

Sol-gel processing of titanium-containing thin coatings

Part III *Properties*

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Some investigations of the thickness, spectral transmittance and reflection, refraction index, abrasion protection, ageing, boiling-water and alkaline-solution treatment have been carried out on coatings deposited by the dip-coating process on a glass substrate. As a starting system, $\text{Ti}(\text{OBU}^n)_4\text{-C}_2\text{H}_5\text{OH-H}_2\text{O}$ was used. The dependence of the properties of the coatings as a function of composition, dipping speed, and the number of deposited layers on the conditions of thermal treatment, was investigated. Introducing 3d-transition elements into the sol solution causes a stable colouring effect, thus decreasing the spectral transmittance of the layers. A correlation between the data from the properties investigated and the structural characteristics of the layers has been made.

1. Introduction

It has been shown [1] that oxide titanate coatings with or without modifier may be successfully synthesized through the sol-gel method. As a starting system, $\text{Te}(\text{OBU}^n)_4\text{-C}_2\text{H}_5\text{OH-H}_2\text{O}$ was chosen. The gel formation concentration range was defined, as well as the boundaries of formation of stable layer structure and the sol-solution immiscibility dome. Some structural characteristics [1] were also defined, and detailed X-ray photoelectron spectroscopy (XPS) investigations were carried out on the chemical composition and valency state of the elements in pure titanate and in titanate modified by SnO_2 , Fe_2O_3 and SiO_2 coatings [2].

The most accurate studies were performed with compositions in the $\text{TiO}_2\text{-SiO}_2$ system, with respect to both synthesis of stable bulk samples and of coatings. It is well known that coatings from the system possess antireflective properties, while coatings on SiO_2 -bases containing transition metal oxides show interesting colour effects [3, 4]. Titanium-containing thin films, applied in building architecture and the car industry as sun-protection glasses, have been investigated by Dislich [5]. Yoko *et al.* [6] report the additional protection with modified titanate coatings of a TiO_2 electrode obtained through the sol-gel technology. Several authors [7–9] have investigated the thickness, optical characteristics and chemical durability of modified titanate coatings in relation to their chemical composition and the technological production conditions.

The present work aimed to study some chosen properties of TiO_2 -based thin layers, obtained through sol-gel technology using the dip-coating process on a glass substrate, and to investigate the vari-

ations in thickness and optical properties with the dipping speed and the number of the consecutively deposited layers. It was also aimed to investigate some important physical and chemical properties of the coatings, e.g. the integral transmittance and reflection ability, the mechanical stability and chemical durability, etc. A correlation between the properties investigated and the structural characteristics was sought; the latter was discussed in Parts I and II [1, 2].

2. Experimental procedure

Titanate thin layers of the initial composition presented in Table I were investigated. The technology for the preparation of ready-for-dip process sol solutions was described in Part I [1]. All coatings obtained were dried at room temperature and tempered at 500 °C for 10 min. The transparency and homogeneity of the coatings were read visually and spectrophotometrically. Part of the samples were characterized by SEM (Jeol JSM-T200) to determine their uniformity and surface defects.

Spectral transmittance, refractive index and coating thickness were studied as a function of the dipping speed, the number of consecutively deposited layers, as well as a function of the thermal treatment temperature. The thickness and the refraction index were taken ellipsometrically on a He-Ne laser device, constructed at Sofia University [10, 11] (a second thickness test was carried using a Talystep, Rank Taylor Hobson, UK to compare the results). Transmittance and reflection spectra were taken with a spectrophotometer type SPECORD UV/VIS and NIR (Carl Zeiss Jena, Germany).

TABLE I Sol compositions

Code of composition	Ti(OBu ⁿ) ₄ (mol %)	C ₂ H ₅ OH (mol %)	H ₂ O (mol %)	Second component (mol %)	Coatings in oxide composition (wt %)
001	3.0	97.0	–	–	100 TiO ₂
002	3.0	85.0	12.0	–	100 TiO ₂
004	4.5	95.0	–	0.5 (SnCl ₄)	82.54 TiO ₂ 14.96 SnO ₂
008	9.9	83.0	6.0	1.1 (Fe(NO ₃) ₃ ·9H ₂ O)	90.48 TiO ₂ 9.52 Fe ₂ O ₃
009	10.0	82.0	3.0	5.0 (Fe(NO ₃) ₃ ·9H ₂ O)	66.70 TiO ₂ 33.30 Fe ₂ O ₃
012	10.0	85.9	3.0	1.1 (Mn(CH ₃ COO) ₂ ·4H ₂ O)	91.0 TiO ₂ 8.9 MnO
013	10.0	84.5	3.0	2.5 (Mn(CH ₃ COO) ₂ ·4H ₂ O)	81.84 TiO ₂ 18.16 MnO
103	1.2	50.0	40.0	8.8 (C ₂ H ₅ OH) ₄ Si	15.35 TiO ₂ 84.65 SiO ₂

Tests for defining ageing, abrasive protection, boiling-water and alkaline-solution treatment, were carried out according to the literature [12] for six identical samples of dimensions corresponding to the parameters of the spectrometer (the standards adopted here and valid for the moment (ISO, ASTM, DIN) for glass properties determination are not suitable for thin-layer investigation, therefore samples were tested according to the branch recommended standard [12]). The suitable coatings of high quality intended for treatment as sun-protective glasses for architectural building purposes would possess transmittance spectra differing less than 6% before spectrophotometry was carried out.

Layer ageing ability was defined [12] for two sets of samples. For the first series the samples were positioned at 500 mm from a 900 W mercury lamp for 6 days, and the second series were put in a drier at 110 ± 1 °C at atmospheric humidity for 6 weeks, after which both sets were spectrophotometrically tested and then compared.

Abrasion protection was defined for six samples tested on a polisher covered with a thick cloth rotating at 100 000 r.p.m. at a pressure of 1500 N m⁻². Subsequently, spectrophotometry was carried out and finally a comparison was made of results from before and after the test.

To define the boiling-water resistance of the coatings, samples were placed vertically in a plastic vessel. To avoid touching and sticking, glass sticks were positioned between the samples. Distilled water was then poured over the samples until they were entirely covered. The vessel was heated to boiling point while the water level was kept constant throughout the test by adding small quantities. After 1 h the samples were removed, dried on filter paper and left for 30 min at standard conditions (room temperature 13–35 °C and air humidity 45%–75%). Then spectrophotometry was carried out and the spectra compared. For a quantitative analysis of the sample, an extract solution was subjected to an ICP–AES test [13] on a ICP spectrometer (Spectro Analytical Instruments, Germany).

The alkaline-solution resistance of the coatings was investigated by placing samples in a glass vessel in the vertical position, not touching one another. They were covered with a 1% solution of sodium and potassium phosphates, and the vessels were then placed in a boiling-water bath. After 30 min the glasses are removed, washed, dried on filter paper and left for 30 min at standard air conditions to stabilize. Transmittance spectra did not differ more than 6%.

3. Results and discussion

3.1. Thickness and optical properties of the coatings

It is well known [14] that the coating thickness depends mainly on the concentration of the solution, the speed and angle of dipping, the temperature and duration of the thermal treatment. Fig. 1 shows the dependence of the thickness of consecutively deposited layers on the dipping rate of the process, for a sample of code 001. It is clearly seen that on increasing the rate of dipping the thickness of the samples also increases. A high dipping speed predetermines the outline deposition of comparatively thick coatings which, because of internal tension during the drying process, tend to crack. This is overcome by the consecutive deposition and firing of thin layers to form coatings of the desired thickness.

The dependence of the thickness of the coatings on the number of deposited layers at different dipping rates is presented in Fig. 2. It is seen that for a given dipping rate the thickness of the coating is proportional to the number of deposited layers, because on increasing the dipping rate the slope of the curves is also increased. The results obtained correlate with investigations cited elsewhere [15, 16].

It was proved [2] that the structure of titanate coatings during the heating process is influenced by thermal diffusion from the glass substrate towards the layer. On a substrate free of alkaline ions (e.g. sapphire substrate), TiO₂ crystallizes as the anatase phase, while at temperatures up to 1000 °C, the predominant crystalline phase is rutile [1]. In the case of substrates

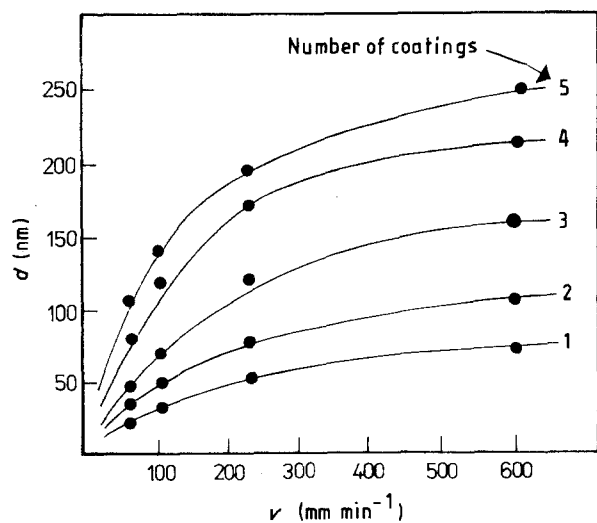


Figure 1 Thickness of the coatings versus dipping speed for 1, 2, 3, 4 and 5 coatings as consecutively deposited layers.

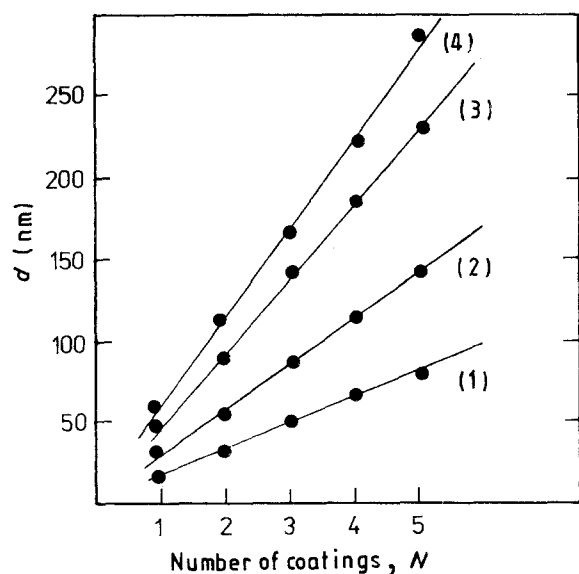


Figure 2 Thickness of the coatings versus the number of layers at different dipping speeds: (1) 6 mm min^{-1} , (2) 120 mm min^{-1} , (3) 240 mm min^{-1} and (4) 600 mm min^{-1} .

with an alkaline coating network, sodium ions diffuse in the film and probably stimulate the formation of structural types such as $\text{Na}_2\text{O}-\text{TiO}_2$. Analogous results were reported by Pulker [17] who established that anatase, brookite, rutile and $\text{Na}_2\text{O}-\text{TiO}_2$ in TiO_2 films is strongly dependent on the type of solution used, the thermal treatment and the migration of alkaline ions from the substrate, such as soda-lime window glass.

It is known [17] that titanate coatings of different crystalline structure show differences in their optical properties. In comparison with the coating possessing anatase-type structure, coatings with $\text{Na}_2\text{O} \cdot \text{TiO}_2$ are formed at a lower rate of heating and have a lower refractive index. The sodium-ions diffusion process in and through the titanate film is rapid even after crystal formation of the main phase. The concentration gradient of the sodium diffused in the thicker layers may be optically registered by the decrease of the refractive

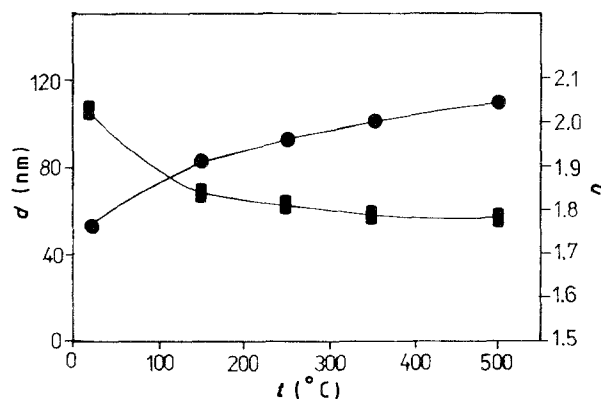


Figure 3 (●) Refractive index, n , and (■) thickness d of the coatings versus temperature.

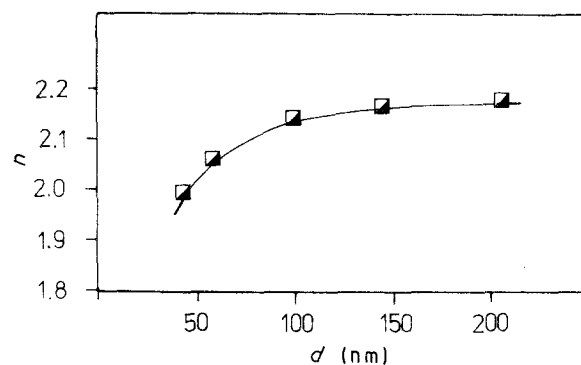


Figure 4 Refractive index and thickness of a monolayer of TiO_2 , composition code 001.

index with depth from the boundary "air/film" surface into the substrate itself. SiO_2 -based vitreous coatings obtained in the same manner from a sol solution exhibit quite a different behaviour. For 20 nm thickness they offer an excellent diffusion barrier for sodium ions [17]. This was reported earlier [2], where it was established that there was no sodium diffusion process taking place from the substrate towards the silicate layers.

Fig. 3 shows the dependence of the refractive index and the coating thickness on the heating temperature. It is obvious that the refraction index, n , is a function of the densification of the layer as the temperature increases. As the diffusion of alkaline substances from the substrate towards and through the layer is performed for some period of time, its influence on the layer structure decreases from the "layer/substrate" boundary towards the surface, depending on the layer thickness, d . Therefore, a thin titanate film deposited on an alkaline-containing glass substrate possesses a lower refraction index compared with a thicker film deposited on the same type of substrate. This is very well illustrated in Fig. 4 for titanate coatings treated at 500°C for 10 min. This is also analogous with Pulker's results [17].

Fig. 5 shows the transmittance spectra of titanate coatings depending on their thickness and dipping rate. A decrease in the transmittance is noticed with increasing coating thickness. Fig. 6 shows the changes in coating transmittance with temperature change and

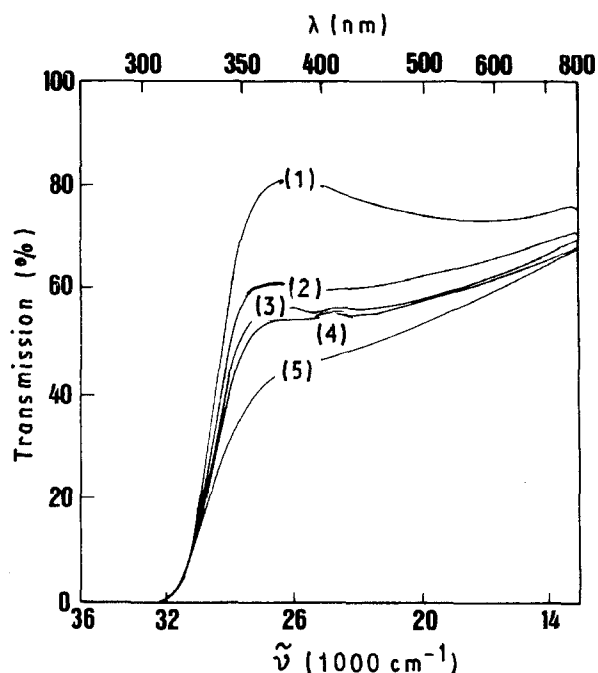


Figure 5 Variation of transmittance spectra of titanate coatings with the dipping speed: (1) 24 mm min⁻¹, (2) 60 mm min⁻¹, (3) 120 mm min⁻¹, (4) 240 mm min⁻¹ and (5) 600 mm min⁻¹, thermally treated at 500°C for 10 min.

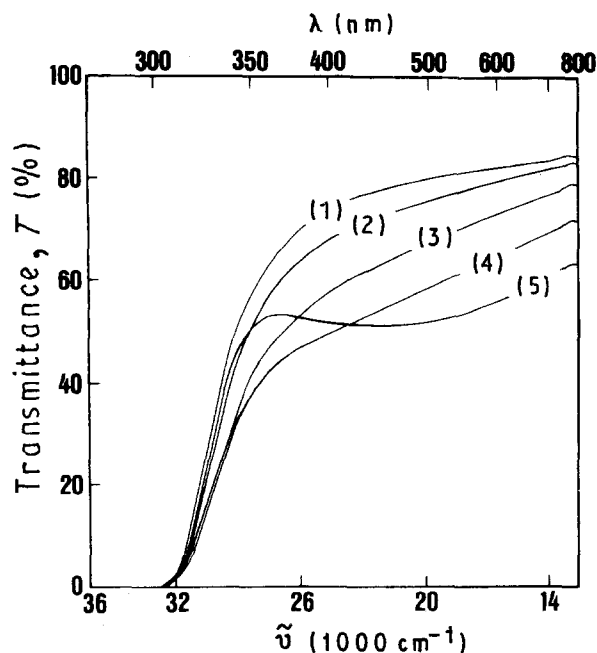


Figure 6 Transmittance spectra of titanate coatings versus temperature: (1) 25°C, (2) 150°C, (3) 250°C, (4) 350°C and (5) 500°C, thermally treated for 10 min.

the densification. It is seen that after thermal treatment, transmittance decreases because of the layer densification process taking place.

Titanate coatings can be easily modified by several oxides of the transition 3d-elements such as iron, chromium, manganese and vanadium. The effect of the change in the optical properties is achieved as reflection, transmittance, colour, etc. For example, Fig. 7 illustrates the change in the transmittance spectra of iron and manganese in titanate coatings depending on the concentration of the 3d-transition ions and the wavelength. On the other hand, through a combination of titanate coatings with high and low refractive indices, stacks of layers may be obtained possessing interesting interference properties [18].

Table II gives the experimentally obtained data on transmittance and reflection of different samples, as well as for layers modified by Fe(III) ions. It is obvious that they exhibit acceptable integral transmittance over 40% and the respective reflection in the visible spectral region. In the near-infrared spectral region, one-layer coatings do not possess a high reflection but are at the limits of the branch-recommended standard [12].

3.2. Mechanical properties and chemical durability

Coatings for commercial application must possess excellent chemical durability and mechanical strength. The dip coatings obtained were tested for physical and chemical properties according to the literature [12].

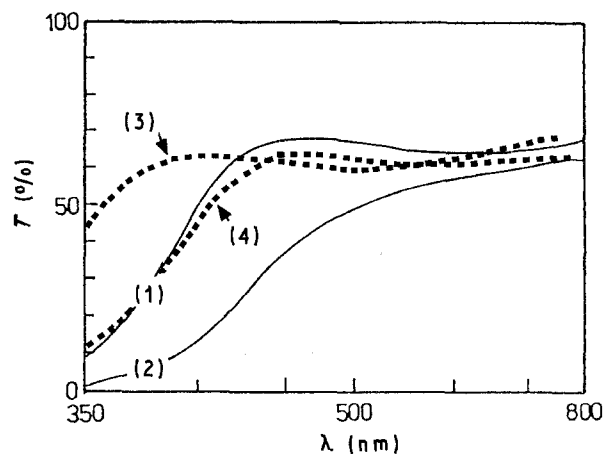


Figure 7 Transmittance spectra of titanate coatings modified by transition metal ions: (1) sample 008, (2) sample 009, (3) sample 012 and (4) sample 013.

TABLE II Integral coefficients of transmittance, \bar{T} , and reflection, \bar{R} , of selected titanate coatings in the visible (VIS) and near-infrared (NIR) ranges

Code of composition	VIS range (380–780 nm)		NIR range (800 nm– μ m)	
	\bar{T} (%)	\bar{R} (%)	\bar{T} (%)	\bar{R} (%)
001	63.0	29.2	79.9	16.8
008	53.2	26.7	77.0	8.6
009	39.2	50.1	74.9	19.4
103	80.0	15.6	–	–

The recommended standard for glass branch refers to a test for flat sun-protective glass with a metal oxide or pure metallic coating or a combination of both. Requirements do not depend on the type of coating or its thickness. Investigations were focused on defining chemical durability and mechanical strength (abrasion protection).

Coatings were intended for use in the open air so atmospheric resistance was also investigated. Some preliminary investigations were carried out to define their ageing, chemical durability (boiling-water and alkaline-solution resistance) and abrasion protection.

Fig. 8 shows a comparison of spectra before and after ageing by short wavelength beams from a mer-

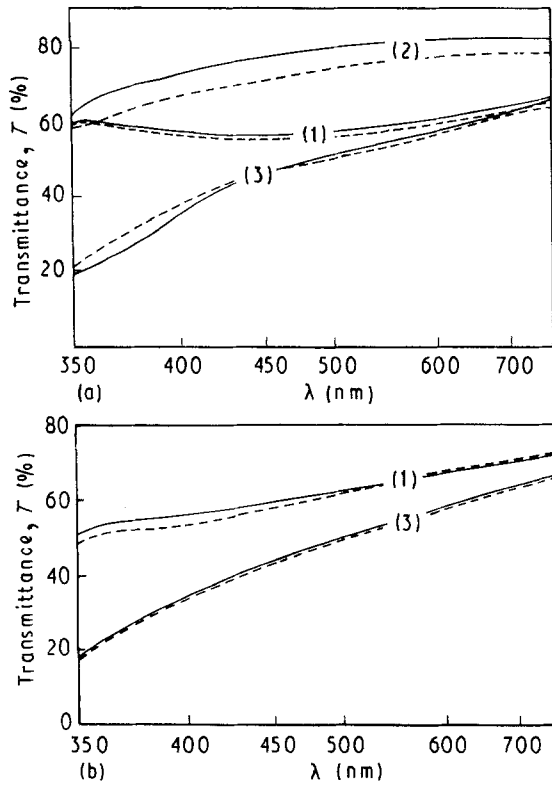


Figure 8 Transmittance spectra for ageing tests of coatings of compositional code (1) 001, (2) 103, and (3) 009; (a) short wavelength treatment and (b) after thermal treatment; (—) before and (---) after the test.

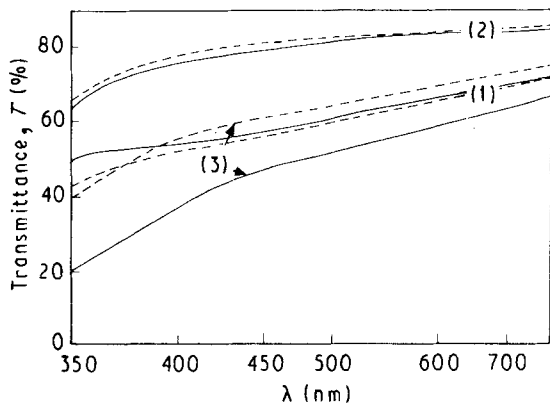


Figure 9 Transmittance spectra for abrasive protection of coatings with code sample (1) 001, (2) 103 and, (3) 009, (—) before and (---) after the test.

cury lamp, as well as the spectra of some selected thermally treated coatings.

Fig. 9 shows spectra of the transmittance of coatings with code numbers 001, 009 and 103 before and after the abrasion stability test. It is seen that the results obtained satisfy the requirements, because only sample 009 (Curve 3) shows $\Delta T \approx 20\%$. In this case the adhesion model of the TiO_2 layer to a silicate substrate discussed in Part I [1], is valid. The experimental data from the investigations on samples to define their resistance to boiling-water treatment are presented in Fig. 10a. From the difference in spectral transmittance of samples before and after treatment, it is seen that they show good stability to boiling-water treatment.

The alkaline-solution resistance is an important property in practice and industrial application. The difference in spectral transmittance must not exceed 6% for the visible spectral region. The results obtained are presented in Fig. 10b. It was established that they correspond to the respective limits for chemical resistance in alkaline media. Sample 3 is an exception, showing a slight lightening of the layer after alkaline treatment.

4. Conclusions

1. It was shown that for a successfully selected composition and with appropriate technology, the sol-gel process is a suitable method for preparation of titanate coatings of high uniformity and good substrate adhesion in the system $\text{Ti}(\text{OBu})_4\text{-C}_2\text{H}_5\text{-OH-H}_2\text{O}$.

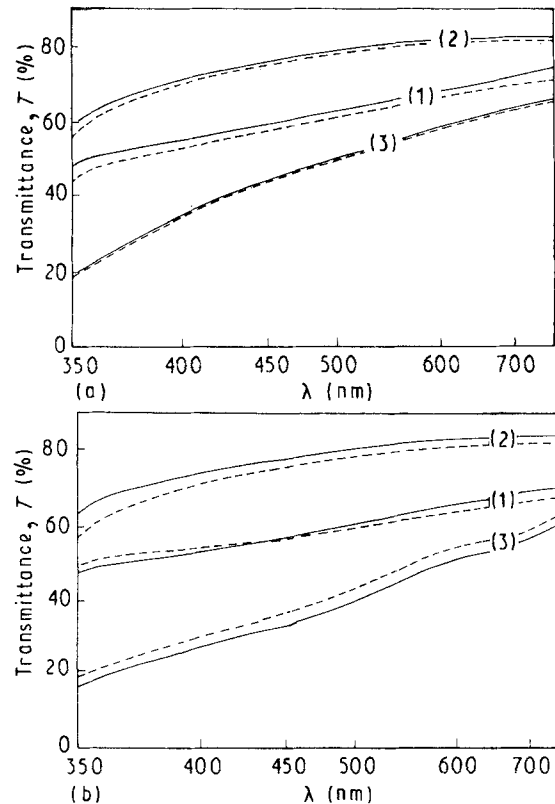


Figure 10 Transmittance spectra for (a) boiling-water resistance and (b) alkaline-solution resistance of coatings of code (1) 001, (2) 103 and (3) 009, (—) before and (---) after the tests.

2. Coating thickness is immensely affected by the composition, viscosity of the sol solution and the dipping rate. It was established that increasing the dipping rate under otherwise stable conditions will increase the thickness. For a given dipping rate, the thickness is proportional to the number of layers and the relationship is linear.

3. The refractive index increases with increasing temperature and is a function of the layer densification which depends on the thermal treatment, and thus the layer thickness slowly falls.

4. The spectral transmittance decreases with increasing layer thickness, and with increasing dipping rate. All other conditions being stable, the spectral transmittance decreases with densification increases. Introducing 3d-transition metal ions gives a stable colouring effect in the layers, combined with a decrease in spectral transmittance.

5. It was established that abrasion protection, ageing and boiling-water and alkaline-solution treatment resistance is sufficiently high for their practical application as sun-protective metaloxide coatings on glass substrates.

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