

# Performance Evaluation of Dimethyl Silicone Oil as Archaeological Dry Leather Lubricant

by

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## Abstract

This study aimed to investigate the treatment effect of dimethyl silicone oil on archaeological dried leather. Leather samples, without treatment and treated in a vacuum, were submitted to an accelerated aging at 100°C for 72 hours. In order to evaluate the efficacy of treatment, leather characteristics were examined before and after treatment with dimethyl silicone oil and after accelerated aging. Colorimetry, ATR-FTIR spectroscopy, shrinkage temperature measurement and differential scanning calorimetry were used to examine the leather characteristics and the effectiveness and stability of treatment. The results revealed that the dimethyl silicone oil has a suitable performance in the treatment of dry leather. The results also showed that the use of dimethyl silicone oil significantly reduces the changes in leather during accelerated aging. In other words, dimethyl silicone oil treatment improves the leather stability against deterioration.

## Introduction

Leather making is no doubt one of the earliest technologies of mankind, and leather is one of the first biomaterials ever made.<sup>1,2</sup> Archeological excavations have shown that leather products have been useful materials since the dawn of human history as vessels, upholstery, clothing, furniture, footwear, writing support, bookbinding, et cetera. A lot of leather has been found in archaeological excavations, due to the widespread use of leather from ancient times and today constitute an important and large part of museum and archival objects.<sup>3</sup> However, leather is considered as one of the most sensitive materials towards burial conditions, environmental factors, biological attacks, chemicals, hard use, etc.,<sup>4</sup> and therefore, their preservation is one of the biggest challenges in conservation. The deterioration of leather is a complex process in which there are a great number of contributing factors. These factors, in combination with the leather and tanning chemistry, lead to very diverse and complex degradation mechanisms.<sup>5</sup> One of the major problems and forms of decay facing the archaeological and historical leathers is excessive desiccating and drying. Dressings and lubricants are the most commonly used treatment for dried leathers. The dressings are usually applied in an attempt to slow deterioration,

improve the appearance of leather and, perhaps, restore some of its former strength and flexibility.<sup>5-7</sup>

There are, to date, several different methods for treatment of dry leathers, such as neat's-foot oil, lanolin, glycerin, British museum leather dressing (BML), Bavon, Marney's leather dressing, pliantine, and SC6000 and / or leather cream recommended by Larsen in 2007, the Dutch emulsion recommended by the Koninklijke Bibliotheek, The Hague, a modified leather dressing suggested by Fuchs in 2005, and Cire 213 recommended by the National Library of France.<sup>5, 7-10</sup> Main compounds of these traditional treatments are usually oils, fats and waxes.<sup>10</sup> As the base components of these materials are fatty substances containing varying concentrations of unsaturated fatty acids, overuse of traditional dressings and lubricants can cause oxidization and stiffening, discoloration and staining, a tacky surface, depositing of spew on the surface, exacerbate the growth of microorganisms and hamper of future conservation efforts.<sup>5, 10</sup> Also, according to previous studies, almost invariably the researchers conclude that the traditional dressings have no preservative effect and do not increase the durability and stability of the leathers.<sup>6, 10, 11</sup> These materials do not contribute to the preservation of the constituent moisture and destabilize collagen and, as a result, they can cause excessive dryness of the leather fibers.<sup>3</sup> Accordingly, the use or non-use of these materials in the treatment of vegetable-tanned leathers has for several decades been a concern for conservators, because it may intensify the degradation of the leather. Therefore, a great deal of attention has been paid by leather conservators to the application of synthetic polymer material which did not have previous problems. However, an accurate and comprehensive evaluation of a new treatment method is necessary before introducing and using.

Among various materials, silicone oil is a common polymer in treatment of both dried and waterlogged leathers. Several studies have been conducted and introduced for evaluation of silicone oil in conservation of historic leathers.<sup>3, 5</sup> Nevertheless, it is very important that used treatments have a long-term stability. In other words, these materials should not break down into harmful degradation products for leather over a long period of time.

This paper will evaluate the effect and stability of silicone oil on archaeological leather treatment. In fact, the present paper is the

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continuation of our previous paper,<sup>3</sup> in which we investigated the effect of silicone oil and PEG (with and without antioxidant ascorbic acid) in lubrication of new traditional dried leather. The results of the study showed better performance of silicone oil, however, it is essential to consider its function as a treatment in historic dried leather. Although lubrication on historical-ethnographic leathers is a controversial subject in leather conservation, dimethyl silicone oil can be used in the treatment of historic dry leather, especially bookbinding, if approved for proper performance. Therefore, the aim of current paper is to investigate the effectiveness of dimethyl silicone oil treatment on historic dried leather.

## Materials and Methods

### Leather Treatment and Accelerated Aging

Studies were performed on an archaeological vegetable tanned leather piece. These leathers were excavated from Ghalee-Kooh-i Ghaen (a historic stronghold from the Seljuk period, 11th-13th centuries) in the South Khorasan province of Iran.<sup>12</sup> Part of leather sample, 2×10cm, was treated with dimethyl silicone oil (KCC Co., South Korea) in a vacuum tank at 170mm Hg pressure for 2 hours and rest for 20 hours. Then, excessive treatment materials were removed by dryer paper and samples were dried in a desiccator. After treatment, a sample of both treated and untreated leathers were artificially aged to evaluate the long-term stability of the treatment and its effects on leather properties. The aging process was accomplished according to ISO 17228:2005.<sup>13</sup> Samples were placed in oven at a 100°C for 72 hours.

### Colorimetry

The colorimetric properties of leather samples were analyzed with Salutron® Colortector Alpha apparatus as a portable colorimeter in terms of CIE L\*a\*b\* color coordinates. The total color difference ( $\Delta E^*$ ) was calculated according equation 1.<sup>14</sup> Color values were measured five times for each leather sample, and their average was considered as CIE L\*a\*b\* color coordinates.

$$\text{Equation 1.} \quad \Delta E = \sqrt{[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]}$$

### ATR-FTIR Spectroscopy

Samples of the corium layer were analyzed by using a Nicolet 470 FTIR spectrometer and OMNIC 6.1a software (Nicolet instrument corporation, USA) equipped with PIKE MIRacle attenuated total reflectance (ATR) accessory with zinc selenide (ZnSe) crystal plate. The leathers were split and their corium surface was placed on the crystal of the ATR cell. All spectra were collected in the range of 4000-600 $\text{cm}^{-1}$  at 4 $\text{cm}^{-1}$  resolution with 32 numbers of scan, and were baseline corrected between 900 and 1800  $\text{cm}^{-1}$ .

### Shrinkage Temperature

Shrinkage temperatures of the leather samples were determined according to ASTM D6076-03.<sup>15</sup> The sample specimens, in the form of 12.5×76 mm strips, were soaked in water tank equipped with a vacuum pump. The wet specimens were inserted into the bath of water at room temperature (25°C). The water was heated at 3-4°C/min rate and the temperature at the first definite sign of shrinking was recorded.

### Differential Scanning Calorimetry (DSC)

The measurements were performed using a Mettler Toledo DSC calorimeter and STARe SW 9.10 software (Mettler Toledo, Switzerland). For studies of denaturation in dry state, the leather samples typically weighing 5-15 mg were placed in aluminum pans, and their DSC curves were recorded between room temperature (25°C) and 350°C at the heating rate of 10°C/min, in N<sub>2</sub> flow.

## Results and Discussion

Table I presents the colorimetric data in CIE L\*a\*b\* system for leather samples, before and after treatment and accelerated aging. The greatest change after treatment has occurred in parameter L\*, which shows a decrease of 12 units. This is due to the return of the leather surface black gloss after treatment, which was damaged due to the long burial of the leather under the soil. The extreme change in L\* caused a large color difference ( $\Delta E^*$ ) after treatment. However, results indicate a great color stability of treated leather, after accelerated aging process, with compared to untreated leather.

**Table I**  
Colorimetric data for leather samples

Colorimetric parameter	Ref	A-Ref	SiT	A-SiT	Ref to A-Ref	Ref to SiT	SiT to A-SiT
L* (mean±SD)	31.58±1.96	26.96±1.37	19.33±1.32	20.5±1.24	-	-	-
a* (mean±SD)	-0.72±0.06	-0.70±0.05	-0.61±0.08	-0.75±0.08	-	-	-
b* (mean±SD)	2.35±0.21	3.12±0.19	1.31±0.11	1.80±0.13	-	-	-
$\Delta L^*$	-	-	-	-	-4.62	-12.25	1.17
$\Delta a^*$	-	-	-	-	0.02	0.11	-0.14
$\Delta b^*$	-	-	-	-	0.77	-1.04	0.49
$\Delta E^*$	-	-	-	-	4.68	12.29	1.28

Ref: Untreated leather; A-Ref: Aged untreated leather; SiT: Treated leather; A-SiT: Aged treated leather

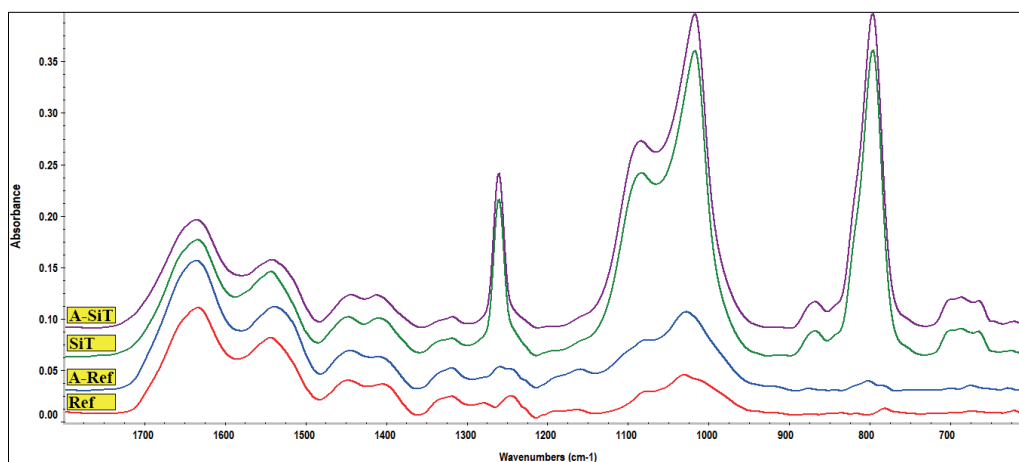


Figure 1. ATR-FTIR spectra of untreated (Ref) and treated (SiT) leathers, before and after (A-) accelerated aging

The ATR-FTIR spectra of leathers are given in Figure 1. IR bands around  $1635\text{cm}^{-1}$  (Amide I),  $1540\text{cm}^{-1}$  (Amide II),  $1350\text{-}1490\text{cm}^{-1}$  (C-H),  $1220\text{-}1320\text{cm}^{-1}$  (Amide III) and  $950\text{-}1200\text{cm}^{-1}$  (C-O) were assigned to the structure of collagen polypeptide chains.<sup>3, 12</sup> According to SiT and A-SiT spectra, the dimethyl silicone oil treatment has produced absorption bands related to its structure in the leather spectrum. In ATR-FTIR spectra of SiT and A-SiT, a strong absorption band between  $730\text{ and }900\text{cm}^{-1}$  was assigned to Si-C group. The peaks at  $700\text{ and }1015\text{cm}^{-1}$  represented Si-O and at  $1080\text{cm}^{-1}$  respectively suggested vibration of Si-C group.<sup>16-18</sup> However, ATR-FTIR spectra of treated and untreated leathers does not show a significant visible change after accelerated aging. In the FTIR spectra, the position and intensity of amide I and II absorptions can reflect the molecular structure of collagen. Based on previous studies, accelerated aging can change the intensity and position by destroying collagen. The intensity ratio of amide I and amide II bands,  $I_{\text{AI}}/I_{\text{AII}}$ , indicates the hydrolysis degree of the collagen, whereas their position difference,  $\Delta\nu$ , is related to collagen denaturation. Previous research has shown that dimethyl silicon absorption bands do not affect the vibrations of amide I and II in FTIR spectrum of collagen.<sup>3</sup>

Hence, the denaturation and the hydrolysis degree of collagen were examined for a more accurate evaluation. The peaks at  $1650\text{cm}^{-1}$  for the amide I and  $1550\text{cm}^{-1}$  for the amide II absorptions are interesting for this purpose as the  $\Delta\nu$  ( $\nu_{\text{AI}}-\nu_{\text{AII}}$ ) value is corresponding to collagen denaturation, and or gelatinization, and the value is around  $90\text{-}100\text{cm}^{-1}$  for new leathers, which increases with deterioration. Also, the hydrolysis degree of the polypeptide chains can be semi-quantified using the amide I/amide II band intensity ratio ( $I_{\text{AI}}/I_{\text{AII}}$ ), which is about 1.25 - 1.30 for new leathers and increases with deterioration.<sup>3, 19-21</sup> The  $I_{\text{AI}}/I_{\text{AII}}$  and  $\Delta\nu$  values are presented in Table II. The results obtained clearly suggest that untreated leather is more denatured and hydrolyzed compared to treated leather, according to  $I_{\text{AI}}/I_{\text{AII}}$  and  $\Delta\nu$  values in ATR-FTIR spectra. In the other words, the

Table II

$\Delta\nu$  and  $I_{\text{AI}}/I_{\text{AII}}$  as deterioration indices in ATR-FTIR spectra of leather samples

Sample	$\nu_{\text{AI}}$	$\nu_{\text{AII}}$	$I_{\text{AI}}$	$I_{\text{AII}}$	$\Delta\nu$ ( $\text{cm}^{-1}$ )	$I_{\text{AI}}/I_{\text{AII}}$
Ref	1633.34	1542.83	0.097	0.063	90.51	1.54
A-Ref	1635.63	1538.56	0.119	0.069	97.07	1.72
SiT	1633.69	1542.54	0.107	0.071	91.15	1.51
A-SiT	1634.59	1541.66	0.101	0.062	92.93	1.63

ATR-FTIR results indicate that the dimethyl silicone oil treatment increased stability of leather. Its evaluation on new leather has also confirmed its proper performance in improving leather stability, both chemical and mechanical.<sup>3</sup>

DSC curves of leathers are shown in Figure 2. At temperatures less than  $100^\circ\text{C}$ , leathers have exhibited endothermic peaks, corresponding to the loss of leather humidity.<sup>22</sup> An endothermic peak at above  $100^\circ\text{C}$  ( $100\text{-}200^\circ\text{C}$ ) indicated the denaturation temperature ( $T_d$ ) of the dry leather samples.<sup>23</sup> This reaction can be described by the amorphous-crystalline structure of collagen, according to which the crystalline triple-helix is embedded into an amorphous matrix.<sup>22</sup> As a result, this process in leather might be related to the softening of crystalline part of collagen.<sup>22</sup> Figure 3 shows the denaturation temperature of leathers (for  $T_d < 200^\circ\text{C}$ ). The  $T_d$  of untreated leather is  $108^\circ\text{C}$ , which accelerated aging reduced it to  $106.5^\circ\text{C}$ . However, the dimethyl silicone oil treatment has increased the  $T_d$  to  $137^\circ\text{C}$  and has reached to  $153.5^\circ\text{C}$  after accelerated aging. This increase in denaturation temperature can be caused by increased cross-linking during aging process.

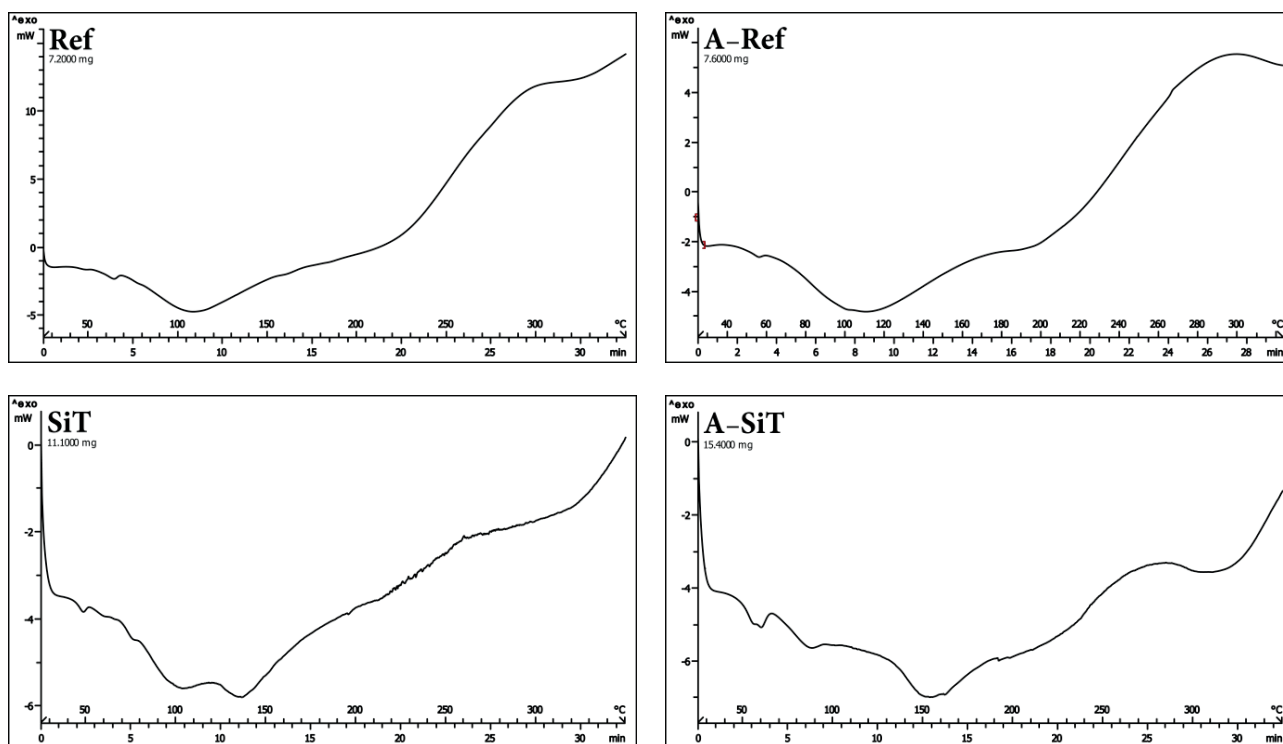


Figure 2. DSC curves recorded at the analysis of leather samples in N<sub>2</sub> flow

Figure 3 shows the shrinkage temperatures (Ts) of leathers, in addition to Td. The untreated leather exhibited a Ts of 42°C, which is reduced to 41°C after aging, while the new vegetable tanned leather has a Ts value from about 70° to 85°C.<sup>24</sup> This indicates the severe decay of the leather studied. However, dimethyl silicone oil improved the hydrothermal stability of leather and Ts has increased from 42° to 59°C, which is only 2°C lowered after aging.

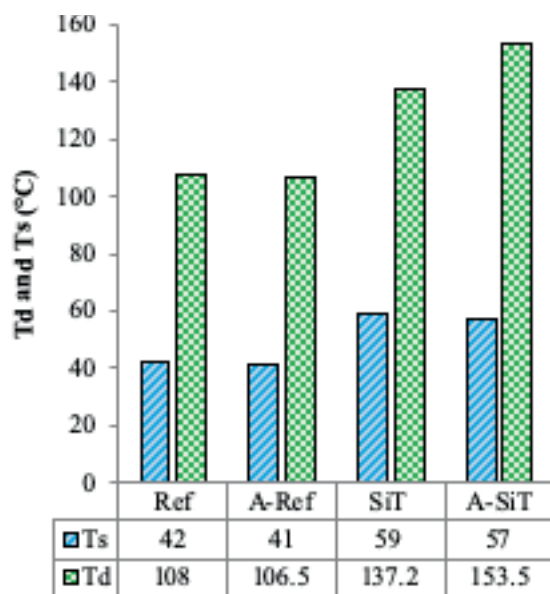


Figure 3. Td and Ts values for the leather samples

## Conclusions

The treatment of historical dried leathers is one of the major concerns for conservators because traditional and conventional dry leather treatment methods have some negative effects. Therefore, in this study, dimethyl silicone oil was evaluated for its effectiveness in the treatment of archaeological dry leather as well as its chemical stability.

Colorimetric results showed that the color stability of the dimethyl silicone oil treated leather is more than untreated leather. Also, the results of the ATR-FTIR spectroscopy clearly showed that the use of dimethyl silicone oil reduces the denaturation and hydrolysis of the leather. In the other words, the ATR-FTIR results indicate that the dimethyl silicone oil treatment increased stability of leather. In addition, the evaluation of the shrinkage temperature and the DSC curves showed that dimethyl silicone oil greatly increases the Ts and Td of the leather. After the accelerated aging process, the treated leather also indicates a great stability. Therefore, the dimethyl silicone oil is a stable and appropriate treatment for archaeological dry leathers.

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