Scientific paper

Modified Silica Sol Coatings for Surface Enhancement of Leather

Boris Mahltig,[1*] Lutz Vossebein,[1] Andrea Ehrmann,[1] Nicolas Cheval[2] and Amir Fahmi[2,3]

[1] *Niederrhein University of Applied Sciences, Faculty of Textile and Clothing Technology, Webschulstrasse 31, 41065 Mönchengladbach, Germany*

[2] *University of Nottingham, Department of Mechanical, Materials and Manufacturing Engineering, University Park, Nottingham, NG7 2RD, England, UK*

[3] *Rhein-Waal University of Applied Sciences, Faculty of Technology and Bionics, Nollenburgerweg 115, 46446 Emmerich, Germany*

* *Corresponding author: E-mail: boris.mahltig@hs-niederrhein.de*
Tel.: +49 2161 186 6028; Fax: +49 2161 186 6013

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Abstract

The presented study reports on differently modified silica sols for coating applications on leather. Silica sols are prepared by acidic hydrolysis of tetraethoxysilane and modified by silane compounds with fluorinated and non-fluorinated alkylgroups. In contrast to many earlier investigations regarding sol-gel applications on leather, no acrylic resin is used together with the silica sols when applying on leather. The modified silica particles are supposed to aggregate after application, forming thus a modified silica coating on the leather substrate. Scanning electron microscopy investigation shows that the applied silica coatings do not fill up or close the pores of the leather substrate. However, even if the pores of the leather are not sealed by this sol-gel coating, an improvement of the water repellent and oil repellent properties of the leather substrates are observed. These improved properties of leather by application of modified silica sols can provide the opportunity to develop sol-gel products for leather materials present in daily life.

Keywords: Leather, SiO_2, hydrophobic, oleophobic, abrasion resistance

1. Introduction

Nearly 20 years ago, researchers started to evaluate sol-gel applications for the modification of natural materials like wood.[1,2] About 10 years ago, textiles as another substrate for sol-gel treatment came into the focus of researchers.[3,4]

Starting from these early reports, many different groups world-wide developed sol-gel applications on wood and textiles to bring new functionalities and new properties to those materials.[5–12] This is a strong ongoing research leading also recently to new results especially in respect to realize antimicrobial, self-cleaning, water and stain repellent textile or wood.[13–19]

As wood or textiles, leather is also a material original from natural resources with high economic impact due to applications in clothes, shoes, furniture or in the automotive section. However, in contrast to the strong efforts to develop sol-gel applications for wood and textiles, only few investigations are reported on the development of sol-gel applications for the treatment of leather. Longer experiences are available for the modification of leather by plasma or plasmapolymerisation to improve mechanical properties and to reach water repellent effects.[20,21] For these different plasma treatments a change of the water up-take capability and hygroscopic properties of leather is reported. Silane reagents like aminopropyltriethoxysilane are also used for the enhancement of the adhesion of an afterwards applied interpenetrating network on leather.[22] By this combination of a silane precursor and the network, the abrasion stability of the treated leather was reached.

Since 2006, some studies are reporting on the use of SiO_2 particles prepared by a sol-gel process as an additive for acrylic resins applied onto leather materials.[23–25] In these applications silica particles are used as additives in acrylic resins offering to several advantages such as the decrease of water up-take capability or the improvement of physical and mechanical properties. Remarkably, especially the capability for the up-take of liquid water is decreased while simultaneously the permeability for water vapor is increased.[23–25] However, for these investigations the sol-gel prepared particles are used only as an additive in a resin and not as a coating forming agent itself.

Gelatin modified silica sols used for preparation of transparent coatings have also been suggested for the use as coating agent for leather materials.[26,27] As reported by Smitha *et al.*, the silica particles of the coating agent are supposed to agglomerate with each other during the coating and drying process, so the resulting sol-gel coating is supposed to be a three-dimensional network as a result of agglomerated silica particles. While the preparation of these sol-gel coating agents and their applications on glass substrates are well described, the application on leather substrates is only suggested and less experimental results for leather substrates are reported by Smitha et al.[26,27]

Because of the small number of results reported on sol-gel coatings applied on leather up to now, the aim of the now presented investigation is to depict the effects of differently modified silica sols used as coating agent for leather refinement. The investigated silica particles are not used as additive in an acrylic resin, they are the coating forming agents themselves and they are modified by silane containing compounds to gain water and oil repellent effects.

The water and oil repellent properties of leather substrates after application of differently modified silica sols are intensively investigated after the sol application and after an abrasion test has been performed at the coated samples. These investigations are accompanied by scanning electron microcopy.

Due to the sufficient values for repellent properties gained for leather after sol-gel application even if an abrasion is performed, the here presented coating agents could be the starting point for the development of various sol-gel applications for leather refinement.

2. Experimental Part

2. 1. Material Preparation

A pure silica sol and modified silica sols are used for the treatment of leather surfaces. The preparation of the silica sols is performed by acidic hydrolysis of tetraethoxysilane (TEOS) (purity >95%) (supplied as DynasilanA from Evonik/Degussa). For this, an amount of 4 ml 0.01 N HCl is added to a mixture of 20 ml TEOS and 84 ml ethanol under strong stirring. After further stirring for 24 hours at room temperature the silica sol is ready to be used as coating agent. The silica sols are modified by adding three different additives alternatively in an amount of 4 vol.–% to the prepared silica sol. Various additives are used, such as octyltriethoxysilane (purity > 95 %) (supplied as Dynasilan OCTEO from Evonik/Degussa), triethoxytridecafluorooctylsilane (purity > 95 %) (supplied as Dynasilan F8261 from Evonik/Degussa) and a fluorinated polysiloxane (supplied as Dynasilan F8800 – recipe containing 70% fluoralkyl- and aminoalkyl-containing polysiloxane in 30% ethanol). After addition of the additive to the mixture, the solution is strongly stirred for at least 30 minutes before applying on leather. By these combinations, altogether four different recipes are realized and used for application onto leather samples. These recipes are summarized in table 1.

Possible safety hazards of the described recipes can result from the addition of fluorinated organic compounds. Fluorinated organic compounds are known for long time to contain an acute toxicity and they are also bioaccumulative.[28–30] Thus it is necessary to avoid exposition during preparation and application of the used recipes. This is the reason why the recipes are applied on the leather by a rolling process and no spraying process is used. In case of spraying, the risk of inhalation by breathing in the aerosol is too high.

The application of the recipes is performed by a rolling process on leather. After drying the treated leather samples at room temperature, a subsequent treatment at 50 °C for 15 minutes is performed. The leather samples are provided by Wilhelm Kasten GmbH (Lederfabrik, Sternwede, Germany) and used as received, due to the fact that the developed silica sol recipes should be used as an after treatment finishing for leather which is already supplied to the customer. The leather material has a weight of 1154 g/m^2 and is pretreated by the producer with light brown color pigment and a wax.

Table 1: Overview on silica sols used for leather treatment

sol	Composition
1	Pure silica sol
2	Silica sol with octyltriethoxysilane
3	Silica sol with triethoxytridecafluorooctylsilane
4	Silica sol with fluorinated polysiloxane

2. 2. Analytical Methods

Contact angle measurements are conducted to investigate the hydrophobic and oleophobic properties of the leather surfaces. The contact angle measurements were performed by a self-built device containing a digital camera (Digimicro) and a data evaluation by commercial software (Microcapture). The contact angles are determined with two liquids: water and natural oil from thistle.

Drops of these liquids with a volume of 18 microliters are set on the leather surface. The contact angles are determined as a function of time up to 4 minutes.

The contact angle measurements are performed at three different locations on the specimen surface as function of time. The contact angle is recorded after setting the drop of testing liquid onto the surface after setting times of 5, 30, 60, 120 and 240 seconds. This measurement procedure is repeated at three different locations on the surface. From these three measurements the average value for every setting time is calculated and given in the data evaluation. The range of measured contact angle values for every setting time is reflected by the error bars for each data point, so the error bars presented cover the lowest and the highest contact angle measured for each setting time determined from measurements at different locations on the surface.

Scanning electron microscopy (SEM) was used to investigate the surface topography of the sol-gel treated leather samples. Reference measurements are done with SEM for comparison with untreated leather. For all SEM measurements, a SEM from Philips (model XL 30 ESEM FEG Philips) was used. For the measurements, the leather samples were cut by 1 cm * 1 cm and coated with Platinum using a sputter coating process of 60 seconds duration.

The properties of leather samples are tested after the application of the sol-gel coating and after abrasion tests have been performed. The abrasion is done with a commercially available device (New Martindale Abrasion Tester) using an abrasion with a wool fabric for 20,000 cycles.

3. Results and Discussion

The water repellent properties of the investigated leather samples are determined by contact angle measurements (Figure 1). For this, the contact angles of water are determined as function of time after the water drop is set onto the leather surface. Even the investigated non sol-gel treated leather sample shows certain water repellency with contact angles around 103° which is a nearly stable value for at least 4 minutes after drop setting. The application of the pure silica sol recipe 1 leads to a small enhancement of the water repellency compared to the untreated leather. This is especially remarkable, because a pure SiO_2 coating prepared from a silica sol is not supposed to be hydrophobic.[16,31]

An improved water repellent effect could therefore be explained by a kind of barrier effect of the SiO_2 coating, which prevents the water from sinking into the leather substrate. This is comparable to the effects observed for plasma polymers deposited on leather.[20,21] However, it has to be stated that the surface topography of the leather samples is nearly not influenced on the micrometer scale by the sol-gel coating (Figures 2, 3a and 3b). The surface topography of the investigated leather consists of regularly distributed pores with diameters between 60 and 80 micrometers. Those pores are not filled up by the sol-gel coating as it is reported, e.g., for plasma treatments or plasma polymerization (Figures 2, 3a and 3b).[20,21] For this, it should be stated that the applied sol-gel coating is extremely thin and is not able to fill up micrometer sized pores on the leather surfa-

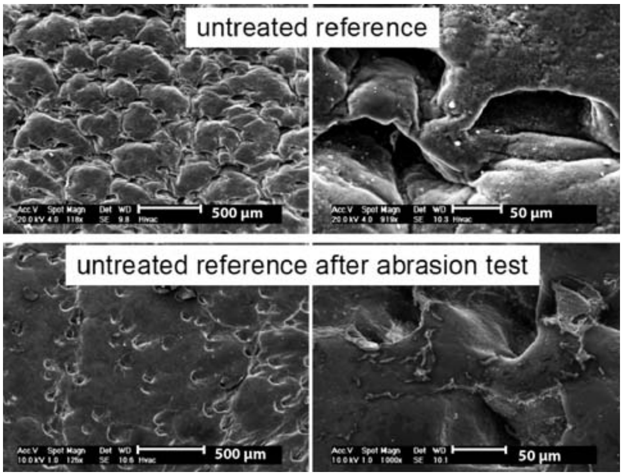

Figure 2: SEM micrographs of untreated leather – before and after an abrasion test is performed.

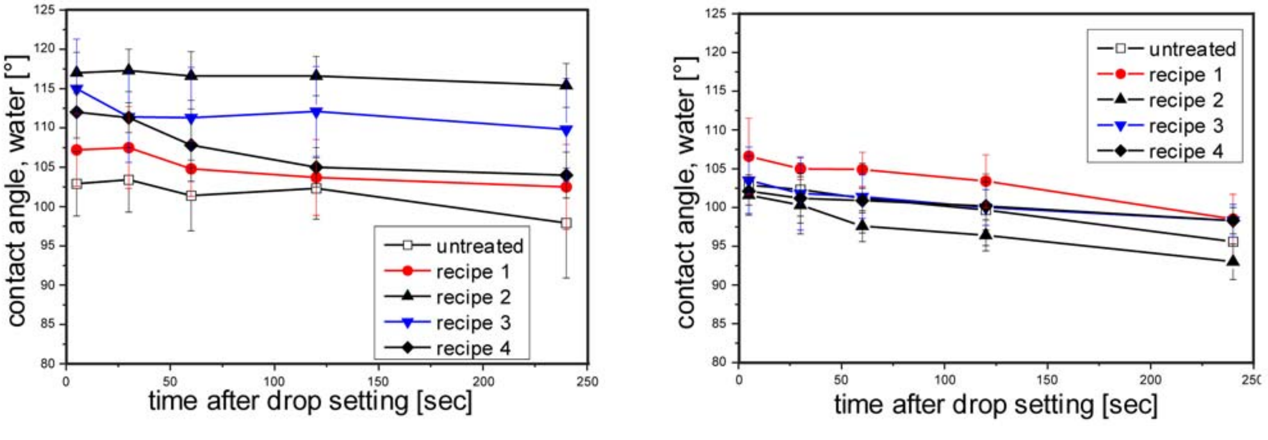

Figure 1: Contact angle of water on leather – after application of different recipes (left image) and after abrasion test (right image)

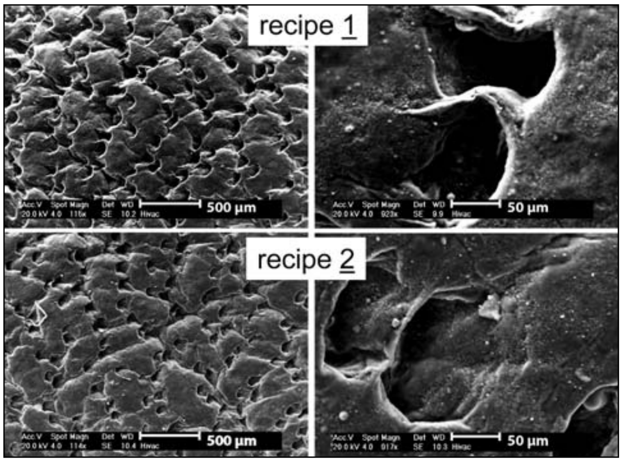

Figure 3a: SEM micrographs of leather samples – after application of the sol recipes 1 and 2.

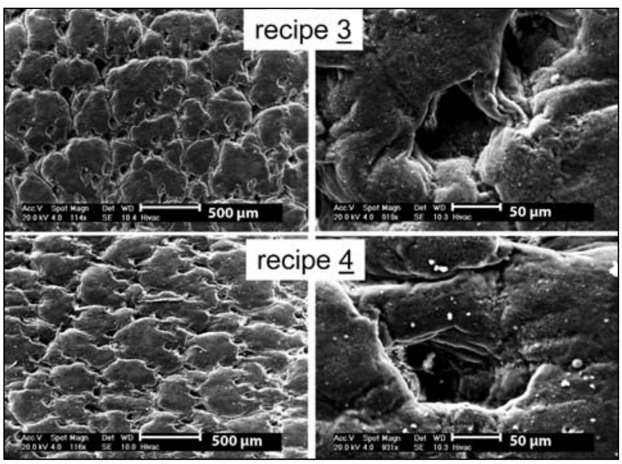

Figure 3b: SEM micrographs of leather samples – after application of the sol recipes 3 and 4.

ce. A certain increase in water repellency after the application of a silica sol can therefore not be explained by a simple sealing of the leather pores by the silica sol. In contrast, it should be supposed that the sol recipe penetrates into the leather pores during the application process and leads to a complete coating of the leather surface including also the inner surface of the pores.

As expected, the different hydrophobic modifications of the silica sols applied as recipes 2, 3 and 4 are leading to a further increase of the hydrophobic properties of treated leather samples (Figure 1). Especially remarkable is for these three recipes that the modification with the non-fluorinated octyltriethoxysilane (recipe 2) yields the highest contact angle against water. Therefore, a combination of SiO_2 with octyltriethoxysilane is most advantageous for improvement of hydrophobic properties of the leather.

An important question for the practical use of the investigated sol-gel coatings is the stability of the gained effects under conditions of usage. For this, an abrasion test is performed on the sol-gel treated and on the untreated leather samples considered as reference. This abrasion test is performed by running 20,000 cycles against a wool fabric on a Martindale device. For the untreated leather samples, it can clearly be observed, that the leather topography is significantly changed by the abrasion process (Figure 2). While the pore size in the leather surface is nearly not influenced by abrasion, the other part of the leather surface loses its roughness. Thus, it can be supposed that a significant amount of leather material is removed by the abrasion.

The same abrasion behavior can be suggested from SEM micrographs for the sol-gel coated leather samples (Figures 3 and 4). The coated samples also exhibit a strong change in the surface topography after abrasion, thus a complete protection against abrasion cannot be expected by the applied sol-gel coating.

This statement is in good relation with the contact angle measurements with water on the leather samples af-

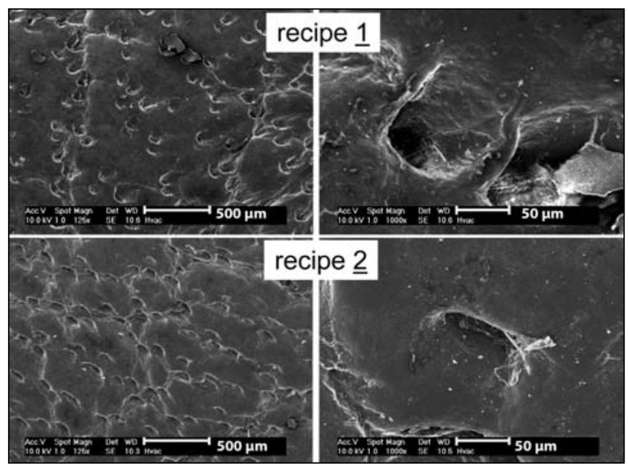

Figure 4a: SEM micrographs of leather samples – treated with the sol recipes 1 and 2, after performance of the abrasion test.

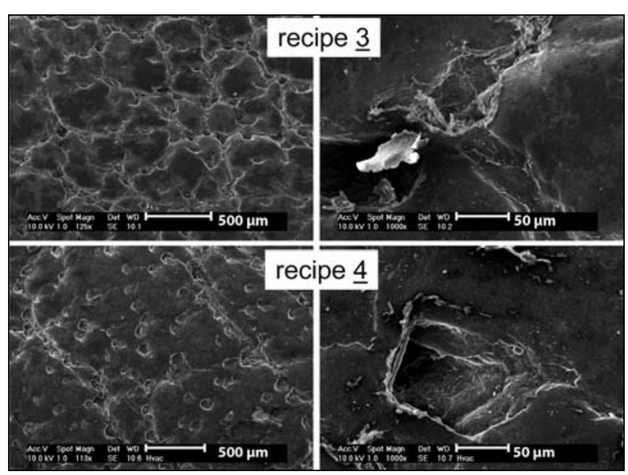

Figure 4b: SEM micrographs of leather samples – treated with the sol recipes 3 and 4, after performance of the abrasion test.

ter the abrasion process (Figure 1). These results demonstrate that the hydrophobic properties of all sol-gel coated samples decrease drastically after abrasion. On the other hand, the water repellent effect of the untreated leather keeps its contact angle against water in the range of 103°. The additional hydrophobic effect gained by all hydrophobically modified sol-gel recipes 2, 3 and 4 is diminished by the abrasion and is nearly similar to contact angles determined for the not sol-gel treated leather (Figure 1). Only for the pure silica sol coating (recipe 1) a slightly higher contact angle against water can be determined even after the abrasion is performed. Hence, certain better abrasion stability may be suggested by application of a pure silica sol compared to the hydrophobically modified SiO_2-sol coatings. However, it should be stated that the measured difference in the contact angle of water after the abrasion tests are less than 5° which is in the range of the error bars reflecting the deviations of the performed contact angle measurements on different positions of the sample.

To complete the investigation, oil repellent properties of the treated leather samples are also investigated by determination of the contact angle of natural oil (Figure 5). Compared to the water repellent properties, the influence of the different sol-gel treatments is more significant on oleophobicity than on hydrophobicity. Even the not sol-gel treated leather contains an initial contact angle of 55° against the used oil. However, after setting the oil drop, the oil drop sinks into the leather substrate, which is reflected by a significant decrease of the contact angles as function of time (Figure 5). The application of the pure silica sol does not lead to a higher initial contact angle of oil but to a decrease of this contact angle as function of time. Thus, it should be estimated that the applied SiO_2 coating is not oleophobic itself but a kind of sealing of the leather surface may be suggested, due to the lower decrease of the oil contact angle with the increasing deposition time.

Higher initial contact angles against oil, between 65° to 70°, are reached by the application of the modified silica sols (recipes 2 and 3). These silica sols are modified with fluorinated and non-fluorinated octyltriethoxysilane. Remarkably, both recipes lead to certain oil repellent effects. In comparison, the strong oil repellent effect gained by the coating with the sol recipe 4 is especially significant. By applying this recipe, an initial high contact angle of oil of 85° can be reached. Additionally, the contact angle value is stable even as function of time after setting the oil drop onto the leather surface. Recipe 4 contains a silica sol modified with a fluorinated polysiloxane which is obviously the most effective modification for realization of oleophobic properties. This recipe 4 is probably useful to reach a permanent oil repellent effect on leather which could lead to stain repellent applications.

Compared to the water repellent properties, the oil repellent properties are strongly influenced by the performed abrasion test (Figure 5). The oil repellency of the untreated leather specimen is significantly decreased after abrasion test and after two minutes after setting the oil drop is nearly completely sunk into the leather surface. The tendency of oil to sink into the leather surface is smaller, if the leather sample is treated with the sol-gel recipes before the abrasion process.

The pure silica sol recipe 1 leads to the same initial contact angle of oil. However, even after 4 minutes this oil drop is not completely sunk into the leather surface. Hence, it can be stated that obviously not the complete SiO_2 sol coating is abraded from the leather surface and the remaining SiO_2 should have a certain effect on the oil up-take capability of the leather. The recipes 2 and 3 containing the modified silica sols lead to slightly higher contact angles against oil and contain also a slower sinking into the leather surface as a function of time after the drop setting (Figure 5). The behavior after application of recipe 4 is especially remarkable. For this recipe, an initial contact angle of 50° is observed which is stable as a function of time. Due to the fact that the SEM images indicate for all leather samples a high amount of abraded material by abrasion test, the remaining oil repellency of the sol-gel

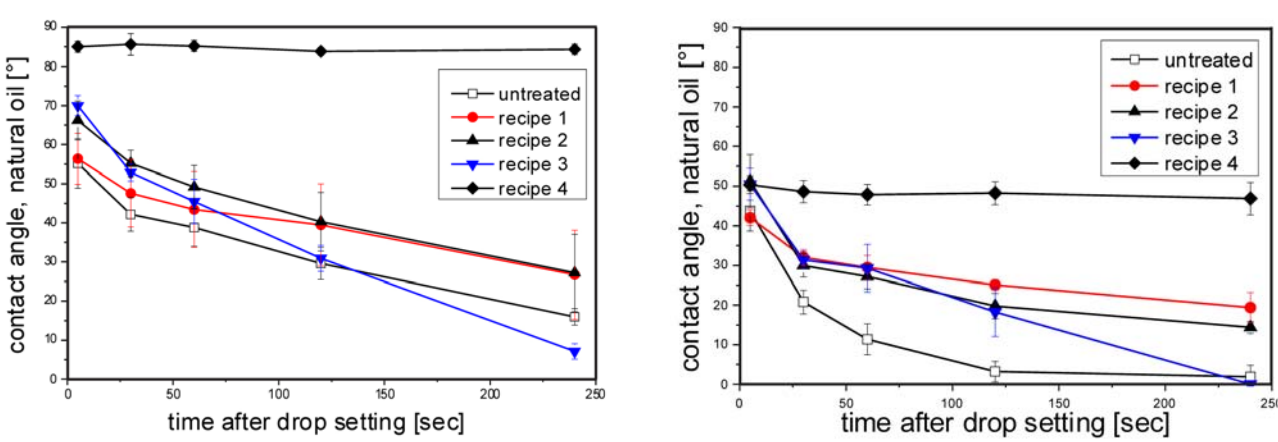

Figure 5: Contact angle of natural oil onto leather – after application of different recipes (left image) and after abrasion test (right image)

treated leather is surprising, because it should be assumed that together with the abraded leather also the sol-gel coating is removed during the abrasion test. The still present oil repellency may be explained by the fact that the abrasion affects mainly the leather topography but not the pores in the leather surface. The inner surface of the pores is obviously not abraded and the remaining sol-gel coating on the inner surfaces is able to lead to a certain oil repellent effect.

Because of the strong difference of water and oil repellent properties, it can be concluded that the oil repellency could be related to the properties of the inner surface of the pores. Probably the sinking of oil into the leather material is going through those pores. If a sol-gel application is able to cover and therefore to protect also the inner surface of the leather pores, a significant oil repellent effect will be introduced on the leather material.

4. Conclusions

Self crosslinking modified silica sols can be used as coating agents onto leather substrates. It has been observed that the water and especially the oil repellency of the leather materials can be significantly enhanced. The enhanced properties are also present in weaker form after an abrasion test is performed on the coated samples. This remaining repellency together with results gained by SEM investigations indicate that the sol coating does not only effect the surface of the leather topography but also the inner surface of the pores present in the leather material.

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Povzetek

V študiji poročamo o različno modificiranih solih silicijevega oksida, ki bi bili uporabni kot prevleke na usnju. Soli so bili pripravljeni s hidrolizo silicijevega etoksida v kislem mediju in modificirani s silani s fluoriniranimi in ne-fluoriniranimi alkilnimi skupinami. Za razliko od predhodnih raziskav sol-gel postopka za zaščito usnja v pričujoči študiji akrilati niso bili uporabljeni v kombinaciji s silicijevimi soli. Delci modificiranega silicijevega oksida predvidoma agregirajo ob nanosu na podlago in tvorijo prevleko na površini usnja. Preiskave z vrstičnim elektronskim mikroskopom so potrdile, da prevleka ne zapolni por usnjene podlage. Kljub temu smo opazili, da so se vodo- in olje- odbojne lastnosti podlage izboljšale. Izboljšane lastnosti usnja z nanešeno prevleko na osnovi modificiranih silicijevih solov predstavljajo priložnost za razvoj izdelkov, pripravljenih po sol-gel postopku, za usnjene materiale, ki so prisotni v vsakdanjem življenju.