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QUANTITATIVE DESCRIPTION OF COLOR CHANGES OF 18 KARAT GOLD ALLOYS DURING TARNISHING TESTS

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INTRODUCTION

Red gold alloys are highly valued for their aesthetic qualities, particularly in luxury goods and jewelry. The possibility of changing the color of the alloys to a certain extent by changing the chemical composition without losing the gold content, makes them very interesting from a design point of view.

In general, alloying with suitable elements such as copper (Cu) and silver (Ag) ensures the mechanical properties required for use as jewelry without sacrificing the noble luster appearance of Au. For example, a significant increase in the hardness of red gold can be achieved by increasing the Cu content.[1] However, alloying with other, less precious elements, such as Cu provides the properties required for the application, but reduces the chemical stability of the precious metal. Hence, these alloys are therefore more susceptible to corrosive attacks, such as those caused by contact with skin, when worn. Maintaining their color over time remains a persistent challenge due to environmental exposure. These trade-offs are critical for designing alloys that balance functionality and durability in specific applications, such as jewelry or industrial materials. Understanding how these elements interact within the alloy matrix is essential for improving performance and extending the lifespan of gold alloys. Color stability is crucial for aesthetic reasons, therefore standardized quality requirements exist such as those defined in ISO 8654,[2] which categorizes gold alloy colors based on chromaticity, which is measured using CIE

colorimetry. Permissible tolerance ranges are defined within these categories. Each category has a specific tolerance range that defines acceptable deviations in color caused by manufacturing or environmental factors. For red gold, maintaining its characteristic reddish hue within the defined tolerance range is critical for consumer acceptance and compliance with standards. Exceeding the tolerance limits can cause color changes that differ greatly from the actual desired color of the alloy.

Efforts to improve the color stability of red and dental gold alloys have been already reported in.[3,4] There are patents dealing with the improvement of resistance against discoloring of some 18K Au alloys in correlation to the content of palladium (Pd) and some additional elements such as platinum (Pt), indium (In) and tin (Sn).[5–8] However, it is difficult to compare the data and draw conclusions because the test conditions in the different studies are not the same.

In general, tarnishing is defined as the visibly detectable discoloration of a metal caused by a thin adherent layer of a reaction product, such as an oxide or a sulfide, induced by a chemical reaction between the metal and the environment.[1] There is analytical evidence that in Au-Cu-Ag alloys the formation of Ag and Cu-sulfides play a crucial role when the parts are exposed to sulphur-containing environments.[9–11] Tarnishing of Au alloys is similar to that of Ag alloys.[11] The formation of AgS is dominant for the tarnishing since it was found mainly in the reaction layer.[9,11] Tarnishing correlates with the Ag/Cu content in Au alloys and the corrosion product on the surface leads to loss of metallic polish, lustre and color.[11] It was shown, that the reaction of silver with hydrogen sulphide[1] is endothermic, so that reaction takes place only when it is heated or an oxidizing agent is present (2).[12] From there, oxygen accelerates the redox reaction with sulphur.

$$2Ag(s) + H_2S(s) \leftrightarrow Ag_2S(s) + H_2(g) \quad (1)$$

$$4Ag(s) + 2H_20(g) + O_2(g) = 2Ag_2S(s) + 2H_20(g) \quad (2)$$

In the context of the oxidation mechanism of tarnishing, Yuan et al reports about a tarnishing mechanism of 18K rosy Au alloy based on the oxidation of Cu, when immersed in artificial sweat. Copper oxide forms on the sample's surface when it was immersed in artificial sweat for a certain time. It results in a gradually color change of the surface from red to yellow.

It should be noted here, that no sulfur containing molecule was listed to be part of the sweat solution in this study.[3]

Furthermore, it is reported that Cu is dissolved from gold jewelry in contact with artificial sweat,[13,14] which also causes a chemical change on the surface. For improving the tarnishing resistance it was found that Zn has a positive effect on the tarnishing since Zn has a deoxidizing purpose in yellow gold alloys.[11,15] Further, Ohta et. al. states a positive effect of Pd on the discoloring resistance of dental Au alloys with nobility < 50%.[4] However, the mechanism of discoloration is not fully described yet since systematic studies are limited.

From there, in this work an overview on the findings of the patents regarding the color and the discoloring of 18K Au alloys was obtained to identify potential alloy compositions. Since different aging conditions were used in the patents, the focus of the present study was set on a systematically experimental investigation under standard conditions. Therefore tests were carried out under three defined conditions to investigate the effect of different ageing conditions on the color change of the same alloys.

They consisted of immersion in artificial sweat and exposure to artificial sweat vapor over a defined period of time and measuring the color at defined time intervals. Furthermore, long-term exposure tests were conducted under air in which the color was also measured at defined intervals. Hence, the change of color could be determined and the color stability of a 2N yellow gold and a 5N 18K red gold alloy was evaluated under standardized conditions. Although these do not correspond exactly to the realistic conditions of the realistic usage scenario, which would be better simulated by a wear test, for example, but in contrast to this, they ensure the reproducibility and systematic nature of the experiments.

1. MATERIALS AND METHODS

1.1 Materials

Two 18K gold alloys were purchased from C.Hafner GmbH + Co.KG (Germany) as sheet material, a 2N yellow gold alloy and a 5N red gold alloy. The Ag/Cu ratio of the alloys used can be determined from the respective nominal concentrations in the Table 1. Before the start of the corrosion tests, the samples were metallographically polished according to the standard for color measurement DIN EN ISO 8654_2020-05 and a first color

measurement was done within one hour after polishing as initial state of the alloys before corrosion testing.

The influence of the main alloying elements silver and copper on the color of the gold alloy is wellknown in the literature and there are already existing ternery phase diagrams published.[16]

Table 1: Designation of the alloys used and the nominal Ag/Cu concentrations

Standard color	Alloy	Ag	Cu
2N	751 GG 16	150	89
5N	751 RT 32	40	199

1.2 Corossion tests and color measurements

The tarnish testing was done in synthetic sweat solution according to DIN8237 (NIHS96-50) and in air. In total ten samples were tested as given in the Table 2. The testing in synthetic sweat was either done by exposure to the sweat vapor (as described in the testing standard) or by immersion into the synthetic sweat solution. The second type of testing was chosen in order to avoid stains on the samples from droplets of the testing solution. The samples tested in synthetic sweat vapor and in synthetic sweat solution are designated “xxx-SSV” and “xxx-SIM”, respectively. Two identical samples were tested for each alloy in these two tests. The total testing duration in synthetic sweat solution was approximately 500h. The testing in air was done under office atmosphere at room temperature. Direct sunlight was avoided during testing. The samples are designated “xxx-AIR”.

Table 2: Samples and testing conditions for tarnish testing

Sample ID	Test type	Temp. [°C]	Standard
2N-1 SSV	synthetic sweat vapor	40 ± 2	DIN8237 (NIHS96-50)
2N-2 SSV	synthetic sweat vapor	40 ± 2	DIN8237 (NIHS96-50)
2N-3 SIM	synthetic sweat immersion	40 ± 2	DIN8237 solution
2N-4 SIM	synthetic sweat immersion	40 ± 2	DIN8237 solution
2N-5 AIR	air testing	23 ± 4	--
5N-1 SSV	synthetic sweat vapor	40 ± 2	DIN8237 (NIHS96-50)
5N-2 SSV	synthetic sweat vapor	40 ± 2	DIN8237 (NIHS96-50)
5N-3 SIM	synthetic sweat immersion	40 ± 2	DIN8237 solution
5N-4 SIM	synthetic sweat immersion	40 ± 2	DIN8237 solution
5N-5 AIR	air testing	23 ± 4	--

During testing, the color was measured repeatedly and plotted as function of time. During the interrupted tarnishing test, the samples were taken out of the solution, cleaned with deionized water and dried. Color measurements were made with a Konica-Minolta CM-5 spectrophotometer (Konica Minolta Business Solutions Deutschland GmbH, Germany) in the wavelength range of 360-740 nm, with wavelength steps of 10 nm. The system is automatically calibrated with an internal white standard before the measurement. The following conditions were used for color measurements:

- Measurement geometry d/8 diffuse illumination
- Observer 10°
- Light type D65

The color was measured in the CIE- La*b* color space, where the a* value represents a shift in the color space between green and purple and the b* value represents a shift between blue and yellow. The L value can be used to make a statement about gloss, with this being arranged as a vertical axis to the a*b* color space. With all three values, a statement can thus be made about the color as well as about the brigthness.

The color change ΔE relative to the original color before testing was calculated from the L*, a* and b* values before and after testing according to the equation:

$$(1) \qquad \Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}.$$

When considering the categorization of known gold alloys according to their color, from 0N to 5N in relation to the chromatic coordinates L, a*b*, it becomes clear that a wide range of colors is possible according to.[2] This standard describes how the basic composition affects the color of the gold alloy in terms of the copper and silver concentrations and which main colors are standardised. From yellow-green (0N, 14K) to dark red (6N, 18K), a more or less continuous transition takes place.

2. RESULTS

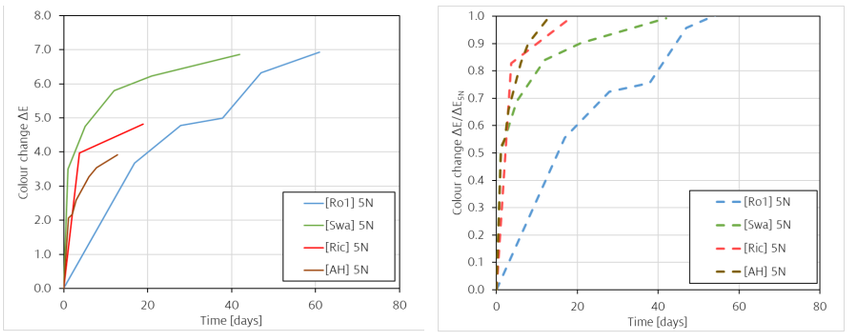
2.1 Evaluation of patents

Patents were evaluated according to the criterion of corrosion resistance and based on their relative color change in salt spray test and an overview of adequate 5N alloy compositions could be provided.[5,6,8,17] Between the test results obtained under nominally identical test conditions of the nominal identical standard 5N alloys for reference purpose, the different patents also show large variations in the color change behavior of this tested 5N alloys. Figure 1 a) shows the extent of the differences in discoloring behavior, with completely different color changes visible after the same corrosion test period. For this reason, it is difficult to compare the results of the various alloy tests with regard to color change. In order to obtain better comparability of the results independently of the respective patent, the corrosion tests were standardized according to the maximum color change of the standard 5N alloy which has been subjected to the identical corrosion tests. This makes it possible to neglect the differences that can be attributed to the small differences in the test procedure of the individual patents. This makes it possible to determine approximately how quickly the maximal measured value of color change documented in the patent for the standard 5N alloy is reached (Figure 1 b) and allows the other alloys tested to be compared in terms of the influence of the alloying elements. All in all it illustrates the difficulty of comparing the results of different corrosion tests under nominally identical conditions.

Figure 2 shows the color difference relative to the respective nominal 5N color change value of each patent (ΔE / ΔE5N) to determine the influence of various alloy components on the

color change. To do this, an equivalent of the possible relevant alloy element concentrations was formed and applied to the standardized color change. It was found during the evaluation of the patent research that the color change does not correlate with the respective copper concentration.

A roughly linear decrease of ΔE with increasing amount of addition in atom-‰ can be observed. Discoloration decreases with increasing amount of Au+Pt+Pd+In+Sn content.



a) *b)*

Figure 1: a) Comparison of the time-dependent color changes ∗E of the standard 5N alloy for four different patents; b) Color change progression normalized according to the maximum color change of the 5N alloy documented in the respective patents

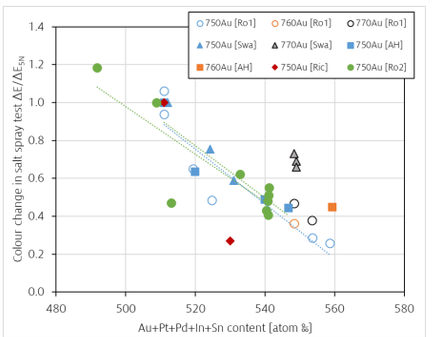
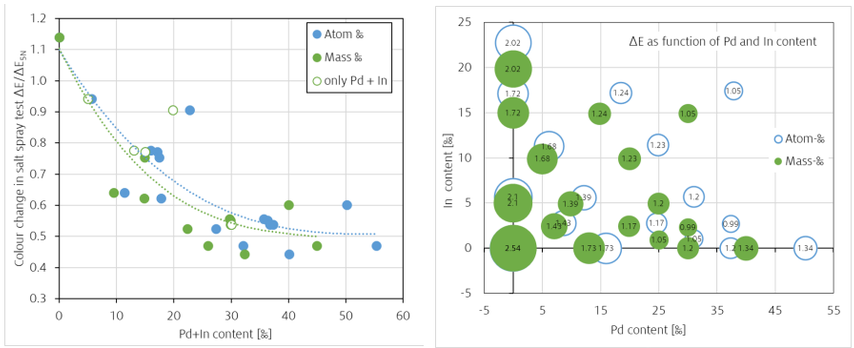


Figure 2: Color change in salt spray test of 5N alloys dependent on the Au+Pt+Pd+In+Sn content.

The effect of Pd and In on the color change of alloys with the composition 750Au (250-x)Cu xPd+In is shown in Figure 3. A

decrease of ΔE with increasing Pd+In content is shown (Figure 3 a). For Pd+In>20/25‰ ΔE becomes constant. To visualize the difference in the effect of Pd and In, ΔE was plotted as a function of both elements in the form of bubbles in Figure 3 b), with bubble size correlating with ΔE. Pd alone reduces clearly color change, whereas In alone shows only a very small effect. Pd combined with only small amounts of In (<5 mass‰) decreases ΔE even more. The highest reduction of ΔE is achieved for 20-30 mass‰ Pd and 1-3 mass‰ In.



a) *b)*

*Figure 3: a) Color change *E/*E5N in dependence of the combination of the Pt+In contents and b) *E in form of the bubble size for visualization of the effect in dependence of the In and Pd contents respectively.*

2.2 Corrosion tests

The development of the color change, according to equation 1, over the time is shown in Figure 4 (left column) and against the square root of time in the right column. Each testing series was conducted on two identical samples (open and full symbols). Figure 4 (upper left), shows the resulting color change after reaction with synthetic sweat, which is significantly higher for the 5N red gold (red line) alloys than that of the 2N yellow gold (yellow line). Thus, the 5N red gold discolor faster and stronger than the 2N yellow gold. The samples immersed in the solution (circles) reveal for both alloys a stronger discoloring compared to the samples in synthetic sweat vapor (triangle). With increasing testing time, the difference in color change for the both testing conditions becomes smaller. Initial discoloring is very fast and appears during the first 25 hours of testing. After that, the further color change slows down significantly and asymtotically approaches a certain value. The two identical samples show small scattering and a good repeatability

of the color change. The curves plotted against the square root of time in Figure 4 (upper right) show clearly the change in slope of the linear increases in ΔE around 25h, which corresponds to a decrease of the reaction rate.

Figure 4 in the bottom row shows the results of discoloring after exposure to air, which is much slower than in synthetic sweat. The color change after 1000 h of testing in air is comparable to the color change that occurs after 4h testing in synthetic sweat. The 2N alloy discolored faster in air than the 5N alloy. Plotting the data against the square root of time (Figure 4 bottom left), enhances a parabolic color change governed by a more or less constant rate, since no change in the slope of the linear increase can be observed.

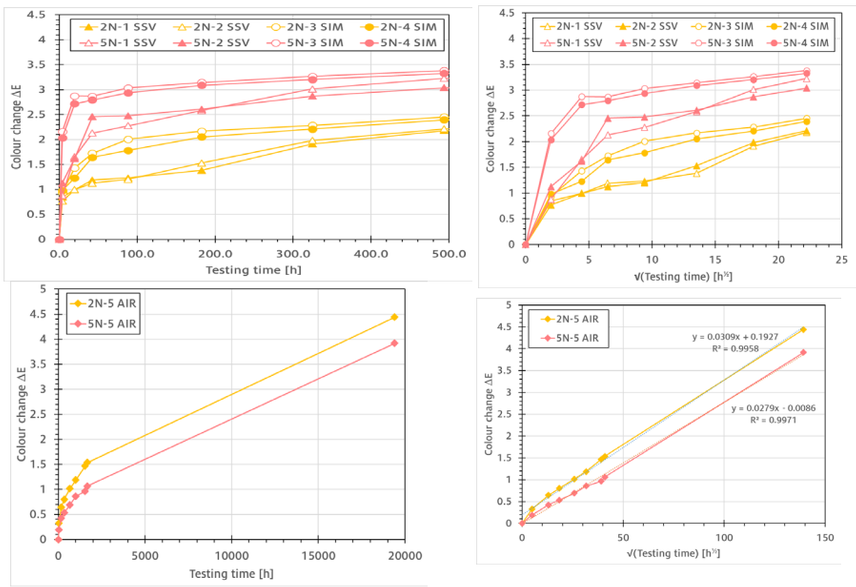


Figure 4: Color change as a function of time for samples in synthetic sweat (upper row) and samples in air (bottom row). The data are plotted against the time (left column) and the square root time (right column)

During the corrosion test the color changes mainly due to an increase of the b* value, especially in case of the 5N red gold. The 2N yellow gold shows also a slight increase of the a* value. The difference of the test in synthetic sweat vapor and of the immersed samples is quite small.

The development of the color parameters L*, a* and b* as a function of testing time is shown in Figure 5. The samples in synthetic sweat are plotted in the left column and the samples tested in air in the right column.

The L* value of the samples is about constant, except for the 2N yellow gold tested in synthetic sweat vapor (Figure 5 top left). These samples show a gradually decreasing L* value. The L* parameter (top left diagram) stays constant during testing for the 5N alloy in synthetic sweat, both in SSV and SIM conditions. Testing in air results in a very small decrease of the L* value. A similar behavior is observed for the 2N alloy. However, the 2N-SSV samples show a constant decrease of the L* value. The a* values of all alloys are nearly constant during testing for all testing conditions. A very small increase of a* is observed for the 2N alloys in SSV and SIM conditions. The 5N alloys show a very weak tendency of decreasing a* values. The most significant color changes are with the b* value. All testing conditions resulted in an increase of b*, which was strong in the beginning of testing. The increase of b* is very strong in the first 48 hours of testing especially for the 5N alloy in SIM conditions. For the 2N alloy both conditions, SIM and SSV, showed similar results. In synthetic sweat (SSV and SIM) b* approached a constant value after 300-500 hours of testing. The testing in air still shows an increase of b* after 1600 hours, but the overall changes are much smaller than in synthetic sweat. The results show that during the tests, the sample surface becomes more yellowish.

The 2N alloy darkens slightly when in contact with oxygen. The 5N alloy only shows this phenomenon when expsoed to air (SSV, air tests).

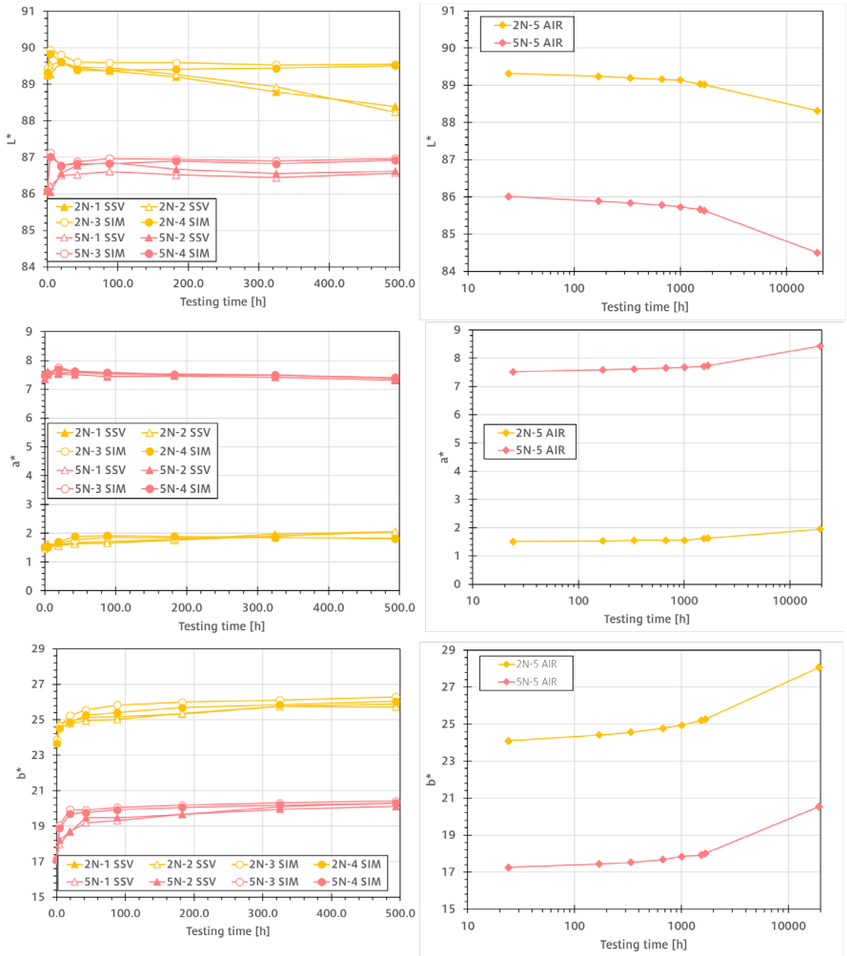


Figure 5: Development of the L (top row) a* (middle row) and b* value (bottom row) during the tarnishing test in synthetic sweat (left column) and in air (right column).*

DISCUSSION

The patent research carried out has shown how important it is to know the exact testing conditions of the corrosion tests. Without this information, it is not possible to make reliable comparisons of the color changes of different alloys. For this reason, the color change of two standard alloys (2N and 5N) was systematically examined under different test conditions in this study.
The discoloration behavior of a 2N and a 5N alloy in different

media was studied as a function of time. During the interrupted testing time, the color was documented by color measurement. Testing was done in three different media: air, synthetic sweat vapor and by immersion into synthetic sweat. Both alloys show faster discoloration for the artificial sweat test, than exposed to air. In general, independent on the media, the alloys show a strong color change within the first 25 hours of testing. At longer testing times the color change asymptotically approaches a stable value for the 2N and the 5N when tested in artificial sweat. The color change observed in every medium, is ruled by a diffusion controlled process, showing parabolic behavior, since ΔE increases linearly against the square root of time √t, as it is defined by the second Fick's law.[18] Immersion and wetting with artificial sweat shows a slowdown, whereas exposure to air shows a constant reaction rate over the test period.

As mentioned at the beginning the relative amount of Ag and Cu play a role in the corrosion mechanism. Our study shows a more pronounced discoloring, when immersed in artificial sweat, for the 5N alloy in which the Ag to Cu ratio is due to the high Cu content, 8 times lower than for 2N. Due to the high Cu content, it is assumed that the discoloring mechanism is not based on the formation of AgS, but rather on a process in which Cu plays the main role. The observed parabolic reaction rate process is not in accordance to the linear growth of sulfides found for 14K Au alloys,[10] but it is in accordance to a diffusion controlled process, as the Cu release is and which was found to occure for Au based jewelry alloys.[14,19] As a consequence of the release, Cu depletes on the sample´s surface, resulting in a more yellowish color, and measured by the increase of b*. The reaction slowdown, when tested in artificial sweat, is suggested to occur due to the progressive Cu depletion at the surface. Based on these obervations the discoloration mechanism of the 5N and 2N alloy immersed in artificial sweat, is assumed to be based on the Cu release out of the samples surface instead of tarnishing (oxidation). Comparing the methods amongst each other, faster and stronger discoloring could be observed for all samples that were immersed in the synthetic sweat solution (SIM tests) than the samples that were exposed to synthetic sweat vapor (SSV) or air, which is even slower. A more pronounced effect of oxygen on the discoloration rate is observed for the 2N alloy, which discolored faster on air than the 5N alloy, and which shows slight darkening when vaporized with artificial sweat (SSV), in contrast to immersion (SIM). Darkening is known as a consequence of sulfide formation which manifest themselves as a reaction layer.[10,11] In general, in the SSV test the samples tend to form stains that make it more

difficult to evaluate the color change. However, these results suggest that 2N, which contains 8 times more Ag than Cu, tends to react with the environmental air, as it is describes by equation (2). Since oxygen or heat is needed for the reaction, the 2N alloy, which contains more Ag, tarnishes in air and vapor, whereas the immersion in artificial sweat is assumed to effect only Cu release followed by discoloration.

It is also worth noting that wearing a piece of jewelry in real life involves additional abrasive wear. This can result in the mechanical removal of the surface discoloration so that it is not particularly noticeable when worn. However, the corrosive attack during wearing is uneven, e.g. through local skin contact, composition of the sweat, general humidity, temperature etc.. Fromthere, an uneven discoloring results, which is even more troublesome.

CONCLUSION

The aim of the study was to describe the influence of various corrosion tests on color change of two gold alloys. For this reason, the same tests were carried out simultaneously on well-known standard alloys and the color change determined was documented. The necessity for this examination arose from the patent search that was carried out. The search showed that under nominally identical conditions, different color changes can be expected of the same alloy.

Based on these findings, depending on the different chemical exposure due to the various tested media, it is possible to build on the influence of certain alloying elements to improve color resistance.

In this work on two 18K alloys, the discoloring and tarnishing behavior is shown to be led by a diffusion controlled process and is more pronounced for the 5N alloy in the artificial sweat test. Since immersion shows stronger discoloring than exposure to air, the discoloring mechanism is determined by element release. However, discoloring is supported by the presence of oxygen for the 2N alloy and tarnishing is suggest to occur. Although the corrosion mechanism was not investigated in detail here, these findings confirm the negative role of increasing Ag/Cu ratio. The discoloring is controlled by an increase of the b* value, resulting in a yellowish surface.

The results show that both alloys exhibit significant color changes over time. This pronounced color shift, even under mild

conditions, underscores the need for a deeper understanding of the discoloration mechanism of multicomponent gold alloys, based on Au-Ag-Cu. To investigate the individual factors that play a role in the decolorisation process, as e.g the ordering transformation or passivation effects, further tests are needed. Therefore, investigations on a range of alloys in which the chemical composition varies systematically, and which were tested in different media, should be conducted in order to gain a scientific understanding of the different discoloring processes. Further, in-depth studies on the surface as Auger spectroscopy or XPS analys should be carried out to make the reaction layer visible.

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