

# CHAPTER 29

## Colored Coatings with Metal Colloids

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### INTRODUCTION

Metal colloids have been used for staining glass since hundreds of years (Weyl, 1951), e.g. yellow and ruby church window glasses with silver and gold colloids respectively. Today it is known from the Drude theory (Kittel, 1976) that the color of these nano composites (nano-sized metal particles in a dielectric matrix) is due to a surface plasmon resonance effect of the conductive electrons, which leads to a selective absorbance in the visible range of light. The molar coefficient of absorbance of this effect is in the range of  $10^5$ – $10^6$  l/mol cm, which makes metal colloids very interesting as efficient dyes for colored sol-gel-coatings with thicknesses around 1  $\mu$ m. Furthermore their extremely high UV and thermal stability are favorable for practical applications. Beside this their non-linear optical properties ( $\chi^{(3)}$ -effects) have been studied recently (Hache, 1988) and could be mainly attributed to effects of “hot electrons” with ps relaxation times (Hache, 1988). It is interesting that Au colloids in SiO<sub>2</sub> layers prepared by sol-gel processing (Matsuoka, 1993) showed larger  $\chi_m^{(3)}$  coefficients (e.g. the specific non-linearity of the metal particle) compared to Au particles incorporated in glasses by ion implantation (Fukumi, 1991), by RF sputtering (Kadono, 1993) or by melting (Hache, 1988). This effect was explained by non-equilibrium states of the Au colloids, frozen in by the sol-gel preparation route (Matsuoka, 1993).

Both fields of possible applications: stable colored sol-gel-coatings and highly efficient non-linear optical materials were the motivation for the development of appropriate synthesis and processing routes which will be reviewed in this paper. But at first an overview on the linear optical properties of metal colloids in dielectric media shall be given, because the theoretical knowledge can be used to determine colloidal size and concentration from simple absorbance measurements and is helpful for the generation of desired colors.

### THEORETICAL BACKGROUND

An excellent overview on the optical properties of metal colloids in dielectric media is given by Kreibig and Vollmer (1995). For diluted systems the absorbance coefficient  $k$  can be calculated according to the MIE theory (Mie, 1908) using Eq. (29-1)

$$k = \frac{6\pi n_d NV}{\lambda} \operatorname{Im} \left\{ \sum_{v=1}^{\infty} a_v + p_v \right\} \quad (29-1)$$

where  $NV$  denotes the volume concentration of the particles,  $n_d$  the refractive index of the dielectric, non absorbing matrix and  $\lambda$  the vacuum wavelength of light.  $a_v$  and  $p_v$  represent the contributions of electric and magnetic partial waves, which can be calculated as a function of  $\lambda$ ,  $n_d$  and the real ( $\epsilon_{1m}$ ) and imaginary part ( $\epsilon_{2m}$ ) of the dielectric function of the metal particles. Kreibig had shown (Kreibig, 1996, 1970); that due to the small size of the metal nanoparticles additional collisions of the electrons occur with the particle walls. This “mean free path effect” leads to an increase of the collision frequency of the electrons by adding  $v_F/R$  ( $v_F$  = Fermi velocity,  $R$  = radius) and therefore to particle size dependent expressions for  $\epsilon_{1m}$  and  $\epsilon_{2m}$ . Finally the absorbance  $k$  can be calculated using

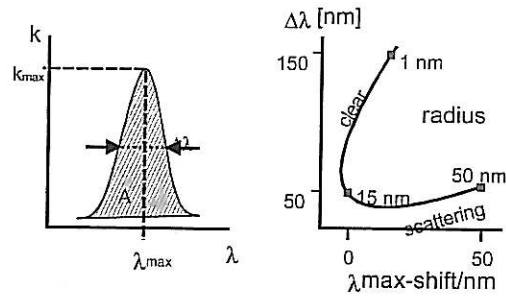


Figure 29-1. Dependence of peak position shift and half band width of absorbance bands of Ag and Au colloids in dielectric media, summarized from (Mennig, 1993; Berg, 1991; Fröhlich, 1982).

numeric methods (Kreibig, 1995; Dusemund, 1991; Mennig, 1993; Porstendorfer, 1996) as a function of  $\lambda$ ,  $n_d$ ,  $NV$ ,  $\epsilon_{1m}(R)$  and  $\epsilon_{2m}(R)$ .

The absorbance bands of the colloids are characterized by the spectral position of the plasmon peak  $\lambda_{\max}$ , the height of the peak ( $k_{\max}$ ) and the half band width of the absorbance band  $\Delta\lambda$ . Investigations on Ag (Berg, 1991; Fröhlich, 1982) and Au colloids (Mennig, 1993) in glass lead to the following result, summarized in Figure 29-1.

Figure 29-1 shows that for small particles with radii between 1 and approximately 15–20 nm, the half width strongly decreases with increasing particle size, whereas the peak position of the absorbance band remains almost unchanged. Appropriate glasses appear clear and transparent, since scattering can be neglected for such small particles and the absorbance is due to absorption. With further increasing particle size the half width increases again and the peak shifts slightly to longer wavelengths. Here scattering becomes more and more evident and appropriate composites appear translucent. The parameter diagram of Figure 29-1 can be used to determine the average colloid size from spectroscopic data, since it has been shown, that measured values of  $\Delta\lambda$  and  $\lambda_{\max}$  are in good agreement with the theoretically obtained curve of Figure 29-1 for several investigations on Ag (Berg, 1991; Fröhlich, 1982; Mennig, 1992) and Au colloids (Mennig, 1993, 1994a).

Furthermore the area beneath the absorbance curve is proportional to the volume concentration of colloidal metal (Fröhlich, 1982). The proportionality factor only slightly depends on the particle size (Fröhlich, 1982; Mennig, 1984), but depends on the refractive index of the matrix. These theoretical and experimental investigations lead to the conclusion that for a given matrix the color obtained by metal colloids strongly depends on the type of metal and cannot be changed significantly by the particle size, when scattering has to be excluded. Figure 29-2 shows the absorbance spectra of Ag, Au, Pd and Cu colloids embedded in a matrix with  $n_d = 1.5$ , calculated numerically according to (Porstendorfer, 1996).

As one can see from Figure 29-2, Pd colloids show a rather strong and broad absorbance with its peak in the UV and a long “tail” in the visible range, which leads to brownish colors. Ag colloids show a sharp and strong peak at around 400 nm wavelength (yellow color). Au and Cu colloids create reddish colors with peaks at about 530 nm and 600 nm respectively. The plasmon peak is overlapped by interband transitions which occur for wavelengths  $\lambda < \lambda_{\max}$ .

As already mentioned above, the color of metal colloid containing composites does not only depend on the type of the metal, but also on the refractive index of the matrix,

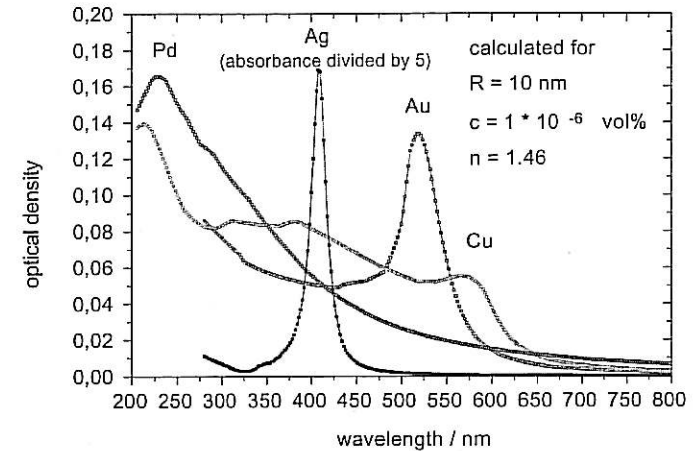


Figure 29-2. Calculated spectra of different metal colloids (Pd, Cu, Ag, Au with 10 nm radius, concentration  $10^{-4}$  vol.% in a dielectric matrix (thickness 1 mm) with refractive index  $n_d = 1.46$ , according to (Porstendorfer, 1996).

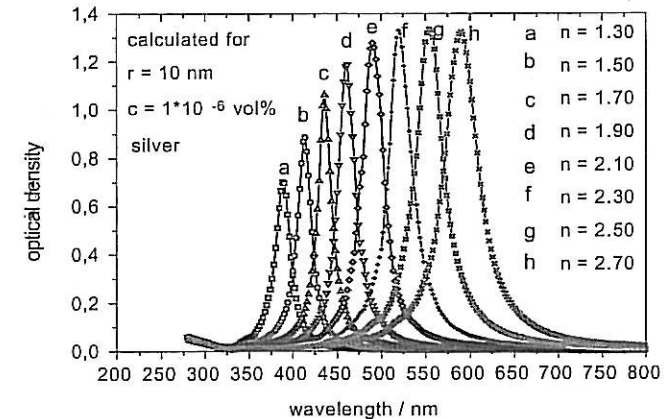


Figure 29-3. Calculated absorbance spectra of Ag colloids (10 nm radius,  $10^{-6}$  vol.% in dielectric matrices (thickness 1 mm) of different refractive index, by numeric programs according to (Porstendorfer, 1996).

as one can see from Eq. (29-1). In order to illustrate this influence absorbance spectra of Ag colloids have been calculated using numeric programs of (Porstendorfer, 1996) for matrices with refractive indices varying from 1.3 (water) to 2.7 ( $\text{TiO}_2$ , rutile).

As one can see from Figure 29-3, the absorbance of the Ag colloids is shifted to longer wavelengths and the height of the absorbance increases significantly with increasing refractive index of the matrix, ranging from 1.3 to 2.7. First experiments with different noble metal colloids in sol-gel derived  $\text{TiO}_2$  films, densified at 500 °C (Sakka, 1994) and with Ag and Au colloids in  $\text{TiO}_2$  layers densified at temperatures between 200 and 600 °C with

different refractive indices (Mennig, 1997a) are qualitatively in good agreement with this theoretical result.

#### SYNTHESIS ROUTES TO METAL COLLOID CONTAINING COATINGS ON GLASS

Au colloids have already been generated in SiO<sub>2</sub> coatings on glass by dissolving of AuHCl<sub>4</sub> in tetraethoxysilane (TEOS) sols (Matsuoka, 1993; Fernandez Navarro, 1992; Sakka, 1998) or by incorporation of appropriate precursors in ormosil matrices (Tseng, 1992). There have also been only few attempts for the generation of Ag colloids in SiO<sub>2</sub> matrices by dissolving AgNO<sub>3</sub> in sols prepared from TEOS sols (Datta, 1992) or tetraethoxysilane (Reisfeld, 1988), using different reducing agents like formaldehyde (Datta, 1992) or Sn<sup>2+</sup> (Reisfeld, 1988) or by adding an aqueous colloidal Ag solution to a TEOS sol (Hinsch, 1990). In a similar manner Au colloids have been prepared in TiO<sub>2</sub> coatings on silica (Sakka, 1994, 1998). The common problem of these approaches is, that mechanisms for the control of the colloid size are missing. From the rather broad absorbance spectra and from TEM pictures it had to be concluded that broad size distributions of the colloids were obtained and agglomeration could not be avoided completely.

From several investigations of the generation of metal colloids in solutions and polymers, it is known that agglomeration can be avoided by stabilization with surface ligands, leading to a minimum of the Gibbs free energy of the system. Henglein (Henglein, 1988, 1989, 1992) described the generation of colloidal metal and semiconductor nanoparticles (e.g. HgS, Ag<sub>3</sub>S–CdS, PbS, Ag, Au, Pd) in alcoholic solutions by wet chemical or photochemical (photolytical decomposition of acetone) reactions of appropriate organometallic complexes. The stabilization of the colloidal particles was obtained by organic surface ligands, which had been used as complex forming agents for the noble metal ions, before the nucleation and growth reactions had been initiated. Schmid (Schmid, 1991, 1992) prepared Au-, Pt- and Pd-colloids and bimetallic colloids (Au/Pt, Au/Pd, Pd/Pt) by dissolving appropriate metal salts (e.g. H<sub>2</sub>PdCl<sub>4</sub>, H<sub>2</sub>PtCl<sub>6</sub> or H<sub>2</sub>AuCl<sub>4</sub>) in water and by redox reactions with citrates. For the stabilization of the colloids phosphoric salts (P(m-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na)<sub>3</sub>, p-H<sub>2</sub>N–C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na) were used. Bönnemann describes an elegant way for the preparation of noble metal colloids, stabilized with tetra alkyl amines, by reduction and simultaneous stabilization of the noble metal salts with tetra alkyl boronhydride (Bönnemann, 1991a, 1991b). For composite materials, metal nano particles are generated and stabilized in reverse micelles, polymers and zeoliths (Cheong, 1992a, 1992b). In (Schubert, 1990; Breitscheidel, 1991) functionalized silanes are described to be suitable for the stabilization of metal colloids (Au, Ag, Pd) in appropriate SiO<sub>2</sub> xerogel powders by densification in air and a second thermal treatment in H<sub>2</sub> gas atmosphere.

Based on this knowledge new synthesis and processing routes have been developed recently, which lead to Au colloids in organic–inorganic hybrid (Nanomer®) coatings on glass (Spanhel, 1992; Mennig, 1995), to Pd colloids in SiO<sub>2</sub> coatings (Burkhart, 1994) and organic–inorganic monoliths (Catalano, 1994), to Au (Mennig, 1994a), Cu (Mennig, 1994b) and Ag (Mennig, 1997b) in SiO<sub>2</sub> coatings and also in SiO<sub>2</sub>–PbO-coatings (Mennig, 1994c; Schmitt, 1997).

The basic idea for these synthesis routes (for details see ref. Mennig, 1994a, 1994b, 1994c, 1995, 1997b; Spanhel, 1992; Burkhart, 1994; Catalano, 1994; Schmitt, 1997) was to use functionalized silanes (aminosilanes like 3-amino propyl triethoxy silane (APTS), N-(2-amino ethyl)-3-amino propyl trimethoxy silane (DIAMO), trimethoxy silyl propyl diethylen triamin (TRIAMO) or thiosilanes like 3-mercapto propyl trimethoxy silane

THIO)) for the stabilization of the noble metal ions by formation of appropriate complexes in alcoholic solution and to add this to the coating sol, in order to avoid spontaneous reduction and colloid formation in the sol or during wet film preparation. Colloids are formed afterwards during the densification step of the matrix, which can be an organic–inorganic hybrid (Nanomer®), or a glass-like or ceramic material.

The synthesis of metal colloids in Nanomer® coatings has not been investigated systematically so far. For Au–DIAMO complexes in a MPTS/ZrO<sub>2</sub> matrix sol however, it could be shown (Mennig, 1995) that controlled colloid formation could be obtained by a combined UV-IR irradiation of the wet film in presence of a suitable photo initiator within about 1 minute. During this process the matrix was cured simultaneously. It is assumed that the photoreaction leads to reduction of Au<sup>3+</sup> ions and the aminosilane simultaneously catalyzes the curing of the matrix, but further experiments are required to prove this hypothesis.

State-of-the-art SiO<sub>2</sub> coating sols (Brinker, 1990) like acid catalyzed TEOS sols could not be used for the formation of metal colloids in glass-like SiO<sub>2</sub> and SiO<sub>2</sub>–PbO coatings, because of rapid gelation due to pH increase obtained from the metal-aminosilane or -thiosilane complexes. This problem could be overcome by using sols prepared from 3-glycidoxypropyl triethoxysilane (GPTS) and TEOS (Schmidt, 1993). Surprisingly it was found, that despite of the high organic content of this sol, clear, transparent and crack-free coatings with thicknesses up to 0.8 μm could be obtained on glass after firing at temperatures between 500 and 700°C (Schmidt, 1993) even in N<sub>2</sub> and N<sub>2</sub>/H<sub>2</sub> atmosphere.

The colloid formation occurs by nucleation and growth processes during the densification of the matrix while thermal decomposition of the organic residuals allows reduction of the noble metal ions in the temperature range between 250 and 400°C (Mennig, 1994a, 1997b). In addition, their mobility in the coating matrix is decreased by the densification process of the surrounding matrix. These processes can be controlled by the processing parameters (temperature and time, reducing gas atmosphere) and also by the kind and concentration of the used stabilizer, as it has been shown for Au colloids in SiO<sub>2</sub> (Mennig, 1994a), where average colloid sizes between 3 and about 30 nm could be obtained. This model is consistent with results of SAXS measurements on Au colloid containing SiO<sub>2</sub> coatings on glass as a function of densification temperature, which indicate a fuzzy colloid to matrix interface at intermediate temperatures around 300°C (Kutsch, 1997a, 1997b).

The principle of stabilization of the metal ions in the sol could also successfully be used for the formation of Au, Ag and Pd colloids in first experiments with TiO<sub>2</sub> coatings (Mennig, 1997a). In this case silanes cannot be used as stabilizers. Therefore chlorocomplexes were used for Au<sup>3+</sup> and Pd<sup>2+</sup> and Ag<sup>+</sup> ions were stabilized with ethylenediamine. Again the colloid formation occurs during the densification of the matrix where reducing gas atmosphere has to be used for Ag and Pd. The TiO<sub>2</sub> matrix was synthesized from titanium isopropoxide using state-of-the-art synthesis routes (Sakka, 1994).

#### NON-LINEAR OPTICAL PROPERTIES

The non-linear optical properties of Au colloid containing composite coatings with glass-like (Mennig, 1994a) and Nanomer® matrices (Mennig, 1995) have been investigated as a function of the wavelength using degenerated four wave mixing experiments (laser induced gratings) with copolarized laser beams of an excimer laser pumped dye laser with a pulse length of 20 ns (Mennig, 1995). The results of these measurements are presented in Figure 29-4. It shows the non-linear response of the composite film ( $\chi^{(3)}$ ),

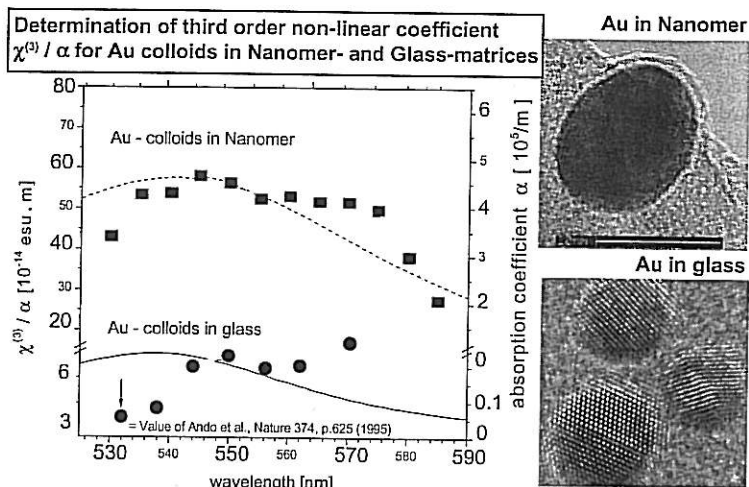


Figure 29-4. Non-linear optical response  $\chi^{(3)}/\alpha$  (data points) and absorption coefficient (dashed and solid line) of Au colloid containing glass-like ( $\text{SiO}_2$ ; Mennig, 1994a) and Nanomer<sup>®</sup> coatings (Mennig, 1995) on glass, determined from degenerated four wave mixing experiments with 20 ns pulses (Mennig, 1995).

related to the absorbance coefficient  $\alpha$ . This quotient is assumed to be the figure of merit for the characterization of the resonant  $\chi^{(3)}$  effect.

As one can see from Figure 29-4, the  $\chi^{(3)}/\alpha$ -values obtained in the glass like coating are in very good agreement to the data point, obtained from colloids in glass by melting (Adono, 1995), which proves the correct adjustment of the measurement equipment. They are about one order of magnitude smaller compared to the Nanomer matrix. It is assumed that this is due to an enhanced local electric field (Hache, 1988). The local field enhancement may be attributed to the distorted shape (spheroidal) and probably also to the influence of the ligand (DIAMO; Mennig, 1995), as one can see from the high resolution micrographs (upper picture Au colloid in Nanomer matrix, lower picture Au colloids in glass-like coating). Despite this remarkable effect, the diffraction efficiencies obtained in the Nanomer coating are still in the range of about  $10^{-3}$  (Mennig, 1995), which is still too low for practical applications. The reason is, that the relaxation times of the third order non-linear effect of several ps (Hache, 1988) are much shorter than the pulse duration of the used laser beams (20 ns).

Recently pump and probe experiments were performed on Au colloid containing  $\text{SiO}_2$  (Mennig, 1994a) and  $\text{TiO}_2$  (Mennig, 1997a) coatings by Feldmann et al. (1997) using fs laser pulses. Relative transmittance changes (bleaching) near the plasmon peak of about 15% in the case of  $\text{SiO}_2$  and of about 30% in the case of the  $\text{TiO}_2$  matrix were obtained in the ps range. Since ultra short laser pulses are required to obtain this large effect, there is no practical application for the moment.

## DECORATIVE COATINGS ON GLASS

Based on the synthesis routes described in Chapter 3 of this paper, transparent colored coatings have been developed for silicate prescription eye glass lenses (Mennig, 1997c) on

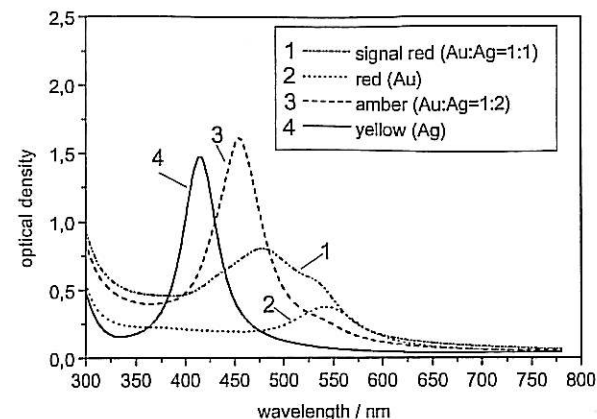


Figure 29-5. Absorbance spectra of  $\text{SiO}_2$ - $\text{PbO}$  coatings containing Au and Ag colloids and Ag-Au mixtures on glass after densification at  $600^\circ\text{C}$  in air (coating thickness  $0.2$ - $0.4\ \mu\text{m}$ , metal content about 1 at.%) from Mennig (1997d).

an industrial level and for flat glass (Mennig, 1997a) and halogen lamps (Mennig, 1997d; Endres, 1996) on lab scale. Since the color range to be obtained with different metals in a given matrix is limited, mixtures of Ag and Au containing sols have been developed (Mennig, 1997d), in order to obtain amber and red colors for signal applications. The result is presented in Figure 29-5.

The molar ratio between  $\text{PbO}$  and  $\text{SiO}_2$  was chosen to 1:7, in order to obtain complete densification of the coating at about  $500^\circ\text{C}$  and to adapt the refractive index of the coating to that of optical and flat glass, in order to avoid colored interference effects. As one can see from Figure 29-5, sufficient optical densities can be obtained with coating thicknesses of about  $0.3\ \mu\text{m}$  (on both sides of the substrate) and metal contents of only about 1 at.%. Furthermore one can clearly see that the absorbance spectra of the mixed systems (curves 1 and 3) cannot be obtained by weighted addition of the spectra of the single components (curve 2 for Au and curve 3 for Ag). It is assumed that Ag-Au alloy colloids or core shell structures are formed in the coatings, prepared from the Ag-Au mixtures. Further investigations are required for a final explanation.

Another possibility to extend the color range of metal colloid containing coatings on glass is shown in Figure 29-6.

It represents the absorbance spectra of Ag colloids in  $\text{SiO}_2$ - $\text{PbO}$  (Schmitt, 1997; Mennig, 1997c) with a refractive index of 1.57 and in  $\text{TiO}_2$  (Mennig, 1997a) coating (refractive index 2.35) on silicate glass after densification at  $500^\circ\text{C}$  in air ( $\text{SiO}_2$ - $\text{PbO}$ ) and  $\text{N}_2/\text{H}_2$  atmosphere ( $\text{TiO}_2$ ). In the  $\text{TiO}_2$  coating, which shows a deep violet color, the absorbance peak of the Ag colloids is shifted to 520 nm wavelength. This is in very good agreement with the calculated values (compare Fig. 29-2) of about 520 nm peak position for a refractive index of 2.30. Further investigations are required for the control of the Ag colloid size by variation of the synthesis and processing parameters.

The described decorative coatings show excellent adhesion on fused silica, boron silicate (Borofloat) and float glass. Stability tests have been performed with the  $\text{PbO}$ - $\text{SiO}_2$  coatings. No change in the absorbance spectra (difference in transmittance  $<1$  were obtained after 8 days at  $500^\circ\text{C}$ , 14 days of suntest and 12 days of climate test. The scratch resistance

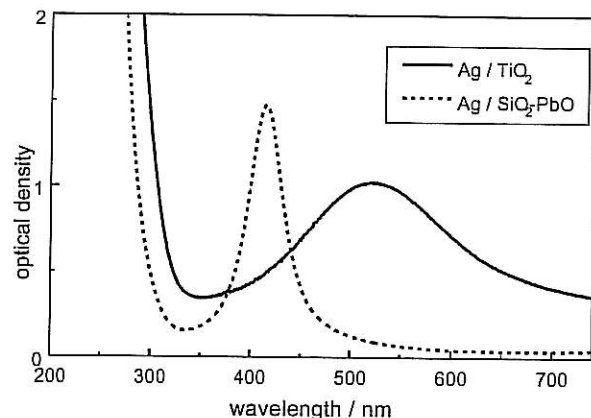


Figure 29-6. absorbance spectra of Ag colloids in a 100 nm thick  $\text{TiO}_2$  and in a 300 nm thick  $\text{SiO}_2\text{-PbO}$  coating on glass (Mennig, 1997a).

of the coatings is the same as for silicate glass and therefore these coatings fulfill a general demand for the application of colored coatings on glass. For the application on prescription eye glass lenses a technology has been developed, which allows to prepare coatings with four different colors using one and the same matrix sol, to coat lenses of all possible geometries with one and the same process parameters by spin coating and to densify the coatings for all colors in one and the same furnace. Therefore an efficient production of colored eye glass lens became possible on industrial scale.

#### APPLICATION OF NEW COATING TECHNOLOGIES

The dip-coating technology is well established for the deposition of optical coatings on large area glass substrates. It is used industrially for the deposition of high quality, dielectric multilayer interference coatings on large area flat glass substrates. The disadvantage of this coating technique are the rather slow deposition rate of several cm/min and the long pot life which is required for the coating sols.

Recently, the flat spray technique has been applied successfully on pilot scale for the homogeneous deposition of Au colloid containing lead silicate glass coatings on 1 m<sup>2</sup> size float glass panes (Fink-Straube, 1998/2002). The appropriate coating line (producer Venjakob) is shown in Figure 29-7.

The glass substrates are transported on stainless steel belts from the right to the left in Figure 29-7. They enter the spray booth, where two spray guns with special nozzles (high volume low pressure nozzles) are moving perpendicularly to the line direction. After spraying, the substrates move through a flash-off zone into the dryer, which can be heated to temperatures up to 350°C. After cooling at the end of the line, the coated glass panes are taken off and the coating has to be fully densified in an appropriate tunnel or batch furnace. It could be shown by interferometric measurements, that a coating thickness of about 270 nm with a homogeneity of  $\pm 5\%$  could be obtained by adding some high boiling point solvents to the coating sol, usually used for dip-coating. This rather small thickness variation is hard to see with the naked eye. It could also be shown, that the high boiling point solvent could be removed during the thermal densification step without leading to



Figure 29-7. Flat spray coating line (Venjakob) for the deposition of metal colloid containing coatings on flat glass.

a decrease in optical quality or chemical durability of the coatings, compared to similar coatings, prepared by dip-coating without the appropriate high boiling point additive. The line speed for the flat spray process was adjusted to 2 m/min, which is significantly faster than dip-coating.

As another alternative, the so-called flexo-printing technique has been used for the fast deposition of Au colloid containing coatings on glass substrates of 50 cm  $\times$  50 cm in size (Mennig, private communication). The principle of this technique is shown in Figure 29-8.

The coating sol is deposited on a doctor roll by a sol dispenser and is transferred from there to an anilox roll with small cavities. From this roll, the sol is transported to the printing

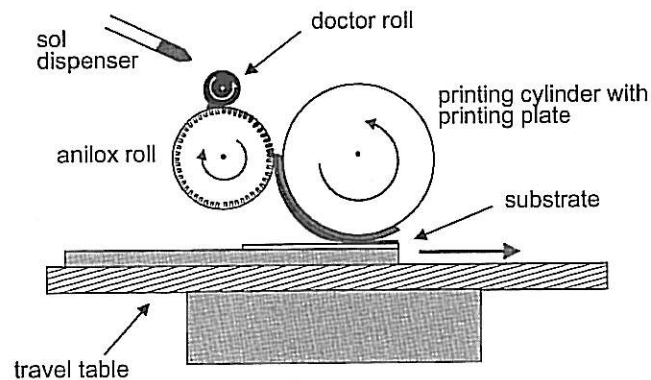


Figure 29-8. Principle of flexo-printing for the deposition of metal colloid containing coatings on glass.

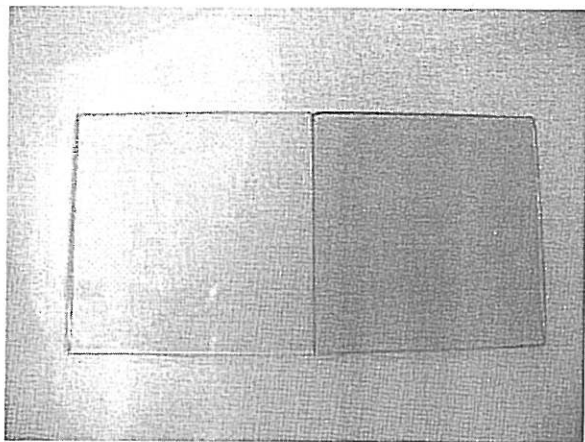


Figure 29-9. Au colloid containing coating on glass deposited by the flexo-printing technique with a deposition speed of 10 m/min (right side) having a thickness of  $220 \pm 11$  nm and uncoated glass (left side).

cylinder with the printing plate. The glass substrate is moved on the travel plate underneath the printing cylinder. During this process, the wet film is deposited. Using coating sols similar to those used for the flat spray application, homogeneous coatings with a thickness of  $220 \pm 11$  nm have been realized, using travel speeds of up to 10 m/min! One example is shown in Figure 29-9.

## CONCLUSION

It can be concluded that metal colloids in glass-like sol gel coatings offer interesting possibilities to obtain highly durable colored coatings on glass. The sol-gel technique allows the preparation of new colors by mixtures of different metals and by high refractive index matrices. Furthermore the synthesis and processing parameters can be well adapted to industrial needs, which will favor further applications in the future. New high-throughput techniques like flat spray coating or flexo-printing offer great opportunities for the cost-effective production of colored coated glass in comparably small, individual series.

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