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Evaluation of the effect of UV stabilizers on the change in colour of a silicone elastomer following ageing by three different methods. An In-Vitro Study

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Abstract:

Aim and objective-To compare and evaluate the effect of UV stabilizers (UV absorbers and Hindered Amine Light Stabilizers-HALS) on the colour change of a commonly used silicone elastomer subjected to ageing by three different methods.

Materials and methods- 4 groups of 30 samples each were studied; Group A-Control, Group B-Silicone+ UVA (Chimassorb 81), Group C- Silicone+ HALS (Uvinul 5050) and Group D-Silicone + Combination (UVA+ HALS) (Chimassorb 81+Uvinul 5050). Each group was further divided into groups of 10 samples each based on the method of ageing- accelerated weathering chamber (Weather-Ometer), artificial perspiration and a cleansing agent. CIE Lab colour values L*, a* and b* were measured for all samples before and after weathering and change in colour (Delta-E) was calculated. One-way ANOVA was applied to compare the mean values of the 4 groups and the Post Hoc Tukey test was carried out to compare between 2 groups.

Results- All groups showed a significant colour change. For Group A the colour change (average Delta E) for accelerated weathering, artificial perspiration and cleansing agent was 1.479, 0.617 and 0.62 respectively. Similarly, for Group B it was 1.109, 0.509 and 0.507; for Group C it was 1.866, 0.652 and 0.997 and for Group D it was 1.303, 0.829
and 1.033 respectively. UVA (Chimassorb 81) showed the least change consistently in all 3 types of ageing.

Conclusion-Addition of UV stabilizer Chimassorb 81 showed a reduction in colour change of the silicone elastomer. Following studies on the effect of these additives on the physical properties of elastomers has shown that they can have a potential use in maxillofacial prosthetic rehabilitation.

Keywords: Maxillofacial prosthesis, Silicone elastomer, UV stabilizers, Colour change

Introduction: Silicone elastomers are successfully being used to rehabilitate patients with extra-oral defects that are either present congenitally or as a result of trauma, burns and surgical resections.¹

These elastomers are biocompatible, durable, inert, and easy to manipulate and colour to match the natural skin. However, one of the main drawbacks of prostheses made from these elastomers is that they degrade and discolour over a period of time.²⁻⁶ This requires the prostheses to be remade periodically, generally every 6 months-2 years, increasing the cost of rehabilitation.³⁻⁷ The color change has been attributed to factors like UV radiation, temperature changes, humidity, and the use of adhesives, cosmetics, cleansing agents, and exposure to body fluids.⁷⁻¹²

The popularity and increasing demand for these elastomers has increased the interest of researchers to improve their properties. Current research strategies have been
directed towards improving the mechanical properties and color stability of pigmented elastomers. The addition of UV stabilizers, thermochromic pigments and opacifiers to improve the colour stability of pigmented elastomers have been tried in the past with varying results.$^{13-17}$

UV degradation occurs on constant exposure to UV rays produced by the sun and depends to a large extent on their duration, extent and intensity. UV stabilizers have been used extensively in the polymer,$^{18}$ paint, cosmetic and plastic industries as well as for wood$^{19}$ and cellulose fabrics$^{20}$ to prevent colour degradation and increase the life of these products. UV stabilizers are a broad term which includes UV absorbers (UVA), and Hindered amine light stabilizers (HALS), both having different modes of action.

Studies by Gary et al.$^{21}$ and Hatamleh et al.$^{22}$ have shown that the change in colour has been attributed to the degradation in the elastomer itself. Hence, the first strategy towards increasing the longevity of prostheses by reducing its colour change should be towards improving colour stability of the silicone elastomer itself. In order to understand fully the behavior of silicones and UV stabilizers, three common modes of weathering need to be studied, namely, the accelerated environmental weathering in a weathering chamber, artificial perspiration and a cleansing agent. The change in colour following such weathering methods is expressed as a Delta E value. A Delta E value greater than 1 (Kiat-Amnuay et al.$^{13}$, Lemon et al.$^{7}$, Haug et al.$^{3}$), 2 (Beatty et al.$^{23}$, Polyzois et al.$^{24}$) and 3 (Kantola et al.$^{14}$) has been considered perceptible to the human eye. This research study is an attempt to evaluate the effect of UV stabilizers on the colour change of unpigmented silicone elastomer, using three different methods of weathering.
Materials And Methodology:

A commonly used platinum based maxillofacial silicone elastomer Z004 (Technovent Pvt. Ltd., UK) was used in a 1:1 base: catalyst ratio with no pigments added.

UV stabilizers namely UV absorber (Chimassorb 81, BASF, India) and HALS (Uvinul 5050, BASF, India) were used as additives.

A total of 4 groups were studied with 30 samples each. These were Group A- Control, Group B- UVA (Chimassorb 81), Group C-HALS (Uvinul 5050) and Group D- Combination of UVA and HALS (Chimassorb 81+Uvinul 5050). (Table 1) These groups were further divided into sub groups of 10 samples each according to those aged by accelerated weathering in a chamber, artificial perspiration and cleansing agent. (Table 2)

Stainless steel sheets of 4mm thickness were wire cut (`Precision Wire EDM` machine, Sodick, Germany) into square plates of 10cms X 10 cms. They were paired into sets of 3. The middle sheet was further wire cut to obtain square shaped cavities for samples of 2cm X 2cms. Holes to retain nuts and bolts were made at the 4 corners of the sheets to secure the assembly.

1% by weight of respective UV stabilizer for Groups B (Chimassorb 81) and C (Uvinul 5050) and 0.5% by weight of each UV stabilizer (Chimassorb 81 and Uvinul 5050) for Group D were weighed, added and thoroughly mixed with the silicone (base +catalyst) manually using a metal spatula for 5 minutes. The moulds were carefully loaded and clamped under pressure for 24 hours to allow the silicone to polymerize. The samples
were then retrieved, the excess cut away carefully and cleaned thoroughly with acetone and cotton.

The samples obtained were randomly distributed into 3 groups for ageing- Accelerated weathering (Weather-Ometer, Xenon Arc Ci 4000, Atlas Material Testing Technology, USA), ageing using artificial perspiration and ageing using a cleansing agent for Groups A,B,C and D.

The designated samples were placed in the Weather-Ometer for 300 hours. Alternating light and dark cycles for a total of 180 minutes completed one cycle. The light cycle (120 minutes) included an irradiance of 340nm of 0.55W/m², humidity of 50% and a chamber temperature of 47 degrees Celsius with water spray for 60 minutes. This was followed by 60 minutes without water spray. The dark cycle lasted for 60 minutes with a temperature of 38 degrees Celsius, humidity of 95% and irradiance at 340nm of 0.55W/m². These parameters were selected keeping in mind tropical climatic conditions.

Artificial perspiration was prepared in the laboratory. The composition included 0.5 grams L- histidine monohydrochloride monohydrate, 5 grams Sodium Chloride (NaCl), 5 grams Disodium hydrogen orthophosphate dodecaceahydrate (Na₂HPO₄×12 H₂O) and 2.2 grams Sodium dihydrogen orthophosphate dehydrate (Na₂HPO₄×2 H₂O) in 1 litre of distilled water. All chemicals were supplied by Sigma-Aldrich Co. LLC. Bangalore, India. The pH of the perspiration was adjusted to a neutral pH of 7 using 0.1 mol/l Sodium Hydroxide (NaOH).

The cleansing agent included a 1:1 dilution of commercially available Dettol Sensitive (Reckitt Banckiser Ltd., India) with tap water. For ageing using the artificial perspiration
and cleansing agent, the samples were immersed in the respective solutions for a period of 100 hours.

Testing of samples was carried out before and after ageing by the respective methods. For the groups subjected to accelerated weathering in a weathering chamber, (AA, BA, CA, DA), the colour was measured at 100 and 300 hours whereas for the other it was only measured at 100 hours. The samples for all groups were thoroughly cleaned with cotton and acetone prior to testing.

The colour variables L*,a*,b* according to the CIE (Commission Internationale d’Eclairage) Lab system were measured using a spectrophotometer (TES-135 Color Meter, Instruments and Machinery Sales Corporation, Mumbai, India) before and after ageing.

The L* parameter corresponds to the degree of lightness and darkness (100 ideal white, 0 ideal black), while a* and b* coordinates correspond to red or green chroma (+a = red, −a = green) and yellow or blue chroma (+b = yellow, −b = blue), respectively. The Delta E (change in color) was calculated for each sample using a software with the formula

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

where Delta L*, Delta a* and Delta b* are the difference in L, a and b values before and after ageing.

One-way ANOVA was applied to compare the mean values of the 4 groups. A further analysis, the Post Hoc Tukey test was carried out to compare between 2 groups. The significance level was considered at 0.05 and a confidence interval was 95%.
Results:

Average Delta E values obtained for Groups A, B, C and D were obtained. (Table 3)

1. For samples subjected to accelerated weathering in the chamber, at 100 hours there was no statistical difference between the groups. However, at 300 hours, Group B (Chimassorb 81) showed the least change and this change was statistically significant between Group B (Chimassorb 81) and C (Uvinul 5050) (P<0.05). Hence, between the UVA and HALS, the UVA showed the least colour change. (Fig.1)

2. For samples subjected to artificial perspiration, Group B (Chimassorb 81) showed the least colour change, the difference being statistically significant between Group B (Chimassorb 81) and D (Combination) (P<0.05). (Fig.2)

3. For the samples subjected to the cleansing agent, Group B (Chimassorb 81) again showed the least colour change. However, this change was not statistically significant as compared to the other groups. (Fig.3)

4. An addition of the Delta E values of all 3 methods of ageing showed highly statistically significant results. This was highly significant (P<0.01) between Group B (Chimassorb 81) and C (Uvinul 5050). It was statistically significant (P<0.05) between Groups A (Control) and C (Uvinul 5050) and Groups B (Chimassorb 81) and D (Combination). (Fig.4)

Discussion:
Degradation of silicone elastomers during the course of their use is known to have a multifactorial etiology.\textsuperscript{25} Such degradation usually occurring over a period of 1-2 years frequently necessitate re-makes that are cumbersome for the patient and the clinician alike. One of the main causes of colour deterioration is a constant exposure to UV rays produced by the sun and is dependent on the duration, extent and intensity of the exposure. UV stabilizers have been used extensively in the polymer, paint, cosmetic and plastic industries as well as for wood and cellulose fabrics to prevent color degradation and increase the life of these products.\textsuperscript{18-20}

A UV stabilizer is a broad term including UV absorbers (UVA) and Hindered amine light stabilizers (HALS), both of which have different mechanisms of actions. The empirical requirements for optimal action of the stabilizers are high solubility, minimal diffusion and high distribution homogeneity.\textsuperscript{18} The literature has reported on UV degradation of elastomers and a subsequent change in their mechanical and optical properties.\textsuperscript{7-10,24} The strategies for stabilization of elastomers have included the use of UV stabilizers, thermochromic pigments and opacifiers.\textsuperscript{7,13-17}

Such attempts at stabilization of elastomers have yielded mixed results. Kantola\textsuperscript{14} found that thermochromic pigments were very sensitive to UV radiation and not suitable for prosthetic application whereas Kiat-amnuay\textsuperscript{13} studied various concentrations of opacifiers and found that they prevent colour degradation overtime. In this study, Chimassorb 81, a benzophenone UV absorber (UVA) and Uvinul 5050, an oligomeric Hindered amine light stabilizer (HALS) were studied.
In the past, varying concentrations of UV stabilizers have been documented by researchers with mixed results (Chu and Fischer et al.\textsuperscript{16} used 1.5% weight UVA and found that it was effective in reducing yellowing of the elastomer, Lemon et al.\textsuperscript{7} used 12%, .25% by weight UVA and found that these did not protect the samples and Tran et al.\textsuperscript{15} used 75% by weight UVA and HALS and found that this was effective only for a certain pigmented groups). In this study 1% by weight of UVA (Chimassorb 81) and 1% by weight of HALS (Uvinul 5050) for Groups B and C respectively and 0.5% of each for Group D was used. All these additives are FDA approved biocompatible additives manufactured by BASF Chemicals, Mumbai, India Division.

Since the discolouration of silicone elastomers has been documented to be brought about by a myriad of sources of photo chemical insults, the authors believe at least 3 types of weathering methods should be evaluated to understand the colour change during clinical use. This study has utilized accelerated ageing, artificial perspiration and a cleansing agent for simulating photo-chemical insult to the silicone. Ageing parameters for accelerated weathering in a chamber, use of artificial perspiration and cleansing agent were based on protocols followed by Hatamleh et al\textsuperscript{22} and Eleni et al.\textsuperscript{26} Artificial perspiration solution was obtained by following the methodology described by Hatamleh et al.\textsuperscript{22} and Polyzois et al..\textsuperscript{24} Such a solution has been used as a standard for exposure of the silicone elastomer samples to simulated body fluids. The cleansing agent chosen for the study was one of the most popular agents used by patients for cleaning and disinfecting prostheses in India. Care was taken to ensure that a diluted solution was used and that the solution was clear and colourless in order to eliminate any potential discolouration of the silicone.
For the samples subjected to accelerated weathering in a chamber (Weather-Ometer), the greatest change in colour was seen with samples stabilized by Uvinul 5050 (Delta E -1.866), followed by Control samples (Delta E -1.479) and those stabilized by a combination of UV stabilizers (Delta E -1.303). The least discolouration was seen with Chimassorb 81 stabilized samples (Delta E -1.109) (Fig.4). The weathering was done for 300 hours in this phase of the study.

The effect of UV radiation has been known to enhance cross linking, break down of polymer chain bonds, reduce polymerization and decompose the elastomers, all of which may contribute to color instability. It is likely that Chimassorb 81 compound is able to better absorb UV rays from sunlight and dissipate this energy throughout the polymer matrix, thereby preventing degradation.

For the samples subjected to artificial perspiration, the greatest colour change was seen with the samples stabilized by a combination of UV stabilizers (Delta E -0.829) followed by the samples stabilized by Uvinul 5050 (Delta E -0.652) and the Control samples (Delta E -0.617). The least change in colour was again seen with Chimassorb 81 stabilized samples (Delta E -0.509) (Fig.5).

Perspiration can modify surface characteristics and result in extraction of some compounds from the elastomer into the solution, thereby accelerating the interaction of fatty acids with silicone. This has been known to contribute to the colour change. It is likely that Uvinul 5050 which is present in the groups that showed the greatest amount of discoloration promotes the extraction of siloxane compounds, this effect being more
prominent in the samples that were stabilized using the combination of UV stabilizers (Chimassorb 81 and Uvinul 5050).

For samples subjected to ageing using a cleansing agent, the greatest colour change was seen with the samples stabilized with a combination of UV stabilizers and the least change was seen with the Chimassorb 81 stabilized samples (Delta E =0.507) (Fig.6).

This study utilized a 100 hour immersion protocol in comparison to a previous study by Eleni26 that used 30 hours of immersion in the disinfectant to simulate 1 year of use. A 100 hour protocol was followed keeping in mind the tropical conditions, increased perspiration and pollution in the Indian environment. Colour change with this group of samples can be attributed to the contents of the cleansing agent and their interaction with the silicone surface producing surface alterations.

A similar phenomenon has been described by Eleni et al26 where four disinfecting agents were used and demonstrated that chemical insult results in colour change following surface modulations. It is also probable that a difference in surface hydrophobicity following use of stabilizers can contribute to changes in the absorption and adsorption of the soap solutions on the silicone surface thereby producing a colour change over time.28,29

It must also be noted that this study used unpigmented elastomers which have been shown to discolour more than pigmented elastomers as pigments are known to add stability to elastomers.3 As reported by Mancuso et al.,28 this colour change of the elastomer itself can be attributed to inherent chemical alterations in the silicone and a
probability of absorption and adsorption of substances that can take place from the surface of the silicone.

Amongst the stabilizers studied in this research, Chimassorb 81 (UVA) showed the least colour change. Chimassorb 81 (Fig.8), chemical name Methanone, [2-hydroxy-4-(octyloxy)phenyl]phenyl, and molecular weight of 326.4 g/mol; is preferably used for thick films of materials (>100µm) especially plasticized PVC and rubbers. The thickness of the samples or absorption depth in this study was 4mm contributing to protection of the polymer. As the name suggests, UV absorbers soak up harmful UV rays from sunlight converting this energy into heat energy which is then dissipated. They prevent the formation of harmful free radicals. On the other hand, HALS protect the basic material structure and help neutralize the harmful photochemical free radicals. HALS regenerate themselves and hence provide protection over a longer period of time. It is probable that Chimassorb absorbs heat energy, preventing photosensitization. Its colour is transparent to visible light and does not alter the appearance of the elastomer thereby contributing to its stabilizing effect.

The accelerated weathering chamber is used to simulate weathering conditions and includes parameters like UV lighting and radiation, water spray to simulate humidity and temperature. A combined effect of these can probably cause a more pronounced change compared to that produced by one parameter alone. UV irradiation can
contribute to enhancing cross linking leading to breaking down of chain bonds and decomposing of elastomer.\textsuperscript{22}

The samples subjected to artificial perspiration showed least colour change when compared to the samples subjected to the cleansing agent. This was not in agreement to a study by Hatamleh\textsuperscript{22} which showed that the antimicrobial cleansing agent produces the least colour change when compared to acidic perspiration. This is probably due the silicone cleaning agent used and the weathering protocol followed which included a 120 minute cycle, 102 minutes of dry weathering and 18 minutes of wet, humidity 70\% and air pressure of 70-1060hPa.

The combination of UVA and HALS in this study did not show satisfactory results. The combination showed more overall colour change (Delta E 3.165) than the UVA alone (Delta E 2.125) (Fig.7). This may be due to the inhibitory action of the HALS on the UVA. Thus a benzophenone UVA such as Chimassorb 81 may be preferred over an oligomeric HALS. Chimassorb 81 (UVA) showed promising results with all 3 methods of ageing. This gives future directions to study this material in different concentrations and compositions, its effect on pigmented samples and physical properties of the elastomer.

This study was an in-vitro simulation of the clinical usage of prostheses and the photochemical insult that they are subjected to. Although standardized protocols for weathering have been followed, the actual clinical use of the prostheses in daily life can be different and variable.

Different types of elastomers, including those different in their compositions and manufacturing protocols can be tested. A variety of other UV stabilizers, their
combinations and concentrations can be evaluated. The effect of these stabilizers on
different pigmented elastomers and their subsequent stabilization can be tried. The
effect of such stabilization on the mechanical properties like hardness, tear strength and
density of the elastomers can be studied. Evaluation over longer periods of time and
combining methods of ageing to simulate natural conditions can also be studied.
Stabilization of the pigments itself is an exciting area of future research.

**Conclusion:**

Within the limitations of the study, it can be concluded that UVA Chimassorb 81
consistently showed least colour change as compared to the other studied groups with
all three methods of ageing. Amongst the methods of ageing, accelerated weathering
(Weather-Ometer) showed the maximum change. Following studies on the effect of
these additives on the physical properties of elastomers, they can have a potential use
in maxillofacial prosthetic rehabilitation.
References:


**Figure legends:**

Figure 1: Comparison of colour change (Delta E) following ageing in an accelerated weathering chamber- 300 hours
Figure 2: Comparison of colour change (Delta E) following ageing in artificial perspiration-100 hours

Figure 3: Comparison of colour change (Delta E) following ageing in a cleansing agent - 100 hours

Figure 4: Comparison of the total colour change following all 3 methods of ageing

**Table legends:**

Table 1: Materials used

Table 2: Groups and subgroups studied

Table 3: Average Delta E values for all groups

<table>
<thead>
<tr>
<th>Materials</th>
<th>Details</th>
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<tbody>
<tr>
<td>Silicone</td>
<td>Z004 (Technovent Pvt. Ltd., UK)</td>
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<td>UV absorber</td>
<td>Chimassorb 81, BASF, India</td>
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<td>HALS</td>
<td>Uvinul 5050, BASF, India</td>
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<tr>
<td>Weather-O-meter</td>
<td>Weather-Ometer, Xenon Arc Ci 4000, Atlas Material Testing Technology, USA</td>
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<tr>
<td>Cleansing agent</td>
<td>Dettol Sensitive (Reckitt Banckiser Ltd., India)</td>
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<tr>
<td>Artificial perspiration</td>
<td>prepared in the laboratory</td>
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</tbody>
</table>

Table 1: Materials used
<p>| GROUP | AGEING | Accelerated weathering chamber (n=10) | Artificial perspiration (n=10) | Cleansing agent (n=10) |</p>
<table>
<thead>
<tr>
<th>Group A- Control</th>
<th>AA</th>
<th>AP</th>
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<td>BA</td>
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<td>BD</td>
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<td>(Chimassorb 81)</td>
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<td>Group C- HALS</td>
<td>CA</td>
<td>CP</td>
<td>CD</td>
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<td>(Uvinul 5050)</td>
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<tr>
<td>Group D-</td>
<td>DA</td>
<td>DP</td>
<td>DD</td>
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<tr>
<td>Combination (UVA+</td>
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<tr>
<td>HALS)</td>
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Table 2: Groups and subgroups studied
<table>
<thead>
<tr>
<th>Group</th>
<th>Average Delta E Value</th>
<th>Standard Deviation</th>
<th>Average SD Value</th>
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<tr>
<td>Group A- Control</td>
<td>1.479</td>
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<td>0.62</td>
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<tr>
<td>Group B- UVA</td>
<td>1.109</td>
<td>0.509</td>
<td>0.507</td>
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<tr>
<td>(Chimassorb 81)</td>
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<tr>
<td>Group C- HALS</td>
<td>1.866</td>
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<td>(Uvinul 5050)</td>
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<td>Group D-</td>
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Table 3: Average Delta E values for all groups