

CHANGES IN GLOSS OF MARBLE SURFACES AS A RESULT OF METHYLCELLULOSE POULTICING

Julie A. Lauffenburger, Carol A. Grissom and A. Elena Charola

Abstract—A range of aqueous methylcellulose mixtures was applied to polished Carrara marble tiles for four hours, 24 hours, and until the poultices had dried to films. The specular gloss of each test area was measured before the poultice was applied and after its removal. When removed wet, poultices made with hard tap-water or deionized water containing a large excess of calcium carbonate or bicarbonates produced little or no change in surface gloss. On the other hand, poultices made with deionized water alone produced significant decreases in specular gloss; this effect was slowed but ultimately not diminished by the addition of ammonium hydroxide to pH 9. After only four hours, AB57 made with EDTA produced severe dissolution of the marble, while AB57 made without EDTA did not appear to alter the surface. Mechanical removal of calcite crystals occurred when poultices were allowed to dry to films. When bulking agents were used, there was little or no reduction in surface gloss. Comparison of the effects of poultices made with methylcellulose of three different molecular weights showed no discernible difference.

1 Introduction

Cellulose ethers have been widely used by conservators as adhesives, consolidants and thickeners [1]. For treatment of stone, they have been used to thicken aqueous cleaning poultices. One major method has been to incorporate cellulose ethers in poultices which remain on the stone for a period of time, but are removed while still wet. Compositions range from methylcellulose poultices with no special additives to complex mixtures such as AB57, used especially in Italy for removal of 'black crusts' from calcareous stone [2]. Sodium carboxymethylcellulose is specified for use in AB57, but some conservators have substituted methylcellulose in the formulation to avoid retention of sodium salts by the stone. A second major method for using cellulose ethers has recently gained popularity around the world as a more effective means of stone cleaning: thick aqueous mixtures of sodium carboxymethyl-

cellulose [3, 4] or methylcellulose [5–7] are applied and then removed after drying to films. These cellulose ether mixtures often include plasticizers to aid in film removal, as well as other additives such as surfactants. Both methods are generally regarded as safe for use on reasonably sound surfaces and, while a few analyses of the effects of actual treatments on stone have been published [6–8], no systematic study has been reported. The purpose of this paper is to determine by means of reflectance measurements the effects on polished marble of a range of methylcellulose poultices, removed both wet and dry.

2 Experimental

2.1 Specular gloss measurements

Specular gloss measurements were taken on the surface of marble test tiles using a Dr Lange Labor-Reflektometer. ASTM Standard Test Method for Specular Gloss (Designation D523-85) [9] was used as a basis for testing. Gloss measurements are based on the ASTM standard of a highly polished, plane, black glass with a refractive index of 1.567 for the sodium D line, which is assigned a gloss value of 100. For this particular instrument, a black glass working standard with a gloss value of 99.3 was used. Initial testing with a 60° geometry indicated that the surfaces had a high gloss more suitable for a 20° geometry, and the latter was therefore used throughout.

Multiple specular gloss readings were recorded before and after treatment for each test area. Each time, five gloss readings were taken at different points for the experiments of set 1, while 15 gloss readings were taken at one centimeter intervals in an easily reproducible pattern for the second and third sets of experiments.

Control readings were taken on untreated areas adjacent to each type of poultice at the same time as readings were taken on poulticed areas before treatment and after all treatments had been completed. For the first set of experi-

Received 23 July 1991

Table 1 Poultrice formulations

Exp. no.	Viscosity in cps. (METHOCEL A type)	Poultrice formulation per 400ml water
1/1	400 (4C)	Tap water
1/2	1500 (15C)	Tap water
1/3	400 (4C)	Deionized water (DI)
1/4	1500 (15C)	DI
1/5	400 (4C)	DI + NH ₄ OH (pH 9)
1/6	1500 (15C)	DI + NH ₄ OH (pH 9)
1/7	400 (4C)	DI + excess CaCO ₃
1/8	1500 (15C)	DI + excess CaCO ₃
1/9	400 (4C)	AB57 without EDTA [11]: DI + 12g NH ₄ HCO ₃ + 20g NaHCO ₃ + 2.5ml Triton X-100 (10% solution)
1/10	1500 (15C)	AB57 without EDTA
2/1	400 (4C)	Tap water (pH 6.5)
2/2	1500 (15C)	Tap water (pH 6.5)
2/3	400 (4C)	DI
2/4	1500 (15C)	DI
2/5	400 (4C)	DI + NH ₄ OH (pH 9)
2/6	1500 (15C)	DI + NH ₄ OH (pH 9)
2/7	400 (4C)	DI + 8ppm CaCO ₃ (pH 9.2)
2/8	1500 (15C)	DI + 8ppm CaCO ₃ (pH 9.2)
2/9	400 (4C)	AB57 without EDTA
2/10	1500 (15C)	AB57 without EDTA
2/11	400 (4C)	AB57 with EDTA [2]: DI + 12g NH ₄ HCO ₃ + 20g NaHCO ₃ + 2.5ml Triton X-100 (10% solution) + 10g disodium EDTA
3/3	1500 (15C)	Tap water (pH 6.5)
3/4	1500 (15C)	Tap water + fumed silica
3/5	1500 (15C)	DI + 15ppm CaCO ₃ (pH 9.2)
3/6	400 (4C)	Tap water (pH 6.9)
3/7	4000 (4M)	Tap water (pH 6.9)

Viscosity in cps.: viscosity in centipoises for a 2% aqueous solution at 20°C; pH measured with a Model 404 Orion Research/Specific Ion Meter

ments, two control areas were measured for each type of poultrice and there were 20 control runs in total. For the second and third sets, one area was measured for each type of poultrice and there were 16 control runs in total.

2.2 Selection of marble test tiles

Carrara marble tiles were selected for the experiment because Carrara marble is commonly used for sculpture. For the first set of experiments, white Gioia Carrara tiles were purchased from Morris Tile of Tuxedo, Maryland, and for the two subsequent sets of experiments, from Sita Tiles of Capitol Heights, Maryland. The samples measured 300 × 300 × 18mm and had been commercially prepared and polished. Inconsis-

tencies in gloss and texture were noted among tiles to the extent that reflectance means varied before treatment from 41.3 to 84.8 gloss units. Variability in surface within single tiles is reflected in the spread of standard deviations. This is most evident in the third set of experiments, for which the tiles had highly irregular surfaces.

2.3 Choice and preparation of poultrices

Aqueous mixtures prepared for the experiments are listed in Table 1. For most of the experiments Dow METHOCEL premium-grade methylcellulose powders of two different viscosities were used: METHOCEL A4C (400 centipoises) and A15C (1500 centipoises); METHOCEL

Changes in gloss of marble surfaces as a result of methylcellulose poulticing

Table 2 Specular gloss measurements for poulticed areas

Poultice	MC	Exp no.	Removed wet at 4 hours				Removed wet at 24 hours				Removed dry at 2-3 days				
			n	\bar{X}_B	s_B	\bar{X}_A	s_A	\bar{X}_B	s_B	\bar{X}_A	s_A	\bar{X}_B	s_B	\bar{X}_A	s_A
Tap water	4C	1/1	5	73.8	1.5	74.1	2.2	51.5	6.8	52.4	5.5	73.8	6.4	44.1	3.8
		2/1	15	80.3	2.9	82.9	2.1	72.7	4.4	73.8	3.6	81.4	3.1	81.8	2.9
		3/6	15	62.9	2.2	63.4	2.1	68.8	4.5	72.4	4.6	82.1	1.6	42.5	7.4
	15C	1/2	5	76.3	1.9	71.8	1.6	53.9	6.0	53.2	6.8	48.8	2.0	32.0	2.6
		2/2	15	79.4	2.8	78.0	3.8	77.4	2.8	76.8	2.7	76.4	5.1	46.0	3.8
	3/3	15	—	—	—	—	—	—	—	—	70.2	2.6	27.3	4.0	
	4M	3/7	15	62.2	1.9	59.3	1.4	71.1	6.5	67.6	2.6	80.8	1.7	33.6	7.5
DI	4C	1/3	5	78.1	1.0	65.4	1.2	57.3	7.8	40.0	4.5	49.1	0.5	31.1	2.8
		2/3	15	71.3	7.1	63.1	7.0	72.7	1.0	54.6	1.5	77.2	3.6	45.2	2.0
	15C	1/4	5	62.6	1.7	47.5	1.0	69.5	3.8	48.0	1.0	73.3	4.3	52.6	6.8
		2/4	15	59.6	4.2	53.5	4.1	71.4	1.3	53.4	2.7	74.6	7.4	45.1	2.7
DI + NH ₄ OH (pH9)	4C	1/5	5	59.3	4.5	54.2	3.6	49.8	2.4	29.7	0.8	61.1	2.3	38.5	5.3
		2/5	15	81.0	3.7	77.1	2.9	63.4	9.4	51.7	6.0	70.7	3.2	46.1	3.6
	15C	1/6	5	63.2	1.3	62.0	1.3	52.0	1.0	35.7	1.2	50.7	8.9	27.4	9.3
		2/6	15	77.1	6.1	74.1	4.5	59.8	4.0	42.7	2.4	71.5	4.1	43.3	3.0
DI + CaCO ₃ excess	4C	1/7	5	51.9	2.0	52.7	2.7	59.5	3.4	56.5	2.2	60.7	0.8	58.4	2.1
		2/7	15	82.3	3.1	73.0	4.0	68.6	1.9	52.6	2.5	78.5	3.2	51.1	3.4
	15C	1/8	5	54.6	2.3	54.5	2.8	60.8	0.9	58.8	2.0	61.1	0.8	56.3	2.2
		2/8	15	78.6	2.5	69.0	3.1	71.2	2.1	50.6	3.4	77.3	4.8	51.0	2.0
	15ppm	3/5	15	66.2	8.4	51.6	8.4	84.8	1.9	65.8	2.5	66.4	10.1	56.7	7.0
DI + AB57 w/o EDTA	4C	1/9	5	54.3	4.2	57.0	3.7	63.5	1.2	60.0	2.9	65.5	2.7	65.6	4.1
		2/9	15	69.8	4.6	69.6	2.3	57.1	6.1	54.2	5.4	70.9	4.5	70.8	4.5
	15C	1/10	5	55.8	2.4	55.4	2.9	68.4	4.3	67.4	1.5	67.7	2.6	65.6	3.4
		2/10	15	70.1	4.4	69.9	4.5	55.0	3.9	56.7	4.7	63.3	7.8	62.5	7.3
w/ EDTA	4C	2/11	15	69.6	9.7	4.1	0.6	79.2	3.6	3.4	0.4	84.7	4.7	3.1	0.4
DI + SiO ₂	15C	3/4	15	—	—	—	—	—	—	—	—	41.3	6.1	35.2	6.5

MC: METHOCEL A type; n: number of pairs of observations; \bar{X}_B : mean of specular gloss measurements before treatment; \bar{X}_A : mean of specular gloss measurements after treatment; s_B : standard deviation of mean before treatment; s_A : standard deviation of mean after treatment.

A4M (4000 centipoises) was used for one experiment. Viscosity is proportional to molecular weight: A4C and A15C are considered to have relatively low molecular weights as conservation materials, while A4M is relatively high. METHOCEL A4C and A15C were substituted for sodium carboxymethylcellulose in the AB57 mixtures (see Table 1), and Triton X-100 for Desogen, which is not available in the USA.

In most cases additives were first mixed in water and the gels were then prepared by adding

5% methylcellulose using the 'dispersion in hot water technique' [10] outlined by Dow. In a few cases the 'dry blending technique' [11] was used with greater success because of the high proportion of added solids compared to METHOCEL powder, e.g., for some AB 57 poultices; however, this change of technique is not believed to have influenced the results.

2.4 Application and removal of poultices

The poultices were individually applied to

Table 3 Specular gloss differences before and after poulticing

Poultice	MC	Exp no.	n	Removed wet at 4 hours		Removed wet at 24 hours		Removed dry at 2-3 days	
				AD	SSD	AD	SSD	AD	SSD
Tap water	4C	1/1	5	0.3	4.0	0.9	13.1	29.7	11.2
	4C	2/1	15	2.6	2.6	1.1	4.1	0.4	3.0
	4C	3/6	5	0.5	2.2	3.6	4.6	39.6	5.4
	15C	1/2	5	4.5	3.7	0.7	13.6	16.8	4.9
	15C	2/2	15	1.4	3.4	0.6	2.8	30.4	4.5
	15C	3/3	15	—	—	—	—	42.9	3.4
	4M	3/7	15	2.9	1.7	(3.5)	5.0	47.2	5.5
Deionized water (DI)	4C	1/3	5	12.7	2.3	17.3	13.5	18.0	4.3
	4C	2/3	15	8.2	7.1	18.1	1.3	32.0	2.9
	15C	1/4	5	15.1	3.0	21.5	5.9	20.7	12.1
	15C	2/4	15	6.1	4.2	18.0	2.1	29.5	5.6
DI + NH ₄ OH (pH 9)	4C	1/5	5	5.1	8.7	20.1	3.8	22.6	8.7
	4C	2/5	15	3.9	3.4	11.7	7.9	24.6	3.4
	15C	1/6	5	1.2	2.8	16.3	2.3	23.3	19.3
	15C	2/6	15	3.0	5.4	17.1	3.2	28.2	3.6
DI + CaCO ₃ excess	4C	1/7	5	0.8	5.0	3.0	6.1	2.3	3.4
	4C	2/7	15	9.3	3.6	16.0	2.2	27.4	3.3
	15C	1/8	5	0.1	5.4	2.0	3.3	4.8	3.5
	15C	2/8	15	9.6	2.8	20.6	2.8	26.3	3.7
	15C	3/5	15	14.6	8.5	19.0	2.2	9.7	8.8
DI + AB57 w/o EDTA	4C	1/9	5	2.7	8.4	3.5	4.7	0.1	7.4
	4C	2/9	15	0.2	3.7	2.9	5.8	0.1	4.5
	15C	1/10	5	0.4	5.7	1.0	6.8	2.1	6.4
	15C	2/10	15	0.2	4.5	1.7	4.4	0.8	7.6
DI + AB57 w/ EDTA	4C	2/11	15	65.5	6.9	75.8	2.6	81.6	3.4
DI + fumed silica	15C	3/4	15	—	—	—	—	6.1	6.4

MC: METHOCEL A type; n: number of pairs of observations; AD: absolute difference of before and after means ($\bar{X}_b - \bar{X}_a$); SSD: statistically significant difference using a two-tailed *t* test at a 99% confidence level [$t\sqrt{(s_B^2 + s_A^2)/n}$]; bold type indicates that the AD > SSD + 1 gloss unit.

75 × 150mm sections on the marble tiles after the surface had been wiped with ethanol, using lint-free cotton pads. A rubber spatula was used to apply the poultices to a thickness of approximately 6mm, and the tiles were left in a laboratory with controlled environment (approximately 50% RH and 21°C). For each mixture, a poultice was removed wet with a rub-

ber spatula at four and 24 hours, and a third poultice was allowed to go to dryness (between two and three days later). Most of the dry poultices pulled away from the stone by themselves, but those which did not were carefully peeled away. No residue of solid material incorporated in the mixtures, such as fumed silica and calcium carbonate, was apparent on the surface after the

Changes in gloss of marble surfaces as a result of methylcellulose poulticing

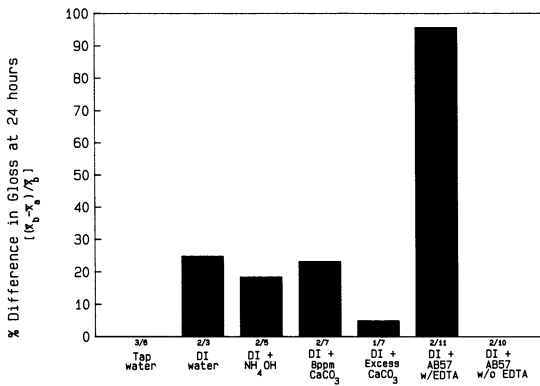


Figure 1 Percent decrease in gloss after poulticing for 24 hours.

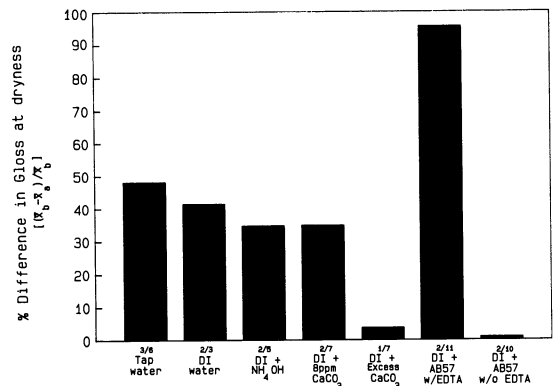


Figure 2 Percent decrease in gloss when poultices dry to films.

poultice had been removed. All marble surfaces were wiped with tap-water and then with ethanol and allowed to dry before readings were taken with the glossmeter.

3 Results

Data are presented in Tables 2 and 3, and statistical procedures are detailed in Appendix 1. Mean values and standard deviations for the specular gloss measurements are given in Table 2. The absolute difference (AD) of the mean values measured before and after treatment are given in Table 3, for comparison with the statistically significant difference (SSD) calculated for each test pair. A significant change in surface gloss is indicated when the AD is greater than the SSD. When the AD is more than one gloss unit greater than the SSD, it is shown in bold type.

The magnitude of significant change in measured gloss gives an indication of the physical degree of change that has occurred. In general, it increased with application time of the poultice and corresponded with visual observations regarding the amount of change on the surface.

Changes in gloss after treatment with a representative selection of poultices are illustrated in Figures 1 and 2. Percent decreases in gloss for surfaces from which poultices were removed wet after 24 hours are shown in Figure 1, and for surfaces from which poultices were removed when dry in Figure 2. In these figures, each bar represents the difference between mean reflectance measurements before and after the

specified treatment, divided by the mean measurement before $[(\bar{X}_b - \bar{X}_a)/\bar{X}_b]$. Note that calculations for these graphs do not take into account standard deviations.

In general, the glossmeter seemed slightly more sensitive than the human eye in differentiating the relative degree of change. However, whenever a significant change was measured it could also be perceived by the human eye, and vice versa.

Instrument repeatability was excellent, as indicated by measurements of control areas made at the same time as those for poulticed areas before and after treatment. With one small exception, there was no significant difference in the control measurements at the 99% confidence level, and generally the AD was much less than the SSD.

4 Discussion

The following discussion is based on a comparison of data listed in Table 3 and visual observations made when the experiments were carried out. All decreases in gloss can be attributed to two different mechanisms: chemical dissolution of the marble and mechanical removal of calcite crystals. Chemical dissolution is indicated by change in gloss measurement for poultices removed wet after four and 24 hours. Chemical dissolution may continue until poultices dry, but mechanical removal of calcite apparently dominates when there is substantial change in gloss measurement between 24 hours and dryness. Figures 1 and 2 illustrate these effects.

An interesting observation for poultices removed after four and 24 hours is the difference between poultices prepared with deionized water and with common tap-water. When made with deionized water, significant differences in surface gloss were measured even for poultices removed after four hours. This can be attributed to the solubility of calcite in water (about 1.4×10^{-4} M or 14ppm [12]; in the presence of CO_2 this value increases [13]). After 24 hours this effect was more pronounced, as would be expected from a dynamic situation that has not reached equilibrium. When made with tap-water, no significant changes in gloss were measured for poultices removed wet. This can be attributed to the common ion effect provided by the relatively high average concentration of calcium ion (1.0×10^{-3} M) as well as other ions in local tap-water [14].

The addition of ammonium hydroxide to the deionized water to adjust the pH to 9, which in theory should decrease attack on the marble surface, seemed to slow the etching effects of the pure deionized water. No significant change in gloss measurement occurred after four hours, but after 24 hours there was a substantial reduction in gloss, similar to that with the pure deionized water. This can be attributed to the fact that at the higher pH the initial dissolution rate is diminished, but over longer periods dissolution is not affected. The dissolution mechanism of calcite between pH 6 and 9 is mainly independent of pH, and the rate of dissolution is surface controlled [15].

Powdered calcium carbonate was added to poultices made with deionized water to see whether adding material of the same composition as the marble itself would have a beneficial effect. Three different amounts were used: 8ppm, 15ppm, and a large excess of calcium carbonate. Poultices made with 8 and 15ppm produced reflectance decreases similar to deionized water, apparently because the solutions were not saturated. While the concentration of calcium ions in a saturated solution of calcite is normally given as 1.4×10^{-4} M (14ppm), empirical testing showed that 8ppm was the maximum amount of calcium carbonate that readily dissolved and that, when 15ppm was added to the water, a slight excess of solids remained visible because of slow dissolution. By contrast, poultices made with a large excess of

calcium carbonate did not produce any change in gloss when removed wet, indicating that no chemical dissolution had taken place. If the solution were not fully saturated, any attack on calcium carbonate would be concentrated on the high specific surface area of the large excess of dispersed powder rather than the marble surface. Poultices made with a solution of sodium and ammonium bicarbonates with excess bicarbonate solids and a detergent (the AB57 mixture for mural paintings) did not change the gloss of the marble surface. The fact that no etching occurred can be attributed to the high concentration of bicarbonate ions. Under these conditions, the equilibrium with carbonate ions is shifted so that the dissolution of calcium carbonate is inhibited.

A poultice made with the same bicarbonate/detergent mixture plus EDTA (the AB57 mixture for stone cleaning) etched the polished marble surface severely compared with all other mixtures. The effect was noted after four hours of poulticing and increased very little thereafter. The rapidity of the etching is attributed to the rate at which EDTA chelates calcium at pH 8.5. Etching of the polished marble was expected, yet the rapidity and severity were surprising.

The second mechanism of damage, mechanical action, was evident when poultices dried to films. Small crystals adhering to the underside of the dry poultice could be felt by touch and were visible to the naked eye throughout, with higher concentrations at the perimeter of the film. The crystals were confirmed as calcite by scanning electron microscopy accompanied by energy dispersive X-ray analysis. In the most extreme cases, losses were visible on the stone at low magnification, corresponding to concentrations of crystals on the poultices. No difference was observed between poultices which detached themselves and those which were peeled away. When comparisons are made between the data for poultices removed wet at 24 hours and those removed after drying, substantial changes confirm mechanical damage (Figures 1 and 2). This is most notable in the case of tap-water poultices, which produced significant decreases in gloss when allowed to dry, although little or no change occurred when the poultices were removed wet.

The addition of bulking and other materials eliminated the mechanical removal of calcite

crystals as the films dried. Most notably, a methylcellulose poultice containing fumed silica and tap-water produced no statistically significant change in surface gloss on drying, although a decrease occurred when the poultice was made with tap-water alone. Poultices made with excess calcium carbonate and bicarbonate salts (AB57 mixtures), which apparently acted as bulking materials, also produced little or no change on drying. Compared to poultices made with bicarbonates alone (data not reported), detergent-containing AB57 produced more slippery poultices and irregular films.

Comparison of data for poultices made with the two low-molecular-weight methylcelluloses showed similar patterns of significant change after treatment. Tap-water poultices made with methylcelluloses of all three molecular weights also produced similar results.

5 Conclusions

Measurement of marble surfaces with a gloss-meter proved to be a reliable and relatively easy method of assessing the effects of a range of aqueous methylcellulose poultices used for cleaning marble. Polished marble tiles provided a good standard from which to evaluate changes in gloss resulting from poulticing. Subtle changes were both observed and measured which might not have been apparent on eroded surfaces. In actual practice, the effects of poulticing on surfaces might be somewhat different. For example, a methylcellulose film does not adhere well to a dirty surface and may therefore be less likely to remove calcite mechanically; conversely, poultice cleaning might do more damage to a deteriorated surface than to polished marble. Nevertheless, we believe that our results are relevant to conservation practice.

Deionized water, frequently used for cleaning marble, decreased surface gloss from four hours onwards, but dissolution was averted by including large excesses of calcium carbonate or bicarbonates. Poultices made with small amounts of calcium carbonate produced approximately the same degree of etching as deionized water alone. Excellent results with a large excess of calcium carbonate suggest that its addition to a poultice made with deionized water might be easier and more reliable than the common practice of soaking marble chips in deionized water before use.

A bicarbonate/detergent mixture (AB57 for wall paintings) also did not change the reflectance of the polished marble, and use of ammonium bicarbonate is recommended as an alternative to calcium carbonate. However, use of sodium bicarbonate is not recommended because of the possible retention of sodium salts by the stone. The addition of ammonia to deionized water to adjust the pH to 9 did not appear to reduce the solubility of the marble, but the use of ammonia in stone cleaning mixtures may be warranted for dirt removal.

Poultices made with local tap-water and removed wet did not cause dissolution of the marble, apparently because of its high calcium content. However, we do not recommend the use of tap-water to clean marble because of the many other undesirable ions in solution, including sodium, iron, copper and chloride.

Results showed severe etching by the AB57 mixture containing EDTA (AB57 for stone cleaning), and this mixture is emphatically not recommended for use on marble, with the exception of a surface which has been altered to a 'black crust' principally composed of calcium sulfate, soot and silica. A marble surface after treatment with the EDTA mixture may appear 'whiter' but this may be attributed to increased scattering of light as a result of etching, not to cleaning.

Mechanical removal of calcite crystals occurred when test poultices were allowed to form films, unless the mixtures had been modified with excess carbonates, excess bicarbonates, or fumed silica. In an effort to reduce mechanical removal of calcite crystals by dry poultices, conservators have typically modified mixtures with plasticizers such as glycol; greater flexibility and reduced adhesiveness of poultice films are reported [3, 6, 7]. Although we did not test plasticizers, we would expect them to diminish or eliminate mechanical damage. Conservators have also reported that low-molecular-weight methylcelluloses produce more flexible and less damaging films than high-molecular-weight ones [6, 7] but no difference was observed in our limited experiments. More work needs to be done, particularly with methylcelluloses of 4000 centipoises and above.

When using methylcellulose poultices, several other factors should be considered which were not tested in this project. Methylcellulose poul-

tices left to dry are extremely efficient in removing dirt from porous surfaces, and the degree of cleaning desired should be established by preliminary testing. Conservators have also noted, particularly when application is uneven, that residues of methylcellulose film can be tedious to remove. Finally, although no residues of admixed materials such as calcium carbonate were evident on the polished test tiles—nor are they expected, because of the adhesive properties of the methylcellulose gel and the manner in which it dries—each surface to be cleaned should be first tested with the poultice mixture to be used, and examined for any deleterious results.

In conclusion, we believe that a methylcellulose poultice made with deionized water, properly modified with calcium carbonate or ammonium bicarbonate and materials to reduce the adhesion of a dried film, can be safely used for cleaning sound marble surfaces.

Acknowledgements

The authors would like to thank Lawrence Becker, currently objects conservator at the Virginia Museum of Fine Arts, for making the first observations that led to this study while he was at the Metropolitan Museum of Art; Robert J. Koestler, who is in charge of the scanning electron microscopy facilities in the Department of Objects Conservation of the Metropolitan Museum of Art, for performing analyses on preliminary test samples; Timothy J. Vitale, senior paper conservator at the Conservation Analytical Laboratory, for his assistance throughout the project, especially with computerization of data; and the Samuel H. Kress Foundation for their support of this interlaboratory collaboration. The experiments were carried out by Julie Lauffenburger for a research project during her postgraduate conservation internship at the Smithsonian Institution Conservation Analytical Laboratory.

Suppliers of materials

Calcium carbonate C-64: Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219, USA.

METHOCEL powders: Dow Chemical Company, Midland, MI 48640, USA.

Triton X-100 wetting agent: Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219, USA.

Appendix: Statistical methods

The means of specular gloss measurements (\bar{X}) and

the standard deviations (s) were calculated by the glossmeter, according to the formulae:

$$\bar{X} = \frac{\sum_{i=1}^n X_i}{n} \quad s = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n-1}}, \text{ where } i = 1, 2, \dots, n$$

observations.

To evaluate whether a statistically significant change occurred after treatment, a two-tailed t test was applied at a 99% confidence level. The paired t test for two samples with equal sample sizes is:

$$t = \frac{X_1 - X_2}{\sqrt{1/n(s_B^2 + s_A^2)}}$$

where the subscripts (B and A) represent before and after treatment values and the degrees of freedom (ϕ) for the test were $n_B + n_A - 2$. At a 99% confidence level, the t values from statistical tables are as follows:

for Set 1 experiments with 5 pairs, i.e. 10 observations, $t_{99\%(\phi=8)} = 3.36$

and for Sets 2 & 3 experiments with 15 pairs, i.e. 30 observations, $t_{99\%(\phi=28)} = 2.76$

By algebraic manipulation of the formula given above we obtain:

$$X_1 - X_2 = t \sqrt{\frac{(s_B^2 + s_A^2)}{n}}$$

and we designate

$$t \sqrt{\frac{(s_B^2 + s_A^2)}{n}} = \text{SSD, the statistically significant difference.}$$

This quantity (SSD) can then be compared to the measured difference of the before and after treatment mean (AD) so that a simple visual inspection of the data shows when a treatment produced a significant effect. Note that for convenience we have used the two-tailed t test, although we have reported the absolute difference of the means.

The t test is strictly applicable only when measurements possess the same inherent standard deviation, i.e., when the data belong to the same population as indicated by the F test for variance homogeneity. The F test compares the ratio of the variances from two sets of data (s^2),

$$F = \frac{s_1^2}{s_2^2}$$

with the critical value of F given for the F distribution from statistical tables. If the calculated value is smaller than the critical value of F , the two sets cannot be said to arise from different populations.

The F values for variance homogeneity were calculated at the 5% level, and most samples passed the test. Rejections can be readily explained. All samples poulticed with the AB57 mixture containing EDTA produced reflectance measurements with very low

Changes in gloss of marble surfaces as a result of methylcellulose poulticing

standard deviations after treatment and were thus rejected; apparently the surfaces had been evenly etched by the EDTA. A few rejections were also obtained for samples poulticed to dryness, apparently because of the erratic mechanical removal of calcite crystals. Since it is well known that the two-tailed *t* test is resistant to non-extreme heterogeneity of variance, we chose to apply this *t* test uniformly to all our experiments.

References

- 1 FELLER, R. L., and WILT, M., *Evaluation of Cellulose Ethers for Conservation*, The Getty Conservation Institute, Marina del Rey, CA (1990).
- 2 URBANI, G., ed., *Problemi di Conservazione*, Editrice Compositori, Bologna (1973) 57, 341-343.
- 3 MEL'NIKOVA, E. A., and LEBEL, M. N., 'Application of polymer films removing surface contaminations from sculptures made of different materials' in *ICOM Committee for Conservation 5th Triennial Meeting*, Zagreb (1978) 78/10/8.
- 4 AGRAWAL, O. P., SINGH, T., and JAIN, K. K., 'Study and conservation of spotted red sandstone of Mathura' in *Case Studies in the Conservation of Stone and Wall Paintings*, IIC, London (1986) 165-169.
- 5 LEHMANN, J., 'The methodology for the cleaning and desalting of stone objects in Goluchow Castle Museum' in *ICOM Committee for Conservation 8th Triennial Meeting*, Sydney (1987) 487-491.
- 6 GRISSOM, C. A., POWER, T., and WEST, S., 'Methyl cellulose poultice cleaning of a large marble sculpture' in *Proceedings VIth International Congress on Deterioration and Conservation of Stone*, Torun (1988) 551-562.
- 7 GOLDBERG, L. A., 'A fresh face for Samuel Gompers: methyl cellulose poultice cleaning', *Journal of the American Institute for Conservation* **28** (1989) 19-29.
- 8 LAZZARINI, L., ASMUS, J. L., and MARCHESINI, L., 'Lasers for the cleaning of statuary: initial results and potentialities' in *1st International Symposium on the Deterioration of Building Stones*, La Rochelle (1972) 89-94.
- 9 *Annual Book ASTM Standards*, 06.01 (1987).
- 10 *How to Prepare a Solution of METHOCEL Cellulose Ethers*, product literature, form no. 192-958-88, Dow Chemical USA.
- 11 MORA, P., MORA, L., and PHILIPPOT, P., *Conservation of Wall Paintings*, Butterworths, London (1984) 342.
- 12 WEAST, R. C., ed., *CRC Handbook of Chemistry*

and Physics, CRC Press, Boca Raton, FL (1984), B-82.

- 13 BATHURST, R. G. C., *Carbonate Sediments and their Diagenesis*, Elsevier Scientific Publishing Company, Amsterdam (1976) 231.
- 14 Data taken from routine analysis of water for the Potomac Water Filtration Plant, revised February 1990.
- 15 SJOBERG, E. L., 'A fundamental equation for calcite dissolution kinetics', *Geochim. Cosmochim. Acta* **40** (1976) 441-447.

JULIE LAUFFENBURGER, BA in art history, Cornell University (1985); MA and Certificate of Advanced Study in Art Conservation, State University College of Buffalo, New York (1989). She is currently Assistant Objects Conservator at The Walters Art Gallery. *Author's address: The Walters Art Gallery, 600 North Charles Street, Baltimore, MD 21201, USA.*

CAROL GRISSOM, BA in art history, Wellesley College (1970); MA in art conservation, Oberlin College (1974). Since 1984 she has been chief objects conservator at the Conservation Analytical Laboratory of the Smithsonian Institution. *Author's address: CAL/MSC, Smithsonian Institution, Washington, DC 20560-0001, USA.*

A. ELENA CHAROLA, PhD in chemistry, University of La Plata, Argentina (1974). She is currently a consultant for ICCROM and coordinator for the Easter Island Program at the World Monuments Fund. *Author's address: 500 East 77th Street, Apt. 1239, New York, NY 10162, USA.*

Résumé—On a appliqué, pour polir des carreaux de marbre de Carrare, des solutions aqueuses de méthylcellulose pendant quatre heures, puis 24 heures, puis jusqu'à ce que les cataplasmes sèchent et pelliculent. Le brillance spéculaire de chaque surface traitée a été mesurée avant et après l'application du cataplasme. Quand ils restent humides, les cataplasmes confectionnés avec de l'eau dure du robinet ou de l'eau déminéralisée contenant du carbonate de calcium ou des bicarbonates en excès produisent peu ou pas de différence dans le brillant de surface. D'autre part, les cataplasmes préparés avec de l'eau déminéralisée seule produisent une décroissance significative de l'effet spéculaire; cet effet est ralenti, mais finalement pas diminué si l'on additionne de l'hydroxyde d'ammoniaque jusqu'à obtention du pH 9. Après seulement quatre heures, l'AB57 mélangé d'EDTA produit une dissolution importante du marbre, tandis que l'AB57 sans EDTA ne paraît pas altérer sa surface. L'usure mécanique des cristaux de calcite se rencon-

tre chaque fois que le cataplasme est laissé jusqu'au séchage complet. Lorsque des agents de charge sont employés, on constate une réduction légère ou nulle au niveau du brillant de surface. Enfin des cataplasmes préparés avec du méthylcellulose de trois masses molaires différentes ne montrent pas de différence visible.

Zusammenfassung—Eine Reihe von Methylcellulosepräparaten wurde in wässriger Lösung an polierten Carrara Marmorplatten erprobt. Ihre Anwendung erfolgte in Form von Gelen, die vier Stunden, 24 Stunden oder solange einwirkten, bis sie zu einem Film abgetrocknet waren. Vor und nach der Anwendung wurden Glanzmessungen auf den behandelten Oberflächen durchgeführt. Gele, die mit hartem Leitungswasser oder deionisiertem Wasser, das Calciumcarbonat oder -hydrogencarbonat im überschuß enthielt, angesetzt worden waren, veränderten—

sofern sie in noch nassem Zustand abgenommen wurden—den Oberflächenglanz nur wenig oder überhaupt nicht. Wurde auf einen Carbonatzusatz verzichtet, nahm der Glanz deutlich ab. Hieran änderte selbst ein Zusatz von Ammoniumhydroxid (bis zu einem pH von 9) nicht viel. Bereits nach vier Stunden löste AB57 mit einem Zusatz von EDTA die Oberfläche des Marmors stark an: Wurde auf einem Zusatz von EDTA verzichtet, konnten dagegen keine Veränderungen beobachtet werden. Trockneten die Gelschichten zu einem Film ab, konnte beobachtet werden, daß dieser bei seiner Abnahme Calcitkristalle aus der Oberfläche mitriß. Falls Dickungstoffe zugesetzt waren, wurde der Oberflächenglanz nur geringfügig oder gar nicht beeinträchtigt. Das Molekulargewicht der Methylcellulose scheint keinen merklichen Einfluß auf die Wirksamkeit der Gele in der geschilderten Anwendung zu haben, was an Hand dreier verschiedener Molekulargewichte ausgetestet wurde.