Stain Removal from a Pigmented Silicone Maxillofacial Elastomer

R. YU, A. KORAN, R.G. CRAIG, and C.N. RAPTIS

The University of Michigan, School of Dentistry, Ann Arbor, Michigan 48109

The removal of environmental stains from a pigmented maxillofacial elastomer was carried out by solvent extraction under network swelling. Silastic 44210 was pigmented with 11 maxillofacial pigments prior to staining. Samples were stained with lipstick, methylene blue, and disclosing solution. These stains were then removed by solvent extraction with 1,1,1-trichloroethane. Color parameter measurements both before and after staining and after solvent extraction demonstrated the effectiveness of removing these stains by solvent extraction while causing little or no change in the color of the pigmented samples.

J Dent Res 61(8):993-996, August 1982

Introduction.

It has been demonstrated in earlier studies[1-3] that the life expectancy of maxillofacial prostheses may be extended by selecting materials which have demonstrated stability in mechanical properties and color. It has also been found that environmental stains could significantly alter the color of maxillofacial elastomers, and that conventional methods of cleaning were ineffective in removing the stains.[4] These results suggested that staining was the principal cause of discoloration of maxillofacial prostheses in a service environment and may, therefore, be responsible for frequent replacement.

In a recent study,[5] stained silicone* samples were cleaned by solvent extraction using toluene, benzene, 1, 1, 1-trichloroethane, or n-hexane. The results indicated that solvent extraction with each of the solvents was highly effective in removing various stains from the base silicone material.

The purpose of the present study was to investigate the potential of solvent extraction for removing stains from pigmented silicone samples in order to establish the clinical efficacy of cleaning silicone maxillofacial prostheses.

Materials and methods.

Silastic 44210 was selected as the base elastomer since: (1) it is an elastomer with proven color and mechanical property stability under conditions of accelerated aging;[1-2] (2) it can easily be pigmented and processed;[3] and (3) it forms a three-dimensional cross-linked network which is essential for successful removal of stains by swelling and extraction with solvents.[6] Samples were prepared following the manufacturers' instructions and were pigmented by incorporating 0.2% by weight of commercially available pigments.† The 11 pigments used were: white (W), yellow (Y), dark buff (Dk Bf), medium brown (MB), light brown (Lt B), red brown (RB), black (Bl), red (R), blue (Bu), light orange (Lt O), and orange yellow (OY). Five samples (6 x 4 x 0.35 cm) were prepared for each pigment in metal molds and under a vacuum to eliminate porosity.

Received for publication June 25, 1981
Accepted for publication December 29, 1981
This study was supported by U.S. Public Health Service Grant DE-04136 from the National Institute of Dental Research, National Institutes of Health, Bethesda, MD 20205.

*Silastic 44210, Dow Corning Corp., Midland, MI 48640
†Artskin Products, Inc., Norfolk, VA 23502

Prior to being stained, the samples were solvent-extracted with 1,1,1-trichloroethane, and the color of each sample was compared before and after solvent extraction to ensure pigment stability. The three common staining agents selected were lipstick, disclosing solution, and methylene blue. The lipstick used was a deep red shade,‡ and this stain was applied to each sample by alternating horizontal and vertical applications until a uniform covering was achieved on the surface. After standing at room temperature for 24 h to allow stain penetration, the samples were wiped with a dry cloth to remove the surface stain, cleaned with a cleansing skin cream,§ washed with soap, and then dried prior to spectrophotometric measurements. The disclosing solution was a product specifically used for disclosing dental plaque and was prepared from 45 g Bismark Brown, 1800 cc glycerine, 15 cc of 95% ethyl alcohol, and 1 cc of oil of anise flavoring. The staining solution was further diluted by one part of the disclosing solution to three parts distilled water. The methylene blue product‖ used was a biological stain, and, for our purposes, it was dissolved in distilled water to form a 0.1% (by weight) solution. Staining was accomplished with the solutions by sample immersion at room temperature for 24 h with constant solution agitation. The samples were cleaned and dried prior to color analysis to remove any surface stain, as described in an earlier study.[5] The removal of the stains was carried out by swelling each sample in 1,1,1-trichloroethane for a period of three d and under constant solvent agitation with a magnetic stirrer. The swollen and extracted samples were then de-swollen by stepwise additions of methanol, and were ultimately dried to constant weight under high vacuum to eliminate all traces of solvent. Spectrophotometric analysis was conducted on each stained, washed, and solvent-extracted sample to determine the effectiveness of the stain removal and to establish whether the color of pigments had been altered.

The methods used for spectrophotometric measurements and color analysis are described in an earlier paper.[5] For each pigment, the means and standard deviations of the color parameters of luminous reflectance, dominant wavelength, and excitation purity were calculated from the results of each experimental condition. The means were statistically compared by analysis of variance[7] and Scheffe intervals[8] at a 95% level of confidence.

Results.

Results of the color analysis are tabulated with the corresponding Scheffe intervals in Tables 1-3. In these Tables, the changes in means and standard deviations of luminous reflectance, dominant wavelength, and excitation purity are listed for each condition.

As seen in Table 1, of the 11 pigments, five pigments (W, Y, Dk Bf, Bl, and OY) demonstrated significant changes

‡Big Apple, #03301, Cover Girl Moisturized Shiny Lipsticks, Noxell Corporation, Baltimore, MD
§Noxema greaseless skin cream, Noxell Corporation, Baltimore, MD
‖Certified for use by the Biological Stain Commission, University of Rochester Medical Center, Rochester, NY

TABLE 1
LUMINOUS REFLECTANCE

Pigment	Lipstick Stain			Methylene Blue Stain			Disclosing Solution Stain		
	Δ After Stained	Δ After Extraction	Scheffe Int.	Δ After Stained	Δ After Extraction	Scheffe Int.	Δ After Stained	Δ After Extraction	Scheffe Int.
W	−9.9	0.2	1.3	−40.3	−0.1	0.9	−17.5	−0.5	1.5
Y	−7.8	−0.1	1.4	−39.8	0.0	0.9	−16.0	−0.7	2.3
Dk Bf	−1.1	0.1	0.8	−20.6	0.3	1.2	− 6.7	−0.7	2.0
M B	0.4	0.1	0.4	− 2.7	0.2	0.6	− 1.0	−0.3	0.4
Lt B	0.2	0.1	0.5	− 8.6	0.0	1.3	− 2.0	−0.1	0.7
R B	0.4	0.0	0.5	− 3.8	0.1	0.7	− 0.5	0.0	1.1
Bl	0.6	0.1	0.2	0.0	0.0	0.2	0.0	0.0	0.2
R	0.4	−0.1	0.5	− 6.7	0.1	0.4	− 0.9	0.0	0.3
Bu	−0.1	0.2	0.7	− 1.4	0.3	0.6	− 2.7	0.1	0.4
Lt O	−0.3	0.3	0.8	−26.3	0.0	1.1	− 7.2	−0.1	0.7
O Y	−4.1	−0.3	0.6	−41.1	0.0	0.8	−11.7	0.0	1.1

TABLE 2
DOMINANT WAVELENGTH

Pigment	Lipstick Stain			Methylene Blue Stain			Disclosing Solution Stain		
	Δ After Stained	Δ After Extraction	Scheffe Int.	Δ After Stained	Δ After Extraction	Scheffe Int.	Δ After Stained	Δ After Extraction	Scheffe Int.
W	33.1	−0.4	0.7	−85.1	−1.3	1.4	8.7	1.8	1.8
Y	2.4	0.0	0.6	−10.7	−0.1	0.3	3.6	1.0	1.3
Dk Bf	1.4	0.0	0.3	−12.2	−0.4	0.6	1.6	0.3	0.5
M B	−1.7	0.0	0.3	− 5.8	−0.2	0.3	− 0.6	−0.1	0.3
Lt B	0.4	0.0	0.2	−11.5	0.0	0.3	1.3	0.3	0.6
R B	−0.9	0.0	0.4	− 4.3	0.0	0.5	−2.5	−0.2	0.9
Bl	17.1	0.1	0.7	− 4.4	0.2	1.3	3.7	0.1	1.0
R	− 2.4	0.0	0.5	− 3.5	−0.1	0.4	− 0.4	−0.1	0.3
Bu	− 0.8	0.4	0.6	1.5	0.5	0.5	9.1	0.3	1.4
Lt O	0.6	−0.1	0.2	− 7.9	0.0	0.5	1.1	0.1	0.3
O Y	1.6	−0.1	0.3	− 9.5	0.0	0.2	2.9	0.0	0.4

TABLE 3
EXCITATION PURITY

Pigment	Lipstick Stain			Methylene Blue Stain			Disclosing Solution Stain		
	Δ After Stained	Δ After Extraction	Scheffe Int.	Δ After Stained	Δ After Extraction	Scheffe Int.	Δ After Stained	Δ After Extraction	Scheffe Int.
W	0.001	−0.001	0.005	0.155	0.000	0.006	0.610	0.045	0.008
Y	−0.010	0.001	0.003	−0.157	0.005	0.010	0.011	0.002	0.005
Dk Bf	−0.009	0.000	0.006	−0.313	−0.002	0.010	0.052	0.002	0.014
M B	−0.026	0.003	0.012	−0.248	0.002	0.006	0.018	−0.002	0.013
Lt B	−0.014	−0.001	0.008	−0.254	0.002	0.007	0.029	0.002	0.008
R B	−0.021	−0.005	0.011	−0.297	−0.002	0.010	0.065	−0.001	0.018
Bl	0.011	0.001	0.003	−0.004	0.000	0.003	0.008	0.000	0.003
R	−0.033	−0.003	0.012	−0.283	−0.003	0.007	0.002	0.001	0.009
Bu	−0.031	−0.006	0.011	0.010	−0.001	0.014	−0.374	−0.020	0.013
Lt O	−0.012	0.001	0.005	−0.169	0.001	0.008	0.002	−0.002	0.005
O Y	−0.009	0.001	0.004	−0.128	0.000	0.005	0.001	0.002	0.003

in luminous reflectance when the lipstick stain was used. The largest change for lipstick stain was seen with the W samples, with a decrease in luminous reflectance of 9.9. The pigment causing the least change was Bl, with an increase in luminous reflectance of 0.6. The values of luminous reflectance for all pigments, except Bl, were significantly changed after methylene blue staining; these changes ranged from 41.1 for OY to 1.4 for Bu. Nine of 11 pigments had significantly lower values of luminous reflectance after exposure to disclosing solution, with differences ranging from 17.5 for W to 0.9 for R. The pigments that remained unchanged with disclosing solution were RB and Bl. All of the original values of luminous reflectance were restored after solvent extraction.

As seen in Table 2, all of the pigmented samples exhibited significant changes in dominant wavelength after

exposure to lipstick, methylene blue, and disclosing solution. The changes in dominant wavelength ranged from 33.1 nm for W to 0.4 nm for Lt B when exposed to lipstick, from 85.1 nm for the W to 1.5 nm for Bu when exposed to methylene blue, and from 8.7 nm for W to 0.4 nm for R when exposed to disclosing solution. Again, the original values of dominant wavelength for each pigment were effectively restored after solvent extraction.

Table 3 presents the results for excitation purity. Lipstick stain altered the excitation purity of all pigmented samples with the exception of W. The observed changes ranged from 0.033 for R to 0.009 for Dk Bf and OY. With the methylene blue stain, the excitation purity of Bu was the only pigment which was unaltered after staining. The changes noted for the pigments ranged from 0.313 for Dk Bf to 0.004 for Bl. The disclosing solution stain was found to produce no effect on the excitation purity of the R, Lt O, and OY pigmented samples, but significantly changed the excitation purity of the other pigments. The changes for these pigmented samples ranged from 0.610 for W to 0.008 for Bl. Following solvent extraction, the excitation purity of the original values for the lipstick and methylene-blue-stained samples was restored. The disclosing solution stain increased the value of excitation purity from 0.051 (before staining) to 0.661 (after staining) for the W pigment, and the value decreased to 0.096 after solvent extraction. Although the change noted was statistically significant, this difference of 0.045 in excitation purity after solvent extraction was small.

Discussion.

After being exposed to lipstick, methylene blue, and disclosing solution, and then being washed, all pigmented samples exhibited significant changes in dominant wavelength, and the values of luminous reflectance and excitation purity for most pigments were also altered. In quantitative color characterization, the parameters of luminous reflectance, dominant wavelength, and excitation purity correspond approximately to value, hue, and chroma, respectively, in the Munsell Color System,[9] in that all colors are presented in a three-dimensional schematic system. Therefore, a change in any of these color parameters will shift the location of a color in the color space, resulting in a distinctive color change as perceived by an observed standard.

The restoration of the original color parameters of luminous reflectance, dominant wavelength, and excitation purity was seen for all pigmented and stained samples after solvent extraction, with the exception of the W pigment. A small but permanent change in excitation purity for the W pigment was observed only with the disclosing solution stain, with an increase of 0.045. This indicates that an interaction between the W pigment and the stain may be responsible for the color change. Although the exact nature of the interaction was not determined, the observed increase in excitation purity of 0.045 at low color saturation is small and would, therefore, be barely perceptible clinically.

During the extraction of stains, the pigment particles were insoluble in the solvent and were permanently entrapped inside the three-dimensional network of the base elastomer, even under the condition of equilibrium swelling. The absorbed solvent acted as a diluting medium and caused the samples to swell such that the increase in elastic free energy from swelling deformation was counteracted by a decrease in the chemical potential for mixing polymer chains and solvent.[6] The presence of solvent in this network matrix could generally be treated as being entirely inert but reducing the number of network chains per unit volume of the swollen sample.[10,11] Lipstick, methylene blue, and disclosing solution stains are soluble in 1,1,1-trichloroethane, and if there is little affinity between the stains and the pigment-polymer matrix, the dissolution of stains would then be expected with solvent extraction. The concentration gradient is the driving force that transports the stains, by diffusion, from the body of the swollen network and into the bulk solvent.

The clinical applicability of this solvent extraction technique was tested on a severely stained maxillofacial prosthesis that had been in service for a period of one year. The results were promising (see the Fig.), since the esthetics of this prosthesis was restored with no noticeable dimensional changes after solvent extraction.

It must also be emphasized that only specific elastomers (those able to form a three-dimensional cross-linked network) are capable of being cleaned by solvent extraction. Unless the base elastomer used for a prosthesis has been evaluated for stability during solvent extraction, this technique should not be employed.

The solvent 1,1,1-trichloroethane is an organic compound, and proper care must be exercised in its use. After a prosthesis has been de-swollen with alcohol and completely dried under a high vacuum (757 mm Hg), no traces of solvent should remain. The residual toxicity of solvent-extracted Silastic 44210 has been evaluated using tissue culture techniques, and the elastomer was non-toxic.[12]

Conclusions.

1. 1,1,1-trichloroethane was effective in removing lipstick, methylene blue, and disclosing solution stains from pigmented Silastic 44210 by solvent extraction.

2. Of 11 pigments evaluated, only the white pigment demonstrated a change in one color parameter. A small but permanent change in excitation purity of the white pigment with the disclosing solution stain was observed after solvent extraction.

3. The solvent extraction of several stains was encouraging and may have direct clinical application.

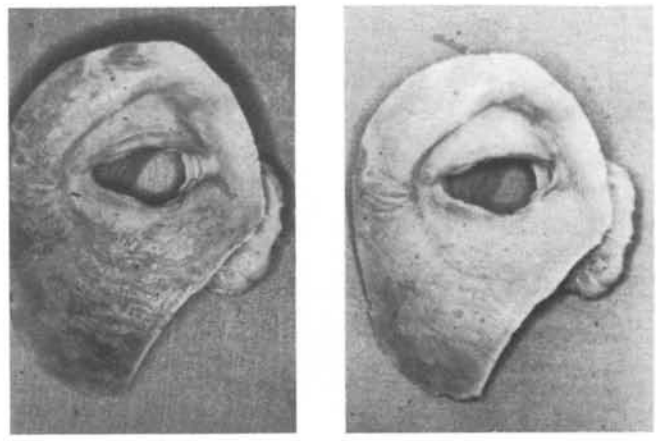

Fig. – Results of solvent extraction on environmentally stained maxillofacial prosthesis. A prosthesis worn by a patient before (left) and after (right) solvent extraction.

REFERENCES

1. YU, R.; KORAN, A.; and CRAIG, R.G.: Physical Properties of Maxillofacial Elastomers under Conditions of Accelerated Aging, *J Dent Res* 59:1041, 1980.
2. CRAIG, R.G.; KORAN, A.; YU, R.; and SPENCER, J.: Color Stability of Elastomers for Maxillofacial Appliances, *J Dent Res* 57:866-871, 1978.
3. KORAN, A.; Yu, R.; POWERS, J.M.; and CRAIG, R.G.: Color Stability of a Pigmented Elastomer for Maxillofacial Appliances, *J Dent Res* 58:1450, 1979.
4. KORAN, A.; LEPEAK, P.; and CRAIG, R.G.: Stain Resistance of Maxillofacial Materials, *J Dent Res* 58:1455, 1979.
5. YU, R.; KORAN, A.; RAPTIS, C.N.; and CRAIG, R.G.: Stain Removal from a Silicone Maxillofacial Elastomer, *J Dent Res* 60:1754-1758, 1981.
6. FLORY, P.J.: Statistical Mechanics of Swelling of Network Structures, *J Chem Phys* 18:108-112, 1950.
7. DALBY, J. (Programmer): BMD8V – Analysis of Variance, Ann Arbor, MI: Statistical Research Laboratory, 1968, 4 pp.
8. GUENTHER, W.C.: **Analysis of Variance**, Englewood Cliffs, NJ: Prentice-Hall, 1964, 199 pp.
9. WYSZECKI, G. and STILES, W.S.: **Color Science**, New York, NY: Wiley and Sons, Inc., 1967, 477 pp.
10. FLORY, P.J.: **Principles of Polymer Chemistry**, Ithaca, NY: Cornell University Press, 1953, Chapter XI.
11. MARK, J.E. and FLORY, P.J.: Stress-Strain Isotherm for Poly (dimethylsiloxane) Networks, *J Appl Phys* 37:4635-4638, 1966.
12. HANKS, T.: Personal Communication, Dental School, University of Michigan, Ann Arbor, MI 48109.

1983 IADR ABSTRACT PACKETS SOON AVAILABLE

Abstract packets for IADR's 1983 meeting (August 1-3, Sydney, Australia) will be available from the Central Office on September 27, 1982. Postcards were mailed to all IADR members (except those in the ANZ Division*) in mid-July, notifying them of this availability. If you would like an abstract packet for this meeting, either contact the Central Office of your Divisional Secretary. Or, simply sign and return the postcard, in an envelope, to the Central Office. Deadline for receipt of these abstracts is January 25, 1983. **PLEASE DO NOT USE AN AADR ABSTRACT FORM TO SUBMIT FOR THE SYDNEY MEETING.**

*Each individual member of the ANZ Division will receive a complete abstract packet.