

New Post-Treatment Process with Enhanced Technical Performance: Corrosion Protection for Electrical Contacts

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The corrosion of metal surfaces is a well-known, but persistent, problem in certain environments. Tarnishing of frequently used metals, such as silver or copper, is one aspect of it. This paper gives an overview of the existing knowledge, which has been accumulated in the last century, and the experience to solve or avoid this problem. Special attention is given to the development of an organic monolayer based on alkanethiols. Some important facts about the structure and functionality of protective coatings are described. Investigations into the properties (corrosion resistance in different media, sliding properties, electrical resistance, bondability and solderability) of metal surfaces, which are protected with an alkanethiol containing anti-tarnish products, are presented. The advantages of using this organic protection are defined.

1 Introduction

Since people discovered how to process metals, as well as metal alloys, and create objects from them, they have faced problems such as corrosion and tarnishing. With the industrialization of society in the 19th century, the increasing technical challenges of the new age required new and variable solutions in terms of protecting the metal surfaces beyond the aesthetic aspects. The need for effective and strong protection has accelerated alongside the opportunities offered by the electroplating of metals. This technique allows for savings in the amounts of metal. There are more and more applications, where the deposited thin metal layers require reliable and better corrosion protection.

The following study has its focus on anti-tarnish systems and processes, which are mainly connected to silver. Some of them are also applicable to other metals, such as Au, Cu and Pd, and their alloys, which inevitably show different kinds of corrosion behaviour. Given the wide range of applications of silver, its tarnishing has been and still is one of the most discussed and investigated topics in industry and science. In decorative applications, tarnishing ruins the appearance. In a technical sense, it causes an increase in contact resistance, while decreasing bondability and solderability.

2 Review

2.1 Tarnish protection: a scientific problem since the 19th century

For more than 60 years, a few methods to prevent silver and its alloys from tarnishing have been subject to research [1, 2]. Mostly, they are connected with creating a protective layer on the metal's surface. Some of the methods and substances (organic thin films), or aspects of them, are still in development. Other processes are no longer commonly used, mainly because of their toxicity (chromate conversion coatings) or low effectiveness (lacquers, chromate conversion coatings). Some patents from the 1980s that are still used involve chromate as a protective coating [3, 4]. Despite the trials undertaken by some companies in the late 1990s with trivalent chromium [5], research and development increasing explored other avenues in the ensuing years.

One relatively old [6] protection method, which is still researched and discussed, involves the use of thin layers (up to 100 nm) from other corrosion resistant metals or oxides, which are applied on top of the deposited metal or alloy [7, 8]. Some recent reports have described the combination of thin protective metal and organic protective layers [9].

Descriptions of some surface protection procedures, which are based on organic substances and show

anti-tarnishing effects, can be found in publications and patents from the first half of the 20th century [10–12]. Organic substances, containing sulfur in the form of sulfhydryl (thiol), also started to be considered as protection against copper corrosion and silver tarnishing [13–16].

2.2 Self-assembled monolayers as the subject of research

From the late 1980s onwards, new studies connected with surface phenomena and thermodynamics, which ran parallel to an expanded demand for new corrosion protection methods, have contributed much to the development of new processes. Investigations into self-assembled monolayers (SAMs) of alkanethiols, preferably on gold [17–19], have provided an opportunity to collate a fundamental understanding of processes such as adsorption (*Fig. 1*), ordering, growth, wetting, lubrication and corrosion. At the beginning of the 1990s, the experience in protecting metal surfaces in industrial applications, as well as developments in fundamental scientific knowledge about SAMs from the second half of the 20th century onwards, led to better and more effective corrosion protection procedures, especially against silver tarnishing [2, 20]. Investigations described in some patents and publications between the end of the 1970s and the beginning of the 1990s show how anti-tarnish products developed [21–25].

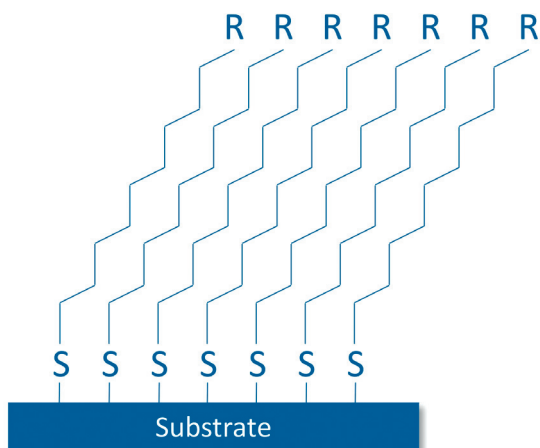


Fig. 1: Schematic drawing of alkanethiol molecules onto metal substrate
Source: Umicore Electroplating

2.3 Thiol-based, water-soluble products

Organic thiols are almost water-insoluble. As such, when the development of this market began, products were mostly based on organic solvents [21–23]. Organic solvents often reveal disadvantages, which prevent their widespread use in industrial applications. They are usually flammable and special precautions are necessary in the production environment. At the beginning of the 1990s, some products appeared, which could be operated in aqueous media [24, 25]. In the second half of the 1990s, some patents dealing with other organic substances, namely azoles, were published [26, 27]. The beginning of the 21st century onwards witnessed a revival of the mainly aqueous thiol-based products, which led to the publication of new patents in this area [28–32]. In addition to thiol-based, water-soluble anti-tarnish products, substances such as fluorinated alkyl thiols and silanes have also been discussed [33–36]. Given their characteristics, there is no remarkable field of application comparable to alkyl thiols.

Since the market requirements are focused on thiol-based, water-soluble products, the main challenge is to design products in order to achieve a proper, stable and reliable aqueous emulsion (*Fig. 2*), thereby assuring the best conditions for adsorption of the thiol-substance on the metal surface.

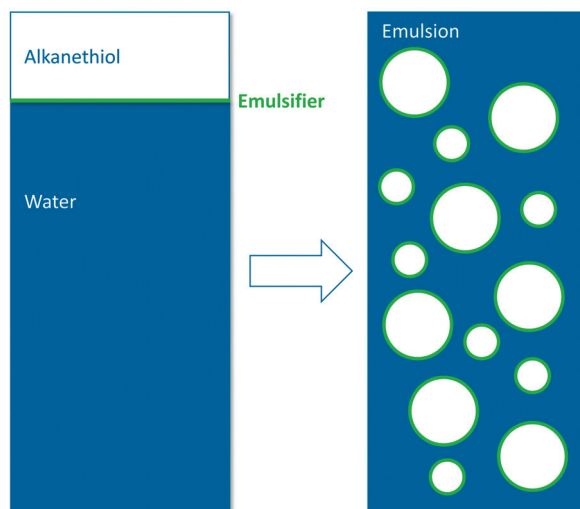


Fig. 2: Schematic drawing of an emulsion of alkanethiol molecules in water
Source: Umicore Electroplating

2.4 Further requirement: reduced post-treatment time

The protection behaviour of the alkyl thiol layer mainly depends on the density of the SAM layers (Fig. 3). Achieving this target, as well as producing a compact coating of close-packed molecules within a minimized exposition time, represents the recent challenge in development, due to the increasing demand in the technical field for faster and reliable protection processes.

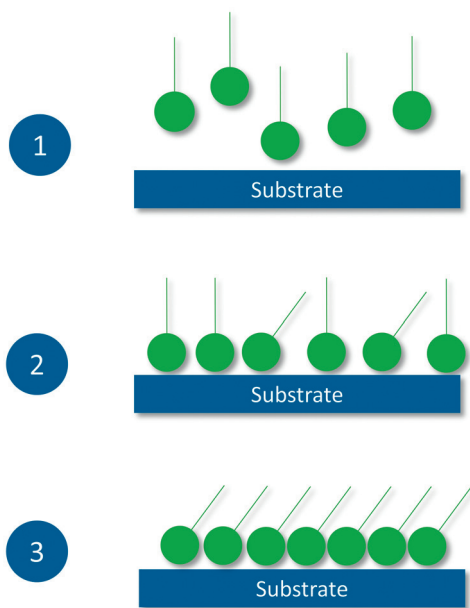


Fig. 3: Adsorption and ordering steps of a self-assembling monolayer of alkanethiols on metal substrate
Source: Umicore Electroplating

Technical coatings in the electronics industry, such as connectors, are increasingly exposed to precious metal savings. The layers, which are to a large extent made of gold, silver, palladium and its alloys, have to fulfil strict technical specifications.

These requirements, however, are hardly achieved by using thinner precious metal layers. In this context, protection technology is increasing the focus of public awareness. Although post-treatment processes will generally offer adequate protection against corrosion, they will still likely leave the main technical properties of the final layer, such as electrical

contact resistance, wear resistance, solderability and bondability, unaffected.

As part of the investigations, well-known and established anti-tarnish processes were benchmarked for further development.

In the interaction with additional additives, the protection capacity could be further enhanced. This is especially the case with electrolytic application, which offers more advantages. Such operations enable protection coating to be applied much more densely and compactly, compared to a simple monolayer involving a dipping process. A second advantage of electrical assistance is that these layers are already fully applied within seconds, thereby providing their full protective potential to a much faster degree.

3 Experimental

3.1 Substrate preparation

In the experiments described below, brass sheets (0.5 dm²) were mostly used. They were plated with 5 to 10 µm of sulfamate nickel and 3 to 5 µm of silver (Arguna® 630). For solderability tests, 3 to 5 µm of silver plated lead frame parts (Arguna® 630) were required. In preparing the samples needed for the neutral salt spray (NSS) test, brass sheets were plated with 3 µm of sulfamate nickel and 0.05 to 0.8 µm of gold (Auruna® 5400).

3.2 Preparation and working conditions of the post-treatment protective solution

The standard post-treatment solution was prepared with 10 m/L of Umicore Sealing 691 Concentrate for the dipping version and an additional 5 g/L of Umicore Sealing 691 Basic Additive for the electrolytic version. The working temperature was 50 °C. The standard exposition times were 3 min for dipping conditions and 10 s for the electrolytic application. For electrolytic usage, 5 V were applied, while MMO 187 anodes were used.

3.3 K₂S test

As silver is highly sensitive to sulphur-containing corrosive media, silver coatings are used to assess the corrosion and tarnish protection performance. A potassium sulphide dip test is commonly performed for the purpose of quality control of the protection processes. Different concentrations of K₂S solution

have been used in this practice. The tests, which are presented in this article, were made in a 2 % K_2S solution. The exposition time of the protected samples was 3 to 10 min at 25 °C.

3.4 Wear resistance

To determine the coefficient of friction the nano-indentation device Universal Nanomechanical Tester (UNAT) from Zwick/ASMEC Advanced Surface Mechanics was used. The test was carried out with a 3 mm gold-coated steel ball at a load of 50 mN; 500 cycles were performed, at a frequency of 16 Hz.

3.5 Electrical contact resistance

The measurements of the contact resistance of silver layers, with and without a top protective layer of Sealing 691, were made using the Kowi 3000 device from wsk Mess- und Datentechnik. The test was made with a contact normal force of 10 cN at a current of 10 mA with a 20 mV limitation in the voltage.

3.6 Bondability test

For gold-wire bonding tests, a Bonder HB16 from TPT, a bond-wire Heraeus HD 2 (25 μ m) and a bond-tool Wedge 4445-2020-3/4-CG-F BKCER were used, with the following bond parameters: US-Power 240 mW; time 60 ms; force 220 mN and bond table temperature 120 °C. The following pull-test was made with the Dage 4000/WP 100 device at a pull angle of 30°.

3.7 Solderability test

The SAT-5100 solder checker from Rhesca, with an SnAgCu solder and an Alpha 100-T flux, was used. The soldering temperature was 255 °C, while the immersion time was 5 s at a speed of 20 mm/s. The test was carried out with an immersion depth of 2 mm.

3.8 NSS test

The NSS test was made, in line with the DIN EN ISO 9227 NSS (September 2012), using equipment from Erichsen (Modell 608), with a volume of 1000 L. The maximum test time was 72 h.

4 Results and discussion

4.1 Anti-tarnish performance by immersion method and by electrolytic application

Silver-coated samples were immersed in a 2 % K_2S solution for testing. The standard anti-tarnish product showed the first signs of corrosion after two minutes, while the samples with the new anti-tarnishing process did not reveal corrosive attacks after five minutes, meaning they were still fully functional.

How well the post-treatment process protects was demonstrated subsequently by test applications with constant voltage. The specimens were immersed for 10 s, with and without a voltage of 5 V (Fig. 4).

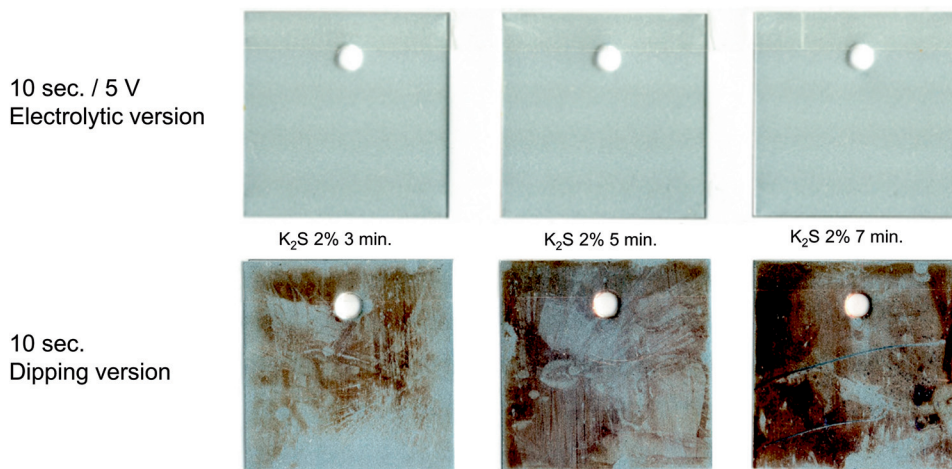


Fig. 4: The electrolytic application shows clearly improved K_2S resistance
Source: Umicore Electroplating

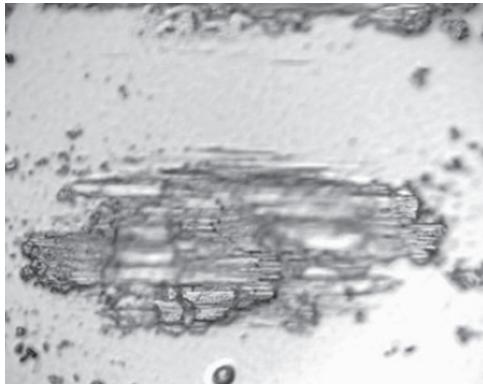
While the dipped parts showed strong discoloration after three minutes of testing in the K_2S solution, the parts with applied voltage did not show any discoloration up to seven minutes later. The advantage offered by the electrolytic application of the product is well demonstrated by these tests. The results show how that best protection can be achieved in a very short exposition time, which makes the process fit with high throughput speed and therefore ideal for use in continuous plating lines.

4.2 Reduced friction force by improved sliding properties

As part of the test series, the mechanical behaviour of electronic components was studied. In the process, the impact of the anti-tarnish solution on the coefficient of friction was examined in relation to connector parts after passivation.

To determine the coefficient of friction of an untreated surface, a pure silver sample was tested by means of a hard gold rivet as a counterpart. The examination of the silver surface with an anti-tarnish layer showed that the coefficient of friction could be reduced by over 95 % (Fig. 5).

These findings make it clear that the new generation of anti-tarnish solution significantly improves sliding properties.



0.76
Coefficient of friction of pure silver
without Umicore Sealing 691

4.3 Electrical properties: stable contact resistance

Particularly in the field of electronic components, a stable contact resistance is one of the fundamental requirements. Thus, even after applying a protective layer, the full functionality of a connector must be given.

In response, Umicore also studied the influence of the new Sealing 691 system on electrical characteristics. During the test series, the change in the contact resistance was primarily investigated.

A reference sample with pure silver coating was benchmarked against samples with a matrix of different concentrations and treatment times in the passivation process. As a result, the contact resistance showed only a slight variation even at the maximum sealing concentration and treatment time.

The investigations showed that the value of the contact resistance was not influenced, as it always remained far below the 10 m Ω limit (Fig. 6).

4.4 Wire bondability thoroughly tested in specifications

The executed gold-wire bond and pull tests clearly met the objectives of the DVS 2811 specification. Under given parameters, it requires a minimum with-



0.04
Coefficient of friction of pure silver
with Umicore Sealing 691

Fig. 5: Wear tracks on the surface and the corresponding coefficients of friction after wear resistance tests of silver coatings show improvement after application of Umicore Sealing 691 (detailed test parameter and equipment: see under 3.4 wear resistance)

Source: Umicore Electroplating

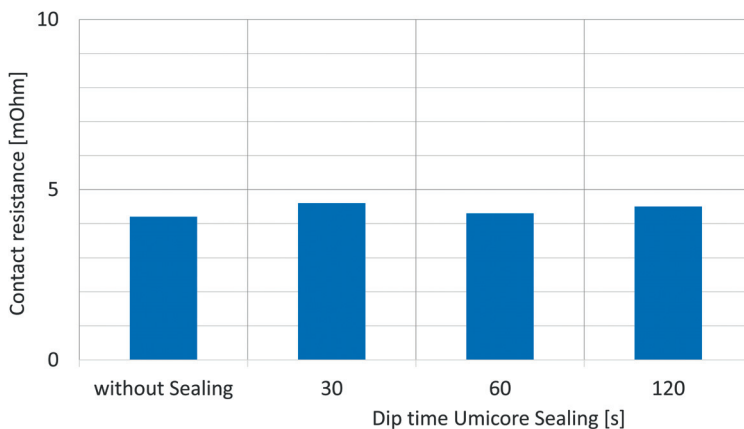


Fig. 6: The contact resistance remains stable, not depending on dipping time
Source: Umicore Electroplating

drawal force of 4 cN; meanwhile, no lift-offs are acceptable in laboratory testing. Overall, all samples in the matrix, with a variation of different concentrations and treatment times, achieved an average pull force in the range of 10 cN, with tight deviations in single values (Fig. 7).

4.5 Solderability remains unaffected

The impact on solderability was determined by recording the zero-cross-time (ZCT) during the solder balance test. As a result, all passivated samples met the specifications of IEC-60068-2-58 and showed a ZCT that was significantly less than 1 s

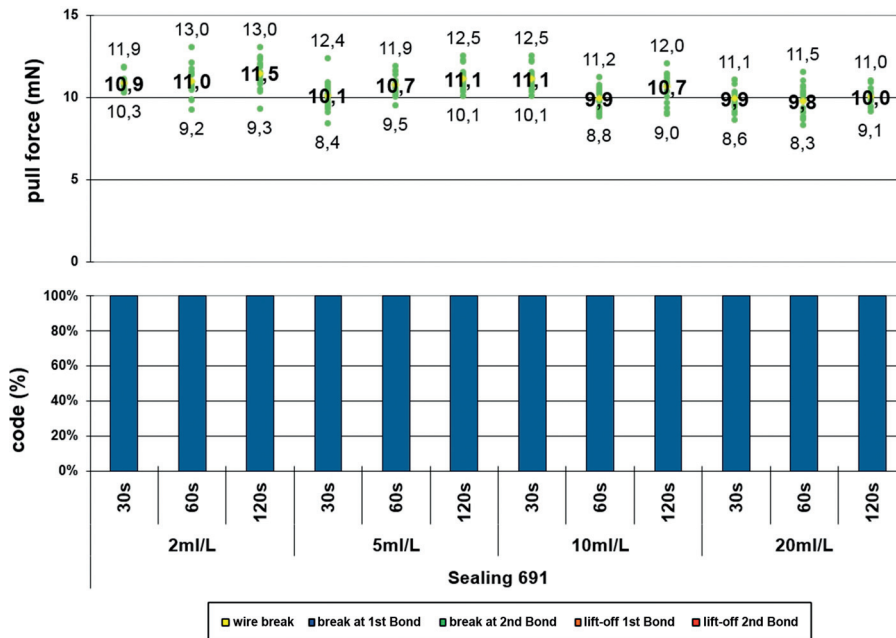


Fig. 7: All samples met the requirements of DVS specification 2811 during the gold wire bond and pull test
Source: Umicore Electroplating

(Fig. 8). Given that the anti-tarnish coating had no negative effect in direct comparison to untreated samples, then, it can be said to be explicitly suitable for solder applications.

4.6 Results after 72 h NSS test

The NSS test, in line with the DIN EN ISO 9227 specifications, is widely used as a standard corro-

sion test. Therefore, the protection performance was studied in combination with a variety of gold layer thicknesses.

A representative example for the strong protection performance in the NSS test is considered as a benchmark result. The reference samples, with the 0.4 μm hard gold coating and no post-treatment on top, showed severe corrosion effects after 72 h. In

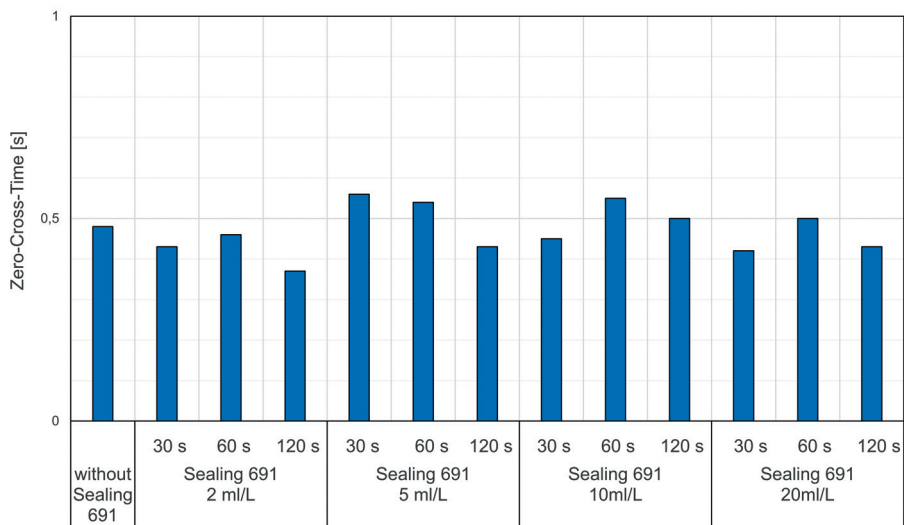


Fig. 8: The zero-cross-time is below one second for all conditions

Source: Umicore Electroplating



Fig. 9: Treated gold samples (0,4 μm) demonstrate the strong protection level during the NSS test

Source: Umicore Electroplating

direct comparison, the 0.4 μm gold layer with only 10 s of post-passivation was fully functional after 72 h and showed no corrosion marks (Fig. 9).

5 Conclusion

The findings verify the huge potential of the new generation of nanoscale anti-tarnish processes. They offer advanced technical performance with a high level of protection in comparison to many other existing systems. The studies demonstrate that the favourable properties of the functional surfaces remain untouched, while some, such as the sliding properties, are even significantly improved.

Used in continuous plating lines, the new anti-tarnishing processes offer strong benefits. The design allows for a very fast application. This is beneficial, especially for reel-to-reel application due to the high throughput rates and short contact times. The standard immersion dipping process can be simply applied, but the complete performance potential is revealed only within a few seconds by use of electrolytic voltage.

The new anti-tarnish protection processes offer the best protection characteristics, the highest application flexibility and, finally, a very high productivity for technical precious metal surfaces, such as gold, silver, palladium and their alloys. The presented processes do not contain HCFCs, CFCs, HCs or chromium. Additionally, they are completely solvent-free and can be successfully applied in aqueous media.

References

- [1] Gay, P.-A.; Berçot, P.; Pagetti, J.: *Plating & Surface Finishing*, 2004 (May), 71–73
- [2] Kartlüke, D.; Scholz, R. R.; Funk, M. J.; Baumgärtner, M. E.: *Galvanotechnik*, 1992, 83(6), 1,918–1,926
- [3] Takakura, Y.: Japanese patent, JPS6213582A, 1987
- [4] Barnes, C.; Ward, J.: European patent, EP0034040A1, 1981
- [5] Susa, H.; Katori, M.: Japanese patent, JPH11152588A, 1999
- [6] Shields, Th.: United States patent, US1949131A, 1934
- [7] Satou, A.; Yamaguchi, Y.; Hashimoto, H.: Japanese patent, JPS637361A, 1988
- [8] Paussa, L.; Guzman, L.; Marin, E.; Isomaki, N.; Fedrizzi, L.: *Surface & Coatings Technology*, 2011, 206(5), 976–980
- [9] Eckert, H. U.; Ryl, M.: European Patent, EP2196563B1, 2013
- [10] McClure, H. B.: *Chemical Engineering News*, 1944, 22, 416–421
- [11] Briggmann, G. F.: United States patent, US2323369A, 1943
- [12] Robertson, L. D.; Robertson, J. W.: United States patent, US2503843A, 1950
- [13] Camp, E.: United States patent, US2522430A, 1950
- [14] Pryor, D.; Cason, L.: United States patent, US3248235A, 1966
- [15] Kroll, H.; Therrien, A.; Bennett, Ph.: United States patent, US3330672A, 1967
- [16] Warner, P. F.; Phillips, T.: German patent, DE1938190A1, 1972
- [17] Folkers, J. P.; Laibinis, P. E.; Whitesides, G. M.: *Langmuir*, 1992, 8, 1330–1341
- [18] Ulman, A.: *Chemical Reviews*, 1996, 96, 1,533–1,554
- [19] Luk, Y.-Y.; Kato, M.; Mrksich, M.: *Langmuir*, 2000, 16, 9604–9608
- [20] Grossmann, H.; Huck, M.; Marka, E.: *Galvanotechnik*, 1991, 82(11), 3837–3841
- [21] Kawana, Y.; Ara, T.: Japanese patent, JPS52111430A (JPS561396B2), 1977
- [22] Nagano, S.; Sakamoto, F.: Japanese patent, JPS59215490A (JPS6155596B), 1984
- [23] German patent, DE3905850A1, 1990
- [24] Grossmann, H.; Marka, E.: European patent, EP0492487B1, 1996
- [25] Grossmann, H.; Marka, E.: German patent, DE4041596A1, 1992
- [26] Kishimoto, M.; Kawashima, J.; Nakamori, S.: Japanese patent, JPH09241532A, 1997
- [27] Aiba, T.; Inabe, S.: Japanese patent, JPH09287082A (JP3373356B2), 1997
- [28] Johns, P.: British patent, GB2402399B, 2005
- [29] Landau, U.; Jolk, I.: EP1969157B1, 2007
- [30] Di, L.: Chinese patent, CN101353800A, 2009
- [31] Huang, H.; Sun, S.: Chinese patent, CN101705483A, 2010
- [32] Abys, J.; Sun, S.; Antonellis, T.: United States patent, US8703243B2, 2014
- [33] Waldeck, D.; Burleigh, T.; Gu, Y.: World patent, WO9948682A1, 1999
- [34] Huang, H.; Sun, S.: Chinese patent, CN101974759A, 2011
- [35] Whitney, D.; Bokisa, G.; Bishop, C.; Vitale, A.: United States patent, US6506314B1, 2003
- [36] Hofmann, U.; Donsbach, H.; Unger, J.: European patent, EP2333021A1, 2011