Stainless Steel Surface Coating with Nanocrystalline Ag Film by Plasma Electrolysis Technology

Ah-Der Lin 1, Chi-Liang Kung 2, You-Qing Cao 2, Chao-Ming Hsu 2,* and Cheng-Yi Chen 3,*

1 Department of Mechanical Engineering, Cheng Shiu University, No.840, Chengcing Rd., Niaosong Dist., Kaohsiung City 83347, Taiwan; k0549@gcloud.csu.edu.tw
2 Department of Mechanical Engineering, National Kaohsiung University of Science and Technology, No.415, Chien Kung Rd., Sanmin Dist., Kaohsiung City 80778, Taiwan; chilane.gong@msa.hinet.net (C.-L.K.); youqing.ca@gmail.com (Y.-Q.C.)
3 Department of Electrical Engineering Cheng Shiu University, No.840, Chengcing Rd., Niaosong Dist., Kaohsiung City 83347, Taiwan
* Correspondence: jammy@cc.kuas.edu.tw (C.-M.H.); k0464@gcloud.csu.edu.tw (C.-Y.C.);
Tel.: +886-7-381-4526 (ext. 5317) (C.-M.H.); +886-7-735-8800 (ext. 3428) (C.-Y.C.)

Received: 28 May 2018; Accepted: 15 June 2018; Published: 17 June 2018

Abstract: This paper describes the use of a plasma electrolysis technique to apply a nanosilver coating to the surface of stainless steel to achieve hydrophobic properties. We propose an experimental reaction system, which includes stainless steel 316 as the two electrodes and an aqueous solution of potassium nitrate (KNO₃), silver nitrate (AgNO₃), and ammonium hydroxide (NH₄OH) as the electrolyte. Better results with a stainless steel surface coated by nanocrystalline Ag film are obtained using optimal parameters chosen through one-factor-at-a-time experiments. The main parameters consist of electrode distance, KNO₃ concentration, and AgNO₃ concentration. The experiment focuses on analyzing the impact of the plasma electrolysis technique on processing time. Variations in KNO₃ concentration show that 3 wt.% yields the worst result because it causes an uneven surface, whereas 5 wt.% gives excellent results because it creates an even, porous surface and the highest contact angle. An AgNO₃ concentration of 0.03 wt.% yields the best contact angle. With the same processing time, silver sediment increases as the KNO₃ concentration increases. With respect to variation in electrode distance, we find that when the distance is set at 20 mm, the contact angle exceeds 100° and results in hydrophobic properties on the specimen surface, while other distances yield a contact angle below 80°, resulting in hydrophilic surfaces. The SEM (scanning electron microscope) results show that the surface of the specimen is full of crater-like cavities that directly affect the contact angle. In this experiment, the contact angle yielding optimum hydrophobic properties is 134° ± 10°. Finally, using distribution patterns obtained by elemental analysis, the experimental results lead to an evenly distributed silver coating on the surface of specimens subjected to plasma electrolysis treatment. The study confirms that plasma electrolysis can be used to coat nanosilver onto stainless steel 316.

Keywords: plasma electrolytic technology; coating Ag; SUS 316; contact angle

1. Introduction

Surface treatment requires the use of physical, chemical, or mechanical methods to alter the surface characteristics of a material—for example, to change the surface crystal microstructure, increase the surface hardness, or add a coating to increase corrosion resistance—and thereby endow the material with multiple characteristics. The initial purpose of surface treatment is mostly to enhance the material’s appearance through alterations such as anodizing, electrolytic polishing, and so on. Another goal may be to improve the material’s functionality, such as with powder-coating, hot-dip galvanizing,
and electroless nickel plating. Surface treatment technology can be roughly divided into two major types [1]: (1) dry surface treatment and (2) wet surface treatment. Dry surface treatment can be subdivided into physical vapor deposition and chemical vapor deposition. Workpiece processing is usually performed in a vacuum and has drawbacks: the workpiece is limited by the size of the cabin, and the equipment is very expensive. Wet surface treatment is subdivided into electrochemical reactions and chemical reactions. Usually, the workpiece is processed in an aqueous solution. A large workpiece can be processed, but water pollution is a huge problem.

Plasma was initially discovered by Crookes [2] in 1879. Subsequent research yielded plasma electrolytic treatment and glow–discharge electrolysis [3–5]. Gupta et al. [6] published a review paper on plasma electrolytic technology. In 2010, Aliofkhazraei et al. [7] integrated plasma electrolytic technology into a specialist book. Practically, plasma electrolytic technology can be divided into two categories: anodic plasma electrolytic (APE) and cathodic plasma electrolytic (CPE) technology. The application of anodic plasma electrolytic technology can be classified as either the oxidation of metals or the fabrication of nanostructures [7]. This technology is mainly used for the treatment of light metals or the special treatment of metals. With regard to metal oxidation, Gu et al. [8] discussed the deposition of aluminum compound coating on a steel plate using a comprehensive method of arc spraying and plasma electrolytic oxidation. Lukiyanchuk et al. [9] applied plasma-electrolytic oxidation technology to coat Fe and Cu on an aluminum alloy. Parfenov et al. [10] summarized plasma electrolytic technology and proposed a theoretical model to further observe the reaction process. Wu et al. [11] employed anodic plasma electrolytic technology to coat a hardened oxide layer on medium carbon steel, conferring wear resistance.

Cathodic plasma electrolytic technology can also be applied to achieve nanocrystalline coatings, cleaning, the fabrication of nanostructures, and heat treatment. Nanocrystalline coatings and cleaning are the most common uses. In 2009, Aliofkhazraei et al. [12] studied the relationship between nanostructure and corrosion resistance in a composite coating on stainless steel 316 and discussed the parameters for forming nanostructural layers on CP–Ti using plasma electrolytic technology. In a subsequent study, Aliofkhazraei et al. [13] applied CPE techniques to achieve nanocoating on the surfaces of a wide range of metallic substrates. Quan et al. [14] proposed a novel cobalt coating on stainless steel 304 using CPE technology. Wang et al. [15] used CPE deposition technology to fabricate an Al2O3 ceramic coating on a TiAl alloy. Lopes et al. [16] studied the influence of different parameters in the formation of TiO2 thin films on stainless steel using a cathodic plasma deposition technique, since TiO2 has high anti-corrosive properties.

Silver is known to have antibacterial characteristics. For example, in 2004 Kim et al. [17] used self-synthesized nanosilver particles as an antibacterial agent to test its antibacterial effect on Escherichia coli; their results showed that nanosilver particles could significantly increase the permeability of the cell wall and eventually cause cell death. Jeon et al. [18] mixed silver with antibacterial properties into silica materials using a sol-gel method. The resulting silica film mixed with silver was used as an antibacterial glass. Other researchers [19,20] synthesized pure titanium and titanium alloy plates coated with nanosilver particles and analyzed their cell adhesion properties on treated titanium surfaces. Analysis showed that the silver nanoparticles were successfully coated on the surface of the titanium material and had a bactericidal effect.

This study uses plasma electrolytic technology to coat a stainless steel surface with nanosilver, yielding stainless steel with antibacterial properties. Based on the one-factor-at-a-time experimental approach, we determined the parameters required to effectively coat nanosilver on stainless steel 316 and achieve a hydrophobic effect on the surface. After treatment with plasma electrolytic technology, the surface appearance of the specimens was observed with field emission gun scanning electron microscopy (FE–SEM), and its compositions were analyzed using an energy dispersive spectrometer (EDS). Finally, the specimens underwent contact angle measurement. The expectation was that a contact angle greater than 100° would yield hydrophobicity.
2. Materials and Methods

2.1. Experimental Procedure

Before carrying out experimental equipment plan and parameter design, the proposed experiment was tested to assess the design and exclude infeasible parameters. The results allowed us to refine the experimental equipment with respect to setting the parameters. When observing the phenomenon of plasma electrolytic coating, the best parameters for silver coating were found in processed test blocks that had been subjected to SEM (SUPRA™ 55, Carl Zeiss AG, Oberkochen, Germany) AFM (atomic force microscopes, NTEGRA, NT-MDT, Moscow, Russia), EDS (SU8000, Hitachi High-Technologies Corporation, Tokyo, Japan), and contact angle measurement (FTA-1000B First Ten Angstroms, Inc., Cincinnati, OH, USA), which were retested to exclude repeatability. We analyzed the effects and tendencies of the various parameters for nanosilver coated using plasma electrolytic technology. The processing area is related to the current \([9]\). Due to the limitations of the proposed equipment for this experiment, the processing area was set at 10 mm \(\times\) 10 mm after testing. The first test was run with traces of \(\text{AgNO}_3\), and the results demonstrated no arcing when electrical conductivity was insufficient. \(\text{KNO}_3\) was added to make up for the deficient conductivity, after which arcing was observed and a series of experiments could proceed.

2.2. Experimental Equipment

The proposed experimental equipment applied plasma electrolytic technology to coat silver on the surface of the stainless steel specimen plate to give it hydrophobicity. The proposed plasma electrolysis system consisted of a power supply system and a plasma electrolytic reaction system. The power supply system was built using a DC power supply unit (N8741A, 300 V, 11 A, 3300 W; Keysight Technologies, Inc., Santa Clara, CA, USA) and a pulse generator (SPIK2000A; Shen Chang Electric Co., Ltd., Taipei, Taiwan). N8741A DC power supply could provide the required voltage and current to an SPIK2000A pulse generator such that it can generate 3 kW power with 50 kHz to the plasma electrolytic reaction system via the connection wire. Note that the pulse generator played a parameter-adjusting role for the pulse power supplied to the plasma electrolytic reaction system. The plasma electrolytic reaction system is practically configured as shown in Figure 1 and equipped with a ruler, a reactive tank, a cathode electrode clamp fixture, and an anode electrode clamp fixture. The reactive tank was a transparent, barrel-shaped glass jar, convenient for observing the results in the plasma electrolytic reaction system. The size of the reaction vessel container was 170 mm (diameter) \(\times\) 150 mm (height) and could carry up to 3.4 L. In an experiment, the electrolyte liquid covered the entire processing area. The ruler was used to adjust the distance between the anode and cathode electrodes. The anodic electrode clamp fixture was used to settle the electrode. In addition to clamping down the specimen, the cathode electrode clamp fixture limited the specimen’s electrolytic range.

![Image of the actual plasma electrolytic reaction system](image-url)

**Figure 1.** The actual plasma electrolytic reaction system.
2.3. Setting the Parameters

In the design of the clamp fixture, the anodic surface was 30 mm × 40 mm, while the cathodic surface was 20 mm × 30 mm. The cathode and anode were stainless steel 316. The anodic surface was entirely exposed, and the cathodic surface was limited in the processing area by the clamp fixture, whose processing area was 10 mm × 10 mm. The reason for limiting the cathodic surface was to keep the required electrical power within the limitations of the experimental equipment. The voltage was 200 V, the working time (Ton+) was 15 µs, the working time (Toff+) was 5 µs, and the frequency was 50 kHz. The main components of the electrolyte were deionized water, KNO₃, AgNO₃, and ammonium hydroxide. Since the commercial KNO₃ product often contains chloride ions, it can easily react with AgNO₃ in the electrolyte solution to precipitate AgCl. The added ammonium hydroxide is used to react with AgCl in the solution to form the diamine silver hydroxide, as shown in Equation (1), to enhance the plasma electrolytic reaction. In this study, the amount of ammonium hydroxide in electrolyte solution is configured as 20 mL.

\[
\text{AgCl} + 2\text{NH}_4\text{OH} \rightarrow \text{Ag}([\text{NH}_3]_2) + \text{Cl}^- + 2\text{H}_2\text{O} \quad (1)
\]

Parameter setting in this study was divided into three major parts. The first part was changing the KNO₃ concentration, which affected the arcing and the size of the surface holes during plasma electrolysis. The second was exploring the effect of AgNO₃ concentration on the plasma electrolytic coating technology; the amount of AgNO₃ affected the silver content of the coating. The third was changing the distance between the electrodes to explore the effect on the coating. Another important parameter when coating is processing time. The experiment was repeated five times for each parameter.

2.4. Post-Processing

After the plasma electrolytic technology was processed, the specimen was washed with clear water, then put into an ultrasonic washing machine for 5 min for further cleaning. Since the specimen was soaked in the electrolyte, its surface contained numerous holes. To prevent residual electrolyte remaining in the holes, the specimen was put into an ultrasonic washing machine for a further 5 min of cleaning. This ensured the subsequent analysis of the specimen would not be affected by contaminants.

3. Results and Discussion

These experiments aimed to determine the optimum parameters for coating based on one-factor-at-a-time experimentation, to achieve a specimen surface with hydrophobicity. This section discusses the experiments in three parts. First, we look at the effect of different KNO₃ concentrations on the plasma electrolytic coating. The higher the KNO₃ concentration, the better the electrical conductivity of the solution, which affects the coating deposition speed. Next, we examine the effect of different AgNO₃ concentrations upon the plasma electrolytic coating. Note that AgNO₃ is a precious metal and must be used sparingly. The higher the AgNO₃ concentration, the higher the coating rate; at the same time, the surface hydrophobicity is depressed. Third, we look at the effect of electrode distance on plasma electrolysis. This distance affects the energy consumed in the current flow. It also confirms whether high or low energy will affect the coating weight of silver. Finally, we discuss the effect of surface hydrophobicity after plasma electrolysis. The aim is to measure the contact angle, then determine the change in surface hydrophobicity after treatment. In the experiment, after the material was processed with plasma electrolytic technology, the surface of the specimens was coated by nanosilver particles. The particle size after plasma electrolysis was confirmed to be about 30–50 nm on the surface of the specimen, as shown in Figure 2, which was within the particle size range of nanosilver. EDS was conducted to analyze the surface composition, as shown in Figure 3; the main component was silver (see Table 1).
was subjected to SEM, EDS, and contact angle measurement, as shown in Figure 4. When the ambient temperature affected the electrical conductivity. That is, lower conductivity resulted from insufficient. With multiple repeated experiments, we observed that the results were affected by the temperature of the electrolyte is about 25°C during the processing. After plasma electrolytic coating with different KNO₃ concentrations, the electrical conductivity was small enough that the plasma electrolytic reaction was incomplete and the processing surface was uneven. Achieving an even surface required a processing time of more than 25 s, but the overall surface uniformity was still insufficient. With multiple repeated experiments, we observed that the results were affected by the external ambient temperature. When the ambient temperature was low, normal arcing could not start because the temperature affected the electrical conductivity. That is, lower conductivity resulted from

Table 1. Composition analysis of surface particles treated by plasma electrolysis.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Cr (at.%)</th>
<th>Fe (at.%)</th>
<th>Ni (at.%)</th>
<th>Ag (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A9</td>
<td>5.39</td>
<td>2.87</td>
<td>0.55</td>
<td>90.65</td>
</tr>
<tr>
<td>A10</td>
<td>1.07</td>
<td>0.00</td>
<td>0.00</td>
<td>98.93</td>
</tr>
<tr>
<td>A11</td>
<td>12.23</td>
<td>3.94</td>
<td>0.52</td>
<td>83.32</td>
</tr>
<tr>
<td>A12</td>
<td>4.29</td>
<td>2.13</td>
<td>0.24</td>
<td>93.39</td>
</tr>
</tbody>
</table>

3.1. The Effect of Different KNO₃ Concentrations on the Plasma Electrolytic Coating

After plasma electrolytic coating with different KNO₃ concentrations, the cathodic specimen was subjected to SEM, EDS, and contact angle measurement, as shown in Figure 4. When the KNO₃ concentration was 3 wt.%, the electrical conductivity was small enough that the plasma electrolytic reaction was incomplete and the processing surface was uneven. Achieving an even surface required a processing time of more than 25 s, but the overall surface uniformity was still insufficient. With multiple repeated experiments, we observed that the results were affected by the external ambient temperature. When the ambient temperature was low, normal arcing could not start because the temperature affected the electrical conductivity. That is, lower conductivity resulted from
lower temperatures, while higher conductivity was achieved with higher temperatures. In this study, the temperature of the electrolyte is about 25–35 °C during the processing.

![Graphs showing surface roughness, contact angle, and silver coating weight](image)

**Figure 4.** Comparison of the effects of different KNO₃ concentrations and processing times during plasma electrolytic coating when AgNO₃ concentration is 0.06 wt.% and an electrode distance of 20 mm are fixed: (a) surface roughness Rq; (b) contact angle; and (c) silver coating.

When the KNO₃ concentration was increased to 5, 7 and 9 wt.%, the RMS surface roughness (Rq) peaked and the surface was uniform. As shown in Figure 4a, the trends of the three curves at 5, 7 and 9 wt.% are quite similar because their differences are within the measurement error since the standard deviation is about 6%. When the processing time was longer, the surface was increasingly rough. When the concentration was increased to 11 wt.%, the surface roughness dramatically declined. We conjecture that the higher the electrical conductivity of the electrolyte, the more violent the plasma electrolytic reaction. This higher electrical conductivity causes the coating deposition speed to be greater than the speed at which holes are created during the plasma electrolytic reaction. This results in fewer holes on the surface of the stainless steel, with some parts being flat and devoid of holes.

The contact angle measurements for different KNO₃ concentrations are presented in Figure 4b. It was observed that the trends of the three curves at KNO₃ concentrations of 5, 7 and 9 wt.% are almost the same because the diagram clearly shows that the contact angle gradually increased as the treatment time increased. However, a KNO₃ concentration of 5 wt.% is suggested as a better parameter for achieving the desired contact angle because this trend is more consistent. Figure 4c compares the silver coating weight for different KNO₃ concentrations and processing times. We found that the silver coating weight on the surface gradually increased with time. With the exception of a KNO₃
concentration of 3 wt.%, the remaining four concentrations caused the surface to be coated with more than 60 at. % silver within 30 s. A KNO$_3$ concentration of 3 wt.% induced low electrical conductivity, so a starting arc was not achieved and hence the Ag coating was not uniform or, in some cases, complete. The above suggests that a KNO$_3$ concentration of 5 wt.% was optimal for coating Ag on the surface of the stainless steel using plasma electrolysis.

3.2. Effect of Different AgNO$_3$ Concentrations on Plasma Electrolytic Coating

As discussed in Section 3.1, a KNO$_3$ concentration of 5 wt.% was found to be optimal and was therefore used during these experiments. Figure 5 compares the contact angle data for different AgNO$_3$ concentrations and processing times. When the AgNO$_3$ concentration was 0.03 wt.% with a processing time from 10 s to 25 s, the contact angle gradually increased from 105° to the widest angle of 123.02°, demonstrating hydrophobicity. Since the standard deviations are average and all within 10%, the trends of the four curves, except 0.06 wt.%, are quite similar. It can be conducted that the variation on the concentration of AgNO$_3$ has a little influence on contact angle. Figure 7 presented that the size of the surface holes for a processing time of 15 s was not uniform; there were some larger holes among the small holes, causing uneven drops on the material surface as well as a narrowing of the contact angle. Therefore, the processing time plays a key effect on contact angle.

![Figure 5](image-url)

**Figure 5.** Comparison of the measured mean value and standard deviation of contact angles for different AgNO$_3$ concentrations and processing times, when KNO$_3$ concentration of 5 wt.% and an electrode distance of 20 mm are fixed.
Figure 6. Surface appearance for different processing times with an AgNO\textsubscript{3} concentration of 0.03 wt.%: (a) 10 s; (b) 20 s; and (c) 30 s.

Figure 7. Surface appearance for processing time 15 s and an AgNO\textsubscript{3} concentration of 0.09 wt.%.

Figure 8 presents the measured mean value and standard deviation of the silver coating weight for different AgNO\textsubscript{3} concentrations and processing times. The silver coating weight gradually increased when the processing time increased for AgNO\textsubscript{3} concentrations of 0.03 wt.%, 0.04 wt.%, 0.06 wt.%, 0.07 wt.%, and 0.09 wt.%. An AgNO\textsubscript{3} concentration of 0.03 wt.% yielded the least silver coating on the surface, followed by an AgNO\textsubscript{3} concentration of 0.05 wt.%, whereas at concentrations of 0.06 wt.%, 0.07 wt.%, and 0.09 wt.%, the difference in coating amount was not significant. Figures 5 and 8 suggest that an AgNO\textsubscript{3} concentration of 0.03 wt.% was optimal for getting a water drop contact angle that
achieved hydrophobicity and produced the least silver coating on the surface. The thick of Ag coating film is about 600 nm.

![Graph showing Ag coating weight for different AgNO₃ concentrations and processing times.](image)

**Figure 8.** Comparison of the measured values and standard deviations of silver coating weight for different AgNO₃ concentrations and processing times, when KNO₃ concentration of 5 wt.% and an electrode distance of 20 mm are fixed.

3.3. Effect of Different Plate Distances on Plasma Electrolytic Coating

Based on the above discussion, we set the silver KNO₃ concentration at 3 wt.% and the silver nitrate concentration at 0.03 wt.% in the following experiments to determine the effect of varying the electrode distance. Figure 9 presents photos of contact angle measurement with respect to processing time with an electrode distance of 20 mm, and Figure 10 compares the measured mean value and standard deviation of the contact angle for different electrode distances and processing times. From Figure 10, we see that an electrode distance of 20 mm yielded the best contact angle. For distances of 10 mm, 30 mm, 40 mm, and 50 mm, the dependences of the contact angle was practically coincided and almost the same. The standard deviation range for electrode distances of 10 mm and 50 mm was large, exceeding 10%, whereas for distances of 20 mm, 30 mm, and 40 mm, the standard deviation was within 10%.

Figure 11 compares the measured mean values and standard deviations of the silver-coating weight for different electrode distances and processing times. The longer the processing time, the heavier the silver-coating weight. When the electrode distance was 10 mm, the silver-coating weight was lower than with the other four greater electrode distances. This may have been because when the electrode distance was too small, the electrical resistance dropped and the plasma electrolytic reaction became fiercer, such that the coated silver element was destroyed, creating a new hole. This prevented the silver from completely coating the surface of the material. The above results suggest that the best contact angle and lower coating weight were achieved with an electrode distance of 20 mm.
**Figure 9.** Contact angle measurement with respect to processing time 25 s and electrode distance of 20 mm.

**Figure 10.** Comparison of measured mean values and standard deviations of contact angle for different electrode distances and processing times, when KNO₃ concentration of 5 wt.% and AgNO₃ concentration of 0.03 wt.% are fixed.

**Figure 11.** Comparison of measured mean values and standard deviations of silver coating weight for different electrode distances and processing times, when KNO₃ concentration of 5 wt.% and AgNO₃ concentration of 0.03 wt.% are fixed.
4. Conclusions

This paper has successfully applied plasma electrolytic technology to coat nanosilver on the surface of stainless steel 316, achieving a relatively uniform distribution. The optimal parameters for KNO$_3$ concentration, AgNO$_3$ concentration, and electrode distance were obtained using the one-factor-at-a-time experimental approach. The KNO$_3$ concentration affects the electrical conductivity, depending on the ambient temperature in the plasma electrolytic reaction system. The experimental results show that a KNO$_3$ concentration of 5 wt.% yields better performance and boosts the contact angle above 100° to achieve hydrophobicity. In terms of AgNO$_3$ concentration, the higher the concentration, the more silver will be deposited on the surface. Therefore, we suggest an AgNO$_3$ concentration of 0.03 wt.% to achieve a larger contact angle and therefore hydrophobicity, as well as a thinner silver coating on the surface with uniform distribution. When the electrode distance is set at 10 mm, the plasma electrolytic reaction is quite violent, since the two electrodes are too close. As a result, the silver cannot be completely coated on the surface, and the contact angle is smaller than in the original material. An electrode distance of 20 mm was found to be optimal for producing a hydrophobic coating. The contact angle of the 316 stainless steel is about 75.75°, producing a hydrophilic material. However, the contact angle of the specimen after the plasma electrolytic silver coating treatment is about 134° ± 10°, yielding a hydrophobic surface. Our experiments show that this silver-coating treatment using plasma electrolytic technology can change the surface of stainless steel from hydrophilic to hydrophobic and make it water-free. In the future, we will explore other properties of nanosilver coatings on stainless steel, such as strength, oxidation resistance, and aging.

Author Contributions: Conceiving and designing the experiments, C.-M.H. and A.-D.L.; Performing the experiments and measurements, C.-L.K. and Y.-Q.C.; Analyzing the data and writing and editing the paper, C.-Y.C.

Funding: This research was partially funded by the Ministry of Science and Technology, Taiwan (105-2622-E-151-010-CC3, 106-2221-E-151-017 and 106-2622-E-110-009-CC2).

Conflicts of Interest: The authors declare no conflicts of interest. The founding sponsors had no role in the design of the study, in the collection, analyses, or interpretation of data, in the writing of the manuscript, or in the decision to publish the results.

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