig. 19 : White metallic plaque

PLATE IV

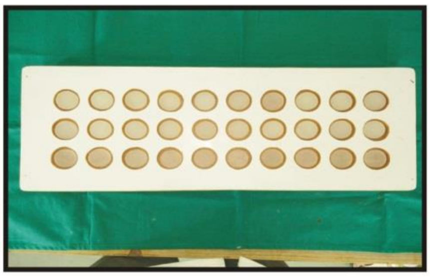

Fig. 20 : Samples exposed to outdoor weathering

Fig. 21 : Samples exposed to acidic perspiration

Fig. 22 : Samples exposed to sebum solution

Fig. 23 : Samples stored in closed box

PLATE V

SAMPLES

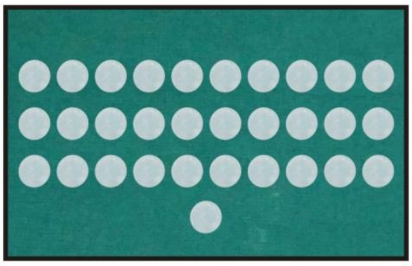

Fig. 24 : Group A before exposure

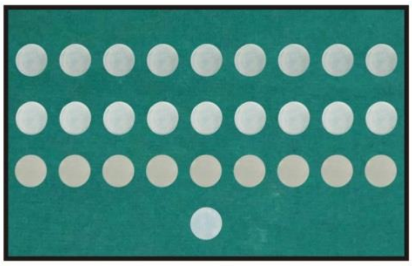

Fig. 27: Group A after exposure

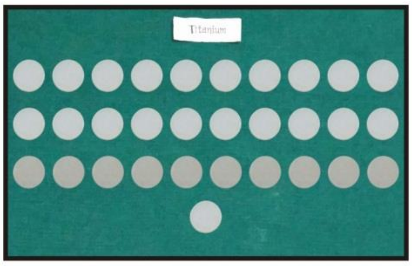

Fig. 25 : Group B before exposure

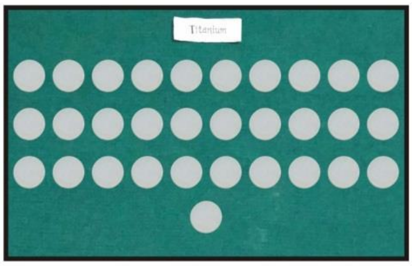

Fig. 28 : Group B after exposure

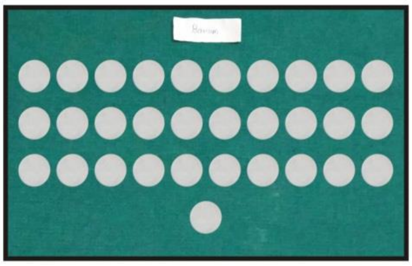

Fig. 26 : Group C before exposure

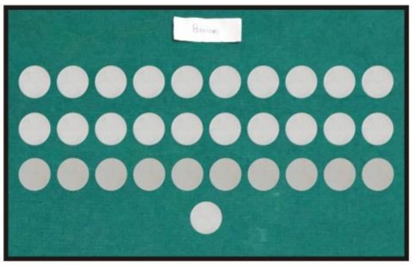

Fig. 29 : Group C after exposure

Results

In the present study color stability of maxillofacial elastomer incorporated with the nano particle pigment and opacifier and exposed to human and environmental aging conditions was evaluated.

Baseline color measurements were done before 6 month using a spectrophotometer, then samples were exposed to environmental and human aging conditions and again color was evaluated by spectrophotometer.

Visual analysis was also done in the present study. Samples were visually compared following their exposure to environmental and different human aging conditions, with samples that did not go through this aging process. The visual reading was carried out among sample of the same group and not among the different groups.

93 samples were divided into 1 control and 2 experimental groups

The three main groups were further divided into four sub groups containing ten samples in each sub group for testing color stability under human and environmental aging conditions and one subgroup having one sample which was kept in closed box and later used as a control sample for visual analysis.

	Control group - Group A (n)	**samples containing titanium dioxide Group B (n)**	**samples containing barium sulphate- Group C (n)**
Outdoor weathering	A_1(10)	B_1(10)	C_1(10)
Acidic perspiration	**A_2(10)**	**B_2(10)**	**C_2(10)**
Sebum solution	A_3(10)	B_3(10)	C_3(10)
Closed box	A_4(1)*	C_4(1)*	C_4(1)*
Total	31	31	31

After 6 month spectrophotometric analysis was again done for measurements for color change.

Color difference were determined using following equation:

$$\Delta E = \sqrt{[\Delta L^*]^2 + [\Delta a^*]^2 + [\Delta b^*]^2}$$

The master chart shows **ΔE** values of all samples of group A, group B, group C.

[ANNEXURE]

STATISTICAL ANALYSIS

The data on pre- and post-exposure parameters i.e. L (degree of lightness and darkness), a (red or green chroma) and b (yellow or blue chroma) were obtained for each sample and accordingly change in color (ΔE) was determined using expression:

- $\Delta E = \sqrt{[\Delta L^*]^2 + [\Delta a^*]^2 + [\Delta b^*]^2}$

The statistical parameters like mean, standard deviation, minimum, maximum and standard error were obtained for pre and post-exposures for each parameter, as well as for color change. The statistical comparison of mean color change across exposures in different groups was performed using one-way analysis of variance. Pair wise comparison was done using Tukey's post-hoc test. Similar analyses were performed for comparing mean color change across treatments for each exposure types. Further, 'percent agreement' method was used to determine the consensus between two observers for visual methods of evaluation of color change. All the analyses were done using SPSS ver. 20.0 (IBM Corp) and statistical significance was tested at 5% level.

1. DESCRIPTIVE STATISTICS

Table 1 provides mean, standard deviation, minimum, maximum and standard error for each parameter as well as color change (ΔE) for samples in Group A, before and after different exposures. The mean color change for samples exposed to outdoor weather was 3.69 ±0.49, with a minimum of 2.78, maximum of 4.21, and standard error of 0.155. For acidic perspiration, the mean was 3.58 ±0.68, with a minimum of 2.02, maximum of 4.49, and standard error of 0.215. For sebum exposed samples, the mean color change was 7.53 ±0.22, with a minimum of 7.28, maximum of 8.02, and a standard error of 0.069. The difference of mean across group was statistically highly significant with p-value < 0.0001. A graphical representation of data is given in Graph 1a, 1b, 1c and 1d.

Table 2 provides mean, standard deviation, minimum, maximum and standard error for each parameter as well as color change (ΔE) for samples in Group B, before and after different exposures. The mean color change for samples exposed to outdoor weather was 2.60 ± 0.24, with a minimum of 2.33, maximum of 3.01, and standard error of 0.076. For acidic perspiration, the mean was 2.35 ± 0.13, with a minimum of 2.18, maximum of 2.62, and standard error of 0.041. For sebum exposed samples, the mean color change was 4.91 ± 0.44, with a minimum of 4.45, maximum of 5.63, and a standard error of 0.139. The difference of mean acrosss groups was statistically highly significant with p-value < 0.0001. A graphical representation of data is given in Graph 2a, 2b, 2c and 2d.

Table 3 provides mean, standard deviation, minimum, maximum and standard error for each parameter as well as color change (ΔE) for samples in Group C, before and after different exposures. It is evident that the mean color change for samples exposed to outdoor weather was 1.59 ±0.28, with a minimum of 1.16, maximum of 1.81, and standard error of 0.089. For acidic perspiration, the mean was 1.46 ±0.28, with a minimum of 1.10, maximum of 1.94, and standard error of 0.089. For sebum exposed samples, the mean color change was 4.03 ±0.57, with a minimum of 3.48, maximum of 4.74, and a standard error of 0.180. The difference of mean across groups was statistically highly significant with p-value < 0.0001. A graphical representation of data is given in Graph 3a, 3b, 3c and 3d.

2. INTRA GROUP ANALYSIS

To determine which group was contributed to overall significance, pair wise analysis was performed and the significance was tested using Tukey's post- hoc test

Table 4 gives the statistical comparison of mean color change for samples exposed to different conditions in Group A using one-way analysis of variance. The difference was statistically highly significant with p-value < 0.0001. Accordingly, pair wise analysis was performed using Tukey's post-hoc test (**Table 4.1**), which revealed that the difference between outdoor weather and acidic perspiration was insignificant, while that of sebum exposure was significantly different than other two exposures.

Table 5 gives the statistical comparison of mean color change for samples exposed to different conditions in Group B using one-way analysis of variance. The difference was statistically highly significant with p-value < 0.0001. Accordingly, pair wise analysis was performed using Tukey's post-hoc test (**Table 5.1**), which revealed that the difference between outdoor weather and acidic perspiration was insignificant, while that of sebum exposure was significantly different than other two exposures.

Table 6 gives the statistical comparison of mean color change for samples exposed to different conditions in Barium treated group using one-way analysis of variance. It is evident that the difference was statistically highly significant with p-value < 0.0001. Accordingly, pair wise analysis was performed using Tukey's post-hoc test (**Table 6.1**)which revealed that the difference between outdoor weather and acidic perspiration was insignificant, while that of sebum exposure was significantly different than other two exposures.

Table 7 provides the comparison of mean color change for samples exposed to outdoor weather and treated with different techniques using one-way analysis of variance. The test resulted into a p-value < 0.0001 indicating statistically highly significant difference of means across treatments. A pair wise analysis using Tukey's post-hoc test (**Table 7.1)** revealed that all the three means differed significantly from each other.

Table 8 provides the comparison of mean color change for samples exposed to acidic perspiration and treated with different techniques using one-way analysis of variance. The test resulted into a p-value < 0.0001 indicating statistically significant difference of means across treatments. A pair wise analysis using Tukey's post-hoc test (**Table 8.1**) revealed that all the three means differed significantly from each other.

Table 9 provides the comparison of mean color change for samples exposed to sebum solution and treated with different techniques using one-way analysis of variance. The test resulted into a p-value < 0.0001 indicating statistically significant difference of means across treatments. A pair wise analysis using Tukey's post-hoc test (**Table 9.1**) revealed that all the three means differed significantly from each other.

Table 10 provides the percent agreement between two observers for visual method of evaluation of color change. For percent agreement, a value of 0.0 indicates no agreement, while a value of 1.0 indicates perfect agreement between observers. Table shows that for barium treated samples, there was perfect agreement between observers as regards change of color as indicated by values of 1.0, irrespective of the exposure. In Titanium treated group, it was 0.8 for all the three exposures, while for Control group, it ranged between 0.7 to 0.9. Thus the null hypothesis was rejected.

Discussion

Extraoral maxillofacial prosthesis is a boon for the patients restoring missing facial structures due to resection, trauma, or congenital anomaly. When surgical reconstruction is not possible, maxillofacial prostheses is the only option which restore the form function and esthetics to large extent and thereby enhances the self confidence of the patient however it is not easy for the patient to accept such prosthesis due to various reasons. Two major problems associated with maxillofacial prostheses are:1) the degradation of static and dynamic physical properties of elastomers, and 2) discoloration of these prostheses in a service environment including sebaceous oils and perspiration. The overall color deterioration of facial prosthesis has also been attributed to certain environmental factors such as solar radiation, temperature, pollution and water.[15] Weathering is the adverse response of a material to climate, often causing unwanted discoloration. Finished facial prosthesis rest on living human skin for long periods and may absorb perspiration and sebum. These absorbed species may cause degradative changes in the elastomer structure, resulting in the ultimate deterioration of the prostheses.[10,11,12,15] **R.M Jani and N.G Schaaf**[21] reported that, of patients who had their prostheses remade within 1 year, 29% had returned for new prostheses because of color change. **Chen MS, Udagama A, Drane JB**[27] conducted a study to evaluate the reactions of patients to their facial prostheses. Color fading was the most frequent response given by the patients for disliking their prostheses.

Silicone elastomers are most commonly used for the fabrication of maxillofacial prostheses due to its advantageous characteristics such as good biocompatibility and bio durability, wide service temperature range, non-adhesive properties, low toxicity, possible optical transparency, low chemical reactivity, and excellent resistance to attack by oxygen, ozone, and sunlight. [45]

Chemically they are known as polydimethyl siloxane and are divided into two basic types: room temperature vulcanizing (RTV silicone) and heat vulcanizing (HTV silicone). Room temperature vulcanizing silicone is a material of choice most commonly to provide best service to the patient due to its better physical properties and color stability.[53,60,65]

Clinical studies demonstrated the average life span of maxillofacial prosthesis is 6 months to 1 year.[11,61] There has been lot of research done on various additions [8,36,41,43,44,45,50,55,57] in maxillofacial silicone in order to improve its color stability like intrinsic addition of opacifiers and nano particle.

Color stability can be evaluated by a instrument or by human eye. Most commonly it is evaluated by a instrument called spectrophotometer however, it is important to co-relate the color degradation detected by spectrophotometer and by visual analysis.[54] Keeping all these factors in mind, present study was carried out to evaluate and compare the color stability of most commonly used maxillofacial silicone elastomer (A-2186) incorporated with nano particle pigment and opacifier after subjecting it to human and environmental aging conditions like; outdoor weathering and skin secretions, color stability was evaluated by visual and spectrophotometric analysis

Materials used in this study, A-2186 room temperature vulcanized silicone elastomer which is most commonly used for fabrication of extra oral prosthesis.[53,60]

Intrinsic addition of opacifiers to facial silicones promoted longer color maintenance.[8,39,41,44,54]

In the present study barium sulphate was used as an opacifier which consists in a white powder, insoluble in water and organic fluids, used in the industry to achieve the white color in paints, glass, and photographic papers. In dentistry, it is used as an opacifier of endodontic cements and in medicine as radiographic contrast. It is also added to sunscreens due to the physical capacity of UV shielding and to obtain an enhanced appearance in cosmetics. The opacifier barium sulphate was added 0.2% by wt to the silicone elastomer. [8,48,49,54,55]

Titanium dioxide nanoparticles were used as additive pigment for maxillofacial silicones with the purpose of improving color stability and imparting white color.[55]

Mayer [32] mentioned in his literature that the nomenclature of pigments can be confusing. A single color can be known by many names or 2 entirely different colors can be known by the same name. Titanium white can be known as titanium dioxide, anatase, or rutile. Nano-oxides are inorganic white powders. TiO2 is widely used as inorganic UV absorbers.[41,44,55] Electrons among nano-particles are forced to vibrate, when ultraviolet light acts on it in the media. As the size of nano-particles is smaller than the ultraviolet wavelength, then some part of ultraviolet light are scattered and some part are absorbed by nano-particles simultaneously. Based on these physical principles, ultraviolet shielding is the result of nano-particles absorption and scattering. The smaller the size of nano-oxide, the more ultraviolet shielding.[61]Addition of these polymer can improve the mechanical and optical properties of the polymer due to their small size, large specific area, quantum effect, and strong interfacial interaction between the organic polymer and inorganic nanoparticles, respectively. [65]

While preparing the samples, a precise stainless steel die measuring 30 mm in diameter and 6 mm in thickness was customized. The stainless steel die was then used as an initial mold for the duplication of the diameter and the thickness of die achieved by using polyvinyl siloxane impression material (putty viscosity).[8,62]

The mechanical mixing was done under vacuum mixer in this study. The vacuum mixing was carried out at 28 inches Hg for 10 minutes. After vacuum mixing the uniform mix free of air bubbles was obtained. Mixture was then loaded into a syringe and injected into each gypsum mold [28,65] this was done in order to reduce pore numbers and percentages in comparison to manual mixing.

Samples were exposed to Indian environmental condition, as one of the most desirable performance characteristics of an ideal facial prosthetic elastomer is the ability to withstand color change when exposed to sunlight over an extended period. Hence, information was required on the long-term outdoor performance of a material, and not only on its performance against artificial weathering. Artificial weathering can be used to approximate the outdoor performance of polymers, so that it can predict the lifetime of polymers under service conditions. However, accelerated artificial weathering can influence the degradation mechanism and results into inaccurate estimation of the lifetime of polymers. [66] The quality and quantity and amount of absorption of radiant energy affects the degradation characteristics of materials when it is exposed to outdoor weathering.[11, 61]

It is difficult for an individual to be outdoors for 24 hours of a day. In general if we consider an average of 8 to 12 hours daily outdoor exposure of a facial prosthesis. then six months exposure period could be equivalent to 1 to 1.5 years of clinical service. The storage period in the solutions simulates 1.5 years of clinical service, which is enough for clinical application, since the mean lifetime of the prostheses is 14–24 months. For this reasons a period of 6 months was selected that represents from 1 to 1.5 year of clinical use.[45]

The 6 months of weathering ensure the exposure of samples to all the three Indian climatic conditions (seasons).[61] samples were placed on plywood rack 5^0 tilted to horizontal plane on the roof of dental institute for 8 hours daily.[11,45,60,61].

Samples were exposed to outdoor weathering from the month of February 2017 to August 2017. The maximum temperature that was recorded during this time period was 42.7^{0}C in the month of April and May, and the lowest temperature recorded was 29^{0}C in the month of February. The highest amount of rainfall that was recorded was 111 mm in the month of June. However, the average rainfall recorded during this time period was 93.8 mm. The above data was obtained from Regional Meteorological Centre.

In the present study samples were exposed to human aging condition as while resting on living human skin for extended periods, facial prosthetics may absorb perspiration and sebum. Absorption of these secretions may cause changes in materials' structure, resulting in the deterioration of prosthesis. The pH of human skin is 5.5 (mildly acidic). Sweat which is a salty, watery solution and secreted by sweat glands. Mixture of sebum and sweat form a protective layer on skin surface, that protects it from "the elements" (such as wind or pollutants), as well as prevent the growth of harmful bacteria and fungi. A recent research has shown that sebum secretion levels varies as seasonal and environmental changes. The skin secretions, mouth rinse, and other solutions are also responsible for any color changes of the elastomeric prosthetic material. An increase in skin surface pH encourages bacterial growth.[11,67]

Color can be evaluated by various instruments. Spectrophotometer have been shown to be more accurate in measuring the color change than colorimeters hence, was chosen for assessment of color in this study. [25]

For this study, the UV reflection spectrophotometer was well suited for measuring the very small changes in the color of the elastomers. The most common method to describe color is the CIE (commission International d'Eclairage) $L^* a^* b^*$The "L" axis is known as brightness and extends from 0 (black) to 100 (perfect white).

The coordinate “a” represents the amount of red (positive values) and of green (negative values), while the coordinate “b” represents the amount of yellow (positive values) and of blue (negative values). L*a*b* values of each specimen at baseline and after 6 months of exposure to environmental and human aging conditions were measured by placing the measuring head on each specimen, using a standard white background.[8,11]

This system calculates the value of ΔE (color change), between two readings, by means of the formula:

$$\Delta E = \sqrt{[\Delta L^*]^2 + [\Delta a^*]^2 + [\Delta b^*]^2}$$

A color change is considered very low when $\Delta E < 1$. The situation is clinically acceptable if $1 < \Delta E < 3$, and it is considered clinically perceptible if $\Delta E > 3$. [8]

Based on ΔE values of the present study color change observed in all samples of control group (Group A) and all the samples exposed to sebum solution (sub-group B_3 and C_3) was clinically perceptible.

In the present study significant color change was observed in control samples (Group A) exposed to outdoor weathering (P value < 0.0001) and sebum solution and acidic perspiration(P value < 0.0001). These findings were in accordance with studies done by **Haug S, Andres C, Moore B**[39] who concluded that a color change occurred not only to the colored but also to uncolored materials over time. **Hatamleh M and Watts D.**[52] who investigated the color stability of pigmented and non- pigmented maxillofacial silicone elastomer exposed to different human and environmental aging conditions. Sebaceous skin secretions cause the greatest perceivable color change to the silicone and pigments used in this study. He noticed inherent color instability of non-pigmented facial silicone elastomers primarily contributes to the color degradation of extraoral facial prostheses **Al-Harbi F, Ayad N, Saber M, ArRejaie A, Morgano S**[60] concluded that outdoor weathering in a hot and humid climate adversely affected the properties of silicone elastomers. . **Willett E, Beatty M**[68] in their investigation concluded that color changes in unpigmented elastomers have been attributed to chemical changes occurring within the polymer, which produce a change in the index of refraction over time. A study was conducted by **Yanagisawa H**[69] who evaluated the effect of lipids on color stability of two silicone elastomers in which he concluded that lipid absorption itself caused minimal changes in the samples, but the degeneration of the samples resulted from oxidation of the absorbed lipid. Significant color change observed in control samples exposed to sebum solution is attributed to the degeneration of the samples resulting from oxidation of the absorbed lipid rather than the lipid absorption itself.

Samples containing titanium dioxide (Group B) , exposed to environmental and acidic perspiration were color stable. Color stability was less in samples exposed to the sebum solution (P value < 0.0001). These results are in accordance with studies conducted by **Sudarat Kiat-amnuay et al**[44] who evaluated the effect of either pigments or opacifiers on the color stability of maxillofacial elastomers before and after artificial aging. It was concluded that dry pigment Ti white remained the most color stable over time. **Muhanad M. hatamlech& David C. watts** [52] **who** observed the least amount of color change among the pigmented specimens exposed to outdoor weathering, also **Al-Dharrab A, Tayel S, Abodaya M** [70] evaluated the effect of different storage conditions on physical properties and color stability of maxillofacial silicone elastomer. He concluded that silicone rubbers are resistant to salt solution and to dilute solution of acids and base and also resist absorbing organic materials.

Samples incorporated with barium sulphate were most color stable. Color stability was maximum with samples exposed to outdoor weathering followed by acidic perspiration and sebum solution. The difference between outdoor weathering and acidic perspiration was insignificant (P value 0.740), while that of sebum exposure was significantly different than other two exposures (P value< 0.0001). Incorporation of opacifier in the silicone matrix increases material durability and keeps the prosthesis esthetically pleasing in relation to color stability for a long time. These results are in accordance with the studies conducted by**, dos Santos D, Goiato M, Moreno A, Pesqueira A, Haddad M** [54]who concluded that opacifier protects facial silicones against color degradation. **Hatamleh M and Watts D.**[52]also observed the least amount of color change among the pigmented specimens exposed to outdoor weathering **FilieÌ Haddad M et al** [8] evaluated the color stability of maxillofacial elastomer with opacifier addition exposed to chemical disinfection and accelerated aging. They concluded that the barium sulfate opacifier was more stable in all periods. Also **Al-Dharrab A, Tayel S, Abodaya M** [70] evaluated the effect of different storage conditions on physical properties and color stability of maxillofacial silicone elastomer. He concluded that silicone rubbers are resistant to salt solution and to dilute solution of acids and base and also resist absorbing organic materials.

VISUAL ANALYSIS

Samples were visually compared following their exposure to environmental and different human aging conditions, with samples which were kept in closed box.

For the evaluation of this method, scores varying from -5(Extremely dark) to +5(Extremely clear) were used.

Color measurement by spectrophotometry is a reliable, sensitive, and repeatable method; however, some color changes detected by this method can not be observed visually. Only ΔE values higher than 3 can be detected by the human eye. [55] The color change is considered very low when $\Delta E < 1$. The situation is clinically acceptable if $1 < \Delta E < 3$, and it is considered clinically perceptible if $\Delta E > 3$. [8]

For control samples (Group A): Color change was visually detectable in control samples. The highest color change was observed in the samples exposed to sebum solution.

For samples incorporated with titanium dioxide (Group B): Color change that occurred in samples exposed to outdoor weathering and acidic perspiration was not visually detectable. Visually detectable color change was noticed by both the observers in samples exposed to sebum solution.

For samples incorporated with barium sulphate (Group C) : Color change in samples exposed to outdoor weathering and acidic perspiration was not visually detectable. Visually noticeable color change was occurred in samples exposed to sebum solution.

The color stability of tested maxillofacial silicone thus depends upon addition of opacifier and nano particle pigments, environmental and human aging conditions it is subjected to.

The final outcome is subjective to particular patient and depends upon complex interaction among all these factors.

CLINICAL IMPLICATION

Color degradation of a prostheses due to environmental and human aging condition is one of the major reason for early replacement of prosthesis by the patient. Addition of barium sulphate and titanium dioxide nano particle can protect the prosthesis from color degradation due to outdoor weathering and acidic perspiration and increases the life of prosthesis.

LIMITATION OF THE STUDY

1. In order to avoid bias while evaluating the color stability of maxillofacial silicone elastomer, specific color pigments were not added with silicone elastomer. As addition of color pigment depends upon the individuals skin tone and hence it can not be standardized.
2. Visual analysis is very subjective and it can vary person to person and can not be standardized.
3. As with any in vitro study the results are obtained in laboratory set up, it can not be extrapolated completely to a clinical situation.

Summary

The present investigation was carried out to evaluate and compare the color stability of maxillofacial silicone elastomer incorporated with opacifier and nanoparticle pigments exposed to environmental and different human aging condition by spectrophotometric and visual analysis.

A 2186 platinum based maxillofacial silicone elastomer was used for the study. Barium sulphate was used as an opacifier. Titanium dioxide was used as a nanoparticle pigment. Pigment and opacifier was added 0.2% by wt. Samples were exposed to environmental and human aging conditions like outdoor weathering, acidic perspiration and sebum solution for 6 months (February 2017 to August 2017). For the purpose of investigation precise stainless steel die measuring 30 mm in diameter and 6 mm in thickness was customized. Total 93 samples were made.

The samples were finished using standardized method. Samples were divided in 3 groups Control (Group A), Samples containing titanium dioxide (Group B) and samples containing Barium sulphate (Group C). 10 samples from each group were exposed to outdoor weathering (A_1,B_1,C_1), acidic perspiration (A_2,B_2,C_2) and sebum solution (A_3,B_3,C_3). 1 sample from each group was kept in closed box (A_4,B_4,C_4) in a well ventilated area as a reference for visual analysis.

A reflectance spectrophotometer was used to assess the color change. The color measurement was done before and after the exposure of samples to environmental and human aging conditions. The color change was evaluated at the end of 6 months using formula

$$\mathbf{\Delta E = \sqrt{[\Delta L^*]^2 + [\Delta a^*]^2 + [\Delta b^*]^2}}$$

Where ΔL, Δ a, Δb are the differences in the L, a and b values of the samples before and after 6 month

Samples were visually compared following their exposure to environmental and different human aging conditions, with samples which were kept in closed box (A_4,B_4,C_4) . For the evaluation of this method, scores varying from -5 (Extremely dark) to +5(Extremely clear) was used.

The color change is considered very low when $\Delta E < 1$. The situation is clinically acceptable if $1 < \Delta E < 3$, and it is considered clinically perceptible if $\Delta E > 3$.

All the control samples showed the significant color change in environmental and human aging conditions. Mean Δ E of group A_1 –(3.69± 0.49), Group A_2 (3.58± 0.68) and Group A_3-(7.53 ± 0.22).

The results revealed that addition of nano particle pigment and opacifier increases the color stability of maxillofacial silicone elastomer exposed to outdoor weathering and acidic perspiration. Mean ΔE of group B_1–(2.60 ± 0.24) and B_2–(2.35± 0.13). In both these exposure groups, samples containing barium sulphate showed the maximum color stability. Mean ΔE of group C_1- (1.59 ± 0.28), C_2-(1.46 ± 0.28). Least color stability observed in all samples exposed to sebum solution. Mean ΔE of group B_3-(4.91 ± 0.44), C_3-(4.03 ± 0.57).

Color change in all the control samples was visually detectable. Visually detectable color change was observed in samples containing barium sulphate and titanium dioxide and exposed to sebum solution only. In the rest of the groups color change was not visually detectable.

Improvement in color stability was significant with addition of barium sulphate followed by titanium dioxide in outdoor weathering and acidic perspiration. However in sebum solution barium sulphate and titanium dioxide showed significant color change.

Conclusion

Within limitations of this in-vitro study, the following conclusion are drawn:-

1. Color change was observed in all control and experimental groups.
2. Control samples showed the color change in all the aging conditions (outdoor weathering, human aging conditions like acidic perspiration and sebum solution).
3. Addition of opacifier and nano particle pigments protect the silicone elastomer as compared to control group from color degradation.
4. Samples containing barium sulphate were most color stable among all the groups followed by titanium dioxide as tested by both spectrophotometric and visual analysis.

5. Among the different environmental and human aging conditions highest color change was observed in samples exposed to sebum solution as tested by both spectrophotometric and visual analysis.
6. According to ΔE values obtained addition of barium sulphate as an opacifier and titanium dioxide as nano particle pigment resulted in clinically acceptable color change when exposed to outdoor weathering and acidic perspiration but not in sebum solution.

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Table 1

Table 1: Descriptive statistics for color change according to exposures –Group A

Exposure **Outdoor weathering**	**ΔE**	**P value***
Mean ± SD	3.69 ± 0.49	< 0.0001 (HS)
Min	2.78	
Max	4.21	
Acidic perspiration		
Mean ± SD	3.58 ± 0.68	
Min	2.02	
Max	4.49	
Sebum		
Mean ± SD	7.53 ± 0.22	
Min	7.28	
Max	8.02	

*Obtained using ANOVA; HS: Highly Significant

Table 2

Descriptive statistics for color change according to exposures – Group B

Exposure **Outdoor weathering**	ΔE	P-value*
Mean ± SD	2.60 ± 0.24	< 0.0001 (HS)
Min	2.33	
Max	3.01	
Acidic perspiration		
Mean ± SD	2.35 ± 0.13	
Min	2.18	
Max	2.62	
Sebum		
Mean ± SD	4.91 ± 0.44	
Min	4.45	
Max	5.63	

*Obtained using ANOVA; HS: Highly Significant

Table 3

Descriptive statistics for color change according to exposures – Group C

Exposure	ΔE	P-value*
Outdoor weathering		
Mean ± SD	1.59 ± 0.28	< 0.0001 (HS)
Min	1.16	
Max	1.81	
Acidic perspiration		
Mean ± SD	1.46 ± 0.28	
Min	1.10	
Max	1.94	
Sebum		
Mean ± SD	4.03 ± 0.57	
Min	3.48	
Max	4.74	

*****Calculated using One-way ANOVA; HS: Significant

Table 4

Comparison of mean color change across different exposures - Group A

Exposure	**Mean**	**SD**	**P-value***
Outdoor weather	3.69	0.49	< 0.0001 (HS)
Acidic perspiration	3.58	0.68	
Sebum	7.53	0.22	

*Obtained using One-way ANOVA; HS: Significant

Table 4 .1

Pair wise analysis of color change between exposures – Group A

Exposure	**P-value***
Outdoor weather vs. Acidic perspiration	0.883 (NS)
Outdoor weather vs. Sebum	< 0.0001 (HS)
Acidic perspiration vs. Sebum	< 0.0001 (HS)

Obtained***** using Tukey's post-hoc NS: Not significant; HS: Highly Significant

Table 5

Table 5Comparison of mean color change across different exposures – Group B

Exposure	**Mean**	**SD**	**P-value***
Outdoor weather	2.60	0.24	< 0.0001 (HS)
Acidic perspiration	2.35	0.13	
Sebum	4.91	0.44	

*Obtained using ANOVA; HS: Highly Significant

Table 5.1

Pair wise analysis of color change between exposures – Group B

Exposure	**P-value**
Outdoor weather vs. Acidic perspiration	0.1553 (NS)
Outdoor weather vs. Sebum	< 0.0001 (HS)
Acidic perspiration vs. Sebum	< 0.0001 (HS)

*Obtained using Tukey's test; NS: Not significant; HS: Highly Significant

Table 6

Comparison of mean color change across different exposures – Group C

Exposure	Mean	SD	P-value*
Outdoor weather	1.59	0.28	< 0.0001 (HS)
Acidic perspiration	1.46	0.28	
Sebum	4.03	0.71	

*Obtained using One-way ANOVA; HS: Highly Significant

Table 6.1

Pair wise analysis of color change between exposures – Group C

Exposure	P-value*
Outdoor weather vs. Acidic perspiration	0.740 (NS)
Outdoor weather vs. Sebum	< 0.0001 (HS)
Acidic perspiration vs. Sebum	< 0.0001 (HS)

*Obtained using Tukey’s test; NS: Not significant; HS: Highly Significant

Table 7

Comparison of mean color change in samples exposed to outdoor weather across groups

Exposure: Outdoor weather			
Groups	Mean	SD	P-value*
Control	3.69^a	0.49	< 0.0001 (HS)
Barium	1.59^b	0.28	
Titanium	2.60^c	0.24	

*Obtained using One-way ANOVA; HS: Highly Significant

Table 7.1

Pair wise comparison of mean color change in samples exposed to outdoor weather across groups

Groups	**P-value***
Control vs. Barium	< 0.0001 (HS)
Control vs. Titanium	< 0.0001 (HS)
Barium vs. Titanium	< 0.0001 (HS)

Obtained* using Tukey's test;HS: Highly Significant

Table 8

Comparison of mean color change in samples exposed to acidic perspiration across groups

Exposure: Acidic perspiration			
Groups	**Mean**	**SD**	**P-value***
Control	3.58	0.68	< 0.0001 (HS)
Barium	1.46	0.28	
Titanium	2.35	0.13	

* Obtained using One-way ANOVA;HS: Highly Significant

Table 8.1

Pair wise comparison of mean color change in samples exposed to acidic perspiration across groups

Groups	**P-value***
Control vs. Barium	< 0.0001 (HS)
Control vs. Titanium	< 0.0001 (HS)
Barium vs. Titanium	< 0.0001 (HS)

Obtained* using Tukey's test; HS: Highly Significant

Table 9

Comparison of mean color change in samples exposed to sebum across groups

Exposure: Sebum			
Groups	**Mean**	**SD**	**P-value***
Control	7.53	0.22	< 0.0001 (HS)
Barium	4.03	0.71	
Titanium	4.91	0.44	

Obtained*****using One-way ANOVA;HS: Highly Significant

Table 9.1

Pair wise comparison of mean color change in samples exposed to sebum solution across groups

Groups	**P-value***
Control vs. Barium	< 0.0001 (HS)
Control vs. Titanium	< 0.0001 (HS)
Barium vs. Titanium	< 0.0001 (HS)

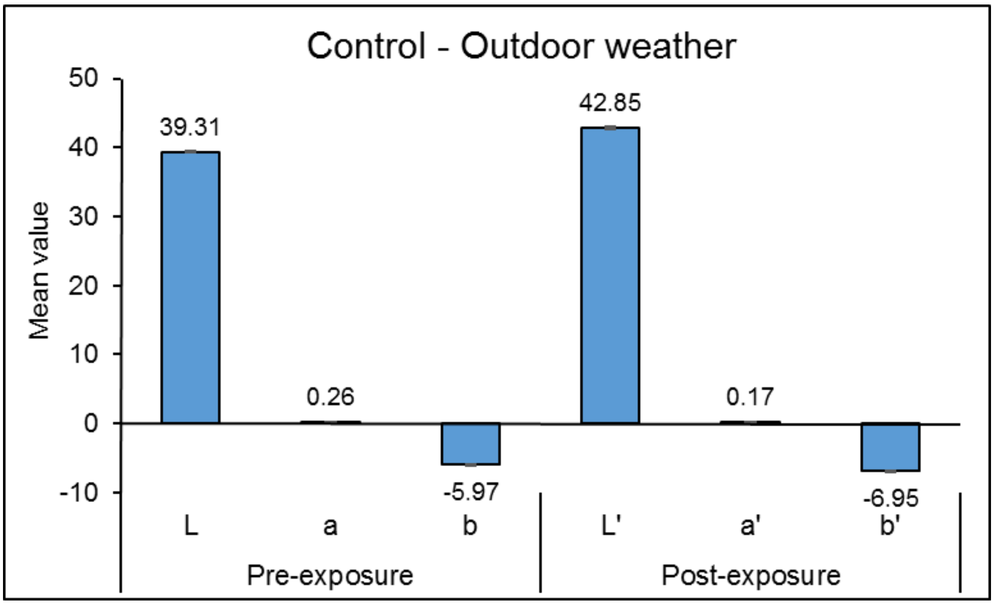
Obtained***** using Tukey’s test;HS: Highly Significant

Table 10

Percent agreement between two observers

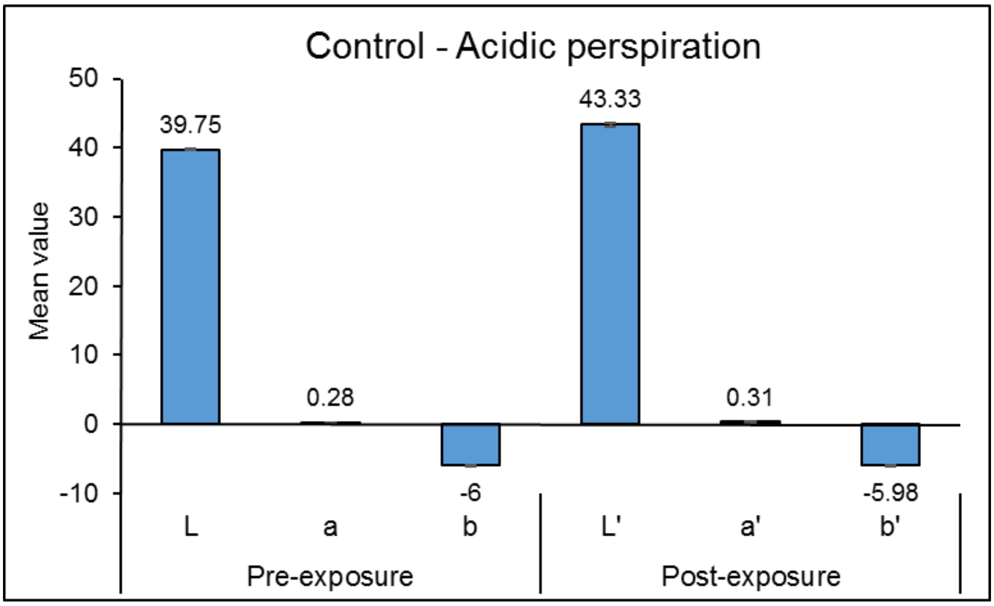
Groups	**Percent agreement**		
	Outdoor weather	**Acidic perspiration**	**Sebum**
Control	0.80	0.90	0.70
Barium	1.00	1.00	1.00
Titanium	0.80	0.80	0.80

Graph 1a



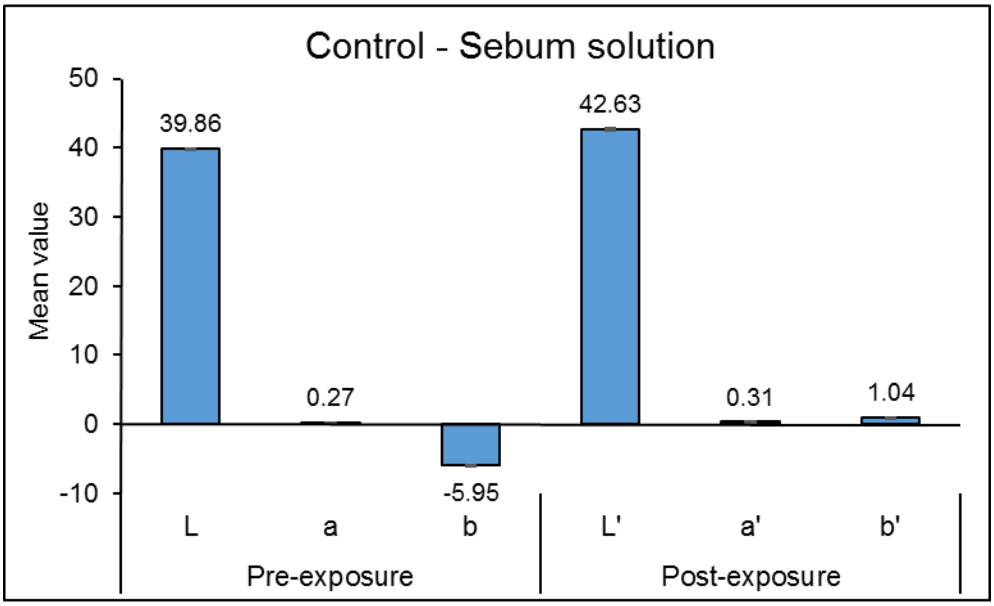
1a: Column chart showing mean levels of parameters for samples exposed to outdoor weather – Group A

Graph 1b



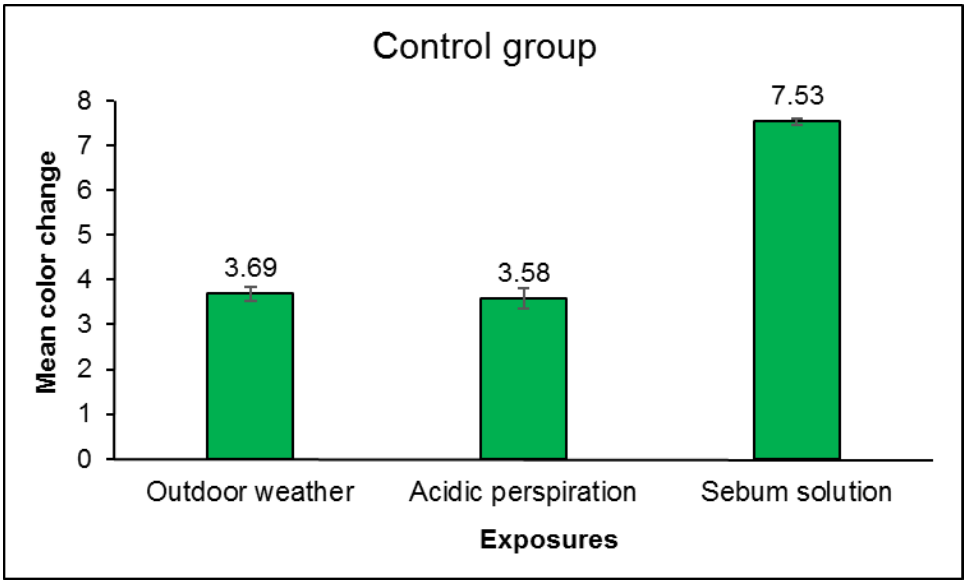
1b: Column chart showing mean levels of parameters for samples exposed to acidic perspiration - Group A

Graph 1c



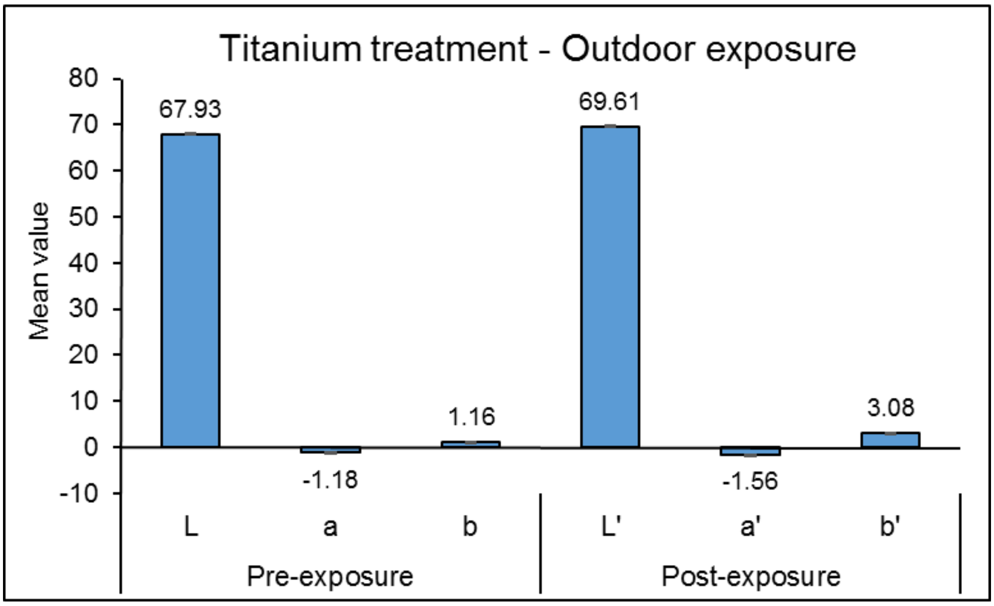
1c: Column chart showing mean levels of parameters for samples exposed to sebum solution - Group A

Graph 1d



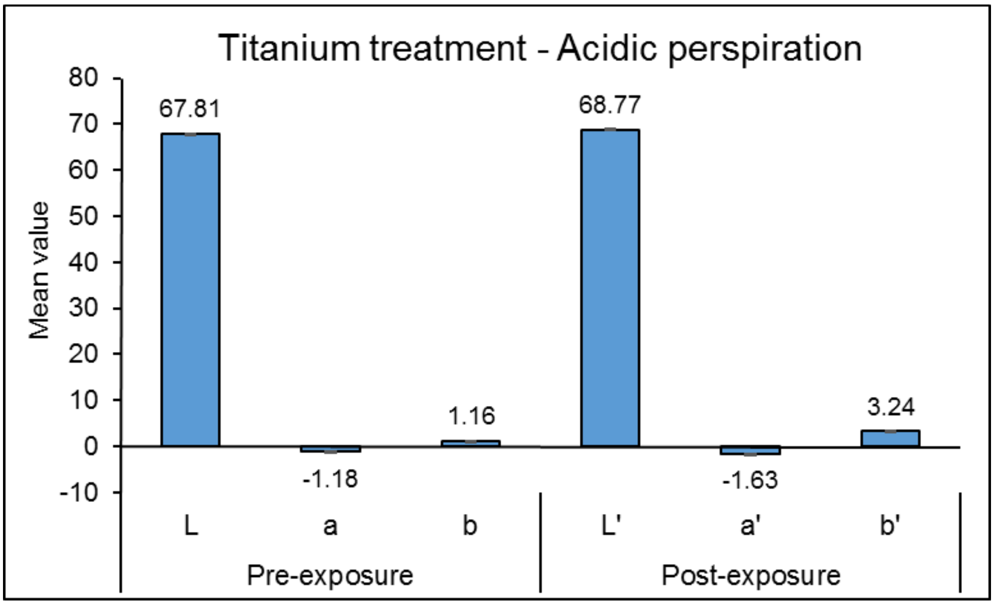
1d :Column chart showing mean color change for samples exposed to three exposures - Group A

Graph 2a



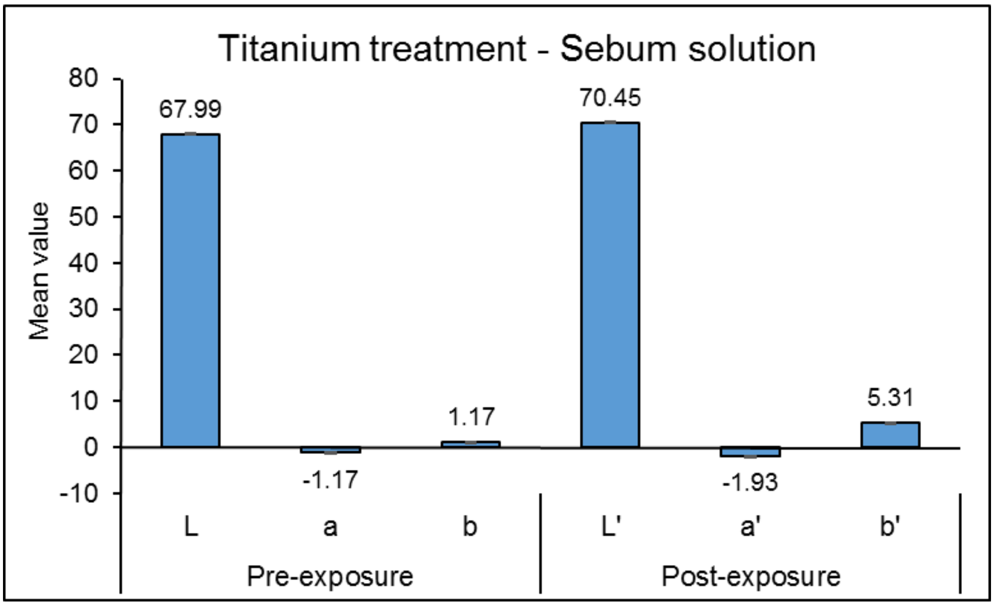
2a: Column chart showing mean levels of parameters for samples exposed to outdoor weather – Group B

Graph 2b



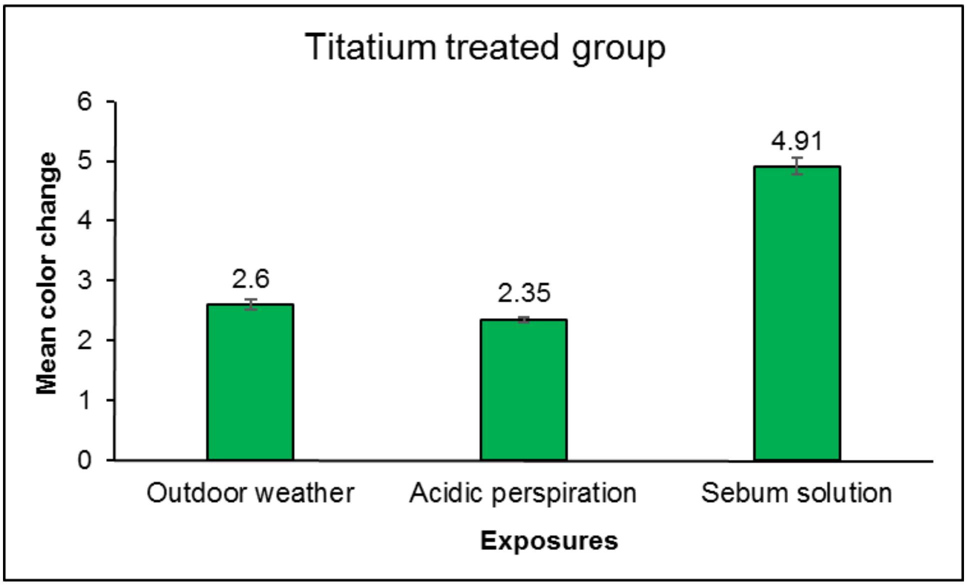
2b: Column chart showing mean levels of parameters for samples exposed to acidic perspiration- Group B

Graph 2c



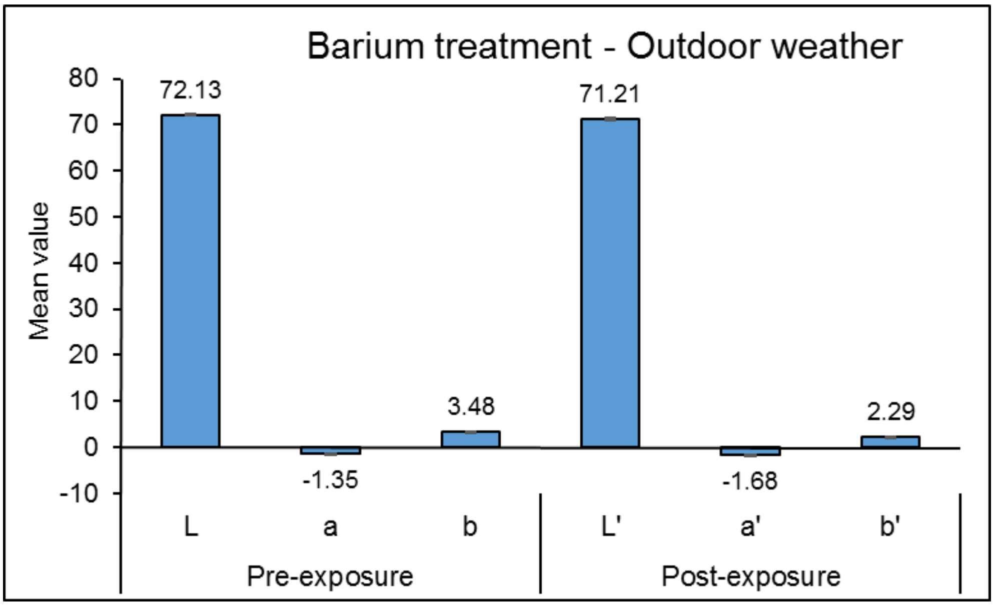
2c: Column chart showing mean levels of parameters for samples exposed to sebum solutions – Group B

Graph 2d



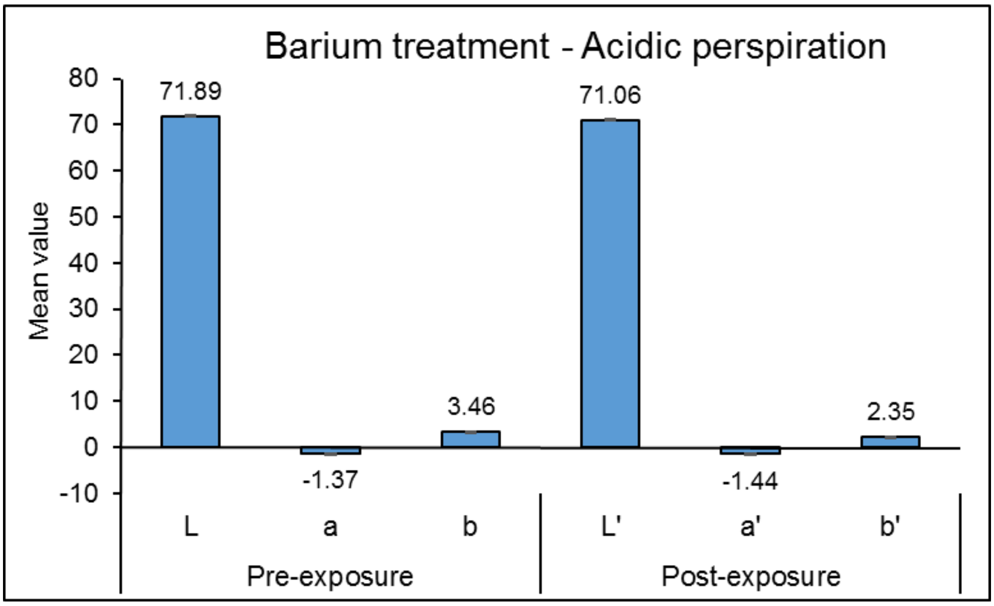
2d: Column chart showing mean color change for samples exposed to three exposures- Group B

Graph 3a



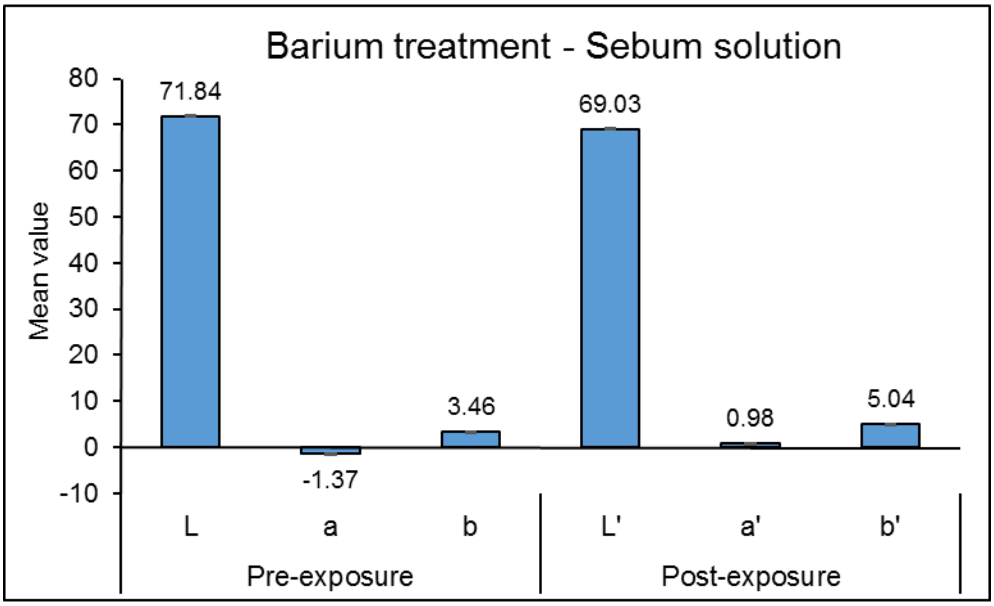
3a: Column chart showing mean levels of parameters for samples exposed to outdoor weather- Group C

Graph 3b



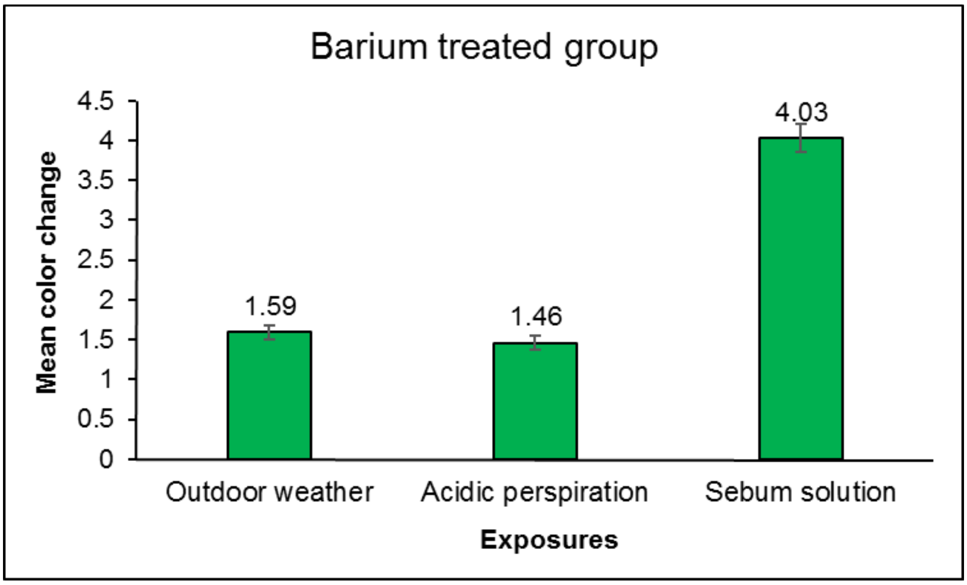
3b: Column chart showing mean levels of parameters for samples exposed to acidic perspiration- Group C

Graph 3c



3c: Column chart showing mean levels of parameters for samples exposed to sebum solution – Group C

Graph 3d



3d: Column chart showing mean color change for samples exposed to three exposures- Group C

MASTER CHAT

ΔE values of Group A

	A_1	A_2	A_3
1	3.717916	7.50689	3.870103
2	3.132555	8.019096	2.020495
3	3.717916	7.295924	3.59007
4	4.205163	7.643363	3.570742
5	3.673758	7.617283	2.930904
6	4.194139	7.516761	3.510185
7	4.105228	7.439207	3.960101
8	3.240895	7.33906	3.870258
9	2.782607	7.626644	4.000162
10	4.105228	7.276414	4.49059

ΔE values of Group B

	B_1	B_2	B_3
1	2.874613	5.455291	2.281272
2	3.005112	5.625416	2.310606
3	2.693604	4.447629	2.286263
4	2.446406	4.544326	2.337755
5	2.530672	4.797593	2.275522
6	2.658834	4.800302	2.310584
7	2.351276	4.773615	2.621965
8	2.337477	4.648064	2.181582
9	2.825757	5.481797	2.3467
10	2.326156	4.533839	2.536257

ΔE values of Group C

	C_1	C_2	C_3
1	1.668652	3.287096	1.199667
2	1.778595	2.584357	1.103947
3	1.814745	2.544917	1.234099
4	1.668652	4.077266	1.628097
5	1.792931	2.670955	1.511059
6	1.261983	4.029764	1.139166
7	1.811657	2.66492	1.543632
8	1.158361	2.641969	1.939948
9	1.756673	4.131513	1.564672
10	1.168118	3.926181	1.703995

VISUAL READINGS

Group A

	A_1		A_2		A_3		A_4	
	Observer 1	Observer 2	Observer 1	Observer 2	Observer 1	Observer 2	Observer 1	Observer 2
1	-1	-1	-1	-1	-2	-2	0	0
2	-1	-1	-1	-1	-2	-1		
3	0	-1	-1	-1	-2	-2		
4	-1	0	-1	-1	-2	-2		
5	-1	-1	0	-1	-1	-1		
6	-1	-1	-1	-1	-1	-2		
7	0	0	-1	-1	-2	-2		
8	-1	-1	-1	-1	-2	-2		
9	-1	-1	-1	-1	-2	-1		
10	-1	-1	-1	-1	-2	-2		

Group B

	B_1		B_2		B_3		B_4	
	Observer 1	Observer 2	Observer 1	Observer 2	Observer 1	Observer 2	Observer 1	Observer 2
1	0	0	-1	0	-1	-1	0	0
2	0	0	0	0	-1	-1		
3	-1	0	0	0	0	-1		
4	0	0	0	0	-1	-1		
5	0	0	0	0	-1	0		
6	0	0	0	0	-1	-1		
7	0	0	0	-1	-1	-1		
8	0	-1	0	0	0	0		
9	0	0	0	0	-1	-1		
10	0	0	0	0	-1	-1		

Group C

	C_1		C_2		C_3		C_4	
	Observer 1	Observer 2	Observer 1	Observer 2	Observer 1	Observer 2	Observer 1	Observer 2
1	0	0	0	0	-1	-1	0	0
2	0	0	0	0	-1	-1		
3	0	0	0	0	-1	-1		
4	0	0	0	0	-1	-1		
5	0	0	0	0	-1	-1		
6	0	0	0	0	-1	-1		
7	0	0	0	0	-2	-2		
8	0	0	0	0	-1	-1		
9	0	0	0	0	-1	-1		
10	0	0	0	0	-1	-1		