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Chromium, cobalt, nickel and copper as pigments of sol–gel glasses

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Abstract

Studies referring to the application of the sol–gel method to obtain coloured coatings on flat glass are reviewed. The authors present their own investigations on the production of coloured gel glasses (bulk and films) of the systems R_nO_m–SiO_2, where R is Cr, Co, Ni or Cu. Based on transmission spectra measurements the valency and the coordination states of transition metals in the starting solutions, gels, bulk glasses and films were determined. The mechanism of colouring of gel glasses containing up to 15 mol of R_nO_m oxides has an ionic character. The most intense colouring is demonstrated by coatings of the Cr_2O_3–SiO_2 system. At higher transition metal concentrations segregation of the respective oxides and selective scattering of light occur. It has been demonstrated that the soda–calcium–silicate glass covered with gel films of R_nO_m–SiO_2 systems are characterized by microhardness which is 30–60 times higher than that of the basic glass.

Keywords: Pigments; Chromium; Cobalt; Nickel; Copper

1. Introduction

Transition metals have been known for a long time as pigments of glasses; when using them one can obtain almost the whole spectrum of colours. However, in the case of glasses obtained by the traditional melting method the content of the transition metals in the glass is limited, and usually does not exceed a few percent. The situation is different for glasses obtained from solutions by the sol–gel method [1]. The process of glass formation is performed here at relatively low temperatures as a result of the reaction of hydrolysis and polycondensation of alcoholates, esters and some inorganic compounds of respective elements. The sol–gel method allows us to obtain glasses containing as much as some tens per cent of the transition metal oxides; these amounts exceed many times those found in melted glasses. The sol–gel method proves very useful when thin, amorphous coatings must be deposited on the surface of various materials; the technique of film deposition in such cases is very simple, and the deposited coatings are characterized by good adherence to the basis. These films allow the modification of the optical, electrical, chemical and other properties of the materials upon which they have been deposited.

Gel coatings, containing oxides of transition metals, deposited on colourless glasses, offer the possibility of obtaining interesting colouring effects. Gel coatings of this type was first reported by Yamamoto et al. [2] and Sakka et al. [3]. The parent solutions for the deposition of the layers were prepared by mixing tetraethoxysilane (TEOS), ethanol, water, hydrochloric acid and nitrates of chromium, cobalt, nickel and copper. The microscopic slides were dipped into the solution and withdrawn at different speeds. After coating the slides were dried and next heated to temperatures of up to 500 °C. The thickness of the films was 0.3–0.5 μm. It has been found that the maximal concentrations of the transition metal oxides that allow us to obtain a transparent, colour covering are as follows: 10 mol.% of Cr_2O_3, 20 mol.% of Mn_2O_3, 45 mol.% of Fe_2O_3, 45 mol.% of CoO, 55 mol.% of NiO and 45 mol.% of CuO. Based on the optical characteristics the authors believe that the mechanism of colouring the gel films by transition metals is of ionic nature, but at high transition metal concentration the crystalline segregation of respective metal oxides also occurs.

Duran, Navarro and others [4–7] have published some papers concerning coloured gel coatings obtained from the same oxide systems as mentioned above. The maximum concentration of the transition metal oxides

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was 30 mol.%. The method of preparing the solutions was close to that described above; the deposition of the films and their thermal treatment were carried out in similar conditions. Based on their investigations the authors conclude that the mechanism of colouring of the gel layers is similar to that of melted glasses. An exception here is gel glasses coloured with chromium, in which chromium occurs mainly at the sixth oxidation state, whereas in melted glasses there are present first of all Cr^{3+} ions in octahedral coordination. The effects of colouring the gel coatings with cobalt and nickel ions, however, are too weak for application; colouring with copper is difficult to control, and the coatings are in practice not reproducible. Investigations of chemical resistance and microhardness have revealed that transition metals reduce the chemical resistance of the coatings in relation to the basis (sodium–calcium–silicate glasses) while increasing its microhardness.

In their subsequent study Da Silva and Navarro [6] conducted similar investigations on gel glasses coloured with copper in the system $5R_2O \times CuO(95-x)SiO_2$, where R = Li, Na or Ca. As a result of heating under oxidizing conditions the obtained gel coatings had a blue–green colour induced by the presence of copper ions Cu^{2+}. When heating glasses with deposited films under reduction conditions they managed, sporadically, to obtain deep red colouring, indicating the presence of reduced copper.

Duran et al. [7] also conducted investigations intended to obtain coatings coloured with two elements of transition metals (Fe–Cr, Fe–Co, Co–Ni, Co–Cr, Cr–Ni and Cr–Mn) and obtained colour effects different from those when only one pigment was used.

Orgaz and Rawson [8] also investigated gel coatings from the system R_nO_m–SiO_2 coloured with cobalt, manganese and chromium, with concentrations of the appropriate transition metals oxides, ranging from 20 to 40 wt.%. They have demonstrated that in the examined films cobalt occurs as Co^{2+} ions in a tetrahedral coordination, and chromium as Cr^{6+} ions, also in a tetrahedral coordination, whereas manganese occurs as Mn^{3+} ions in octahedral coordination. These authors also examined IR spectra drawing on this basis conclusions about the role of the transition metals in the structure of silica glass.

From the above review of the literature it follows that coloured coatings on flat glass represent a problem of current interest. Not all the problems referring both to the mechanism of colouring and to the structure of this type of unique glasses, which cannot be reproduced by the standard melting method, have been fully explained. Moreover, the specific technique of preparing the gel materials requires all researchers to perform their own experiments.

In the present study complex investigations of the production of coloured bulk glasses and gel coatings of the systems: Cr_2O_3–SiO_2, CoO–SiO_2, NiO–SiO_2 and CuO–SiO_2 were carried out. A special effort has been made to determine the valency and the coordination states of the transition metals in bulk gels and gel films as depending on the conditions of thermal treatment and the related mechanism of colouring.

2. Experimental

2.1. *Preparation of solutions*

The starting materials used to obtain gel glasses in the R_nO_m–SiO_2 system, where R = Cr, Co, Ni or Cu, were tetraethoxysilane $Si(OC_2H_5)_4$(TEOS) and nitrates of the respective transition metals. The solution was prepared as follows: TEOS was mixed with ethanol (TEOS:C_2H_5OH = 1:1) for 1 h at a temperature of 50 °C. Hydrochloric acid as a catalyst of the hydrolysis reaction and distilled water were next added, and the solution was mixed, first at a temperature of 50 °C (for 30 min) and afterwards at ambient temperature (for 45 min). The solution obtained in that way was divided into two parts: Part 1 (to be used for coatings) and Part 2 (to be used for bulk glasses).

An appropriate amount of nitrate of the transition metal was added to solution No. 1 and the whole mixed for 45 min. The solution was next subjected to 2–4-fold dilution with ethanol and after careful mixing used to deposit the films by the dip coating process.

In the case of solution No. 2, formamide was added in an amount equivalent to that of added ethanol. The solution was mixed and next proper nitrates were added. The mixture was left under ambient conditions to allow the formation of gel. The gelation time was a few days.

The molar ratio H_2O:TEOS = 1:1 was preserved all the time when preparing the mixtures. The maximum concentrations of the introduced oxides of transition metals at which the obtained glasses and gel layers were of good quality, without any signs of crystallization, are listed in Table 1.

2.2. *Deposition of coatings, thermal treatment*

Solution No. 1 was to be used for the deposition of the coatings on microscopic slides made of sodium–calcium–silicate glass. The microscopic slides were dipped into the solution, withdrawn and heated up to temperatures of 350, 450 and 550 °C in air atmosphere as well as under oxidizing and reducing conditions.

Glasses with deposited films were observed in an optical microscope. Moreover, the transmission in the range of UV and VIS radiation was measured (Specord UV-VIS, ZEISS-Jena) (Figs. 1–4), and selected coatings were subjected to X-ray diffraction analysis (DRON-3 diffractometer) using Ni-filtrated K_α radiation (Fig.

Table 1
Maximum concentration of transition metal oxides (mol.%) in gel glasses of R_nO_m–SiO_2 systems and obtained colouring of materials

Kind of glass	Maximum concentration of R_nO_m (mol.%)		Colouring after thermal treatment	
	Films	Bulk glasses	Films (450 °C)	Bulk glasses (850 °C)
Cr_2O_3–SiO_2	20	20	Yellow	Orange
CoO–SiO_2	40	15	Blue	Blue
NiO–SiO_2	10	20	Colourless (oxidation) Brown (550 °C reduction)	Brown–yellow
CuO–SiO_2	5	5	Blue–green	Blue–green

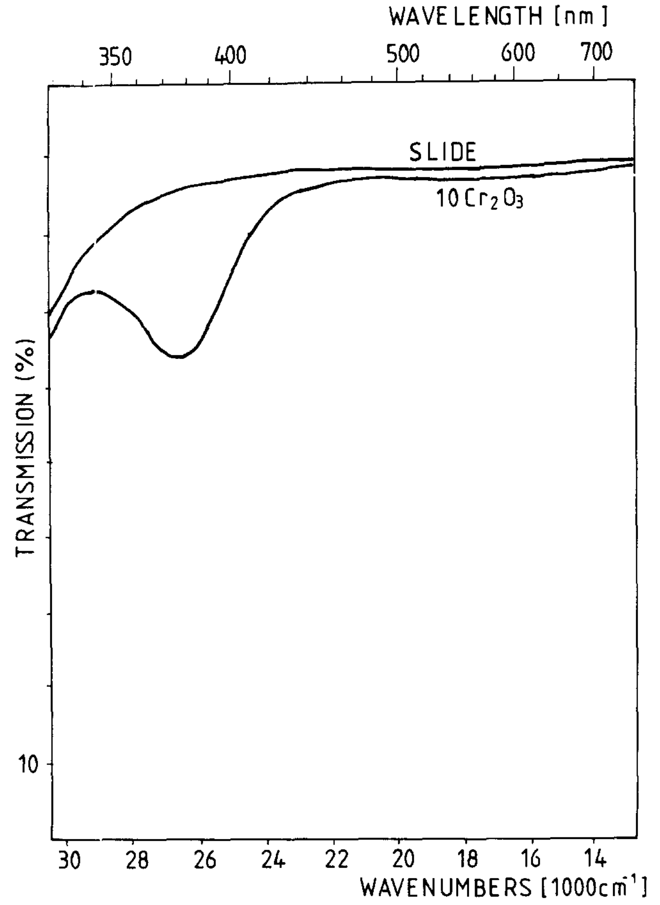

Fig. 1. Transmission spectrum of Cr_2O_3–SiO_2 coating.

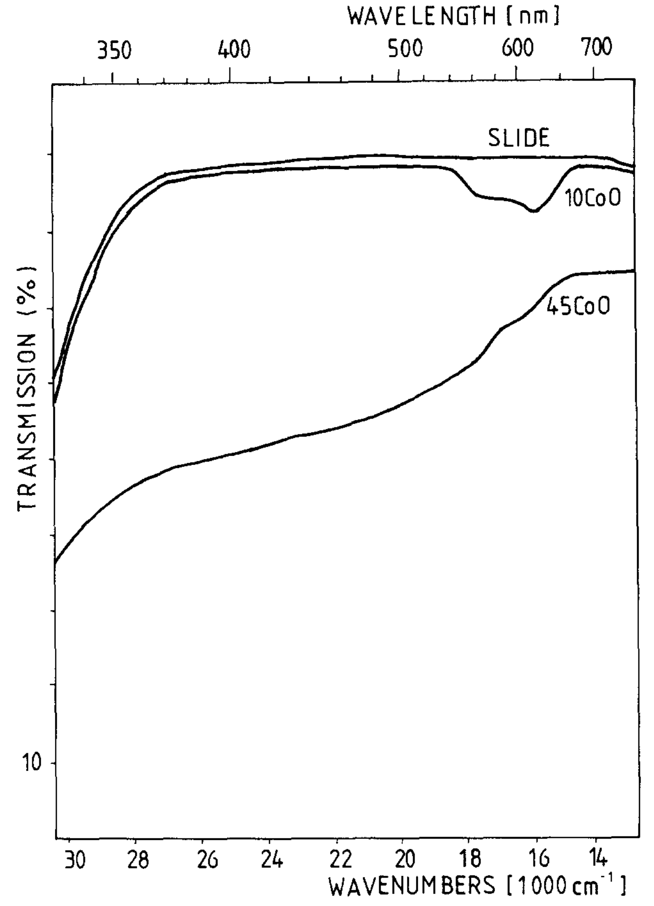

Fig. 2. Transmission spectra of CoO–SiO_2 coatings.

5) and spectroscopic investigation in infrared (Fourier transform spectrophotometer DIGILAB) (Fig. 6). The microhardness by Vickers' method at a loading of 50 gf was also measured (Table 1).

2.3. *Thermal treatment of gels*

Gels dried for a period of one month under ambient conditions were subjected to thermal treatment by heating at a controlled rate up to a temperature of 120 °C for 2 days and next to a temperature of 850 °C for 3 days.

After thermal treatment all gels were subjected to diffraction phase analysis (XRD); the characteristic diffraction patterns are shown in Fig. 5.

In order to determine the valency and the coordination states of the transition metals in the examined gel glasses the transmission in the UV and VIS ranges was investigated (Figs. 7–10).

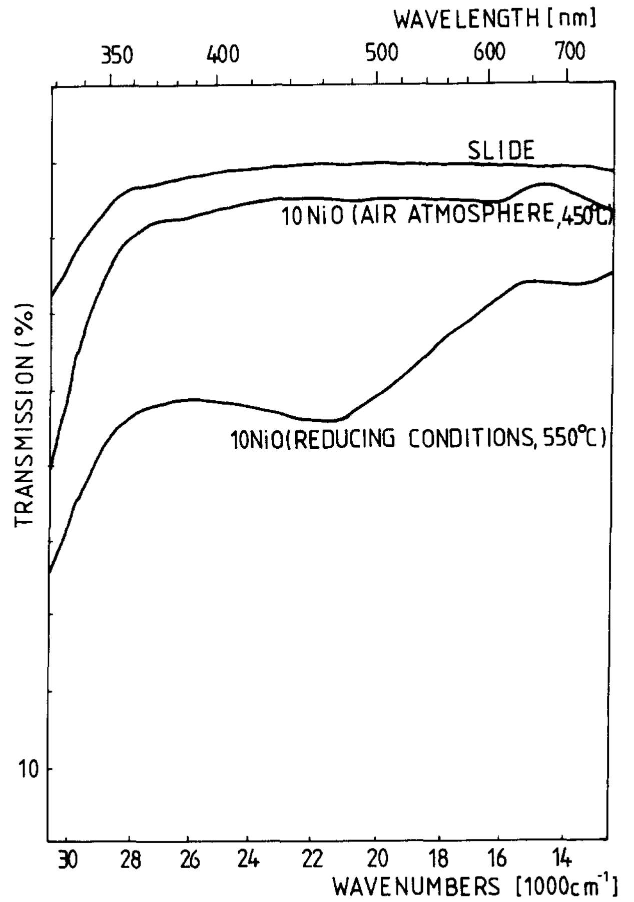

Fig. 3. Transmission spectra of NiO–SiO$_2$ coatings.

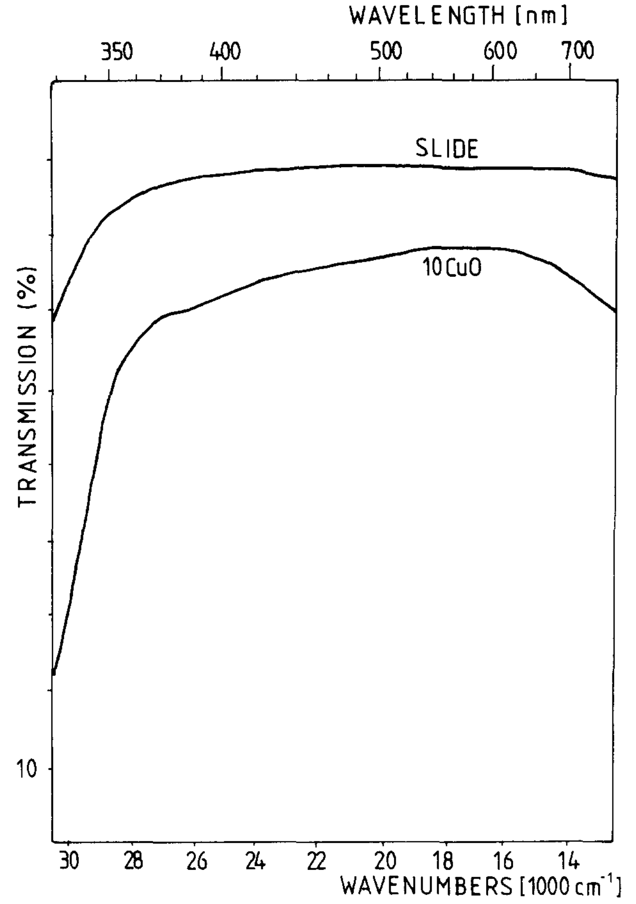

Fig. 4. Transmission spectrum of CuO–SiO$_2$ coating.

3. Results and discussion

3.1. Coatings

The gel films obtained by the dip coating process were of various quality, depending, first of all, on the kind of introduced transition metal oxide and its concentration; thermal treatment proved to be less importance. With repeated deposition (more than 3 times) the quality of the coatings deteriorated. The quality of the coatings was estimated on the basis of visual and microscopic observations.

The highest quality was undoubtedly shown by coatings of the Cr_2O_3–SiO_2 system. Coatings of good quality were also obtained in the CoO–SiO$_2$ and NiO–SiO$_2$ systems (however, in the case of nickel only at NiO concentrations not exceeding 10 mol.%). Coatings of the CuO–SiO$_2$ system were of the poorest quality with visible inhomogeneity already at 10 mol.% concentration of CuO.

3.1.1. Cr_2O_3–SiO_2

In the case of Cr_2O_3–SiO_2 coatings a clear, yellow colouring was obtained; the effect of colouring was here evidently strongest and it did not depend on the heating atmosphere. The transmission spectra (Fig. 1) of this

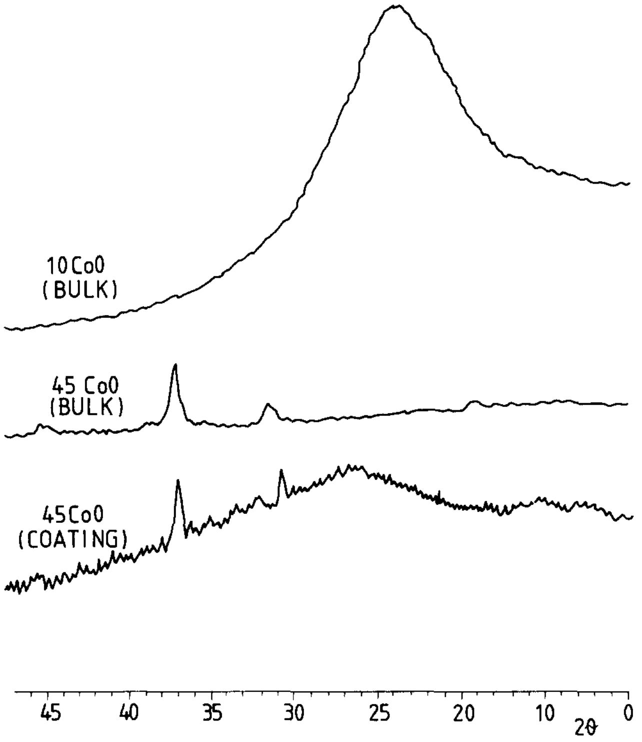

Fig. 5. X-ray diffraction spectra of heat-treated gels (bulk: up to 850 °C; coating: up to 450 °C) of CoO–SiO$_2$ system.

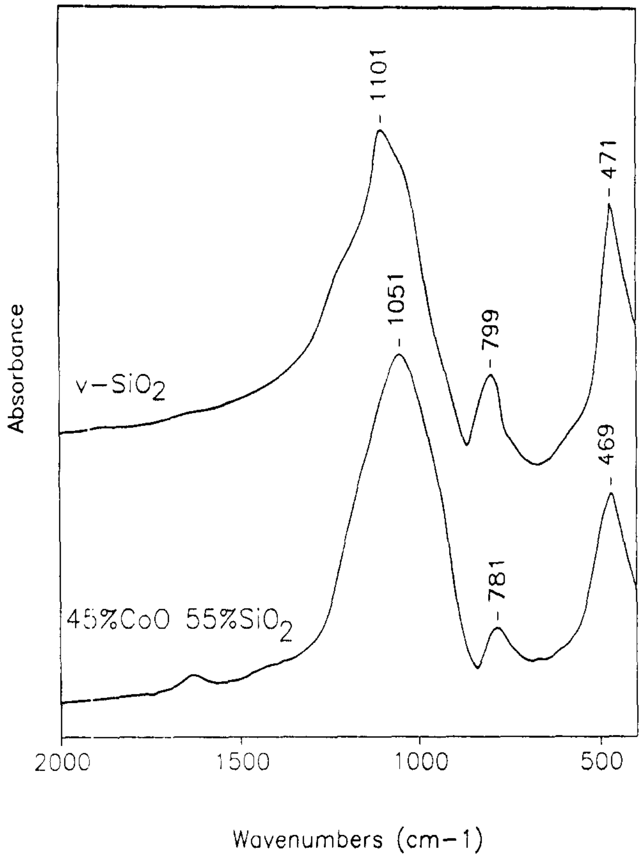

Fig. 6. FTIR spectra of SiO_2 and $CoO-SiO_2$ coatings.

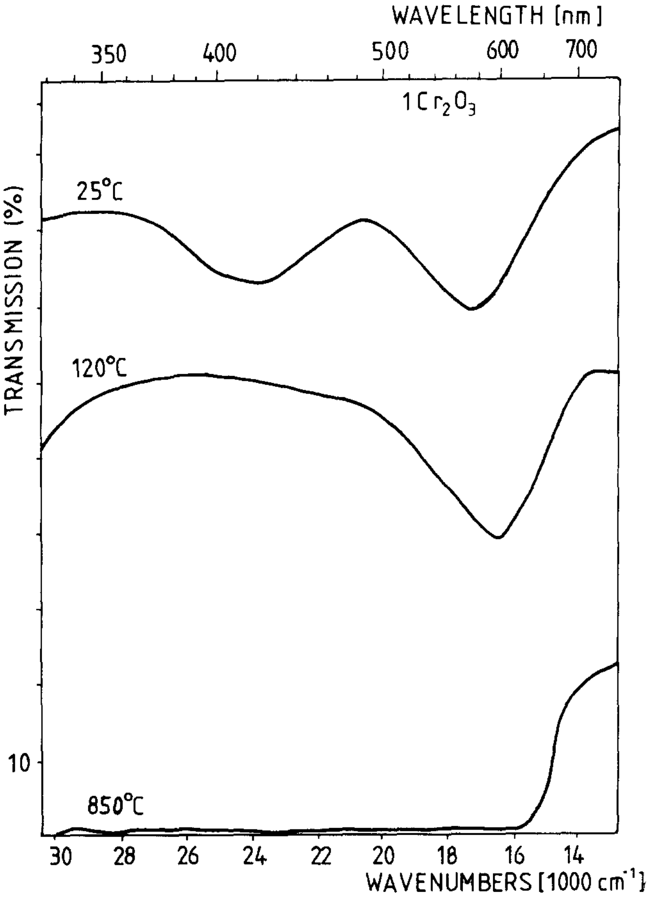

Fig. 7. Transmission spectra of $Cr_2O_3-SiO_2$ gels heat treated at different temperatures.

coating show a very intense "charge transfer" band situated at 365 nm, which may be associated with Cr^{6+} ions in tetrahedral coordination [9].

No traces of bands at 410 and 650 nm, which might indicate the presence of the Cr^{3+} ions in the octahedral coordination, were observed. The results of the author's investigations differ, thus, from the investigation results of Sakka et al. [3] and Duran et al. [4], who obtained layers with green–yellow colouring containing the Cr^{3+} ions in octahedral coordination besides the Cr^{6+} ions in tetrahedral coordination. It is probable that certain differences in the preparation and the method of thermal treatment, of which the authors do not inform in their publication, might have induced the different behaviour of the transition metal elements in gel glasses. Our results, on the other hand, are consistent with the investigation results of Orgaz and Rawson [8] who obtained silica layers containing only chromium Cr^{6+} in a tetrahedral coordination.

3.1.2. $CoO-SiO_2$

Cobalt-coloured coatings showed weakly blue colour at CoO concentrations up to 15 mol.%; at the higher CoO concentrations a dark brown colouring was obtained. The effect of colouring with cobalt was not dependent on temperature nor on the heating atmosphere of the layers. In the first case, the transmission spectra (Fig. 2) were typical for Co^{2+} ions in tetrahedral coordination [9], corresponding to the d–d electron transitions for the $3d^7$ configuration. At higher CoO concentrations decreased transmission in the short range of radiation was observed (Fig. 2); this may be attributed to the segregation of cobalt oxide and light scattering on the suspension. This has been confirmed by XRD analysis of coatings containing 45 mol.% of CaO (Fig. 5); the diffraction pattern shows distinct reflexes (d = 2.82 Å; 3.32 Å) derived from the cobalt oxide.

The results obtained are consistent with the results obtained by other authors examining the colouring of layers by cobalt [3–5,7–8]; this refers to both low (up to 15 mol.%) and high (above 15 mol.%) concentrations of cobalt oxide.

Fig. 6 shows the FTIR transmission spectrum of a gel layer containing 45 mol.% of CoO and, for comparison, the spectrum of a silica gel layer obtained by hydrolysis and polycondensation of TEOS and subjected to identical thermal treatment as the layers coloured with cobalt.

The FTIR spectrum of coatings containing 45 mol.% of CoO is typical for silica glass; however all three bands are shifted towards lower wave number (1052,

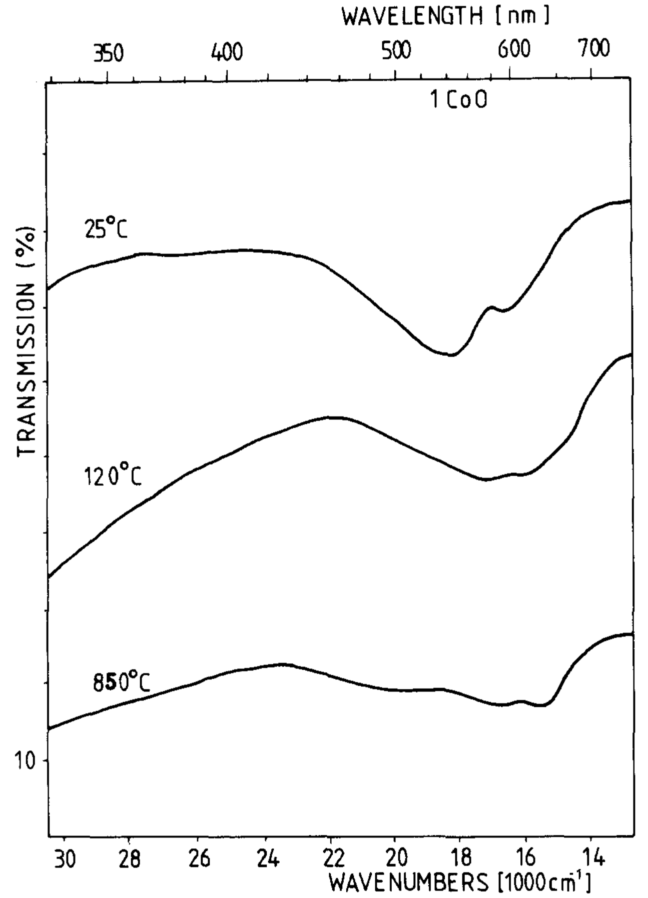

Fig. 8. Transmission spectra of CoO–SiO_2 gels heat-treated at different temperatures.

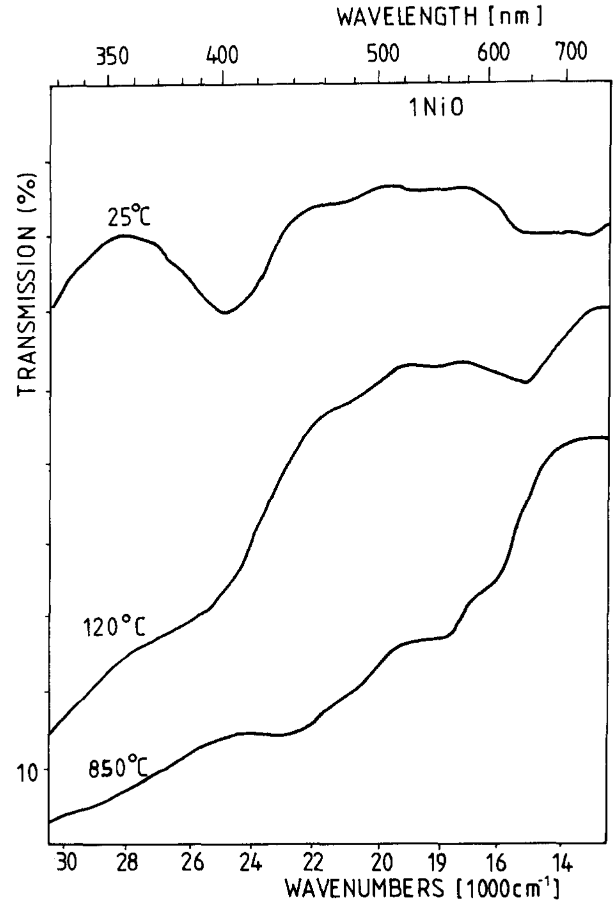

Fig. 9. Transmission spectra of NiO–SiO_2 gels heat-treated at different temperatures.

780 and 468 cm^{-1}) (Fig. 6). This is an indication of the weakening of Si–O bonds in the silica matrix. The weakening of these bonds is not due, most probably, to the presence of the silanol Si–OH groups, since the band at about 925 cm^{-1}, characteristic for these groups, did not appear in the spectrum; on the other hand, it may be due to the incorporation of Co^{2+} ions into the silica matrix in the form of $[CoO_4]$ tetrahedra, which are associated with the presence of mixed Si–O–Co bonds. The vibration frequency of these groups is undoubtedly somewhat different from those of the Si–O–Si groups; these differences, however, are too small to cause the occurrence of a separate band in the spectrum, but great enough, considering the weaker strength of the Co–O bond, to shifting the bands connected with the stretching vibration (Si–O–Si, Si–O–Co) and the bending vibration (O–Si–O, O–Co–O) towards lower frequencies. The weakening of bonds in the silica matrix may also be due to the occurrence of a part of the Co^{2+} ions as a modifier of the silica framework, breaking the bridging bonds in the structure. It follows from the above that the dark brown colouring of the coatings derives only from the part of cobalt bound in the form of oxide, forming a suspension in the glass, while the remaining part occurs in ionic form in the silica matrix.

3.1.3. NiO–SiO_2

At NiO concentrations higher than 10 mol.%, the NiO–SiO_2 coatings showed inhomogeneities. Coatings with NiO concentration up to 10 mol.%, heated in air and under oxidizing conditions, were colourless, while those heated in reducing conditions at a temperature of 550 °C, displayed grey–brown colouring. The transmission spectrum contains a distinct band at about 430 nm. This band is connected with the electron transitions d–d in the Ni^{2+} ions ($3d^8$ configuration) in octahedral coordination [9] (Fig. 3).

From the study by Duran et al. [4] it follows that in the case of silica gel layers containing nickel oxide, a distinct absorption band does not occur until the concentration of nickel oxide NiO reaches a value of 20–40 mol.%. Since in the layers examined by the authors the NiO concentration is low (10 mol.%) the absence of the characteristic bands in the spectrum and the lack of colour in the layers are justified. It is, however, interesting that even at this low concentration the increase in temperature up to 550 °C and the application of the reducing heating conditions resulted

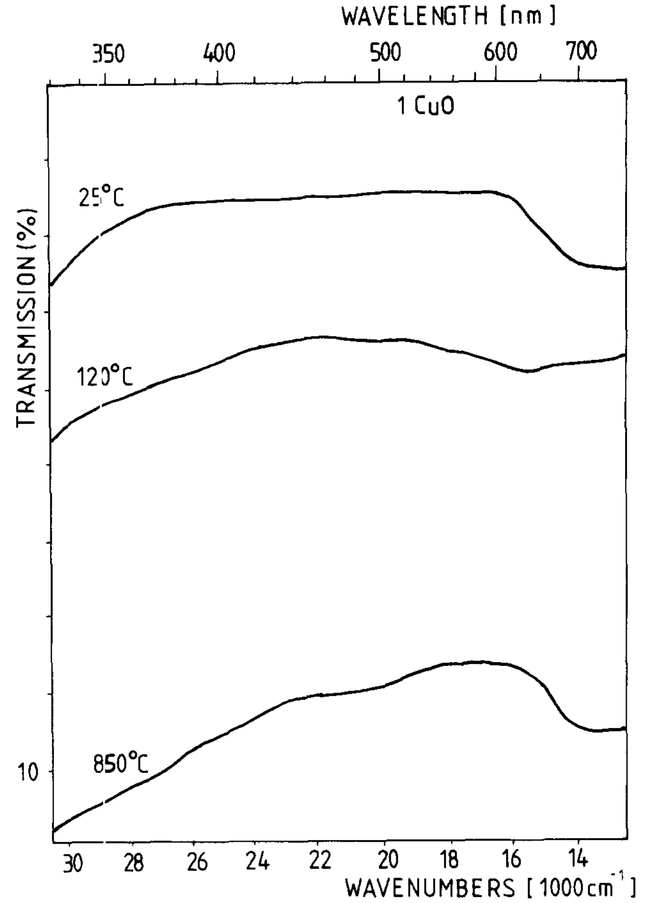

Fig. 10. Transmission spectra of CuO–SiO$_2$ gels heat- treated at different temperatures.

in a distinct "activation" of the colour centres. These are, similar to layers obtained by Duran et al. [4], centres in which the Ni^{2+} ions occur in octahedral coordination with oxygen ions, showing the characteristic absorption band at about 430 nm. The application of reduction conditions of heating did not induce in this case the segregation of nickel oxide NiO, as was the case with bulk silica gel glasses obtained by Silva and Navarro [12].

3.1.4. CuO–SiO$_2$

At CuO concentration up to 10 mol.%, the CuO–SiO$_2$ coatings display weak blue–green colouring. In the transmission spectrum (Fig. 4) an evident decrease of transmission in the long wave range (650–760 nm) can be observed. This is connected with the presence a characteristic band at 790 nm, deriving from d–d electron transitions in the Cu^{2+} ions (3d^9 configuration) in octahedral coordination [9]. Heating in reduction conditions does not change the colouring, which is evidence of the absence of reduced copper (Cu and Cu$_2$O), which gives the deep red colour. Thus, the authors did not manage to reproduce the experiment of Silva and Navarro [6], who obtained the deep red colouring of coatings heated in reduction conditions.

The microhardnesses of the basic slides and those covered with films were measured. The investigations have shown that covering the basic sodium–calcium–silicate glass with silica coatings with addition of 10 mol.% of transition metal oxides greatly increases microhardness. The increase, in relation to basic glass, equals 30–60% (Table 2). This is to be interpreted that in comparison with sodium–calcium–silicate glass the strength of the bonds in silica coatings, containing 10 mol.% of transition metals oxides, is evidently higher. This effect, apart from its practical aspect, is also interesting on account of the fact that in the case of silica gel coatings without an addition of transition metal oxides, deposited on basic glass of the same type, the increase in microhardness is only of the order of a few percent.

3.2. Coloured bulk glasses

As a result of thermal treatment of gels obtained from solution No. 2, monolithic gel glasses in the R_nO_m–SiO$_2$ systems were obtained (Table 1).

Depending on the shape of the glass containers in which gelation performed, the bulk gel glasses had the forms of plates with a surface area of about 1 cm^2 and thickness of about 1 mm; rods with a diameter of about 5 mm and a length of about 10 mm; and irregular pieces of glass.

Distinct colouring of the bulk gel glasses was observed already at 1 mol.% content of the respective oxide.

An analysis of the transmission spectra (Fig. 7–10) of R_nO_m–SiO$_2$ gels after various stages of thermal treatment, has led to the following conclusions.

3.2.1. Cr$_2$O$_3$–SiO$_2$

The starting solution and dried gel had a green colour, and in their transmission spectra there occur two bands (at about 450 and 650 nm) characteristic of Cr^{3+} ions in octahedral coordination with the dipolar water particles as ligands. The increase of the temperature of heating up to 850 °C causes a change of colouring from green to strong orange, accompanied

Table 2
Microhardness, measured by Vickers' method at 50 gf loading, of soda–calcium–silicate slides covered with films containing 10 mol.% of transition metal oxides

Kind of glass	Microhardness (GPa)
Slide 1	3.6
Slide 1+CoO	5.7
Slide 1+NiO	5.3
Slide 1+CuO	5.1
Slide 2	4.2
Slide 2+Cr$_2$O$_3$	5.6
Slide 2+SiO$_2$	4.4

by complete absorption of radiation up to about 600 nm (Fig. 7). It is most probably connected with the presence, within the short wave radiation, of an intense "charge transfer" band, characteristic of Cr^{6+} ions in tetrahedral coordination with oxygen.

3.2.2. $CoO-SiO_2$

Both the solution and wet gel had a pink colouring; the presence of bands in the range 460–650 nm in the transmission spectrum undoubtedly indicated the occurrence of Co^{2+} ions in octahedral coordination (Fig. 8). The role of ligands, in this case, is played by dipolar water particles. With increasing heating temperature the colouring of the gels changes to blue–pink, and the band in the spectrum is shifted to longer waves. The spectrum of gel heated at 850 °C is already typical for Co^{2+} ions in tetrahedral coordination, and the gel glasses obtained have a distinct blue colouring. The results of optical investigations of the gel films and bulk glass are identical, while at the same time being in agreement with the results of other authors [4,5,7]. From the investigations carried out so far on Co behaviour in melted glasses [10], it follows, however, that the coordination equilibrium of Co^{2+} ions depend on the chemical character of basic glass – in high-alkaline glasses tetrahedral coordination is preferred, whereas in glasses of more acid character (low-alkaline, e.g. boron–silicate glasses) cobalt occurs chiefly in octahedral coordination. The phenomenon of cobalt occurrence in tetrahedral coordination in glass of highest acidity, such as silica glass, is thus surprising. The interpretation of this fact from the point of view of the basic–acidic character of glass in this case does not provide the explanation. It seems more appropriate to treat cobalt ions as a "structural probe" of the tetrahedral, continuous framework, in accordance with the earlier studies by Ingram and Duffe [11].

3.2.3. $NiO-SiO_2$

The starting solution and the wet gel display a green colouring. In their transmission spectra there occurs an intensive band at about 400 nm (Fig. 9). This band is associated with the presence of Ni^{2+} ions in octahedral coordination with dipolar water particles as ligands [12]. As a result of thermal treatment, especially above 120 °C, the colour changes to brown–yellow, and the short wave band is shifted towards longer waves (at about 450 nm). The position of this band is similar to that in the case of silicate melted glasses and its origin is ascribed to d–d electron transitions in Ni^{2+} ions in octahedral coordination with oxygen. In the transmission spectrum of gel heated at the temperature 850 °C there appear, however, new, less intense bands (at about 550 and 620 nm), characteristic of Ni^{2+} ions in tetrahedral coordination [12]. This is an indication that increasing the temperature facilitates, as in case of cobalt, the incorporation of nickel into the silica matrix, although this phenomenon occurs on a smaller scale than it does in case of glasses doped with cobalt. The investigations have also confirmed that the strong acidity of the glass does not exclude the possibility of the appearance of transition metal ions in tetrahedral coordination.

3.2.4. $CuO-SiO_2$

In the case of gels and gel glasses coloured with copper, a decrease of transmission in the range of long wave radiation (above 600 nm) is observed independently of the conditions of thermal treatment, which is connected with the presence of an absorption band at about 740–800 nm, characteristic for Cu^{2+} ions in octahedral coordination (Fig. 10). The appearance of copper ions in silica glass exclusively in octahedral coordination may have an influence on the reduced solubility of CuO in the silica matrix; octahedra formed by copper are structurally much more inconsistent with the tetrahedral framework of silica glass when compared with the tetrahedra that can be formed by cobalt and nickel ions.

4. Conclusions

1. Using nitrates of transition metals it is possible, by the sol–gel method, to obtain transparent, homogeneous coatings on flat glass, of yellow, light blue, greenish–blue and dark brown colouring. The colouring effects are visible at the contents of the transition metals oxides not smaller than 10 mol.%. Glasses with the deposited coatings have a microhardness 30–60% higher than that of the basic glass.
2. At a concentration of the transition metal oxides up to about 15 mol.%, the colouring mechanism is of ionic character; at higher concentrations segregation of appropriate oxides occurs and the selective scattering of light is observed.
3. In all starting solutions and bulk gels, obtained at low temperatures, the transition metals show the same degree of oxidation as in the corresponding nitrates used for the synthesis, and they occur in octahedral coordination, forming hydrated ions. During the gel–glass transformation, occurring as a result of thermal treatment up to a temperature of 850 °C, there takes place a rearrangement of the coordination systems of the transition metal ions, and in the case of chromium also a change in the oxidation degree. The characters of these transitions and the accompanying changes in colour are shown in Table 3.
4. The oxidation degree and the coordination state of the transition metals in the coatings after thermal treatment and in bulk gel glasses are in practice the same. Exceptions are the bulk gel glasses with the

Table 3
Character of transitions and changes of colour

20 °C		850 °C
$[Cr^{3+}(H_2O)_6]$ (green)	⟶	$[Cr^{6+}O_4]$ (orange)
$[Co^{2+}(H_2O)_6]$ (pink)	⟶	$[Co^{2+}O_4]$ (blue)
$[Ni^{2+}(H_2O)_6]$ (green)	⟶	$[Ni^{2+}O_6]$ (brown–yellow) $[Ni^{2+}O_4]$ (brown)
$[Cu^{2+}(H_2O)_6]$ (blue)	⟶	$[Cu^{2+}O_6]$ (blue–green)

addition of nickel, in the case of which, besides the $[NiO_4]$ complexes, there also occurs nickel Ni^{2+} in tetrahedral coordination, which is absent in the gel coatings.

5. The possibility of the occurrence of transition metal ions in tetrahedral coordination favours their incorporation in the silica matrix; hence, in the case of cobalt, nickel and chromium it is possible to obtain gel glasses at higher concentration of proper oxides than in the case of copper.

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