New Trends in Decorative Coatings

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Decorative coatings applied with sputter ion plating processes have become a widely accepted application for vacuum technology. Although the deposition itself is only one important step among others, industrial decorative applications require a reproducible and productive coating system. Leybold, as a system manufacturer, is featuring machines with a high level of up-time as well as an extraordinary sales service. In addition, such equipment is able to control all manufacturing steps including the choice of substrate material, the proper machining of it, the advisable heat treatment, the correct surface machining, the appropriate electroplating and the right precleaning. All these factors have an important influence, since a successful product does not depend solely on film properties. All system features required in the performance portfolio need to be fulfilled. In some circumstances, features required for a satisfactory coating can only be determined in extensive field tests.

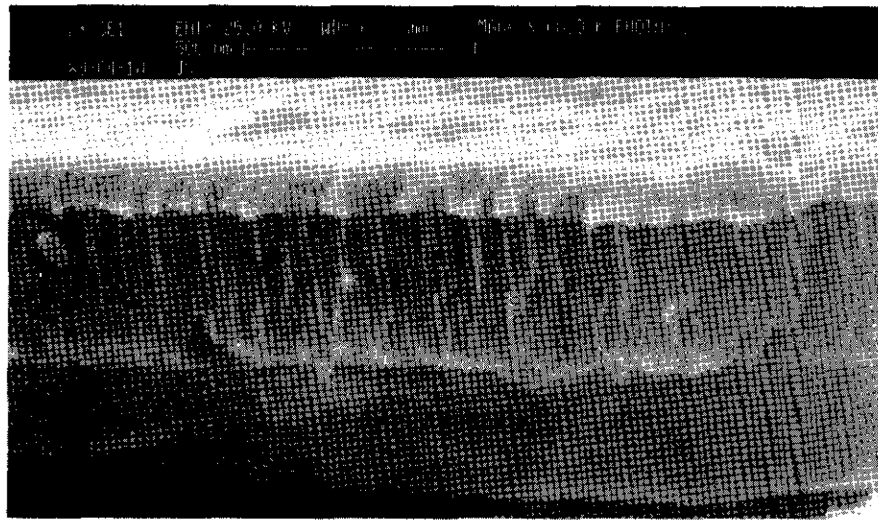

Fig. 1. Scanning electron photomicrograph of a 0.3-µm titanium nitride and 0.1-µm gold-alloy film.

APPLICATIONS FOR DECORATIVE COATINGS

Systems developed for decorative coatings are used in several different applications, including the manufacture of watch parts, eye glass frames and pen parts. Research and development has allowed a broadening of the scope of products on which hard decorative coatings may be applied.

Each type of application is developing more and more special requirements. Decorative coatings can therefore be divided by trends in applications in these fields.

DECORATIVE COATINGS FOR WATCH BANDS AND CASES

After having introduced hard gold-colored films into industrial applications as wear-resistant coatings for tools (especially high-speed steel twist drills), the potential of these materials for use in decoration was also realized. One of the first applications for decorative coatings developed in Japan in the late '70s was in the field of watch parts. For these substrates, gold-colored films are very important. Nowadays, the combination of a hard titanium nitride underlayer with a gold or gold alloy topcoat is the industrial standard (Fig. 1).

A soft metallic film deposited on top of a hard material is assumed to wear relatively quickly; however, most of the surface area remains covered when the first hard tips of the titanium nitride undercoat reach the surface after abrasive wear (Fig. 2); these tips will prevent the soft film from further wear.[1]

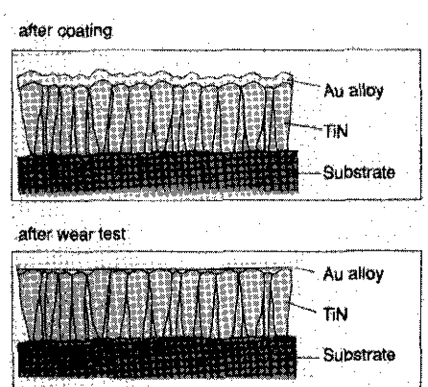

Fig. 2. The gold top layer remains over most of the surface area of the substrate due to the jagged nature of the titanium-nitride undercoating.

Industrial coating systems are available for the deposition of decorative hard coatings using the sputter ion plating process. This process could be performed either in batch-type or in-line type vacuum deposition systems. Figure 3 illustrates the principle of a batch-type system where all process steps are performed with one vacuum chamber. During deposition the sub-

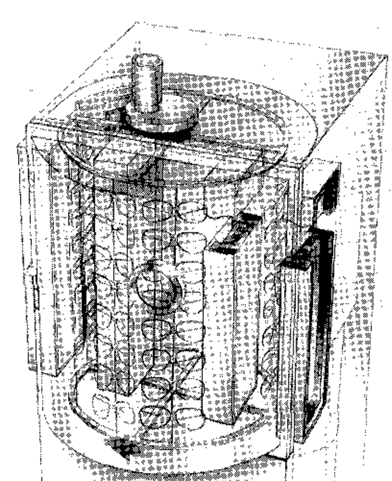

Fig. 3. Schematic of batch-type decorative coating system.

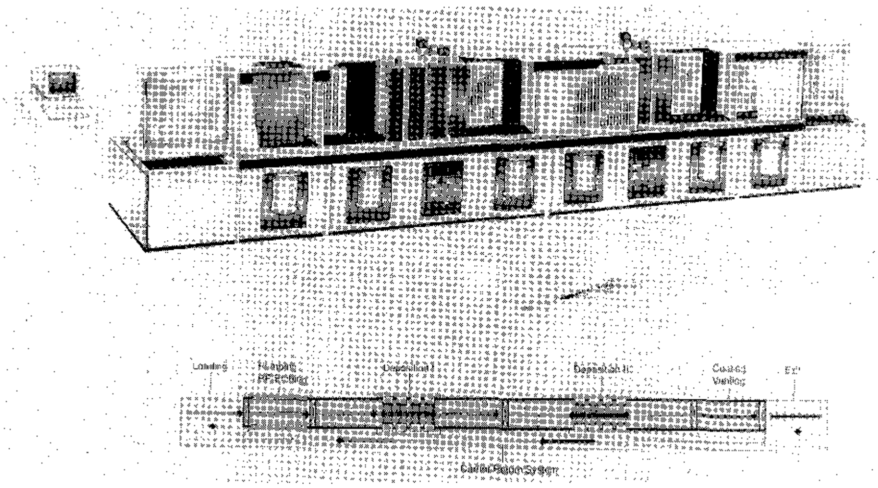

Fig. 4. Schematic of an in-line decorative coating system.

strates to be coated will rotate in a way so that the parts will pass between the two double cathodes, one on the left and one on the right.

The in-line coating system is comprised of four different vacuum chambers used for various deposition process steps. The schematic of the system in Fig. 4 explains the function of the machine. After leaving the loading station, the substrate carrier will be pumped down to the required vacuum level and an rf etching process will be performed. In the first deposition chamber equipped with four double cathodes, the carriers will pass in continuous substrate flow mode (i.e., when the first carrier is in the middle of the cathode arrangement, the second carrier will close up. When the second carrier has reached the same position as the first, the first carrier will leave the first deposition station and move into the second deposition station while the third carrier is closing up. In other words, the cathodes in the first deposition station are operated throughout the production process without interruption. Whereas in the first deposition station only the hard coat is deposited, the rest of the hard coat and the top coat of gold film will be applied in the second deposition station by making use of the oscillating motion of the carrier.

The productivity of these coating systems depends on the type and size of the machine used. Assuming current European economic conditions, coating costs per piece will decline with an increase in productivity. A typical (0.5 µm TiN + 0.1 µm gold alloy) film can be deposited for the same production costs required for deposition of 1.5 to 2 µm of electroplated 18-carat gold.

For watch parts, a titanium nitride and gold alloy coating is, among others [e.g., TiAlC,N (dark blue)], the most important layer system showing extremely good wear resistance compared with electroplated gold. Applying the Taber abrasion test, the volume loss per 1000 rounds per minute for films applied with physical vapor deposition (PVD) is at least one order of magnitude better than volume loss for electroplated coatings (Fig. 5); therefore, a typical film (0.5 µm titanium nitride + 0.1 µm gold alloy) will have at least the same wear resistance as a 5-µm electroplated gold coating.

According to the estimations of the federation of the Swiss watch industry the world production of watches and movements has risen almost by a factor of two within the last ten years. In 1991 the number of units reached a total of 828 million pieces indicating an increase of 6.8% compared with 1990 figures. Although Switzerland is leading the race by value, the largest number of units is produced in Japan covering 46.6% of the market. Despite this fact, there has been a shift of production sites out of Japan to countries offering lower wage levels. Another market trend indicates that moderately-priced watches will disappear.

Existing coating system technology allows reproducible and economical production although there is a need to lower the coating cost per piece. This will also broaden the application of the technology and, hence, lead to further manufacturing cost reduction.

The first goal of process technology when applying decorative hard coatings is to achieve a reproducible gold color according to the Swiss standards for color tones.[2] Although the standards may be used to specify the required composition for any gold color to be deposited, it is important to follow certain fundamental guidelines for standardizing voluminous color definition by using a sputtering target with the correct chemical composition.

First, the color of the sputtered coatings will differ from the color of the bulk material, even if they have the

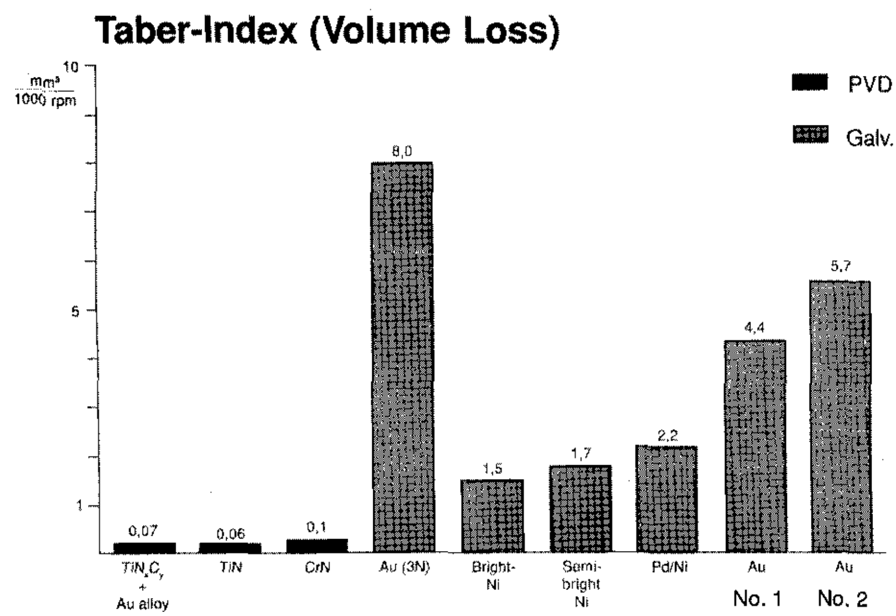

Fig. 5. Taber index (volume loss) for PVD and electroplated coatings.

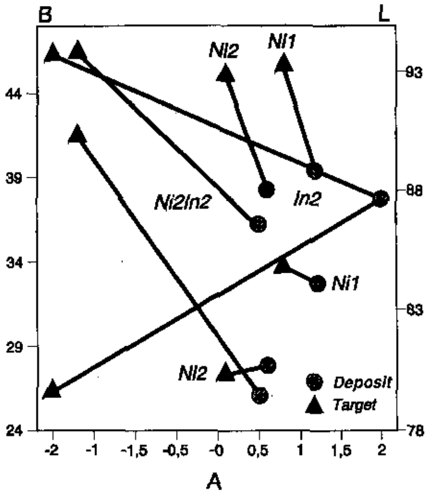

Fig. 6. Change in color coordinates between bulk value and color of sputter-deposited coating for several chemical compositions of target material. L=brilliance, B=yellowness. A=color content.

same chemical composition. A reduction in the brilliance as well in yellowness can be seen in Fig. 6. The color will also depend on the film thickness and the substrate temperature. Figure 7 proves the fact that a minimum thickness of approximately 100 nm is necessary in order to have a color independent of coating thickness. The substrate temperature during deposition should not exceed 280°C in order to avoid a dramatic increase in the delta value (Fig. 8).

A second trend in process technology for watch applications is in the needs for hardness- and color-variable gold targets. Job coaters need to supply a range of slightly different colors for their clients. In addition, a harder gold-alloy film is desirable to partially replace thick gold electroplating, which can be achieved by altering the coating color by introducing reactive sputtering of gold alloys. Using gold-vanadium, 1N14 and 2N18 color tones are achievable with film hardness values in the range of HV 400 (Fig. 9).

DECORATIVE COATINGS FOR EYEGLASS FRAMES

Hard, decorative coatings on eyeglass frames were developed in Japan on early versions of PVD systems. After the introduction of the coated products into the market, the need for a bigger batch-type system was soon recognized. The coating processes required for eyeglass frames are much the same as processes used for watch parts, although a more brownish color tone is applied.

In addition, eyeglass frames have undergone a transition from a medical corrective device to a fashionable accessory, which resulted in a tremendous increase in annual production. This trend seems to be on its way out since the market, at least in the Far East, is already saturated. Alternatively, eyeglass frames are becoming a medical product, at least in Europe, which has strict health restrictions for materials used for the frames.

Due to the nickel allergy problem, manufacturers must mark all products containing free nickel at their surfaces

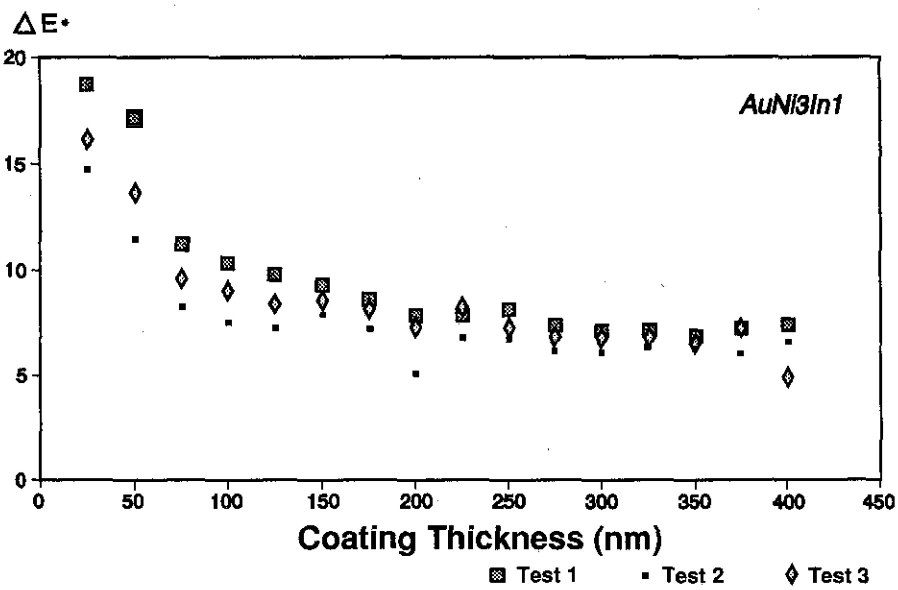

Fig. 7. Variation of coating color with respect to film thickness measured in delta E units.*

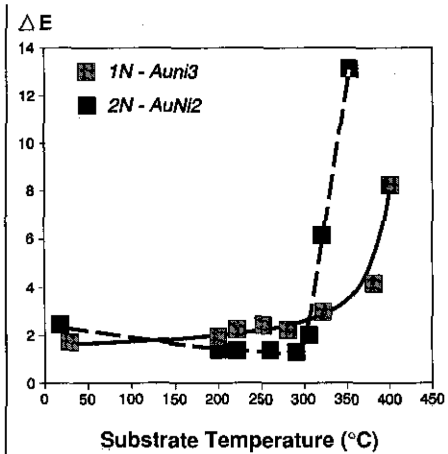

Fig. 8. Variation of coating color with respect to deposition temperature measured in delta E units.*

in some European nations. For example in Denmark, a certain test method is widely used to prove a surface is nickel free. This test can be passed if a 0.5-μm TiAlCN film is sputtered onto a nickel-electroplated coating, whereas a sputter-deposited gold alloy on the same nickel will fail the test.

A field test was organized in which participants wore gold-plated eyeglass chains. Under medical supervision, a number of people having nickel allergy symptoms participated in the experiment. The chains were composed of a copper-based alloy substrate coated with either a nickel, or a nickel and subsequent palladium-nickel electroplate on which the PVD layer system (titanium nitride plus gold alloy) was deposited.

Seven people wore chains with only nickel electroplating, and seven others wore chains with nickel and palladium-nickel coatings. The results of this first test are surprising. Only one person in the group wearing the nickel-plated chains showed an allergic reaction after 14 days. There were two people after a shorter period of time (3 and 4 days, respectively) complaining of irritation in the group who wore chains coated with the nickel/palladium-nickel. It should be noted, however, that the results might have been affected by the quality of the manufacturing process.

The process technology available for eyeglass frames has so far not been able to fulfill all requirements of the application, especially when specific color tones are requested in the market. A pink color is currently being developed, although a variety of materials

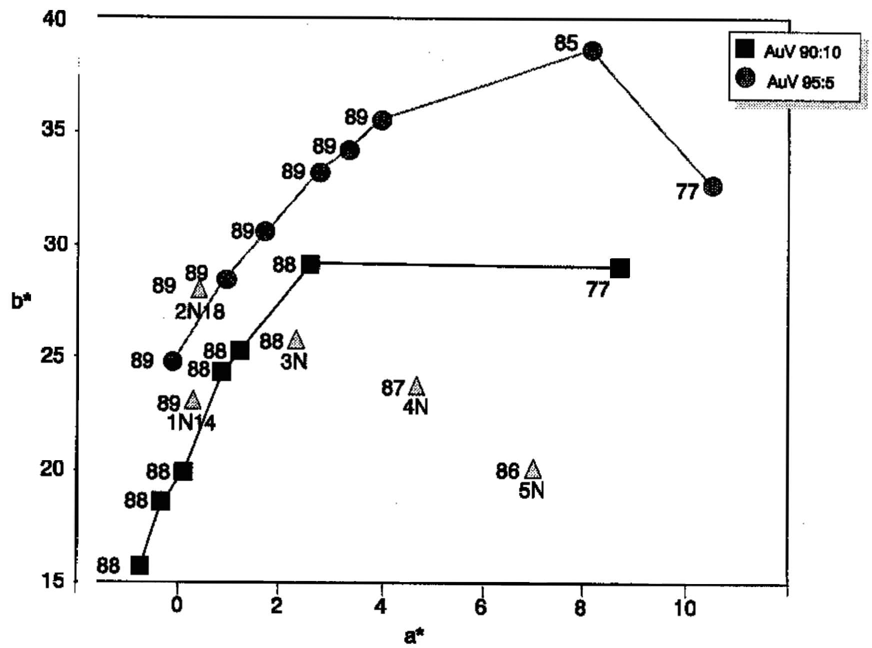

Fig. 9. Variation of color coordinates for different target compositions with respect to N_2-flow.

have been tested unsuccessfully.

Using a titanium-vanadium alloy, it was possible to increase the brilliance to a certain amount, but neither the brilliance nor the redness was sufficient. Even with a pure vanadium target, the color goal was not achievable with any of the tested reactive deposition atmospheres. More details regarding the development of new color tones have been published elsewhere.[3]

DECORATIVE COATINGS FOR PEN PARTS

Decorative coatings on pen parts were one of the early applications of PVD technology. Due to the fact that pen parts usually are small and show large geometric variations, batch-type coating systems seem more useful than in-line machines. On the other hand, pen parts require a low manufacturing cost; therefore, a bigger batch-type machine seems to meet all requirements best.

Directly applying hard coatings on pen barrels is not suitable, since these films are, from an electrochemical point of view, very noble. They could adequately protect the base substrate materials such as brass if they were completely dense; but thin films usually exhibit micropores or are not able to close the coating over obstacles like dust particles. In Fig. 10, the effect of corrosion on films deposited directly onto brass are compared with barrels that have been protected by an electroplated interlayer.[4]

This combination of traditional electroplating and high-tech PVD sputter ion plating allows an industrial solution to the above-mentioned corrosion problem. The best results with respect to corrosion protection have been found employing the layer system as given in Fig. 11. To make use of the electrochemical properties and the dense, pinhole-free structure of the palladium-nickel layer, a coating of 1–3 µm is recommended over the 5–7-µm thick nickel electroplating, which is also used to eliminate surface roughness to some extent.

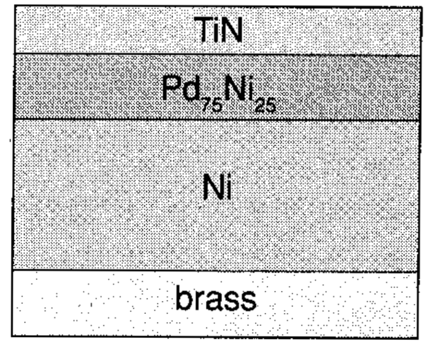

Fig. 11. Layer system for corrosion protection before PVD coating over brass.

Combining electroplating and PVD is not the only possible solution. In the eyes of a coating system manufacturer, a better way is to substitute the substrate material, i.e., using stainless steel or titanium instead of copper-based alloys or low-alloyed steels. To make use of one of the big advantages of the sputter-ion plating technology—its inherent cleanliness with respect to environmental pollution—it is necessary to develop a barrier layer, which may be deposited in vacuum systems.

Such a PVD-barrier layer would provide protection for non–corrosion-resistant substrates in the same way as an electroplated layer would. Although much time and effort has been invested

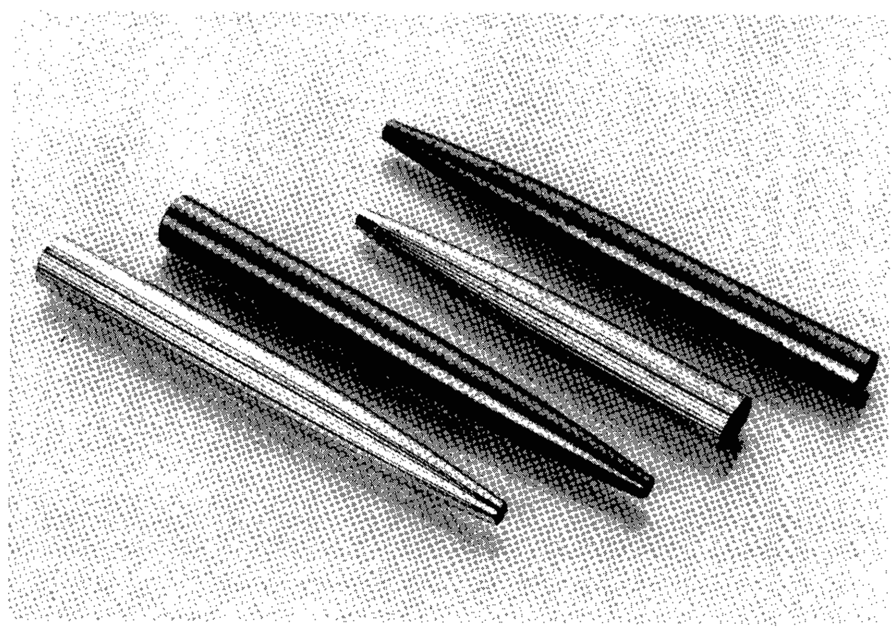

Fig. 10. Effect of corrosion on hard-coated pen barrels made of brass.

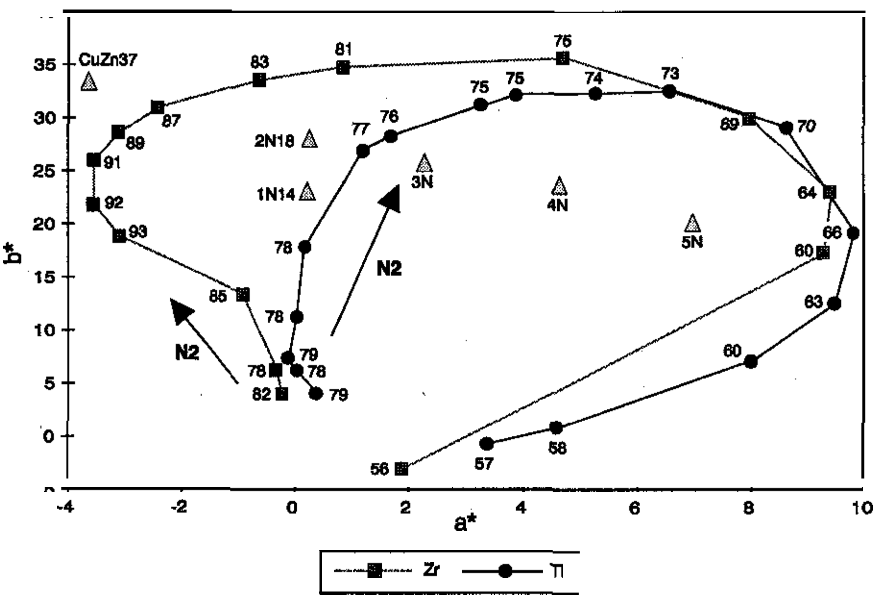

Fig. 12. Comparison of color coordinates of titanium nitride and zirconium nitride with gold and brass standard tones.

in developing such a coating, it is not yet available.

In addition to the aforementioned titanium nitride and gold-alloy layer systems, which are also used for pen parts, there are some significant specialization techniques available.

One color, the so-called "gunmetal" color, is achieved by depositing a certain understoichiometric titanium carbide. Another specialty tone is a bluish gray achieved by depositing TiAlCN.

DECORATIVE COATINGS FOR DOORKNOBS AND FIXTURES

A variety of ordinary parts feature a brass-colored surface. Requirements for corrosion- and wear-protection, especially in outdoor applications, are very stringent. One of the biggest problems is a freshly prepared brass surface that tarnishes quickly unless protected, usually by a clear coat. Sputter ion plating offers the opportunity to apply a wear-resistant coating with a metallic appearance of the same color.

This technology has entered the market in the manufacture of doorknobs and fixtures. The color of titanium nitride and zirconium nitride coatings was compared with respect to color tone standards to see how close the hard coatings' color tone could be matched to brass. Figure 12 shows the brass color as well as the available color tones for titanium nitride and zirconium nitride, each with respect to reactive gas flow.

The introduction of this new surface-finishing method points to a partial replacement of electroplating processes. In addition, the design of doorknobs and other fixtures as well as sanitary fittings will determine the success of sales.

The number and variety of brass-look parts being produced in different industries means that in-line coating systems capable of fulfilling productivity requirements are a necessity.

The ability to coat bigger parts is an objective necessary in order to gain access to other market segments. One of the main differences in this type of equipment will be that the double cathode arrangement will have to be abandoned (i.e., the parts will have to be rotated during the deposition process). Figure 13 shows what the design of this machine will look like. In order to fully cover the parts with plasma, the new PVD machines will implement the so-called ZPT (German abbreviation for interpole target magnetron) cathodes. The first system of this type is already under construction and will be used for research and development and sample coating. The new machines feature a magnetron-type sputtering cathode to improve the target utilization as well as the deposition rate. The idea is to enlarge the width of the target sputtering grove to a more parallel magnetic field and to confine the electrostatic plasma.

In contrast to the conventional magnetron, the surface of the ZPT cathode consists only of the erosion zone; therefore, although the deposition rates per unit of power are almost the same (for Cu, standard high rate cathode 8 A/s per W/cm^2; for ZPT, 9.8 A/s per

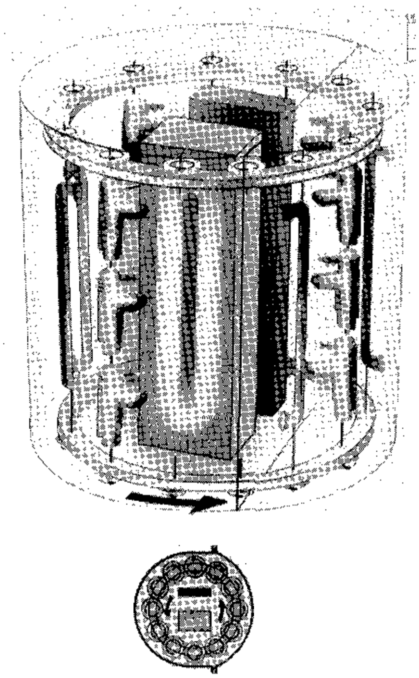

Fig. 13. Schematic drawing of a batch-type coating system for larger parts.

Table I. Colors Available for Interpole Target Magnetron Coating.

Coatings	Colors
CrN_x	metallic gray
TiN_x	light yellow-gold color–brownish yellow
TiC_xN_y	gold color–reddish brown (adjustable to any gold color tone)
$TiZrN_x$	gold colors
Au alloys	gold colors on identically colored TiN_xC_y coatings
Decocoat 031-03 (based on TiAl)	brownish-yellow–violet gray-bluish gray
Decocoat 036-038 (based on TiAl)	reddish brown–copper colored
TiC_x	light gray–dark gray
i:C	black

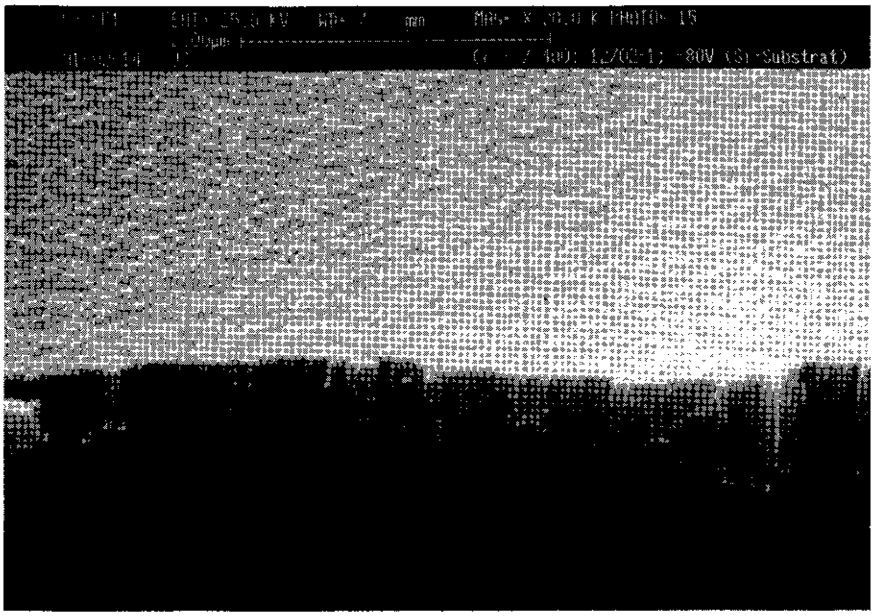

Fig. 14. Typical coating morphology of chromium nitride as seen in the scanning electron microscope.

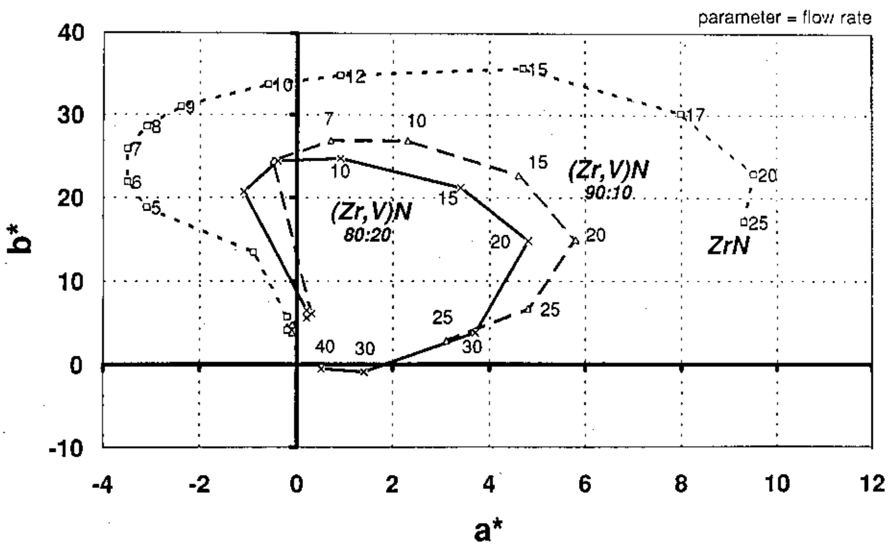

Fig. 15. A and B* values for zirconium nitride and (Zr,V)N with respect to nitrogen flow.*

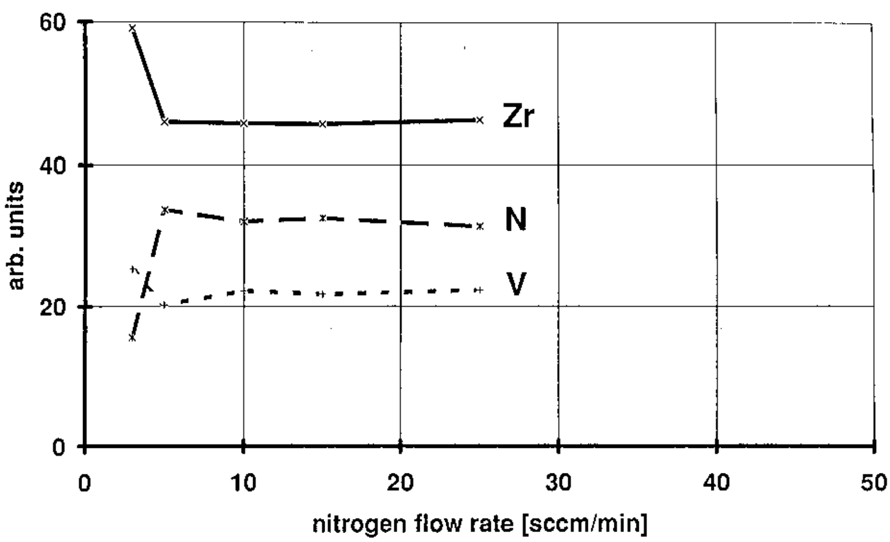

Fig. 16. Chemical composition of (Zr,V)N with respect to nitrogen flow.

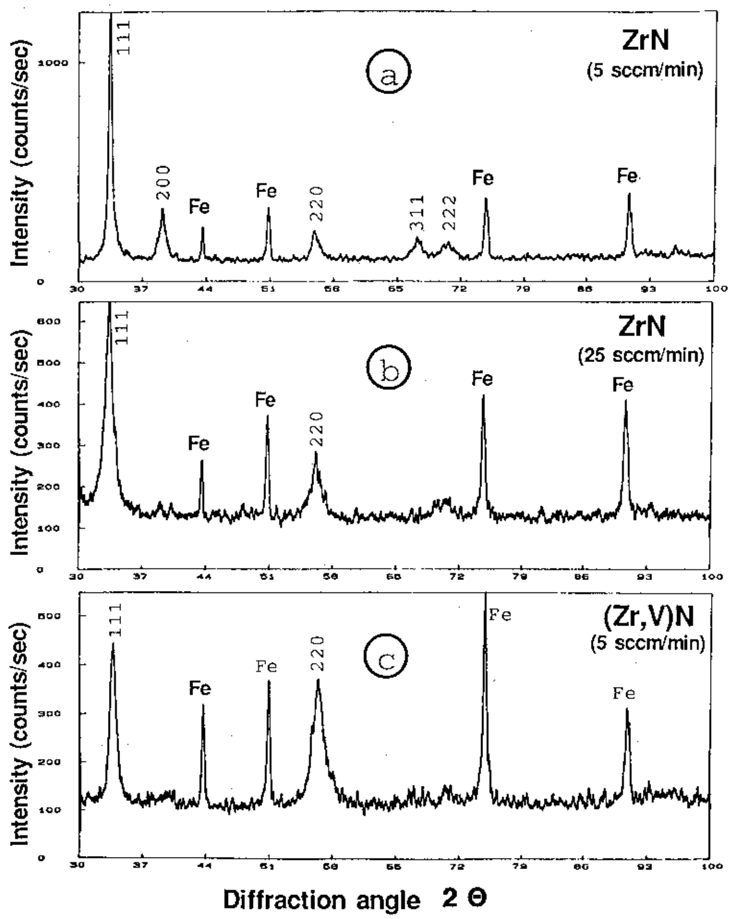

Fig. 17. Texture of zirconium nitride (Zr,V)N coatings.

W/cm^2), the use of the ZPT cathode results in power densities of up to 210 W/cm^2. Since the whole target surface is used, almost no target poisoning is visible. The target efficiency for a ZPT cathode is 55–65% in contrast to 20–30% in the case of the conventional magnetron.

So far, the coating of bigger parts has been restricted only to zirconium nitride. On the other hand, a variety of different coating materials as listed in Table I is available. Certainly, the most important among them for this group of parts will be chromium nitride. A typical coating of this type is shown in the SEM pictures in Fig. 14. The addition of nitrogen to pure chromium leads to a color variation as well as to a higher film hardness.

Reiners et al.[3] have investigated the film texture and chemical composition of zirconium nitride and (Zr,V)N coatings of different colors. Figure 15 denotes the a* and b* values and the N_2 values as parameters. It is clear from Fig. 16 that there is almost no variation in the chemical composition of (Zr,V)N when a certain lowest-reactive gas flow has been overcome. On the other hand, in the case of ZrN, a difference in the X-ray spectra for 5 sccm/min and 25 sccm/min N_2-flow could be detected (cf Fig. 17). This difference in coating texture may be attributed to the color change already recognized. Further studies on this are underway.

DECORATIVE COATINGS FOR STEEL SHEETS

The coating of stainless steel sheets with decorative hard wear resistant films has been developed only recently. In principle, all available color tones that have already been established for other applications may be used for coating stainless steel sheets as well. The size of the machine necessary for these coating processes will be determined by the size of the steel sheets to be coated. The first pilot production system is able to coat steel sheets as large as 1.25×4 m^2.

Coated steel panels are used for walls and ceilings, front sashes, column covers, or partition panels in building materials applications, and for elevators, doors, frames, or interior wall panels. Other applications are side panels of escalators, entrance doors of homes, or interior system kitchen doors. These flat sheets may be combined with three-dimensional parts coated in the same color.

DECORATIVE COATINGS FOR JOB COATERS

All standard decorative coating systems have already been used by job coating shops who use a variety of different deposition processes, among which are processes developed by job coaters themselves. Since the business of such a company is usually specialized for one of the applicational fields, some job coaters are also willing to offer research and development contracts to customers to develop new deposition opportunities.

OUTLOOK FOR DECORATIVE COATINGS

The variety of different applications for decorative coatings examined here cannot overcome every mistake or oversight in surface preparation; only a thorough knowledge of the application can prevent such errors. In addition, preferences of watch and eyeglass frame manufacturers for specialized colors are such that each industry will require its own set of specialized colors, which Leybold anticipates it will be able to supply. **MF**

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