Optical Materials by a Modified Sol-Gel Nanoparticle Process

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1 Introduction

Optical sol-gel materials have been of interest for many years. The reason is that through the preparation of sols with nanoparticulate liquid structures, transparent coatings of many inorganic oxides can be produced [1,2,3]. By using oxides for example with different refractive indices, reflective or antireflective coatings can be fabricated. To obtain stable layers, the gel coatings have to be densified at higher temperatures, in general between 400 and 600 °C. This may be suitable for glass surfaces, but not for temperature sensitive substrates like plastics. In addition to this, if multilayer coatings have to be produced, between each step a densification process has to be carried out before the next coating step takes place. This leads to an unsatisfying situation if industrial low cost processing is required. In addition to this, the dip coating process is not suitable for high speed or large area coating techniques. This is one of the reasons why the sol-gel process never has gained a real high significance for industrial coatings on glass and is limited to special products so far.

Another potential of sol-gel coatings is the embossing of gels before densification. As shown by Tohge [4], the mixture of TiO_2 sols with polyethylene glycol leads to embossable coatings, but due to the low inorganic solid content of such hybrid sols, the height of the embossed structures are in the range of hundreds of nanometers only. As shown by Mennig and co-workers [5], the use of surface modified nanoparticulate SiO_2 sols permits the fabrication of sol-gel thick films (up to 30 µm) with good embossing properties. The surface modification of sol-gel derived nanoparticles in general seems to be an interesting route for the fabrication of "flexible" sols [6, 7]. Nanoparticles are of interest for optics from many reasons, mainly from size (quantum) effects and from scattering effects. Some properties interesting for optics are listed in table 1.

Table 1. Basic properties of nanoparticles interesting for optics

Basic property	effect	application
size	scattering $\gamma_{ext} = 32\pi^4 c \left[\frac{n_p^2 - n_0^2}{n_p^2 - n_0^2}\right] \cdot \left[\frac{r^3}{\lambda^4}\right]$ eq. (1)	glass and transparent polymer matrix nanocomposites for optics
size	quantum size effects in semiconductors	NLO, photocatalysts, UV absorption, fluorescence, photovoltaic
size	plasmon absorption	NLO, colour

As shown in table 1, nanoparticles from metals are of interest for different reasons, for example from their non-linear third order susceptibilities [8, 9] or from their intensive colours based on plasmon surface resonance effects [10]. It could be shown that by complexing ionic precursors of noble metals with aminosilanes a glass like matrix can be obtained by hydrolysis and condensation and that during the heating process, nucleation, diffusion and growth of colloids take place, leading to different colours. In the following paper, an overview over some interesting developments and applications of nanoparticles will be given and discussed.

2 General considerations

2.1 Nanoparticle fabrication

For nanoparticle fabrication mainly gas phase and vacuum technologies are of interest in the scientific literature. However, the largest quantities of nanoparticles presently are fabricated by flame spray oxidation pyrolysis in the areas of SiO_2 (e.g. Aerosil® or Cabosil®). For TiO_2, colloidal routes are used as well as for boehmite or silica sol fabrication, but in general these colloids are not used for processing as powders. Colloidal routes for the fabrication of nanoparticles are known since long time. However, to call this "nanotechnology" only came up recently, since the state of the art for nanoparticles has been improved remarkably [11]. If isolated nanoparticles should be prepared from colloids, meaning that these nanoparticles can be dried and then redispersed, one has to take care of agglomeration. In oxides, in general, surface hydroxyls are present which lead to strong bonds between particles (hydrogen bridges or the formation of metal oxygen metal bonds) and, due to the high surface area of nanoparticles (above 100 m^2/g as a rule), hard agglomerates and redispersion becomes impossible. In solution, colloids in general are stabilized by electric charge stabilization, leading to a pH dependent zeta-potential which also restricts the applicability of sols, especially if they should be processed into polymeric or inorganic matrices. If two charged particles are approached to each other, according to a Sterns theory [12], if the distance between the particles becomes lower than the critical distance, the repulsion changes into an attraction leading to aggregation. This leads to a serious restriction in processing of liquid borne nanoparticles. The third restriction appears if nanoparticles are processed into polymeric or organic matrices. In this case it has to be taken into consideration that the free energy of aggregation never should be lower than the free energy of dispersion, which means that the interfacial free energy between the liquid and the particles has to be lower than the interfacial free energy between two particles. The fourth problem is related to the nucleation and growth process in solution which in general does not follow the La Mers model [13] which should lead to narrow particle size distribution by tailoring the nucleation frequency. For the fabrication of nanoparticles by sol-gel processes, the nucleation should take place over a long period, due to the permanent formation of "unsoluble" nuclei. Narrow particle size distributions have been found in many cases, which were narrower than to be expected for a permanent nucleation process. To explain this effect, various theories have been discussed [14, 15]. If the surface free energy during the nucleation and growth process can be controlled by surface modifiers, as shown elsewhere [16], the interfacial free energy is governing the particle size and particle size distribution. In this case narrow particle sizes can be obtained. Beside the size controlling effect, also the chemical reactivity of the nanoparticles can be tailored, if the surface modifiers are bifunctional, as is schematically shown in figure 1. In addition to this, the surface modifiers can protect the nanoparticles from agglomeration during further processing, for example by hydro-thermal treatment, for example, in order to obtain high crystallinity [17]. And last but not least, the surface modifiers can provide a compatibilisation effect to any matrix if they are chosen properly and thus provide a perfect dispersion. Perfect dispersions of nanoparticles in transparent matrices is an indispensible requirement to obtain high transparency. As shown in equation (1), besides the differences in refractive index between particle and matrix, the particle diameter and the wave length are the governing parameters for the scattering loss.

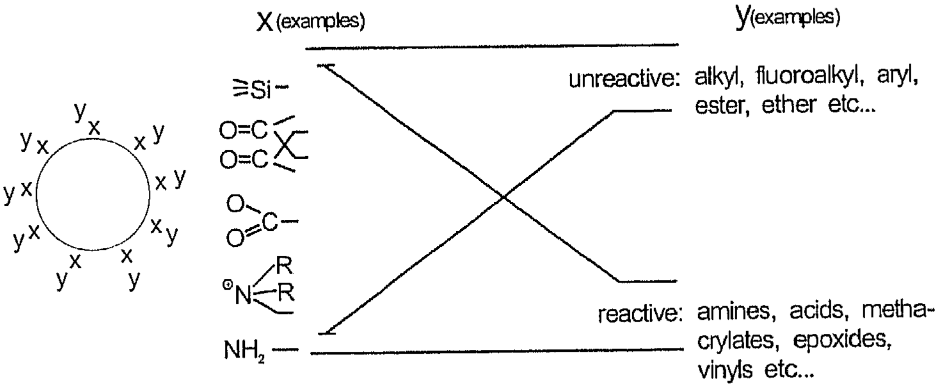

Figure 1 Examples for surface modified nanoparticles (reactive and unreactive modifications)

The use of any kind of nanoparticles opens up an interesting new material strategy for optical materials, the so called optical nanocomposites or nanomers (nanoparticle reinforced polymer matrix composites). As also shown elsewhere, production routes for nanoparticles have been developed which lead to fully redispersible nanoparticles to be dispersed in various matrices. On the other hand, the surface modified nanoparticles also can be used in situ for the fabrication processes. In these processes, the nanoparticles are precipitated and stabilized in situ, e. g. by silanes [18]. These systems also have been used for the fabrication of coatings [19].

2.2 Processing and coating

For optical coatings, the materials processing and the coating and shaping technology is extremely important. Most of the work is carried out by spin or dip coating processes. For spin coating the Landau-Levich equation has been very successfully used for sols and colloids [20] equation (2). Using this approach, the film thicknesses can be calculated within the range of 5 nm of accuracy.

$$h = 0.94 \cdot \frac{(\eta \cdot v)^{2/3}}{\gamma_{LV}^{1/6} (\rho \cdot g)^{1/2}} \quad \text{eq. (2)}$$

h = coating thickness η = viscosity
γ_{LV} = liquid-vapour surface tension ρ = density
γ = gravity

Similar results are obtained from the spin coating process as long as the radius or curvature is not too small (eq (3), Meyerhofer equation [21]).

$$h = (1 - \rho_A / \rho_{A_0}) \cdot \left(\frac{3\eta \cdot m}{2\rho_{A_0} \cdot \omega^2}\right)^{1/3} \quad \text{eq. (3)}$$

ρ_A = mass of volatile solvent per unit volume
ρ_{A_0} = initial value of ρ_A h = final thickness
η = viscosity ω = angular speed
m = evaporation rate of the solvent

The formula is only a rough approach, since the evaporation rate m is temperature dependant and it is not possible to avoid a cooling down by the evaporation during coating.

For planar substrates, especially if anti-reflective coatings have to be prepared, the optical systems in general consist of the substrate and multilayer coatings on both sides. Based on the differences in refractive indices, optical systems can be calculated according to [22]. It has been shown by Schröder [23] in 1969 that by use of angles different from the 90° angle during the dip coating process different layer thicknesses now can be obtained on the top and the bottom side which in general, according to model calculations, lead to a decrease of the numbers of layers necessary for obtaining a specific optical effect compared to coating systems with the same thicknesses on both sides. That means by using an angle dependent dip coating (ADDC) process, process steps and costs can be saved if appropriate calculations are carried out. The question arises whether the angle dependant dipcoating can be used for the coating of curved substrates for optical layers or not. In figure 2, the principle of the angle dependant dipcoating process is shown. One clearly can see from this figure that the variation of the thickness with increasing angle leads to an increase of thickness on the upper and to a decrease of thickness of the lower side of the substrate. However, if small angles are used, the thickness variation is very small, so that calculations have shown that eye glass lenses, which show an angle variation, should be able to be coated with thickness variations not disturbing the optical effects, e. g. anti-reflection. This is explained by the figures 3 and 4. In figure 3, the results of the determination of the film thickness as a function of the angle and the withdrawal speed is given. It is shown that the film thickness increases on the top and decreases at the bottom as expected. It also shows that the thickness change at the top is more sensitive to the withdrawal speed than at the bottom [24]. In figure 4, the dependance of the film thickness is given as a function of different inclination angles and it can be seen that the change in thickness is relatively small with varying angles and in general is below 10%. These estimations have been carried out in order to decide whether it is possible to carry out wet coatings on curved eye glass lenses since in this case, the angle also changes during the dipcoating step, as shown in figure 5. But the thickness of the coatings, especially in the range between 90° and 80° only changes within ≤ 10%, which is considered to be sufficient for optical coatings. This leads to the conclusion that eye glass lenses can be coated by dipcoating processes within the requirements of optical coatings for interference layer if coatings with sufficient differences in refractive indices are available and wet coating and high reflective systems are possible. Since the vast majority of eye glass lenses are made from polymers such as CR 39 and variations, the fabrication of anti-reflective coatings by dipcoating processes only makes sense if the coatings can be cured at temperatures below 100°C and are scratch-resistant at the same time. This topic will be discussed in chapter 3.1 in detail.

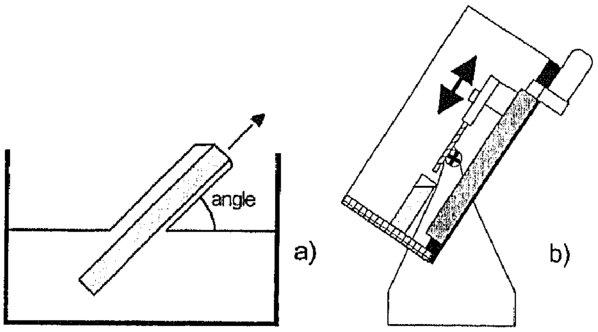

Figure 2 Scheme of the angle dependant dipcoating; a: priciple; b: apparatus

As already mentioned above for large area coatings, dipcoating is not the best process. For this reason, detailed investigations have been carried out for the development of spray-coating process providing a high optical quality. The application of spin-, spray- or spray-spin coating is limited to special cases [25,26] and smaller substrate sizes. The main advantage of the dip coating technique is that the coating thickness can be controlled by the viscosity of the coating sol and the withdrawal speed very precisely. Disadvantages are limited sol pot lives, low pH values for stabilizations of sols leading to equipment corrosion, handling of large panes and vibration-free equipment.

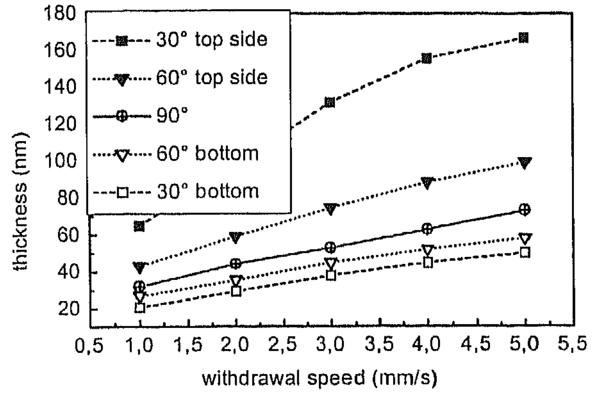

Figure 3 Coating thickness on the top and bottom side for angle dependant dipcoating of a TiO_2 sol with 15 g/l solid content on glass. Curves calculated using data from [24].

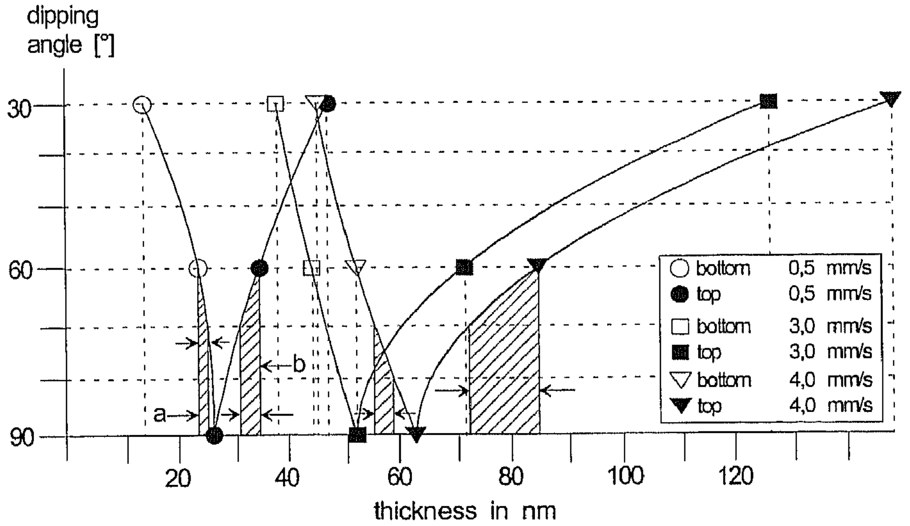

Figure 4 Principles of the process of the angle dependent sol-gel dip coating and dependence of the film thickness as a function of the angle

Since withdrawal speeds are in the range of cm/min, long processing times are required. For example the dip coating process of a 1 m x 1 m glass pane takes about 10 - 15 minutes [27] under industrial conditions. For this reason, spray coating is an interesting alternative if coatings with optical quality in the $\lambda/4$ regime can be realized. Especially the flat-spray coating technique would offer a high throughput. From the state of the art, this technique has only been applied for coatings with thickness in the µm range and not for optical coatings of about 100 nm in thickness. For this reason, investigations have been carried out to develop optical coatings by an automized flat spray technique. As a model system, a SiO_2/PbO/Au system has been chosen [28]. The coating sol was synthesised by preparing a mixture of GPTS (glycidoxypropyltrimethoxysilane) and TEOS (tetraethoxysilane) as SiO_2 precursors and $Pb(ac)_2$ in methanol as lead source (Si : Pb = 7 : 1). Au^{3+} ions were introduced as a complex with DIAMO (N-(2-aminoethyl-3-aminopropyl-trimethoxysilane)) in a concentration of 1.26 weight-% and a Au/DIAMO ratio of 1. After synthesis the sol was diluted (1 : 3) with a mixture of ethanole : isopropanole : n-butanole = 1 : 1 : 1. As additives with low vapour pressure tetraethyleneglycole and butylglycole were added in a concentration of 5 vol.-% each. The flat spray machine [29] is schematically shown in figure 6. The coating is applied in a closed spray booth using 2 high-volume-low-pressure spray guns (Krautzberger HVLP), mounted crosswise on one axis, moving perpendicularly to the direction of substrate transport with a fixed programme. A water curtain is flowing under the conveyor belt and 7000 m^3/h filtered air are circulating in the spray booth for mist control. After passing a flash-off zone, the coating were dried at 150 °C for 15 min and than fired with 150 K/min up to 450 °C, kept for 30 min at this temperature and than cooled down to room temperature within 10 h. In a preliminary screening step [30] the dilution of the coating sol developed for dip-coating was adjusted by manual spraying and visual characterisation of the coating obtained after drying and densification respectively. Both the compounds and their ratio used for dilution were varied resulting in a mixture of ethanole, isopropanole and n-butanole in a ratio of 1:1:3. In case of this mixture the most promising spray coating tests were performed by adding it to the dip-coating sol in a ratio of 1:3. On this basis, flat spraying investigations were carried out. Although the spray coating parameters like spray distance, material pressure, atomising pressure and setting of the spraying guns were varied systematically, only coatings with inhomogeneous thickness (cloudy, stipy, wavy) were obtained. It was assumed that the evaporation of the solvents was too rapid in the µm range droplets, so that no homogeneous liquid film was formed on the substrate. In order to overcome this problem tetraethyleneglycole and butylglycole were used as additives showing a low vapour pressure at room temperature [31,32]. The ratio of tetraethyleneglycole to butylglycole was optimised by visual control of the appearance of the coatings. The best results were obtained using a mixture of tetraethyleneglycole and butylglycole in a ratio of 1:1 and in a content of 10 vol.-% in the coating sol. Both thickness and unevenness of a corresponding coating on float glass densified at 450 C were determined. Figure 7 shows both an interferometric measurement and a FEG-SEM micrograph of such a coating. In the mapping on the left it can be seen that the unevenness of the coating on an area of 80 x 80 mm^2 is less than ± 5%. Besides this, the homogeneity of the coating in the sub-μm range can be demonstrated by FEG-SEM (right side) indicating a high quality coating with a thickness of about 270 nm which was confirmed by profilometry. This means that a process has been developed which permits the high-speed fabrication of wet coatings on flat glasses with rather cheap investment costs compared to vacuum deposition techniques.

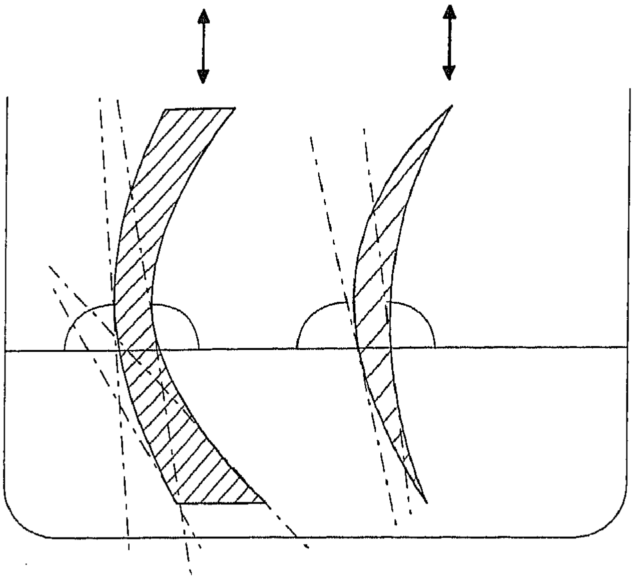

Figure 5 Different and varying angles during the dipcoating of eye glass lenses

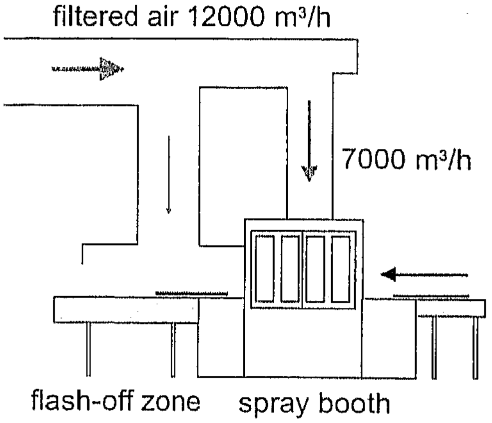

Figure 6 Scheme of the flat spray coater (Venjakob) used for this study

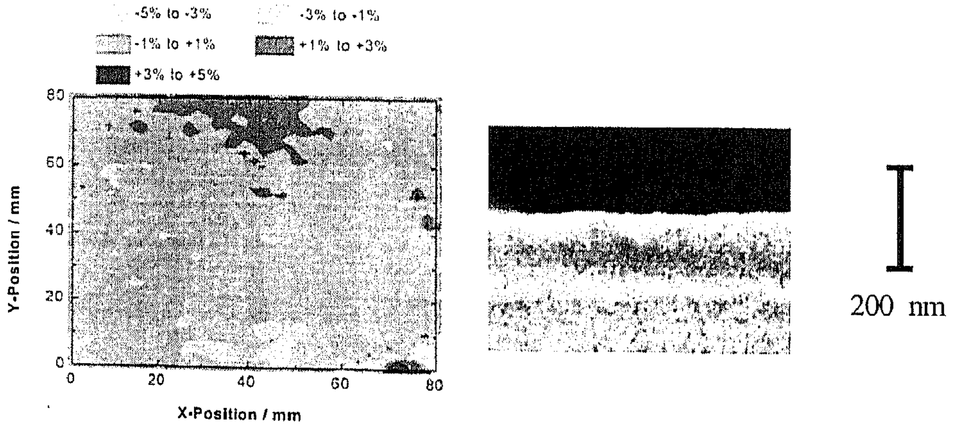

Figure 7	left side:	Mapping (80 x 80 mm^2) of a sprayed Au-colloid coloured coating on float glass (35 x 35 cm) applied by using a coating sol containing: tetraethyleneglycole butylglycole = 1:1; 10 vol.-%.
	right side:	FEG-SEM micrograph of the coating on the left (cross section cut) indicating a thickness of about 270 nm also checked by profilometry

3. Optical coating fabrication

3.1 Interference layers

Sol-gel coatings have been used for the fabrication of anti-reflective coatings in [33]. A multilayer anti-reflective system has been used. In [34] a porous gradient index single step coating has been developed. If high performance reflective or anti-reflective systems are required, multilayer coatings are necessary. For this reason, the Sol-Gel process is difficult as shown by the state of the art and multilayer coatings have to be fabricated step by step with firing steps in between. This reduces the production speed remarkably. That is one of the reasons why this type of coating technology never has gained a large significance in industry. The firing process is necessary in order to avoid dissolution of the sol-gel films in the acid sols. For this reason, as shown in [4] if nanoparticles are coated with reactive molecules, a photopolymerization process can be carried out. In this technology, an in situ coating of TiO_2 and SiO_2 particles by reactive silanes is carried out leading to a particle size of 4 nm in the case of TiO_2 and 10 nm particles from SiO_2, as determined by photon correlation spectroscopy (PCS). The scheme of the process is shown in figure 8. After preparation of the sols and by the addition of photocatalysts for the polymerization of methacryloxy groups or epoxy groups, the layers can be solidified by simple UV irradiation. The details of the processes are described in [35]. The interesting part of the process is that no heating is necessary after each coating and, after finishing all coating steps, a single heating leads to the final interference system without crack formation or loss of adhesion. On plastics, for example, after simple photopolymerization, the interference layers are obtained.

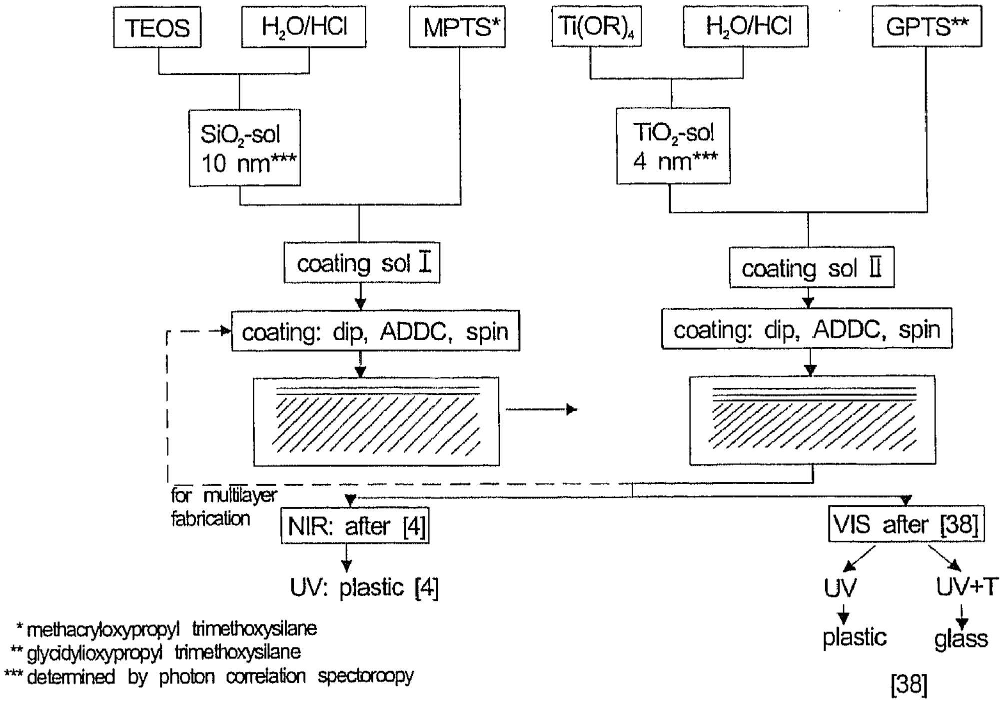

Figure 8 General reaction scheme for the fabrication of interference layers by using polymerizable nanoparticle technology

In figure 9, a stack of five layers on glass is shown as obtained by high resolution scanning electron microscopy. The surprising fact of this technique is that with TiO_2 reactive index numbers up to 1.92 are obtained on plastic substrates which ressembles a package density of about 90% by volume. Compared to conventional sol-gel processing where highly porous gels are obtained, this is a high number which permits to produce anti-reflective layers. The NIR regime on plastics and on glasses is also accessable by this technique. These coatings are prepared by the ADDC-process and it could be shown that the computer simulation of the curves fits almost precisely with the measured curve (figure 10).If the coatings are employed on hard coatings as after [36], the prepared coatings become very scratch resistant compared to uncoated plastics. In a taber abbrader test after 1000 cycles, the haze is only 7% (compared to conventional UV-curing hard coatings on polycarbonate, for example, with 15 - 20% haze). This shows that very interesting optical coatings can be made by the technology of polymerizable nanoparticles. In figure 11, a HR-SEM micrograph with five layers prepared by the described technique on glass after a single firing step is shown.

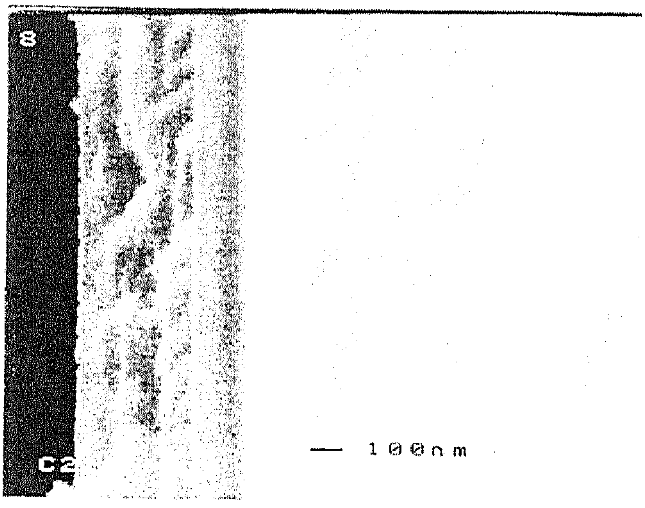

Figure 9 HR-SEM micrograph of a 5-layer stack after firing on glass obtained by polymerizable nanoparticles

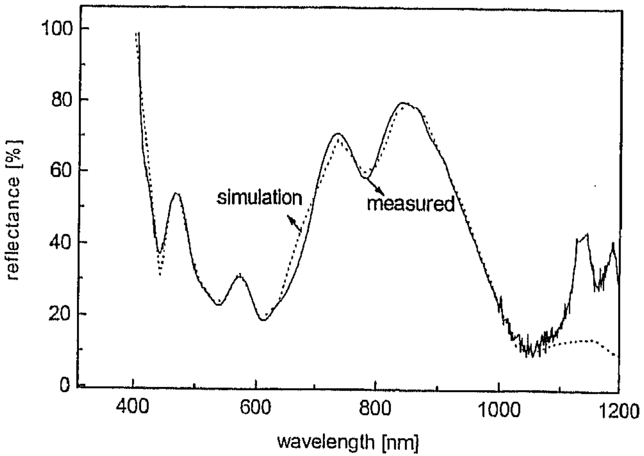

Figure 10 Simulated and measured AR curves [after 38]

3.2 Thick films and embossing

The fabrication of thick films by sol-gel techniques has been described in [5]. The mechanisms for the fabrication of the films with up to 13 μm thickness in a one-step coating technique have been investigated in detail elsewhere [37]. It was shown that by the surface modification of SiO_2 nanoparticles in the range of 6 to 10 nm by methyl group containing silanes (according to figure 11), the flexibility and the relaxation behaviour of the sols is considerably increased. It also could be shown that this effect only is obtained if nanoparticulate SiO_2 sols are treated with methyl group containing silanes. If the nanoparticles are not present, the methyl group containing silanes are forming a three dimensionally cross-linked network which reduces the flexibility and relaxation behaviour drastically. This is schematically shown in figure 12. By using thecoated nanoparticle approach, the film thickness in a one-step coating can be increased from 2 to 14 μm after 500°C heating. The optimization of this process resulted in film thicknesses with particulate gels of up to 50 μm. These films are very soft and now can be patterned by silicon rubber replicas of master stamps or patterns. Due to the flexibility of the silicon rubbers, rolls can be fabricated or curved substrates can be patterned. The interesting part of this technology is that during the densification almost no change of the pattern takes place. This is attributed to the fact that during the densification no viscous flow sintering occurs, so that sharp edges are maintained during the process. This so-called soft gel film (SGF) embossing technique has been used for the fabrication of defractive gratings, V-grooves for fiber to chip-coupling, light traps for solar collectors or glass holograms on coated metals. In figure 13, an overview over results of the SGF technology is given. Due to the densification at 500°C, the SiO_2 is dense up to 98.5%. This is due to the low sintering temperature of the 6 to 10 nm particles. The burnout of the methyl group starts only at 450°C, leaving extremely small pores which close between 450 and 500° [37]. With this technology, it is possible to produce optical micropatterned coatings, consisting of SiO_2. Similar approaches have been carried out with TiO_2 which show that this principle can be generalized to different compositions. The described soft gels also successfully have been used as binders for thick film pastes to print decors, but also functional patterns. To print very fine lines is an attractive feature for electrical contacting; for example, transparent ITO coatings for printing on glass. To obtain very fine lines, the use of glassfrits is difficult from two reasons.

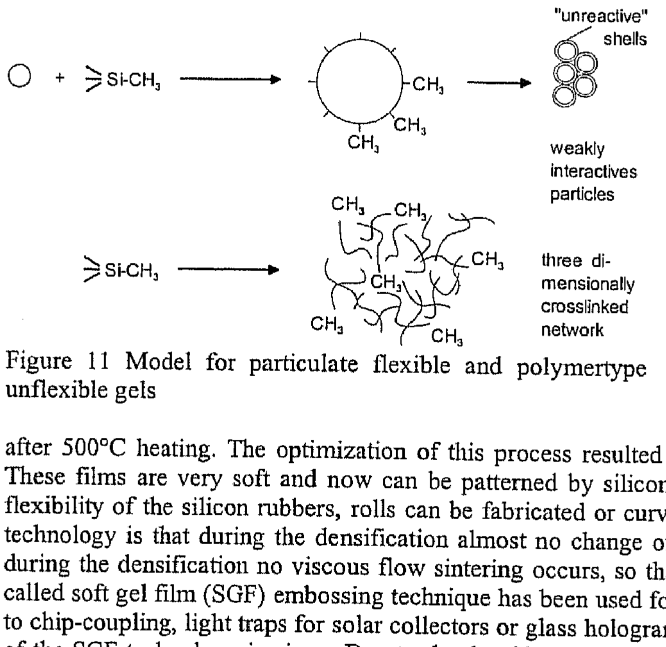

Figure 11 Model for particulate flexible and polymertype unflexible gels

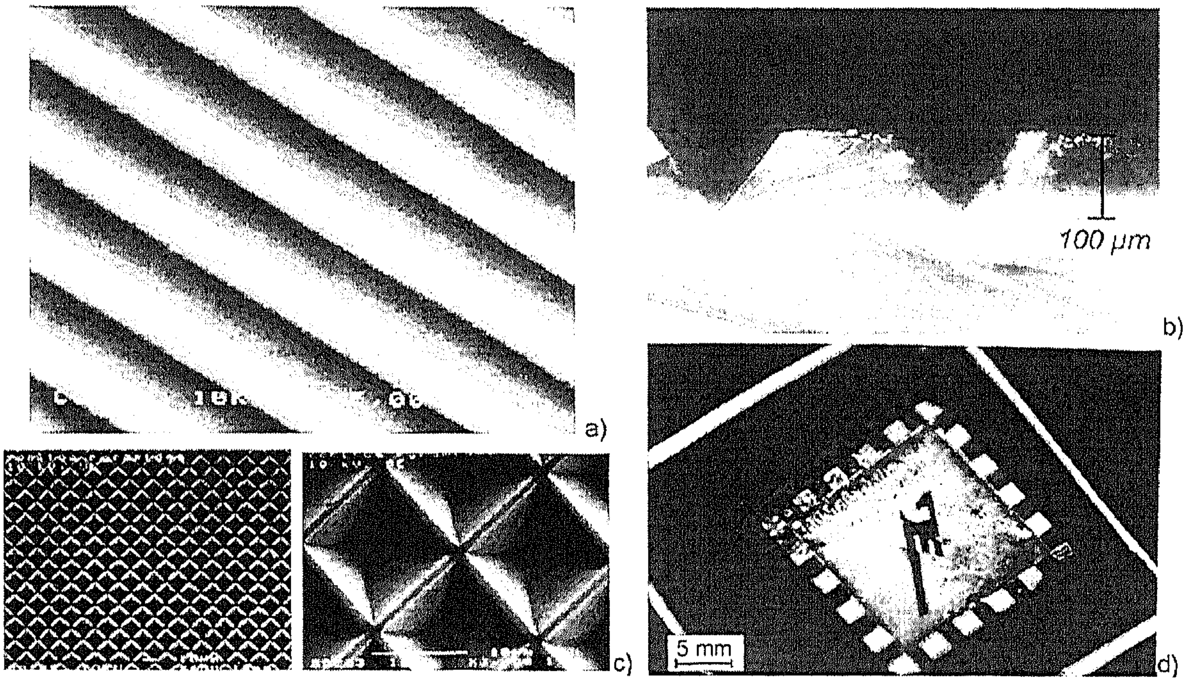

Figure 12 Overview over the glass embossing technology using the SGF method

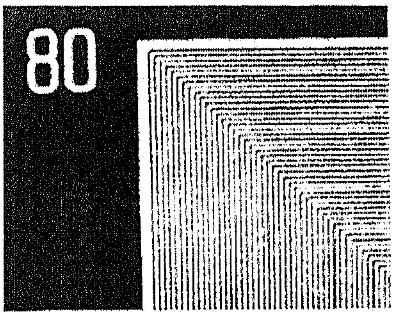

Figure 13 Examples for the printing of very fineline of conductive silver on glass; line width: 80 μm

First, relatively high amounts of glassfrits have to added in order to densify the conducting metal (e. g. silver) containing printing pastes to percolating highly conductive system. And second, due to the viscose flow sintering, a line widening of the lines during the densification cannot be avoided as a rule. Printing pastes have been fabricated containing 98 weight % of silver, particles of a about 20 μm particle size and a mixture of the nanobinder as described in [38] containing about 25% of SiO_2 6 nm particles, surface-modified with methyltriethoxy silane, TEOS or MPTS, respectively, and terpinole as a viscosity controlling agent. With this system, very fine lines could be printed as shown in figure 14. Glass plates of about 80 by 60 cm^2 (figure 15) have been printed on a large area printing equipment in an one step printing process. After firing, the lines are stable against environmental attack and have shown conductivities comparable to commercial available conductive systems. On large area, the fine lines are almost invisible and do not disturb the vision through the glass panes.

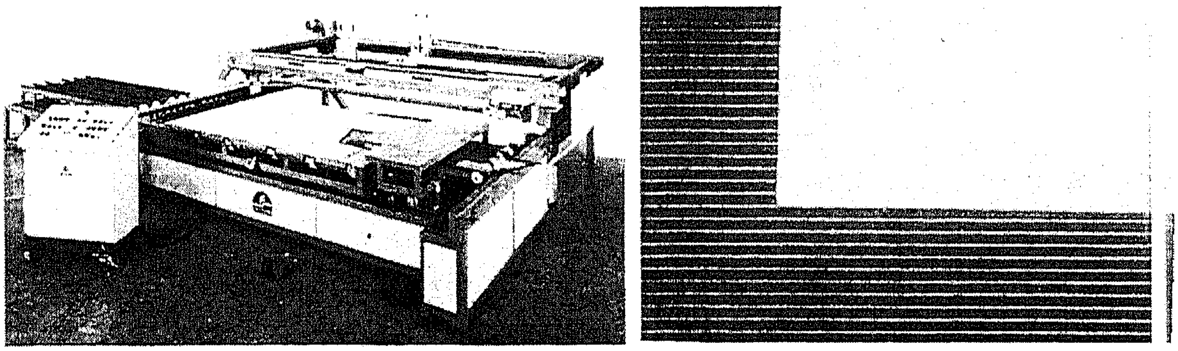

Figure 14 Large area fine line printing on glass using industrial equipment, size: 60 x 80 cm^2

4. Metal colloids for colours on glass

Metal gold colloids are known since centuries (gold ruby glass). In this process, gold salts are mixed to the glass melt and in an anealing process, the gold ruby colour is developed by nucleation and growth. Similar processes are known from silver which leads to a yellow type of colour. For eye glass lenses made from glass, which still has significance in the eye glass industry, this type of colours glasses are not suitable, since, due to the varying thickness of the optical glasses, the colouration is not homogenous. For this reason, a technology based on colloid or ionic coloured metal or metaloxide systems has been developed to be employed in sol-gel films on top of eye glass lenses which should lead to homogenous colouration. As shown in [39] colloid and Co^{2+} ion containing coatings have been developed for obtaining different colours. This is shown in figure 16. As one can see from this figure, a wide variety of colours can be obtained like green, brown, red, grey and blue. For the coating matrix composition, lead silicate glass with a ratio of Si to Pb = 7:1 has been used since the Tg of these systems is in the range between 500 to 520°C. According to the experience in densifying sol-gel films [12], it was assumed that at 480°C a sufficient densification of the lead silicate film for practical use could be obtained. As shown in [39], the Tg can be selected by choice of the SiO_2 to Pb ratio. On this basis, an industrial process has been developed. The scheme of the process is shown in figure 17, and in figure 18 the processing parameters and the firing curve is shown. The coating thickness is about 200 nm and it has to be mentioned that all colours can be obtained in the desired intensity using the same firing procedure and ambient air, so that very small series also can be produced without problems. The colours are very homogeneous and don't change after heat treatment (300°C, 7 days), survive a climate test of 7 days at 40°C and 95% (r. h.), show a good chemical resistance against 1 N NaOH und 1 N H_2SO_4 for four hours at room temperature without changing. They are stable in ultrasonic cleaning machines at 50° for 3 minutes and are very scratch-resistant, (no change after the rubber test). This example shows that by the development of metal colloids in thin glass films, colouration of glass with very stable are possible. The technology has been successfully introduced into the market.

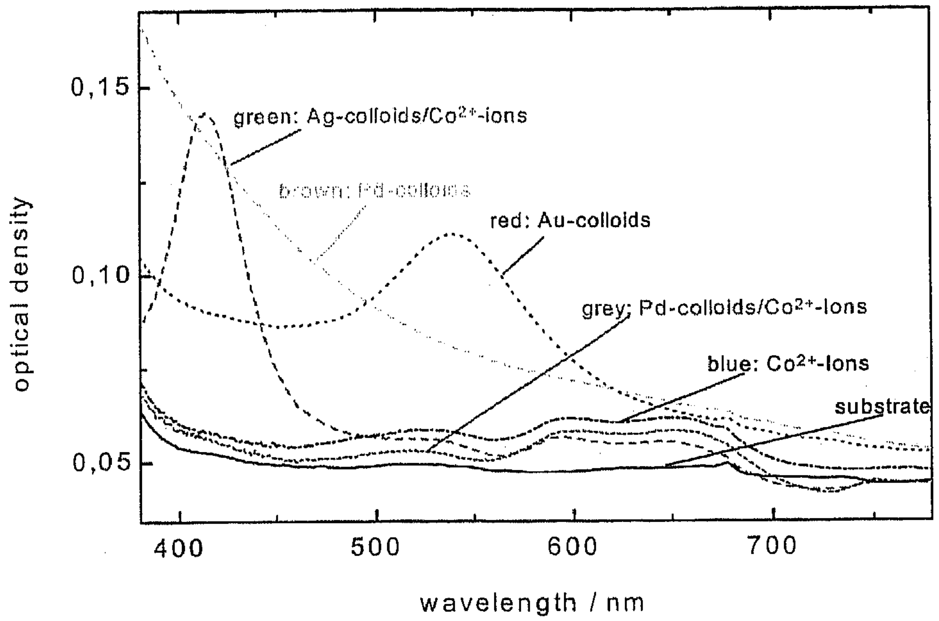

Figure 15 visible spectra of metal colloid and Co^{2+} containing lead silicate glasses.

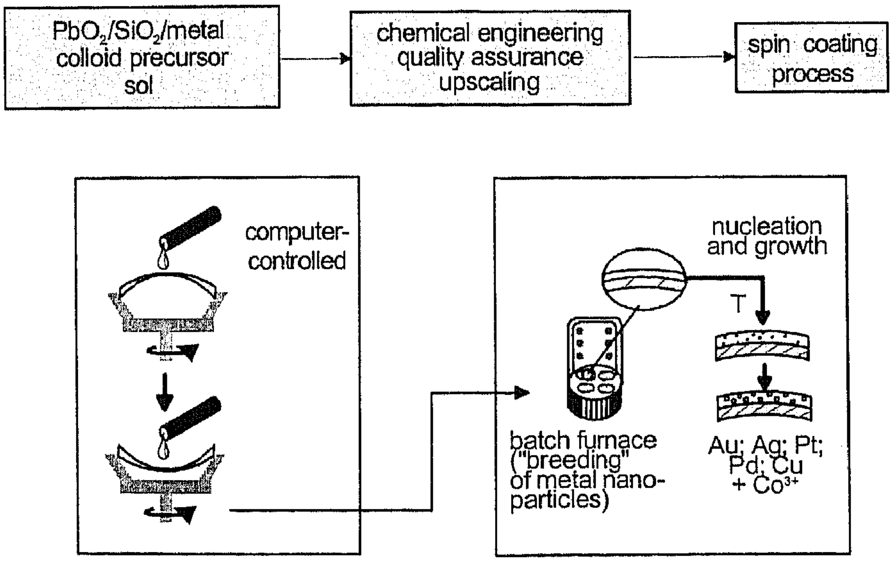

Figure 16 Production scheme for the fabrication of colloid coloured eye glass lenses

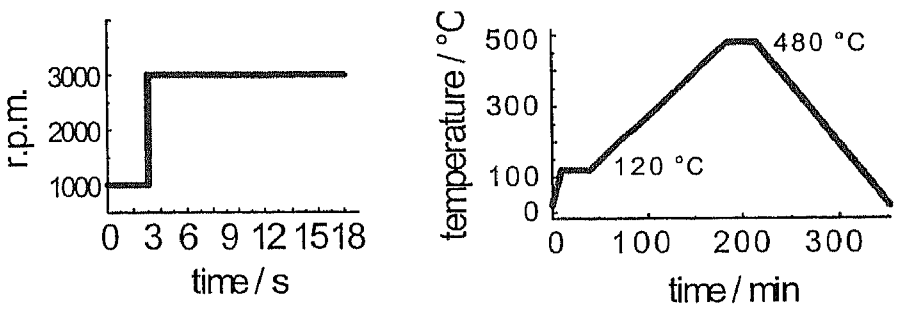

Figure 17 Processing of the lead silicate films: Spin-on process and firing curve in ambient air (identical for all four colours according to figure 16

5. Conclusion

It can be concluded that the use of sol-gel derived nanoparticles leads to interesting new materials and systems for optics. The basic principle, to combine transparent matrices with nanoparticles in sizes below remarkable scattering losses opens up new materials technologies. The processing is almost as simple as sol-gel processing, and the use of polymerizable nanoparticle even leads to high performance coatings by using simple polymer techniques.

6. References

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