

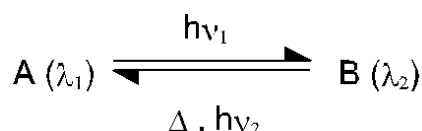
4.2.1 PHOTOCROMIC COATINGS

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1. INTRODUCTION

Photochromism is a part of photochemistry dealing with reversible photochemical reactions. Photochromism was first reported by Fritsche in 1867 [1], who observed that tetracene with air and light produced a colorless material which regenerated to tetracene by heating. Since its discovery, photochromism has received considerable attention and it is still an active field of basic and applied research.

In the early period, photochromism was observed as a color formed under sunlight irradiation during the day, fading away in the night. Scientifically spoken, the phenomenon must be extended to all electromagnetic radiation leading to a general definition: „Photochromism is a reversible transformation of a single chemical species being induced in one or both directions by electromagnetic radiation between two states having distinguishable absorption spectra“ [2-6]. The radiation changes may be induced by UV, visible and IR radiation. Reversibility is an important criterion for the photochromic effect. Figure 1 shows the unimolecular process of a photochromic reaction.



back reaction can be thermally or photochemically activated

Figure 1. Photochromism as a light induced, reversible transfer of a chemical unit between two states with different absorption spectra.

The starting material A (educt), which absorbs the electromagnetic radiation at a wavelength λ_1 , undergoes a transformation into a product B which absorbs usually at a longer wavelength λ_2 . The backward reaction can be activated thermally or photochemically. Forward and backward reactions are running in parallel with different specific reaction rates. Both materials, A and B, are in the electronic ground state, but B is thermodynamically less stable than A.

The photochromic performance is expressed by two characteristic quantities: the darkening ΔA_0 , which is the difference between the absorbance of the color-

less and colored form and the half-fading time $t_{0.5}$, which is the time required for ΔA_0 to decay to 50 % of its initial value after the irradiation is discontinued.

The most common photochromic reactions are of the positive or normal type, in which the initial chemical system comprises a unimolecular A form, which absorbs at a short wavelength (usually in the near UV or blue region) and a B (or colored) form that absorbs at a higher wavelength in the visible spectrum. Bimolecular chemical systems as well as negative or reverse photochromism ($\lambda_{\max(A)} > \lambda_{\max(B)}$) are also possible [7, 8].

There are various classes of photochromic inorganic and organic compounds. Inorganic photochromic glasses can be classified into four groups [9]: rare earth activated silicate glasses [10], silver halide doped borosilicate and aluminophosphate glasses [11-18], silver molybdate or silver wolframate doped borosilicate glasses [19] and copper or cadmium halide doped borosilicate glasses [20-24]. The group of photochromic glasses containing silver halides is the most investigated one. When it is irradiated with ultra-violet or blue light, silver colloids are formed leading to a broad absorption in the visible with a peak around 400 nm. As soon as the irradiation is interrupted, the colloids are destroyed and the absorption disappears. The half-fading time is in the range of several minutes. These processes are not understood completely because questions arise about the role of Cl atoms in the darkened state. As an alternative, pure electronic processes are discussed in [25].

Oxazines [27], pyrans [27], fulgides [28] and dihydroindolizines belong to the group of organic photochromic dyes. Six general categories may be used to classify the mechanisms responsible for the effect: heterolytic/homolytic bond cleavage [29], cis-trans isomerization [30], valence tautomerism, electron transfer systems, pericyclic reactions [31-33] and triplet-triplet absorption [34].

Compared to organic photochromic dyes, the long term stability of Ag halide based photochromic materials is the main advantage. That preparation is described briefly in the next section.

2. STATE-OF-THE-ART OF PHOTOCROMIC GLASSES AND SOL-GEL MATERIALS

Photochromic glasses containing silver halide have been extensively investigated since the first publication by Armistead and Stookey in 1964 [35]. Silver halide colloidal crystallites are embedded into a borosilicate or aluminophosphate glass matrix. The formation of photochromic phases by precipitation of the silver halide crystallites requires an additional thermal treatment (annealing). The formation mechanism of these crystallites is discussed controversially in the literature [17, 36-38]. The growth mechanism is explained as an Ostwald ripening, whereby the average diameter d of the silver halides increases proportionally to $t^{1/3}$. At the beginning of the growth the average diameter of the crystallites is proportional to $t^{1/2}$.

The conditions of the thermal treatment (cooling rate, temperature, time) influence the quantity, the size and the size distribution of the photochromic phases. The photochromic properties of the glasses are mainly determined by the size of the silver halide crystallites, an optimal size being about 10-30 nm [39-41]. Below a critical size of about 5 nm the silver halide phases are not or only slightly photochromic, and when the size is higher than 50 nm, the fading is insufficient [41]. Larger silver halide phases cause a Rayleigh scattering in the visible range depending on the size and the difference of the index of refraction between the particles and the matrix. Not only the kinetic of the photochromic effect is determined by the size of the silver halides, but also the color after irradiation. Glasses containing small silver halide precipitates show a brown color after irradiation due to an absorption with a maximum at 400 nm, characteristic of spherical silver colloids. Photochromic glasses with larger silver halide crystallites darken to a grey or blue violet color. The optical absorption spectra of these glasses are shifted to longer wavelengths [42] compared to those produced by spherical colloids. Their shape is generally ellipsoidal which can lead to a splitting of their absorption maximum [43, 44].

The size of the silver specks formed on the surface of the silver halide crystallites after irradiation is stated in the literature between 1 and 5 nm [42, 43]. There are two types of fading: optical and thermal. During irradiation with light of a wavelength between 550 and 750 nm the electrons are excited leading to the decay of the silver colloids and the recombination of electrons and electron-hole trap centers. In case of thermal fading, the electron-hole trapping centers are thermally excited to deliver their electron-holes. The recombination in the silver colloid centers is described by a tunneling model and electron-hole migration similar to a diffusion process was postulated by Araujo [45].

New synthesis routes for the preparation of photochromic materials are hardly described in literature. Gliemeroth [46] succeeded in the synthesis of photochromic coatings by chemical vapor deposition. He prepared coatings on glass substrates with thicknesses between 150 and 570 nm, but only coatings with a composition in the eutectic region of the ternary Ag-Br-Cu-system showed photochromic properties.

3. STATE OF THE ART OF PHOTOCHROMIC SOL-GEL MATERIALS

The low temperature synthesis of inorganic glasses via sol-gel method allows the incorporation of organic photochromic dyes into the gel matrices [47]. The first incorporation of an organic photochromic dye (Aberchrome 670) into SiO₂ gels was reported in 1986 by Kaufman et al. [48], followed by Levy et al. [49] in 1988 with investigations of the photochromic behavior of spiropyran in silica matrices during the gel-xerogel transition. The results showed, that the local environment of the dye molecules and also the precursor material for the sol preparation have a great influence on the photochromic properties. Preston et al. [50] prepared aluminosilicate sol-gels containing photochromic spiropyran molecules in order to study the photochromic effect by absorption spectroscopy

during the gelation process. The influence of Al_2O_3 content in Al_2O_3 - SiO_2 matrices containing spiropyrans was studied by Nogami and Sugiura [51]. They showed that the photochromic performance decreased with increasing Al_2O_3 content. The investigations of 2,3-diphenylindenone oxide incorporated into aluminosilicate, silica and ormosil sols by Yamamaka et al. [52] showed red colored materials under UV irradiation and back reaction to the colorless form by exposition to visible light with $\lambda > 435$ nm. The photochromic effect of this dye is based on a molecule isomerization. In all three types of materials [51-53], a long lifetime component was obtained (20 s) and in addition, a short lifetime (5 μs) was found in aluminosilicate gels. The gradual decrease of their lifetime with time may result from the increase of the polarity in the gel during aging. Ueda et al. [53] investigated the photoisomerization of 4-methoxy-4'-(2-hydroxyethoxy)-azobenzene in SiO_2 gel films in order to compare it to analogue PMMA films. Furthermore Ueda [54] reported the effect of substituted dye on the photochromic performance.

The feasibility of a sol-gel derived $\text{AgCl}_x\text{Br}_{1-x}$ colloids contained in sodium alumino borosilicate glass powder with photochromic properties was shown in [55, 56]. This powder was obtained by the generation of small silver clusters and colloids in the sol subsequently trapped in the matrix by the gelation step. $\text{AgCl}_x\text{Br}_{1-x}$ crystallites with sizes between 5 and 50 nm in diameter were formed after infiltration of solutions containing Cl^- and Br^- and a heat treatment at about 640 °C. The prepared glass powders darken under UV-irradiation but the recovery had to be activated thermally at temperatures ≥ 150 °C.

The synthesis of coatings of the same matrix is described in [57] and [58]. The starting point was a sodium alumino borosilicate sol. After drying at 130 °C the coatings were exposed to a silver nitrate solution and treated with HCl vapor. The final heat treatment took place at 400 °C. The color of the photoirradiated coatings was brown violet and the transmission at 545 nm (highest sensitivity of the human eye) decreases continuously with increasing irradiation time down to 36 % after 15 minutes (Figure 8).

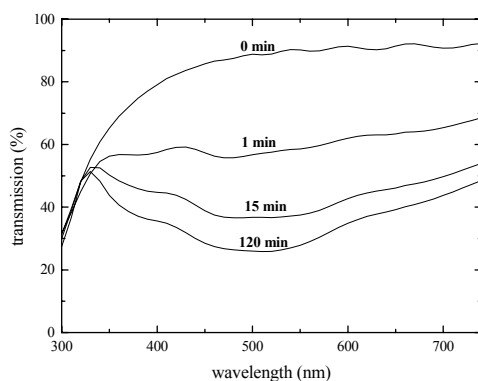


Figure 8. Darkening of the AgCl-doped coating after irradiation (700 W) [57, 58]

In order to obtain a complete fading, temperatures of about 400 °C had to be used. The so prepared coatings were not completely transparent due to a slight scattering which is caused by the transformation of Ag ions into AgCl particles when exposing the coatings to HCl vapor.

An improved synthesis route based on a one-step sol-gel reaction was developed using SiO₂-rich matrices in order to achieve highly transparent coatings on glass with AgCl nanoparticles [59]. In these coatings the silver ions added to the silicate matrix sol are stabilized by complexes such as diamino alkoxysilane N-(2-aminoethyl-3-aminopropyl) trimethoxysilane (DIAMO), which prevent the Ag⁺ ions from spontaneous reduction. Chlorine is introduced into the system by adding 3-chloropropyl trimethoxysilane (CPT) to the sol. During a subsequent thermal treatment, very small Ag colloids (estimated average size of about 1 to 3 nm) are first formed and act as nuclei for the AgCl formation which start at about 200 °C. The Cl⁻ source is the thermal decomposition of the 3-chloropropyl trimethoxysilane. This reaction was applied to a Nanomer[®] system yielding to AgCl crystallites with an average size of about 16 nm as measured by x-ray diffraction. After UV-irradiation (700 W, 15 min) the transmission at $\lambda = 545$ nm decreases from 99 % to 96 % (measured against a silver-free reference sample) in a coating about 0,25 μm thick. A thermal activation between 150 and 200 °C is necessary however to obtain a complete fading within 10 to 15 minutes.

Thus it seems feasible to obtain photochromic sol-gel coatings with thickness about 10 μm showing darkening effects comparable to melted photochromic glasses with a thickness of several mm.

The incorporation of spirooxazine molecules in Nanomer[®] was obtained by Hou et al. [60], who also studied the photochromic properties of photochromic dyes incorporated in aluminosilicate gels during the sol-wet gel-xerogel transformation [61]. The photochromic effect vanishes in the wet gel-xerogel stage of the aluminosilicate gel, while a high photochromic intensity remains almost unchanged for about four months in the Nanomer[®]. For both systems a high color fading speed ($t_{0,5} \approx 2$ s) similar to that in ethanol was obtained, but the photostability was considerably improved. Further investigations with additives were made [62] in order to enhance and to stabilize the photochromic performance of spirooxazine in organic-inorganic hybrid matrices. Addition of fluoroalkylsilane enhances both the darkening and the photostability. It was also shown that a heat treatment is a conflicting factor to the photochromic intensity, photostability and abrasion resistance of photochromic materials. Improved synthesis routes for the development of transparent sol-gel coating material with adjustable photochromic properties for different fields of application are described in [63]. The use of a nanocomposite coating matrix with "hard" and "soft" microstructural units allows the development of photochromic coatings with sufficient free volume for fast switching dyes in combination with macroscopic hard properties. The long term UV stability of photochromic dyes in sol-gel based coatings is one of the crucial points for practical application. The activated photochromic dye is easily degraded by OH-attack, oxidation (O₂ from air, redox reaction with polyvalent components) or degradation by absorption of hard UV light [64]. In order

to improve the photostability, different additives like antioxidants, HALS (Hindered Amine Light Stabilizer) and UV stabilizers were incorporated in the matrix systems. Further the feasibility for obtaining long term UV stabilization for a blue spirooxazine by addition of an UV absorber to the coating matrix has been demonstrated. The influence of tailoring the sol-gel matrices on the kinetic behavior of organic spirooxazines was investigated [65]. The used coating system is compatible with different photochromic dyes like oxazines, pyrans and fulgides and also with surface modified ceramic nanoparticles as filler in order to obtain macroscopic “hard properties“ without changing the photochromic kinetics. A “nonpolar“ spacer did not influence significantly the switching kinetic of the dyes and fast switching times of 2 to 4 s were obtained. On the contrary a “polar“ spacer (aromatic character) showed interactions with the dye molecules, which led to an increase in the switching times of up to 25 s. The retardation of the switching process increased with increasing spacer content and with increasing polar character of the dye molecule.

4. POTENTIAL OF APPLICATION

Inorganic photochromic glasses based on silver halides are currently used for manufacturing photochromic mineral special glass for prescription lenses and sunglasses. They are endowed with a very good durability, but present a slow kinetics and can only be produced as bulk glass with special compositions. Photochromic flat glasses for smart windows cannot be produced, since the glass compositions are not compatible with the float process (evaporation of halides). Consequently the preparation of photochromic coatings is of great importance for many flat glass applications.

The latest research and development in organic-inorganic hybrid matrices containing organic photochromic dyes are very promising and should open a new market and technical innovation. In addition to the application field as coating material for plastics, photochromic coatings on glass lenses could be an alternative to inorganic photochromic ophthalmic lenses. Organic photochromic coatings on glass could further be used in modern art and in the field of decorative applications like window pictures. Also architectural (special double glazing) and automotive glazings (laminated mineral glass car roof) could be innovated that way, but improvement of the long term UV stability of the photochromic effect is necessary.

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