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Optimal Optical Properties–Hardness Ratio of Antireflection Coating Produced from a Silica Sol with Hexadecyltrimethylammonium Bromide on Silicate Glass

B. B. Troitskii[a,] *, A. A. Lokteva[a], M. A. Novikova[a], T. I. Lopatina[a], and I. L. Fedyushkin[a]

[a] *Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, 603950 Russia*
**e-mail: Troitski@iomc.ras.ru*

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Abstract—The effect of the hexadecyltrimethylammonium bromide concentration in the silica sol, which is used to obtain antireflection coatings over silicate glass, on the light transmission of coated glass and the hardness of the coatings was studied. An increase in the concentration of hexadecyltrimethylammonium bromide in the sol from 1.37×10^{-2} to 5.20×10^{-2} M increases the maximum light transmission of glass with an antireflective coating from 94.7 to 99.0%, and minimum, from 84.7 to 93.6%, reduces the refractive index of the coating from 1.43 up to 1.27. The 3H–4H coating hardness acceptable for practice can be achieved provided that the maximum light transmission of glass with a single-layer double-sided coating is ≤96.0–97.0%, the refractive index of the antireflection coating is ≥1.35–1.36, and the maximum volume content of nanopores in the coating is not more than 20.0–23.0 vol % .

Keywords: silica sol; hexadecyltrimethylammonium bromide; silicate glass; antireflection coatings; light transmission; hardness

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Optical coatings that reduce the reflection of light from glass–air interfaces [antireflection coatings (ARC)] are widely used in the manufacture of optical glass products. A general analysis of the current state of the theory and practical applications of ARC on silicate glasses is given in a recently published review [1], the main attention is paid to methods for producing and properties of single-layer quarter-wave antireflection coatings based on nanoporous silicon dioxide as the cheapest and most promising coatings for mass practical application. Coatings obtained from silica sols containing surfactants are one of the variants of this type of ARCs. In 1992, An important discovery was made in the field of nanomaterial synthesis by scientists at Mobil Oil Co. (USA) [2–5]. They developed a matrix method for the synthesis of mesoporous silicates and aluminosilicates. A group of M41S mesoporous materials ((MCM-41—hexagonal mesophase, MCM-48—cubic mesophase, MCM-50—lamellar mesophase) was obtained with a regular, well-defined system of nanoscale structures by conducting a sol-gel process in the presence of a cationic surfactant hexadecyltrimethylammonium bromide (CTAB) [2–4]. In works [5, 6], a method of nanostructure self-organization, important for nanotechnology, was discovered and called the EISA method: Evaporation-Indused Self-Assembly (self-organization of nanostructures caused by solvent evaporation). CTAB is added to the silica sol to form a clear colloidal solution. When the solution is applied to glass by immersion, the solvent evaporates, which leads to an increase in surfactant concentration, and spontaneous formation of various micellar and liquid crystal structures from surfactant molecules occurs. Silicon dioxide nanoparticles are adsorbed on the surface of these structures with the formation of a nanostructured silicon dioxide film. When the film is heated to 500°C, the surfactant is destroyed and a transparent nanoporous silicon dioxide film is formed on the glass, which has the properties of antireflection coatings [7]. For the wide practical use of silicate glasses with ARC, not only the optical properties of the products are important, but also other properties, such as hardness and abrasion resistance of coatings. If the excellent optical properties (maximum light transmission of glass with a coating of ≥98.0–99.0%) are relatively easy to achieve by increasing the concentration of surfactants in the sol, then reaching hardness and abrasion resistance (≥2H–4H) acceptable for practical use is difficult. There are no detailed reports on the relationship between the hardness of optical coatings and the optical properties of glasses with ARC.

The purpose of the work was to study the optical properties of silicate glass with coatings and the hardness of ARCs produced from a silica sol composition containing different concentrations of CTAB.

EXPERIMENTAL

Tetraethoxysilane (Aldrich) purified by distillation three times in vacuo (99.9% content of the basic substance, determined by liquid chromatography), CTAB (Fluka) of substance content > 96.0%, and 2-propanol (Acros Organics) of substance content 99.0%, pydrochloric acid (reagent purity grade) were used. The water was obtained at a DM-1/BK Optima membrane distiller, the specific resistance of water was 14 MΩ cm^{-1}.

To obtain a silica sol by hydrolysis of tetraethoxysilane, 5.0 mL of tetraethoxysilane, 0.6 mL of H_2O, 1.0 ml of 0.1 N HCl, and 3.3 mL of 2-propanol were placed in a 50 mL glass flask and stirred for 4 h at room temperature. The resulting sol was diluted with 2-propanol to a 0.3 M SiO_2 concentration. A certain portion of CTAB was added to a silica sol with a 0.3 M concentration, and the mixture after stirring on a magnetic stirrer for 4 h was left for 24 h at room temperature.

Silicate slides for microscopy 25 × 75 × 1 mm in size were used as a substrate for the preparation of a SiO_2 xerogel film. The refractive index of glass was 1.51. The glass surface was cleaned of contaminants by immersion in a solution of alkali with hydrogen peroxide, then the glasses were washed with water, distilled water, and dried in an thermostat at 150°C for 6–8 h. The coatings were applied to the glass by immersing at 20–25°C and humidity 40-60%. For this purpose, a coating plant designed and manufactured in the laboratory was used. When the mechanism moves down, the glass was immersed in a bath with a sol composition. When the mechanism moves up at a certain speed, the glass was removed from the bath and film coating was applied. Coated glasses were left at room temperature for 1 h to remove most of the volatile compounds from the coatings. Then the glasses were heated to 500°C and kept at this temperature for 60 min. The light transmission of glasses with film coatings in the wavelength range 200–1100 nm was determined on a Perkin Elmer Lambda 25 spectrometer. The refractive index of the coatings was determined on an LEF-3M1 ellipsometer.

The size of the silicon dioxide nanoparticles in the sol was determined by dynamic light scattering (DLS) on a NanoBrook Omni instrument (Brookhaven Instruments, USA) with a solid-state laser (660 nm). The experiments with sols on the device were carried out with a measurement angle of 90°. The signal analyzer was used in multimodal mode. The accuracy of maintaining the temperature of the cell with a suspension of nanoparticles was ± 0.1°.

The hardness (abrasion resistance) of the coatings was determined using a Pencil-type hardness tester, State Standard GOST ISO 15184.

RESULTS AND DISCUSSION

Silicate glass has a maximum transmittance of 91.3% at 520 nm; with an increase in the wavelength of light to 1100 nm, the transmittance decreases to 82.3% (Fig. 1a, curve *1*). This is probably due to the presence in the glass of light-absorbing impurities of iron oxides. The refractive index of glass was 1.51, hardness ≥9H. The light transmission of glasses with single-layer double-sided coatings of silicon dioxide increases in the entire wavelength range of 350–1100 nm (Fig. 1a, curves *2–5*). The maximum transmittance of coated glass increases from 91.3 to 93.4% at λ_{max} = 520 nm (the maximum transmittance of coated and uncoated glasses coincides with λ_{max}) at a coating rate of 28.8 cm min^{-1}. The refractive index of the coating was 1.45, the hardness of the coating was 9H (Table 1).

Coatings (Fig. 1a, curves *2–5*) were produced from silica sols with a concentration of 0.3 M without CTAB; the temperature and cure time of coatings were 500°C, 60 min. The size of the silicon dioxide nanoparticles in the sol, determined by the DLS method, was 1.7 ± 0.4 nm.

An increase in the concentration of CTAB in the sol compositions of silicon dioxide leads to the formation of antireflection coatings on silicate glasses with increased light transmission (Figs. 2–4).

The experimentally calculated values of the maximum light transmission at λ_{max} = 520–550 nm and minimum at λ_{min} = 1100 nm of coated glasses, as well

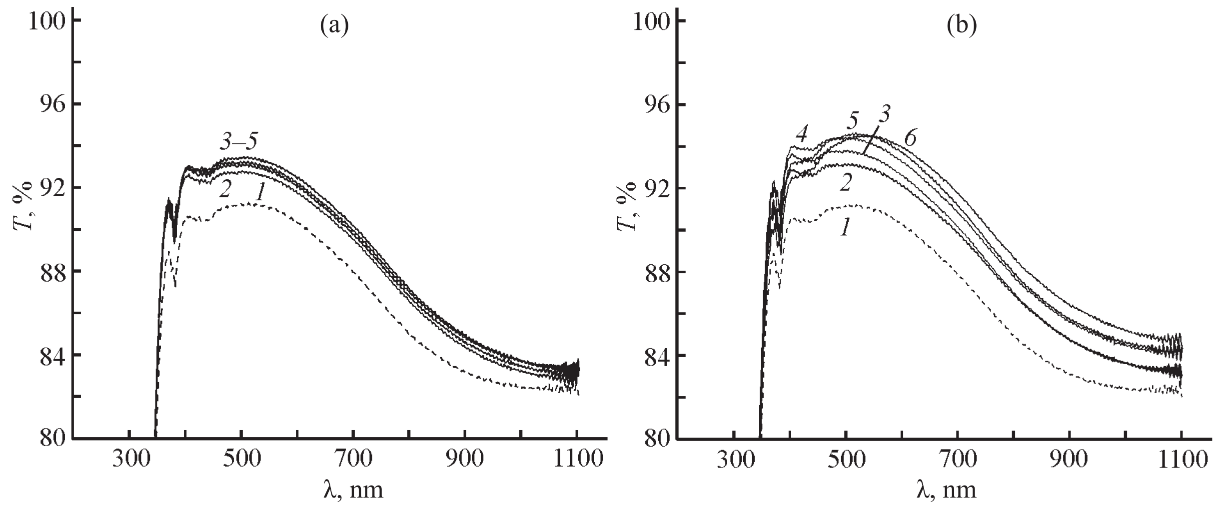

Fig. 1. (*1*) Light transmission of uncoated glasses and (*2*–*6*) with coatings obtained from a silica sol (a) without surfactant and (b) with 0.5 wt % (1.37 × 10^{-2} M) hexadecyltrimethylammonium bromide. Curing of coatings: 500°C, 60 min. Coating rate (cm min^{-1}): (a) (*2*) 12.5, (*3*) 16.3, (*4*) 19.2, (*5*) 28.8; (b) (*2*) 28.8 (silica sol without surfactant), (*3*) 12.5, (*4*) 16.3, (*5*) 19.2, (*6*) 28.8.

Table 1. Maximum wavelengths, maximum and minimum values on the light transmission curves of glasses with ARC, refractive index and hardness of coatings

[SiO_2], M	[Surfactant] × 10^2, M	Coating rate, cm min^{-1}	Maximum wavelengths, nm	Maximum transmittance,%	Minimum transmittance,%	Refractive index	Hardness
0.0	0.0	0.0	520	91.3	82.3	1.51	9H
0.3	0.0	12.5 28.8	510 520	92.7 93.4	82.8 83.5	1.45	9H
0.3	1.37	12.5 16.3 19.2 28.8	480 480 520 540	93.8 94.5 94.6 94.5	83.4 84.3 84.4 84.7	1.43	9H
0.3	1.92	12.5 16.3 19.2 28.8	490 490 550 560	94.6 94.6 95.0 94.5	83.4 84.2 85.8 85.3	1.40	8H
0.3	2.74	12.5 16.3 19.2 28.8	490 490 530 570	96.7 97.0 97.3 96.8	84.3 84.5 85.0 86.6	1.35	3H–4H
0.3	4.10	12.5 16.3 19.2 28.8	490 530 540 570	97.7 98.6 98.0 97.0	85.0 85.5 86.3 86.5	1.30	5B
0.3	5.20	12.5 16.3 19.2 28.8	520 550 600 550	99.0 98.8 98.7 98.0	92.3 92.5 93.6 88.8	1.27	5B

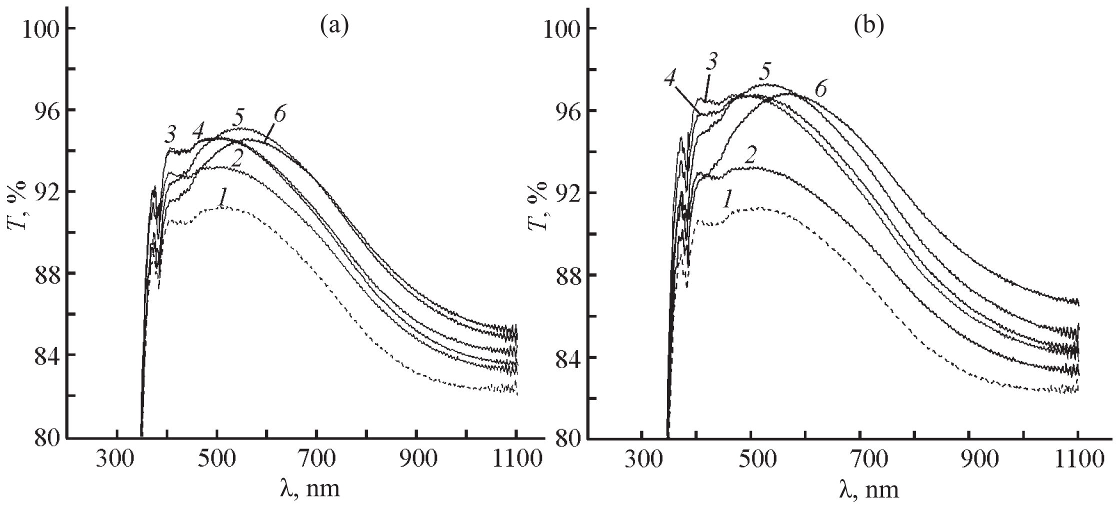

Fig. 2. (*1*) Light transmission of uncoated glasses and (*2*–*6*) with coatings obtained from a silica sol without surfactant and (a) with 0.7 wt% (1.92×10^{-2} M), (b) 1.0 wt % (2.74×10^{-2} M) hexadecyltrimethylammonium bromide. Curing of coatings: 500°C, 60 min. Coating rate (cm min^{-1}): (*3*) 12.5, (*4*) 16.3, (*5*) 19.2, (*6*) 28.8.

as experimentally determined refractive indices of the coatings and their hardness, are given in Table 1.

The dependence of the hardness of antireflective coatings based on nanoporous silicon dioxide on the refractive index of coatings and on the volume percent of nanopores in the coatings is not straightforward (Fig. 5).

The air content in nanopores was calculated according to the Bruggeman formula [8], taking the refractive index of amorphous silicon dioxide equal to 1.46 and using experimentally determined refractive indices of nanoporous coatings (Table 1). Based on the obtained experimental data, the following can be stated.

(1) The maximum transmittance of silicate glass with a single-layer double-sided coating produced from silica sols without surfactant increases by 2.1% compared to the same value of uncoated glass (Table 1, Fig. 1a), which is probably due to a smaller the refractive index of the coating (1.45) compared to glass (1.51). The minimum transmittance at 1100 nm also increases by 1.2% (Table 1).

(2) The light transmittance maxima of glass with antireflection coatings produced from silica sols with CTAB monotonically increase from 94.6 to 99.0% with an increase in the surfactant concentration in the sol from 1.37×10^{-2} (0.5 wt%) to 5.20×10^{-2} M (1.9 wt %) (Table 1, Figs. 1–4). The value of 99.0% is the maximum value of the maximum light transmission of this type of glass with antireflection coatings, since the glass contains impurities, probably iron oxides, which additionally absorb light. The increase in the maximum

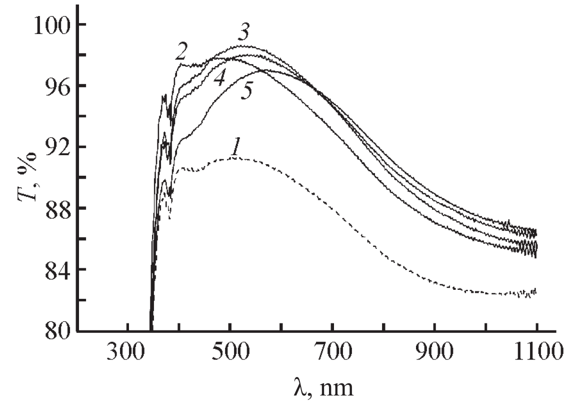

Fig. 3. (*1*) Light transmission of uncoated glasses and (*2*–*5*) with coatings obtained from a silica sol with 1.5 wt % (4.10×10^{-2} M) hexadecyltrimethyl ammonium bromide. Curing of coatings: 500 ° C, 60 min. Coating rate (cm min^{-1}): (*2*) 12.5, (*3*) 16.3, (*4*) 19.2, (*5*) 28.8.

light transmission of glasses with ARC is associated with a monotonic decrease in the refractive index of coatings from 1.43 to 1.27 (Table 1), which indicates an increase in the volume fraction of nanopores in them (Fig. 5). The minimum transmittance at 1100 nm also increases from 84.7 to 93.6% with an increase in the concentration of surfactants in the sol from 1.37×10^{-2} (0.5 wt %) to 5.20×10^{-2} M (1.9 wt %) (Table 1, Figs. 1–4).

(3) The hardness of the coatings decreases from 9H to 6H with a decrease in the refractive index from 1.45 to 1.37, while the volume content of air in nanopores increases from 2.2 to 19.0% (Fig. 5). The hardness of the coatings decreases sharply from 6H to ≤5B with

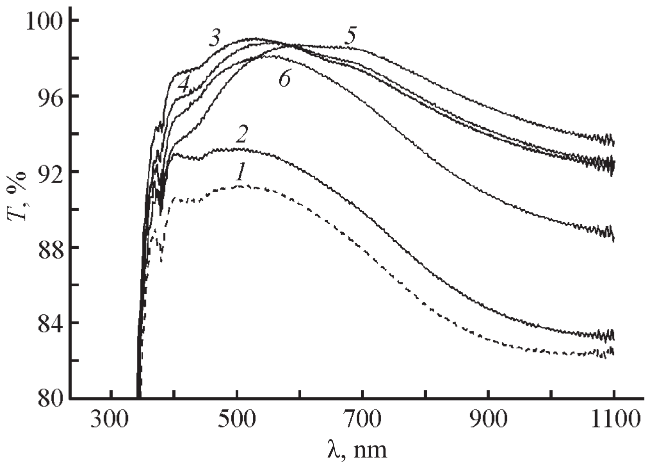

Fig. 4. (*1*) Light transmission of uncoated glasses and (*2*) with coatings obtained from a silica sol without surfactant and with 1.9 wt% (5.20×10^{-2} M) hexadecyltrimethylammonium bromide. Curing of coatings: 500°C, 60 min. Coating rate (cm min^{-1}): (*3*) 12.5, (*4*) 16.3, (*5*) 19.2, (*6*) 28.8.

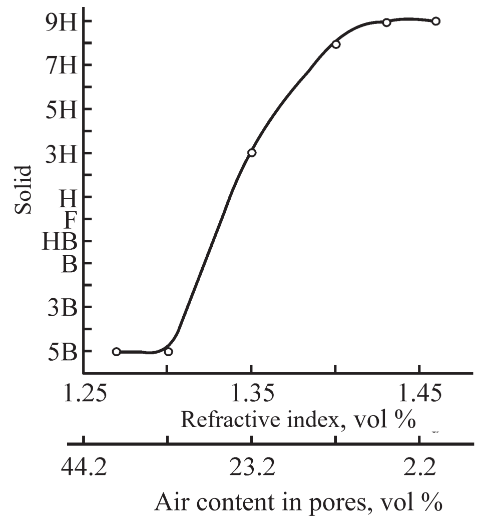

Fig. 5. Hardness of antireflection coatings obtained from sols of silicon dioxide with the addition of hexadecyltrimethylammonium bromide vs. the refractive index and air content in nanopores of antireflection coatings.

a further decrease in the refractive index from 1.37 to 1.32, and the air volume content in nanoporous coatings increases from 19.0 to 30.0% (Fig. 5). With a further decrease in the refractive index of coatings to 1.27, the content of nanopores in them increases to 40.0 vol %, and the hardness remains extremely low: ≤5B (Fig. 5). Figure 5 shows that coatings hardness ≥3H–4H, acceptable for practical use, can be achieved only if the refractive index of the coatings is ≥1.35–1.36 and the maximum volume content of nanopores in them is no more than 20.0–23.0 vol %.

(4) If we compare the experimental data on the maximum light transmission of glass with coatings (Table 1, Figs. 1–4) and the data on hardness of coatings (Fig. 5), we conclude that hardness ≥3H–4H, acceptable for practice, can be achieve if the maximum transmittance is ≤96.0–97.0%.

CONCLUSIONS

As a result of systematic studies of the light transmission of silicate glass with coatings, the hardness of the coatings obtained by immersing the glass in a silica sol composition containing different concentrations of surfactants, heating wet coatings at 500°C for 1 h with the aim of thermal destruction of the surfactant with the formation nanopores and simultaneous curing of the coating, a model was selected,which is the simplest sol composition of silicon dioxide obtained by acid hydrolysis in water–alcohol (isopropyl alcohol) solution widely used in practice and the cheapest silicon-containing compounds of tetraethoxysilane. To this sol, different concentrations of cationic hexadecyltrimethylammonium bromide were added [2–4]. With an increased concentration of surfactants in the sol, glasses with nanoporous antireflection coatings of a maximum transmittance maximum (99.0%) were produced. However, such coatings have a very low hardness (≤5B) and cannot be used in practice. The hardness of coatings acceptable for practice can be achieved provided that the maximum light transmission of glass with a single-layer double-sided coating is ≤96.0–97.0%.

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CONFLICT OF INTEREST

The authors state that they have no conflict of interest.

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