# Industrial Applications of Decorative Coatings - Principles and Advantages of the Sputter Ion Plating Process

U. Kopacz and S. Schulz, Leybold AG, Germany

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## ABSTRACT

For decorative applications coloration is the most decisive factor in surface finishing technology. For example, high valued colored surfaces may be produced using physical vapor deposition processes. Among these sputter ion plating turns out to be most suitable for decorative purposes because stable colors over large areas can be achieved in a reproducible way. In this lecture the principles of the process will be presented and the state of the art with respect to current industrial applications will be outlined. Finally, possible future applications will be addressed.

## 1. INTRODUCTION

Decorative coating of (metallic) surfaces is of major economic importance. It is difficult to give any figures on added values, since decorative surface treatments are used in many different, loosely related or unrelated, fields, and are invariably just one stage among many in overall manufacturing processes. A careful look around should be enough to allow the reader to determine how many of the objects in his immediate vicinity have been given surface decorative treatments. Even if we restrict ourselves to metallic surfaces, as we shall in this article, the number of applications is still large. Most metallic surfaces are treated with paints, lacquers, powder coatings, or electrochemically plated, with corrosion protection often being one of the intended or essential objectives.

Physical vacuum coating processes have also recently become important in several application areas. The significance of these processing methods, jointly designated by the acronym PVD (for physical vapor deposition), can be surmised from the fact that there are already about 100 systems used for decorative coating with hard materials installed worldwide (more than half of them in Japan) and generating an estimated DM 150 million/$ 90 million (in terms of the added values of the coatings themselves) in total annual sales, with annual growth currently at approximately 20 %.

Let us take wristwatches as an example: until about 20 years ago, product function was a major factor in product definition and design; today it is simply taken for granted (Fig. 1).

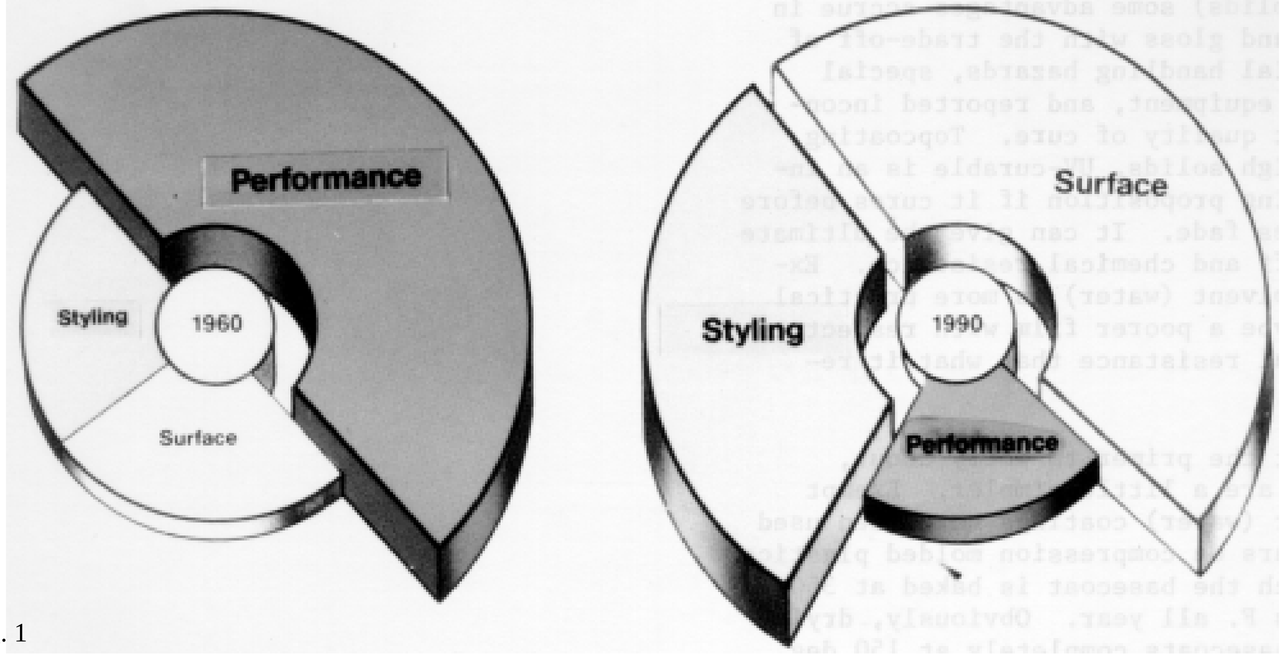


Fig. 1

Means for creating the product differentiations that can determine success or failure in saturated markets thus have come to rest squarely in the area of product “design,” taken as encompassing both styling and choices of surface finish (Fig. 2).

In other words, ion plating can be based on either evaporation or sputtering; of course, both of these processes can be employed without or without use of ion plating [6-9].

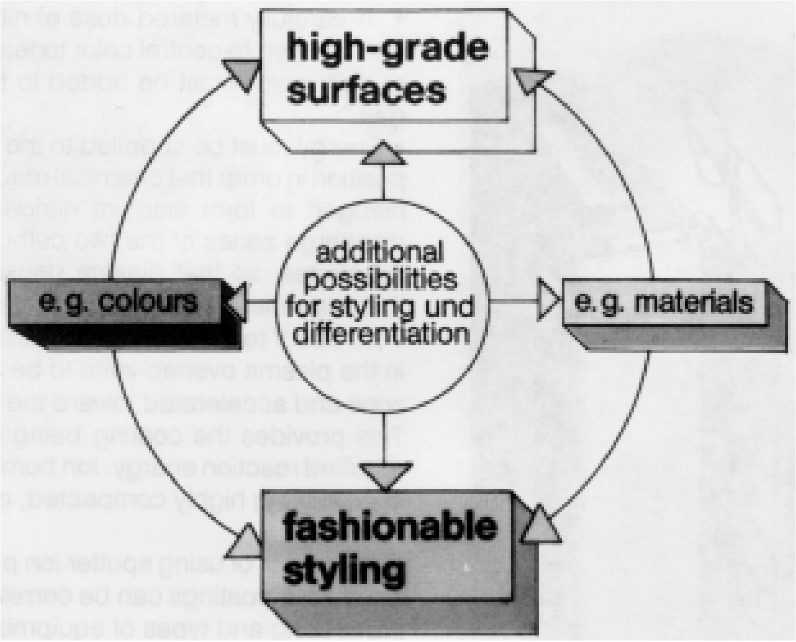


Fig. 2

(The choice of materials used should also be included among the means for creating product differentiations; for example, the use of titanium in consumer products is one path to product differentiation. This development is most easily recognized in semi-luxury consumer products (wristwatches, eyeglass frames, fashion accessories, etc.), but can also be detected in other consumer markets, the automotive market being one example.

## 2. PROCESSING TECHNOLOGY

PVD processing encompasses a number of processing technologies [1-4]. These may be categorized by the methods employed to transfer the material to be deposited from the solid state into the gas phase:

- evaporative processes, or
- sputtering processes.

The term ion plating is used to designate processing methods in which conditions that lead to their surfaces being bombarded by energetic ions during film deposition are created in the vicinity of substrates (the items to be coated), regardless of how the material to be deposited enters the gas phase [5].

We will restrict ourselves to a treatment of sputter ion plating, since this processing method has proven to be particularly effective, affords a high degree of flexibility in the deposition of decorative hard coatings, and also has the greatest potential for further development. However, it should not be forgotten that there are other processing methods that can be used in decorative coating applications. A critical review of all such methods appears in the the article by Matthews [10].
The term sputter ion plating [11, 12] indicates that this method involves processes in which

- all, or some portion of, the materials to be deposited enter the gas phase by means of sputtering processes, and that
- condensation of the materials to be deposited on substrates takes place under constant ion bombardment.

The use of the dual-cathode configuration permits uniform allover coating of (smaller) shaped articles, while providing control over ion bombardment during film deposition [13, 14]. In this approach, two magnetron- cathodes are installed in the vacuum chamber facing one another, separated by a distance of about 10 cm to 15 cm, with the substrates to be coated situated between them (Fig. 3.).

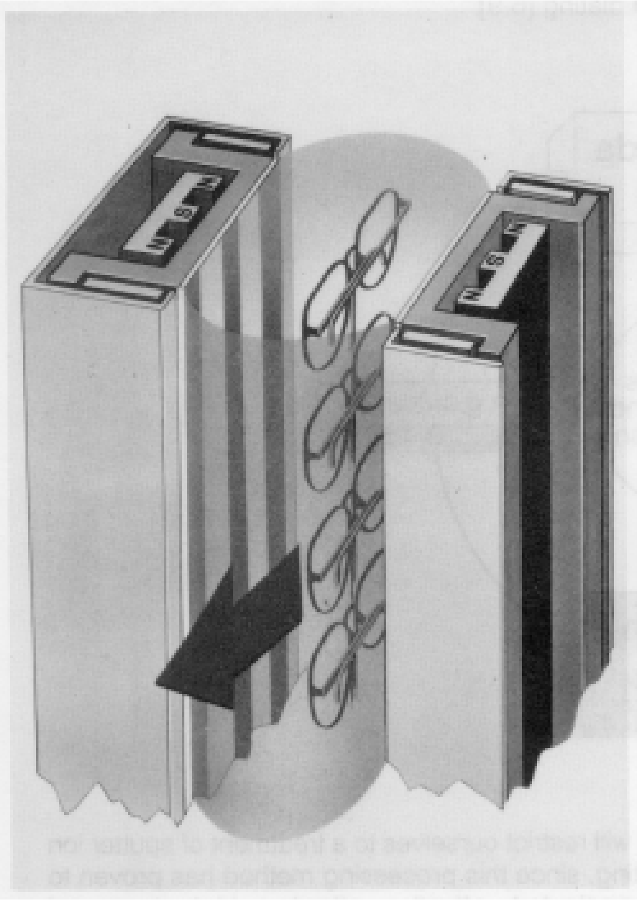


Fig. 3

To deposit, e.g., gold-tone titanium nitride (TiN), a titanium plate several mm thick is bolted onto the cathodes. After evacuation, an inert gas (e.g., argon) to serve as the "working gas" is admitted until a pressure of several times $10^{-3}$ mbar has been reached. A voltage of about-500 V is applied to the cathodes, and a gas discharge is struck in front of the cathodes, resulting in the formation of a "plasma," visible due to its emission of optical radiation. This plasma contains negatively and positively charged current carriers (electrons and ions) in equal numbers.

The positively charged ions are accelerated toward the negatively charged cathodes, and mechanically impact the titanium plates to dislodge (mostly electrically neutral) titanium atoms from them. These titanium atoms then impact nearby objects, condensing out on them. The substrates are moved through the coating zone (i.e., the area between the cathodes) either once only at low speed, or several times at higher speeds. We have thus far considered only purely metallic processes. These methods permit deposition of films of chromium, gold alloys, or of titanium, as in this example. To coat substrates with TiN using "reactive processes," two further conditions must be met:

· A carefully metered dose of nitrogen (the dosage can be used to control color tones, i.e., to obtain light or dark gold) must be added to the argon "working gas."
· Energy must be supplied to the coating during deposition in order that chemical reaction of titanium and nitrogen to form titanium nitride take place. The discharge zones of the two cathodes overlap at the substrates, so that plasma density is greater there than elsewhere (Fig. 3). Applying a bias voltage of-50 V to - 200 V to the substrates causes some of the ions in the plasma overlap zone to be attracted out of the zone and accelerated toward the substrates [13,14]. This provides the coating being deposited with the required reaction energy. Ion bombardment also aids in producing highly compacted, dense, coatings.

The benefits of using sputter ion plating in depositing decorative coatings can be correlated to the types of processing and types of equipment used:

· Use of planar sources (sputtering cathodes) provides uniform (particularly in their colors) coatings without substrates having to be put through complex motions. Substrate mountings can thus be kept quite simple.
· Unlike evaporation rates, sputtering rates remain constant for constant processing conditions, allowing keeping compositions (stoichiometry) of coatings, which strongly affects their final color tones, within narrow tolerances. However, coating stoichiometry can also be deliberately altered in order to obtain various color tones from the same basic type of coating.
· In addition to metals, such as titanium and chromium, alloys, and even "exotic" compounds, such as TiN or TiZrAl, can also be sputtered. A wide range of materials can be deposited using various reactive gases. The, at least in principle, virtually unlimited range of materials that can be deposited translates into a wide choice of colors for use in decorative coating applications.
· Two or more cathode pairs can be installed, depending upon the size of the system used, in order to
- increase effective coating rates,
- be able to simply
deposit multilayer coatings (e.g., TiN covered with a final "flash" of gold alloy),
- deposit "sandwich"
coating stacks, or to

- enhance flexibility in
coating operations (different coating materials can be employed).

· Sputtering methods allow engineering highly productive in-line coating systems, which, in turn, allow achieving very low unit costs.

In view of these significant benefits in processing, it is only fit that sputter ion plating has meanwhile taken over the position of the leading method for depositing decorative hard coatings.

## 3. PROPERTIES OF DECORATIVE HARD COATINGS

The major demands placed on decorative coatings are:

· control of final colors (reproducible, uniform, color tones),
· resistance to wear,
· resistance to corrosion, and
· cost-effectiveness.

Note that only visual appearance (color tones) is solely governed by the coating processes employed. Resistances to wear and corrosion are partly determined by the substrates themselves (substrate materials and geometries) (Fig. 4). Satisfactory coating results can often only be achieved by taking full account of the interactions of coatings and substrates and of the past histories of the substrates used.

### 3.1 COLORS

Their color tones represent by far the most important feature of decorative coatings. Color schemes are probably the simplest approach to creating visible product differentiations in the literal sense of the word. In discussing colors, we implicitly assume that the colors involved are “intrinsic colors” that represent properties of the coating materials themselves or of their component elements. Excluded from consideration are coatings whose colors are due to interference effects, since their colors are strongly dependent on film thicknesses. Films of uniform thicknesses cannot be cost-effectively deposited on complex shapes. In addition, natural wear also affects film thicknesses, and reductions in film thicknesses due to abrasion will lead to conspicuous gradations in color shades appearing on exposed portions of coated articles over time.

### 3.1.1 GOLD TONES

Gold tones continue to represent by far the major decorative colors, and this situation is not likely to change in the foreseeable future. PVD offers the following alternatives for depositing gold-tone coatings:

1.deposition of gold alloy films,
2.deposition of titanium (carbo)nitride films, and
3.deposition of titanium (carbo)nitride films, followed by a thin overlay of a gold alloy.

**Requirements on Deco Coatings**

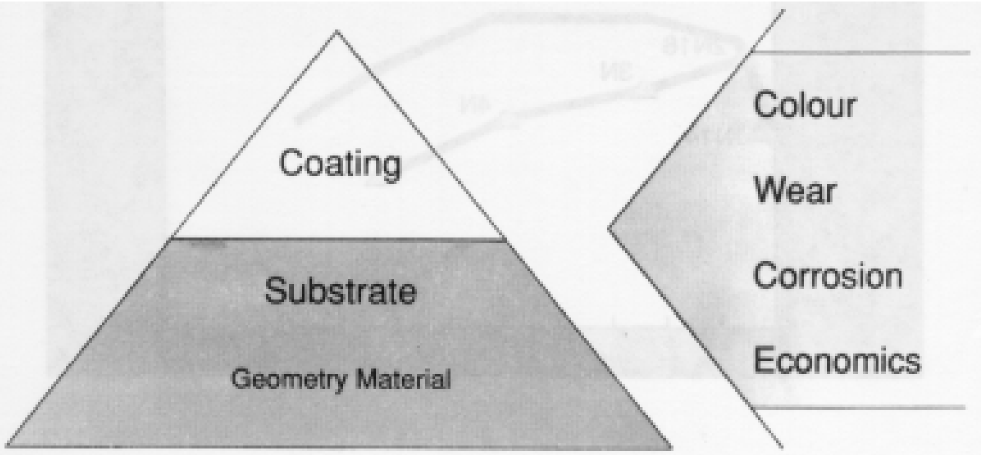


Fig. 4

Thus far, only the third of these alternatives has found application on an industrial scale. Let us now consider these alternatives in detail.

### 3.1.1.1 DEPOSITION OF GOLD ALLOYS

Gold alloys can be deposited relatively simply using sputtering methods employing “purely metallic processes” [15]. The color tones that result are solely determined by the compositions of the gold alloys used.

The particular benefits of sputtering techniques compared to electroplating, for example, are due to the fact that there are no real problems connected with stoichiometric deposition of gold alloys having unusual compositions (e.g., AuTi10) while maintaining the required degrees of color uniformity and color reproducibility. One characteristic of sputtering is that (for metallic processes) the composition of deposited coatings invariably conforms to that of the target materials used. There are also-thus far little explored - options for depositing very ordinary types of gold alloys having unusual colorations. The intermetallic phase AuAl2, which which exceeds 18 kt. gold content and exhibits a violet coloration, can serve as a (somewhat academic) example of what is meant here. This compound has long been known; however, it has hardly any applications due to its extreme brittleness and low resistance to corrosion. Such compounds can be fabricated into targets and deposited by sputtering processes. The ability of sputtering methods to deposit compounds that cannot conceivably be deposited by any other means offers opportunities that have thus far been largely ignored.

### 3.1.1.2 DEPOSITION OF TITANIUM (CARBO) NITRIDE FILMS

Titanium nitride exhibits a gold-like coloration that can be controlled by varying nitrogen content or by adding small amounts of acetylene. Fig. 5 presents a color scale, superimposed on the CIElab-units $a^*$ (positive: red-value; negative: green-value) and $b^*$ (positive: yellow-value; negative: blue-value) [16], with Swiss gold-tone standards [17] entered. Fig. 5 shows that titanium carbonitride films can be given any standard gold-tone by choosing suitable combinations of nitrogen and carbon contents. These types of coatings are, however, not necessarily suitable as gold-tone decorative coatings, since they have low brilliance in comparison to gold alloys, giving them a somewhat greyish appearance.

**Colour of $\text{TiN}_x\text{C}_y$ Films**

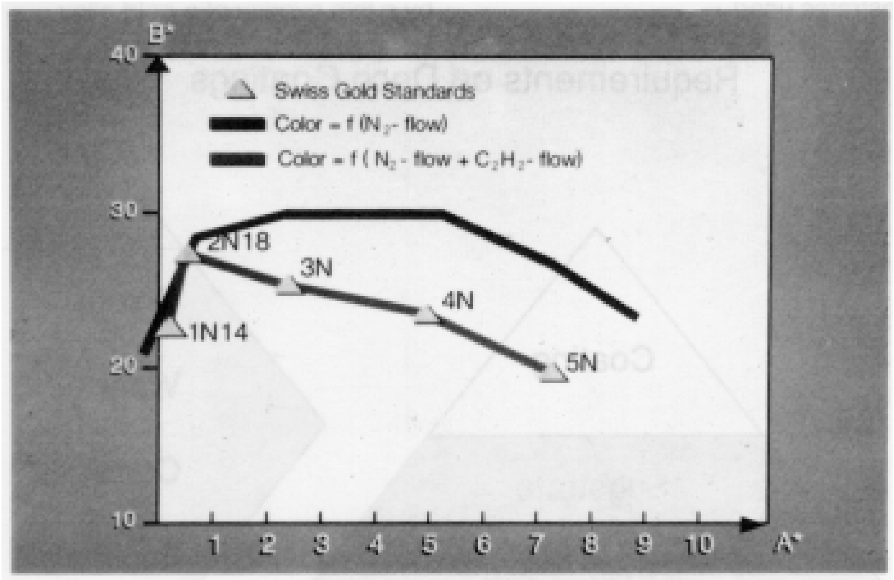


Fig. 5

Brilliance is assessed in terms of the L*-value of the CIElab-units; it lies at about 88 - 91 for gold alloys, but only at about 74 - 76 for titanium carbonitride films. Fig. 6, which gives the wavelength dependence of their reflectivities, provides further clues as to the origins of these differences in visual appearances of gold alloys and titanium nitride. Meaningful color values can be computed from these curves of reflectivity versus wavelength. It seems obvious that the reflectivity curves of gold alloys can be qualitatively approximated by varying the nitrogen and carbon contents of titanium carbonitride films. However, gold alloys have higher reflectivities over the entire wavelength range. The reason for this is of a fundamental nature: differences in electronic structures [18] that will not be considered further here. Their low brilliances mean that used alone these types of coatings will not find application in the gold-tone coating area. Titanium carbonitride films, however, certainly have their uses, e.g., (with much greater carbon contents) in the decorative red-brown coating area.

This approach can also be used in solving the problem of the unacceptable brilliances of titanium (carbo)nitride films. A second film that provides the missing properties is added:

· The desired hardnesses and resistances to wear are obtained using films of titanium (carbo)nitride that also produce the desired gold tones, but with unacceptable brilliances.
· A very thin overlay of gold alloy is added to the film of hard material to produce the needed brilliance. Gold films 0.05 µm thick are sufficient to fully obscure underlying substrates [19].

The obvious objection is that this solution is clearly unacceptable, since the thin gold alloy overlay would rapidly wear off, so that the low brilliance of the underlying titanium (carbo)nitride film would soon determine appearances. Closer analysis indicates otherwise, however:

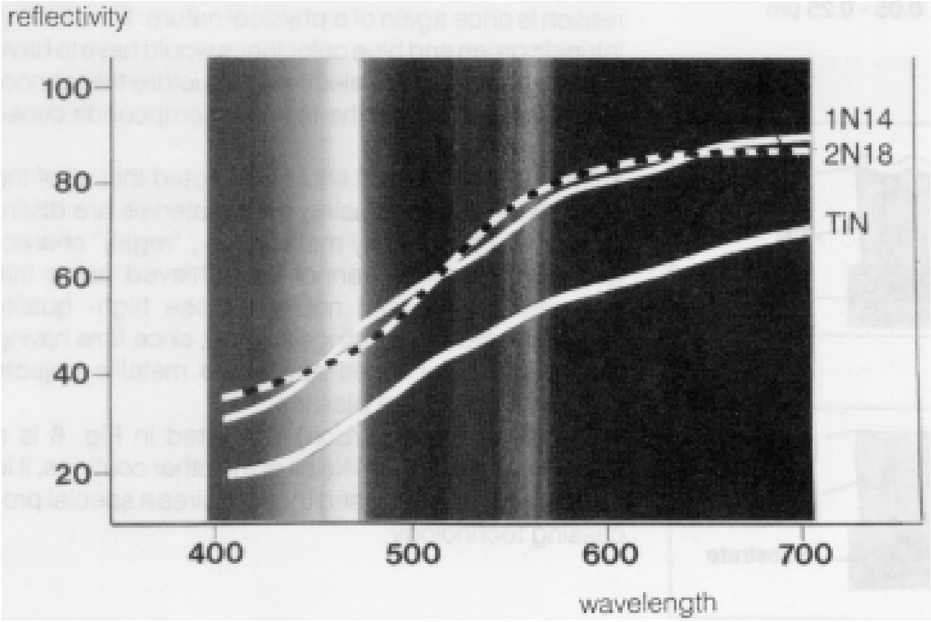


Fig. 6

### 3.1.1.3 DEPOSITION OD TITANIUM (CARBO) NITRIDE FILMS, FOLLOWED BY A THIN OVERLAY OF A GOLD-ALLOY

The basic aim in applying any coating to solid objects is meeting different, often mutually contradictory, sets of requirements placed on basis material and surface properties.

· Wear occurs first at exposed points (along edges and at corners), and is thus initially limited to small portions of the surfaces of coated objects. Since the underlying film has nearly the same color tone as the overlay, these highly localized minor variations in brilliance due to wear go unnoticed.
· Since every surface exhibits microroughness, gold alloy overlays will wear off only at roughness peaks, if at all, and any gold alloy worn off will be deposited in the intervening valleys (Fig. 7).

Furthermore, abrasion is confined to small portions of the total surface area, namely to surface roughness peaks, so that any shifts in color tone remain visually imperceptible. $ The soft gold alloy acts as a lubricating film that effectively reduces abrasion; the film is redistributed over the surface of the object instead of being abraded away. In fact, a composite coating of titanium nitride and gold alloy films was the subject of a patent application [20] very early in the history of the field.

**Effect of Gold Top Layer**

**Typical thickness of gold top layer: 0.05 - 0.25 µm**

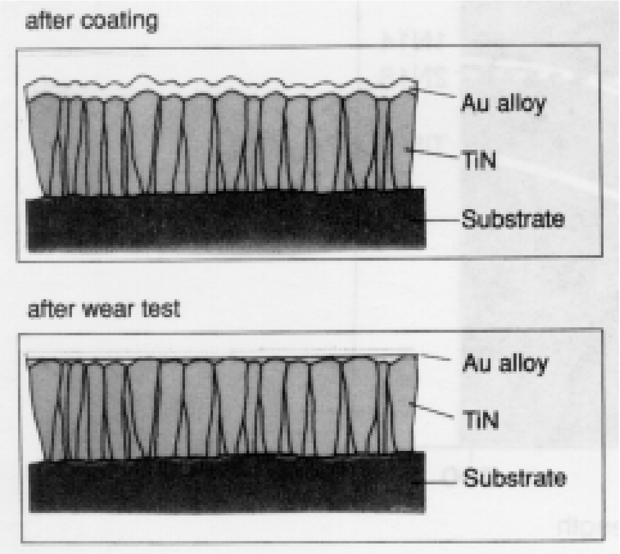


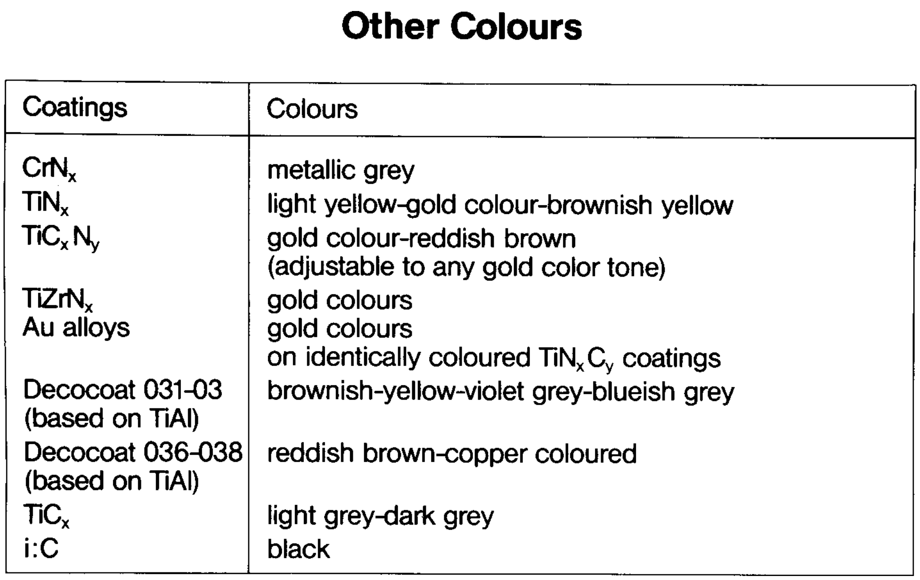
Fig. 7

3.1.2 OTHER COLORS

Color tones are the major justification for using decorative coatings. Fashion aspects of consumer products are acquiring greater importance under the pressure of growing needs for product differentiation, and similar trends are emerging for professional and industrial products, all of which translates into constantly growing demands for new color tones. Modern PVD methods, particularly sputter ion plating, are particularly good choices for meeting these needs.

The virtually unlimited range of materials that can be produced using these methods also provides an enormous untapped potential in terms of new color tones for use in decorative applications. Fig. 8 presents a review of the films thus far used in decorative applications. The following should be noted in this connection:

· The colors available are primarily reddish-yellow and grey tones. Blues and greens are lacking. The reason is once again of a physical nature: films having intrinsic green and blue color tones would have to have a very special type of electronic structure that cannot occur, at least not for the titanium compounds considered here [18].
· On the other hand, it should be noted that all of the color tones obtained using hard materials are distinguished by their highly metallic, i.e., “regal,” characters. Bright colors cannot be achieved using this approach, but would not suit these high-quality “expensive looking” coatings anyhow, since films having very bright color tones applied to metallic objects appear “cheap,” like plastics.
· The black (hard carbon) film listed in Fig. 8 is a special type, since, unlike all of the other coatings, it is electrically insulating, and thus requires a special processing technology.



## Other Colours

| Coatings | Colours |
|---|---|
| $CrN_x$ | metallic grey |
| $TiN_x$ | light yellow-gold colour-brownish yellow |
| $TiC_xN_y$ | gold colour-reddish brown<br>(adjustable to any gold color tone) |
| $TiZrN_x$ | gold colours |
| Au alloys | gold colours<br>on identically coloured $TiN_xC_y$ coatings |
| Decocoat 031-03<br>(based on TiAl) | brownish-yellow-violet grey-blueish grey |
| Decocoat 036-038<br>(based on TiAl) | reddish brown-copper coloured |
| $TiC_x$ | light grey-dark grey |
| i:C | black |

Fig. 8

Fig. 9 illustrates the breadth of color tones that can be covered using a single compound. This shows the various color tones that can be achieved with zirconium carbonitride by varying its nitrogen and carbon contents. Of course, one could consider adding other metallic constituents, such as titanium or chromium, to make still further color tones accessible. In summary, we should remember that the opportunities for creating color tones using PVD methods have been used to no more than a minor extent at best, and have by no means been exhausted.

**Zirkon-carbon-nitride**

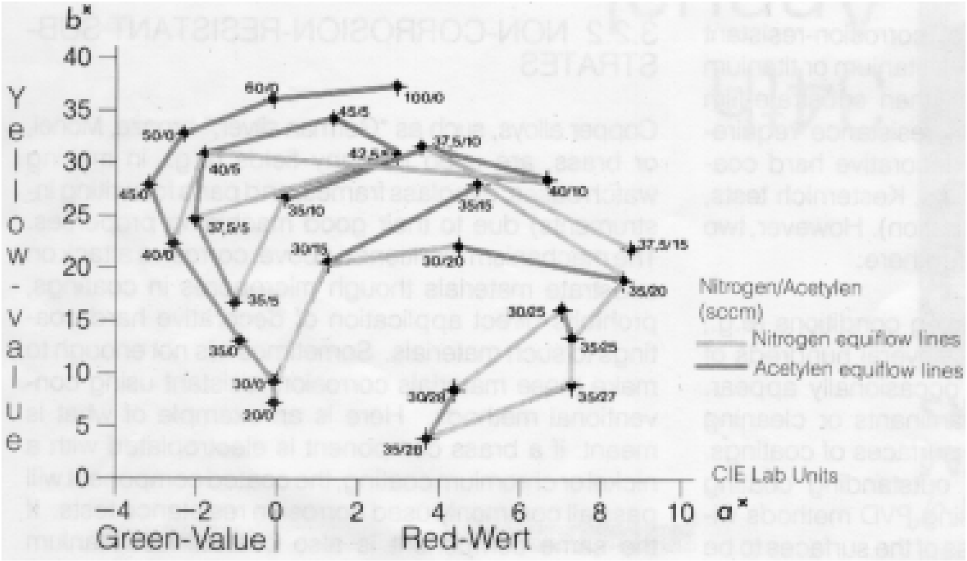


Fig. 9

## 3.2 CORROSION RESISTANCE

The following factors are critical in assessing the corrosion resistances of decorative hard coatings:

· All of the hard materials used are inherently highly resistant to corrosion, and thus have high positive electrochemical potentials.
· The structures of films deposited using PVD methods are characterized by pronounced anisotropies: these films are deposited as many small dendrites oriented perpendicular to the surfaces of their underlying substrates. Films deposited in such forms are nonsmoothing, and closely follow any surface roughness features.
· Decorative hard coatings are very thin (typically of 0.3 µm to 0.7 µm thicknesses).

Small defects, such as scratches, small pores, etc., on the surfaces of engineering materials are a fact of life that cannot readily be prevented.

Film deposition is affected where such occur, due to the anisotropy of deposited films. Micropores originate, and are not covered over as films are deposited, due to the films being insufficiently thick. Micropores permit direct corrosive attack on underlying substrate materials. Thus, the substrate material or material underlying films must be considered in assessing the corrosion resistance of decorative hard coatings. This fact is often overlooked.

### 3.2.1 CORROSION-RESISTANT SUBSTRATES

If substrates themselves are of corrosion-resistant materials, such as stainless steel, titanium or titanium alloys, hard metals, or Inconel, then substrate-film composites will meet corrosion resistance requirements typically demanded of decorative hard coatings (salt-spray tests, CASS-tests, Kesternich tests, and resistance to artificial perspiration). However, two important factors should be noted here:

· Under extremely adverse testing conditions (e.g., salt spray tests extending over several hundreds of hours), corrosion effects may occasionally appear. The causes involved are contaminants or cleaning agent residues residing on the surfaces of coatings. This also makes it clear that outstanding coating adhesions can be achieved using PVD methods without need for perfect cleanliness of the surfaces to be coated. The adhesions of coatings deposited using PVD methods never presents any problems, thanks to the high performance capabilities of ion etching (cf. supra).
· Substrate materials may occasionally be designated as being corrosion resistant even though, strictly speaking, they are not. An example is the stainless steel, often designated 12/12, that, e.g., is the material of choice for watch cases due to its good machining properties. With its approx. 12 % nickel content and approx. 12 % chromium content, this steel borders on the austenitic region, and it also frequently contains ferritic phases. Its corrosion resistance is often adequate in the uncoated state, but can deteriorate when the material is covered with decorative hard coatings. The reason for this is the extremely high electrochemical potential common to all hard materials. The large differences in electrochemical potentials of coating materials and substrate materials can frequently lead to formation of so-called “local elements,” which contribute to corrosive attack at coating-substrate interfaces for corrosive attacks that take place through micropores. The well-known “pitting” corrosion is the result.

Substrate materials, such as titanium or titanium alloys, hard metals, and high-quality stainless steels, that (except for steels) cannot readily be electroplated are particularly suited to coating using PVD methods. This makes it particularly clear that PVD coating methods represent valuable complements to conventional coating methods: they open the door to the use of unconventional materials. This potential has been little exploited to date.

### 3.2.2 NON-CORROSION-RESISTANT SUBSTRATES

Copper alloys, such as “German silver,” bronze, Monel, or brass, are used in many fields (e.g., in making watch cases, eyeglass frames, and parts for writing instruments) due to their good machining properties. The mechanism mentioned above, corrosive attack on substrate materials though micropores in coatings, prohibits direct application of decorative hard coatings to such materials. Sometimes it is not enough to make these materials corrosion resistant using conventional methods. Here is an example of what is meant: if a brass component is electroplated with a nickel or chromium coating, the coated component will pass all commonly used corrosion resistance tests. If the same component is also coated with titanium nitride (and a thin film of gold alloy), then corrosion effects will appear (in the CASS-test, Fig. 10).

**Effect of electrochemical potentials on the corrosion resistance of film systems**

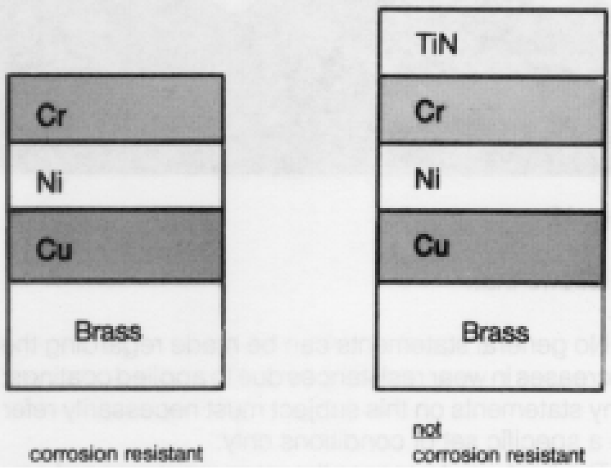


Fig. 10

The cause here comes from electrochemical potentials: chromium has a lower electrochemical potential than does nickel. Local element formation thus cannot occur; corrosive attack proceeds over large areas of the chromium film at low rates, and is visually imperceptible. Titanium nitride has a particularly high electrochemical potential, so that the difference in the potentials of chromium and titanium nitride is large, which can lead to local element formation at micropore sites, and an amplification of corrosion effects. Deposition of a 3-µm to 5-µm thickness nickel film followed by a 1-µm to 2-µm thickness palladium-nickel film brings significant improvement. The type of corrosion protection film needed will depend on requirements. In some applications, a simple nickel film of about 5 µm thickness will be adequate, while in others an additional chromium film will be required, and in still others the palladium-nickel film mentioned above will be required.

## 3.2.3 DEPOSITING ANTI-CORROSION COATINGS USING PVD

Needs for adding anti-corrosion coatings using electroplating lead to production problems, and thus to costing obstacles. An obvious approach would be to deposit anti-corrosion coatings using PVD, since then entire coating complexes (anti-corrosion overlay plus underlying decorative hard color coating) could be applied using a single system, thus greatly simplifying production operations, while providing an economically attractive alternative. This task is simple enough to formulate, but not so easy to convert into actual practice, since a number of crucial factors are involved.

Anti-corrosion coatings deposited using PVD that are acceptable from both engineering and economic standpoints do not yet exist. Preliminary results in this area are shown in Fig. 11 [21]. The total surface areas of corroded spots were taken as indications of the degrees of corrosive attack. The results shown are the means taken over several corrosion test procedures. Marked differences are discernable, and are partly due to the materials used, and partly due to the coating conditions used in depositing them [22].

**Corrosion Resistance of Various Materials**

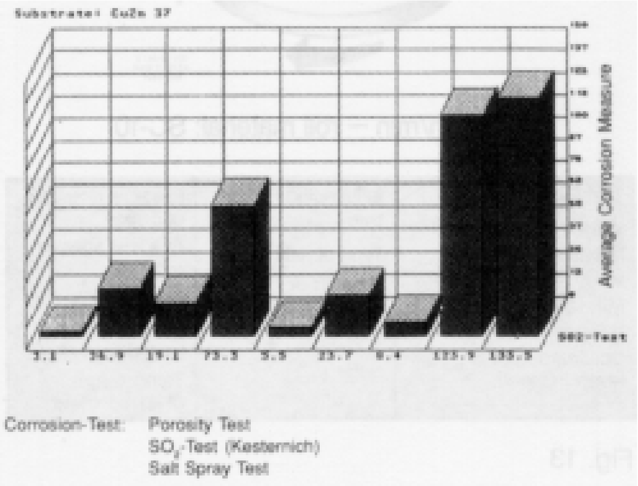


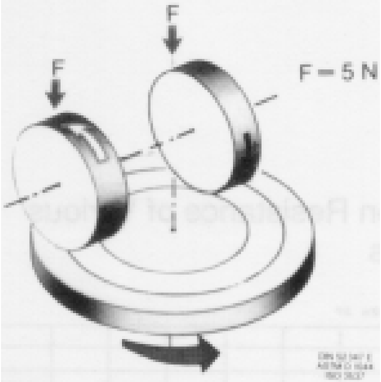
Fig. 11

## 3.3 WEAR RESISTANCE

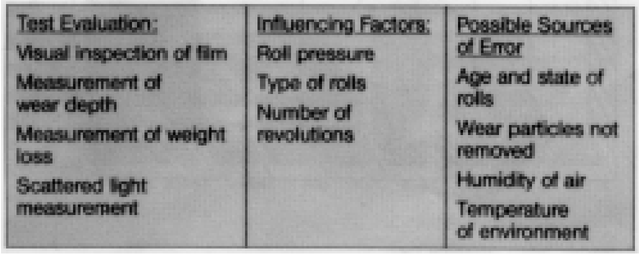
Even consumer products are subject to wear in normal use, due to factors such as clothing fabrics rubbing against wristwatches, including the effects of the dust particles that are likely to be find their way between fabrics and wristwatches, or due to cleaning house-hold utensils, such as tableware, with cleaning agents. These examples are sufficient to indicate that the type of wear is highly dependent upon the types of articles involved, their nominal uses, and the types of treatment they receive.

The degrees to which articles wear are affected by a multitude of factors [23]: the types of materials and the surface properties of objects with which the articles come into contact, the forces acting, the relative speeds of motion involved, whether any intervening media ("lubricants") are present, the natures of any such media, and so on. This complexity is illustrated in Fig. 12. Thus, the films on coated articles are but one of the many factors involved in determining how, and how much, the articles will wear.

**Principle of Taber Abraser Tests (schematic)**



**100 rpm/min — roll material: SC-10**



| Test Evaluation: | Influencing Factors: | Possible Sources of Error |
|---|---|---|
| Visual inspection of film | Roll pressure | Age and state of rolls |
| Measurement of wear depth | Type of rolls | Wear particles not removed |
| Measurement of weight loss | Number of revolutions | Humidity of air |
| Scattered light measurement | | Temperature of environment |

Fig. 13

Schematics of a
Tribological System

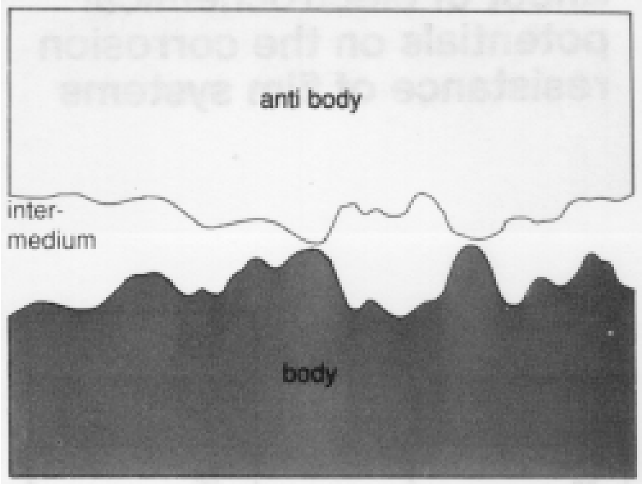


Fig. 12

It follows that:

· No general statements can be made regarding the increases in wear resistances due to applied coatings; any statements on this subject must necessarily refer to a specific set of conditions only.

· The best way to assess the wear resistances of products is to subject them to testing under conditions of actual use, since the wearing factors are precisely those they will normally encounter. Currently demanded for high-quality consumer products is that they retain their original appearance after at least five years of normal use and contact with natural corrosion. This means, among other things, that any coatings applied must not wear off, even locally, exposing the underlying material, over this period.

There are thus a whole series of various test procedures for accelerated assessments of wear resistance intended to simulate the wear that occurs under conditions of actual use. The utility of such test procedures has been empirically confirmed, but should always be additionally confirmed by "real" testing under actual conditions of use, particularly whenever articles themselves undergo any major changes (e.g., new materials are used) or their uses change (e.g., different types of contact or contacting materials come into play). One would logically expect articles having decorative hard coatings to be highly resistant to wear.

**Taber-Index (Volume Loss)**

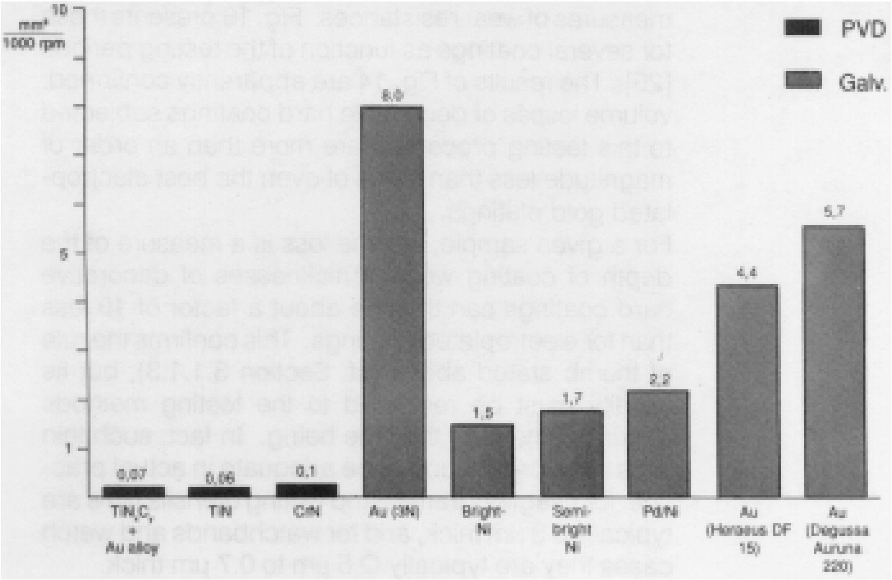
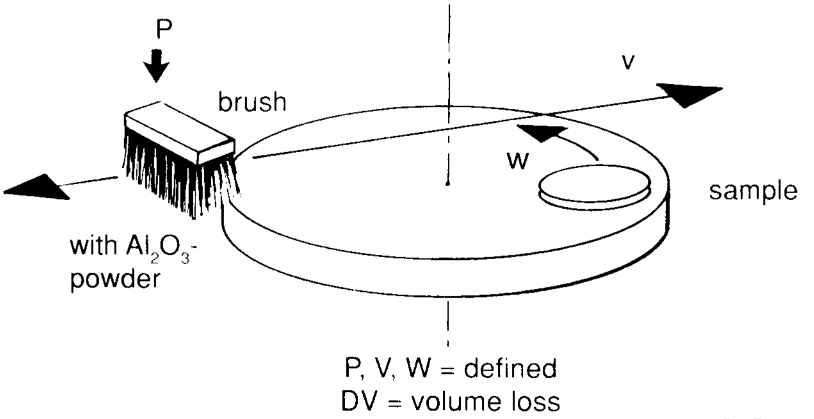


Fig. 14

**Principle**



P, V, W = defined
DV = volume loss

acc. Dr. Riedl, ETA

Fig. 15

This is frequently, but not always, the case. Here are two extremes to illustrate what is meant here:

- Films of TiN less than 0.1 µm thick are extraordinarily resistant to abrasion by polishing wheels.
- However, many of the hard materials, such as TiN or TiAlN, used as decorative coatings exhibit high coefficients of friction with respect to one another. If the surfaces of both of two objects in contact with one another have been coated with such films, high rates of wear will be the result. This example indicated that hardness and wear resistance are two distinct properties, and that hardness alone does not necessarily provide resistance to wear.

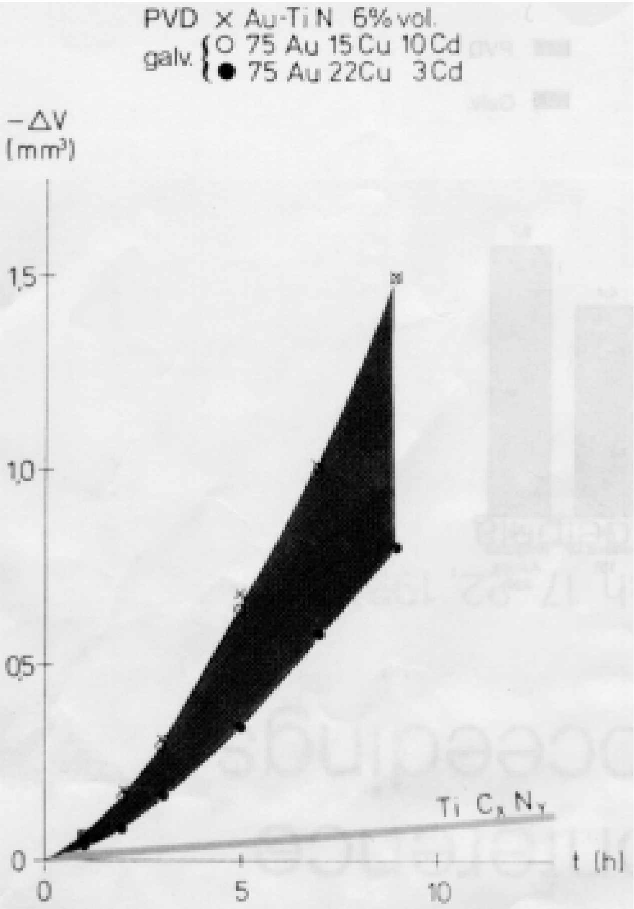


Fig. 16

The significantly improved wear resistances of decorative hard coatings compared to conventional types of coatings can be illustrated through two examples. Fig. 13, together with its explanatory text, schematically depicts the idea behind so-called Taber- abrasion testing. If we take the volume losses sustained over a certain testing period are taken as measures of total wear, then we arrive at results similar to those appearing in Fig. 14 [24]:

· (Metallic) gold films deposited using PVD methods exhibit resistances to wear identical to those of electroplated gold plaques. There appear to be special electroplating procedures that are able to increase gold's resistance to wear.
· The volume losses observed for decorative hard coatings are two orders of magnitude less than for electroplated gold, and an order of magnitude less than for electroplated nickel.
The principle behind another procedure for measuring wear resistance used, e.g., in the watch industry, is shown in Fig. 15. Again volume losses are taken as measures of wear resistances. Fig. 16 presents these for several coatings as function of the testing periods [25]. The results of Fig. 14 are apparently confirmed: volume losses of decorative hard coatings subjected to this testing procedure are more than an order of magnitude less than those of even the best electroplated gold platings.

For a given sample, volume loss is a measure of the depth of coating wear. Thicknesses of decorative hard coatings can thus be about a factor of 10 less than for electroplated coatings. This confirms the rule of thumb stated above (cf. Section 3.1.1.3), but its validity must be restricted to the testing methods described here for the time being. In fact, such thin films have been found to be adequate in actual practice: for eyeglass frames and writing utensils films are typically 0.3 µm thick, and for watchbands and watch cases they are typically O,5 µm to 0.7 µm thick.

## 4. DEVELOPMENT TRENDS

Expansion of the applications base for decorative hard coatings is contingent upon overcoming the existing restrictions. Several approaches to this objective have been mentioned. Here, we will merely summarize current development trends; their detailed treatment will be deferred to a later article.

· Reductions in coating costs due to use of more efficient sputtering sources. As laboratory results show, new types of sputtering sources allow increasing specific sputtering rates by at least a factor of 3 compared to the sources used thus far. This means that coating costs (for the same sets of conditions) can be reduced to half of their current levels. This will open up new application areas, even areas involving larger items other than more sophisticated consumer products (e.g., building hardware and fittings, door knobs, etc.).
· Identification of compounds of hard materials that will yield new color tones, both gold tones and others. The brilliances of gold-tone hard coatings can be markedly enhanced through improvements in processing methods and careful choices of materials. The "brilliance gap" relative to gold alloys is being gradually closed.
· The ability to coat large items. The new sputtering sources mentioned above will permit applying uniform coatings to larger items using the dual- cathode configuration. New approaches to coating large items (not based on the dual-cathode configuration) are being pursued in parallel.

· Deposition of anti-corrosion coatings employing PVD methods.
We reported on this subject in Section 3.2.3. The first promising materials are currently undergoing testing.
· Reductions in coating temperatures. Reactive deposition of hard materials always involves dissipation of energy in the items being coated. The sources of this energy are liberated binding energies, ion impacts, and impacts by so-called "fast-moving neutral particles" (coming from the sputtering cathodes). This can lead to substrate temperatures exceeding 300°C for coating thicknesses of 1 µm. In the meanwhile, it has been demonstrated in the laboratory that 1 mm coatings can be deposited using certain types of arrangements without substrate temperatures exceeding 130°C. If this processing technology can be transferred to production scales, then new avenues into numerous and varied application areas in the coating of (pre-electroplated) die-cast zinc and plastic parts will be opened up.

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