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Synthesis of stable sols based on titanium dioxide, silicon and metal ion for use in photocatalysis

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Abstract. The paper presents the study of physicochemical processes occurring during the preparation of film-forming solutions, as well as the effect of the component composition on the stability of film-forming solutions over time. Compositions of stable film-forming solutions of TBT, TBT-TEOS, TBT-TEOS-$AgNO_3$ suitable for the formation of thin-film coatings have been developed, and the time periods of stability of rheological properties have been determined. It was found that the addition of tetrabutoxytitanium after the establishment of chemical equilibrium in the solution increases the stability of the film-forming solutions. Optimization of the method of solutions preparation for obtaining films with reproducible physicochemical properties has been carried out.

1. Introduction

Photocatalytic methods of purification and disinfection of the air environment are currently being actively developed. The increased activity of research in the field of photocatalysis has created the need for new highly efficient photocatalytic materials. Today titanium dioxide is the most promising photocatalyst. The study of the photocatalytic activity of titanium dioxide began with a study by Fujishima and Honda, published in the 1972 Nature journal [1], which showed the photoelectrochemical decomposition of water molecules under the influence of ultraviolet radiation in the presence of TiO_2. By 1977, the photoactivity of TiO_2 was determined during the decomposition of organic substances [2, 3], and in 1983 titanium dioxide was used for the first time to clean the environment [4, 5]. In the last decade, the antibacterial and antiviral action of TiO_2 has been shown, which has found application in medicine [6].

Despite the large number of studies carried out, specific relationships between the properties of TiO_2 and its activity have not yet been established. In addition, materials based on TiO_2 are mainly synthesized using physical methods: fusion of oxides or magnetron sputtering, which imposes restrictions on studying the characteristics of the system in a wide range of concentrations.

The advantage of using the sol-gel technology to create systems based on titanium dioxide is the ability to manipulate the concentrations of the initial components in a wide range and at the same time achieve a high degree of their homogenization, as well as the purity of the resulting materials. It is necessary to select carefully the compositions of the initial solutions and the concentration ratios of their precursors for the reproducible production of final materials with specified physicochemical parameters and functional properties.

The main conditions for the preparation of time-stable solutions for the synthesis of films are the pH of the medium and the concentration of water. The nature of the solvent and the concentration of the

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metal salt have a significant effect on the viscosity of film-forming solutions. Absolute butanol is more accessible and will not absorb water vapor from the air, like ethanol; therefore, it is more convenient to control the concentration of water in a butanol environment

To obtain thin films, precursor solutions must satisfy a number of conditions defined by the states of the solution. When the precursors dissolve, a time period is required for the formation of a sol. The duration of the formation of a sol can be as short as several minutes, and last several days for substances of various nature. Obtaining film-forming solutions is associated with a sequence of physicochemical processes occurring in the liquid phase, such as dissolution (hydrolysis and solvation); condensation; coagulation, etc.

The aim of this work was to select the concentration ratios of the starting components to obtain stable TiO_2-based sols capable of forming photocatalytic structures.

2. Experimental part

2.1 Materials and experimental procedure.

Film-forming solutions for the preparation of thin-film TiO_2 and TiO_2-SiO_2-Ag were mixed using $Ti(OC_4H_9)_4$, $Si(OC_2H_5)_4$, $AgNO_3$, HNO_3 and distilled H_2O. In of all film-forming solutions, the volume of tetrabutoxytitanium was 0.35 ml (the concentration of $Ti(OC_4H_9)_4$ in the film-forming solutions was 0.1 M). The concentration of $Si(OC_2H_5)_4$ in the solution was varied from 0.1 to 0.5 M, $AgNO_3$ - from 0.001 to 0.005 M, HNO_3 - from 0.01 to 0.06 M, H_2O - from 0.2 to 2 M. Analytical grade butyl alcohol (H_2O content 0.03 wt%) was used as a solvent. The sol formation proceeded at room temperature.

2.2. Research methods.

Viscometry is based on the measurement of the flow time of a liquid of a known volume through a capillary from a measuring tank. The determination of the kinematic viscosity of the film-forming solutions was carried out using a VPZh-2 viscometer with a capillary diameter of 0.99 mm. To calculate the kinematic viscosity, the following equation was used: $\upsilon = (g/9.807) \cdot T \cdot K$, where υ is the kinematic viscosity of the liquid, mm^2/s; g - acceleration of gravity at the measurement point, m/s^2; T is the average time of fluid flow, s; K is the constant of the viscometer, mm^2/s^2.

The pH values were obtained using an ITAN pH meter. A silver chloride electrode was selected as the reference electrode for measurements.

3. Results and Discussion

Sols and gels have been sufficiently studied in liquid solutions. At the first stage, such solutions easily diffuse and have molecular weights corresponding to the monomeric form. However, over time, the molecules in such solutions increase in size and diffusion stops. This is due to an increase in the size of the particles and a decrease in their total number, or as a result of the formation of such particles of larger aggregates, which leads to the formation of a gel. These processes increase the viscosity of solutions, the measurement of the value of which can serve as an indication of all these processes. From the presented dependences, it can be seen that an increase in the concentration of water in a solution leads to a significant decrease in its "lifetime" (Figure 1).

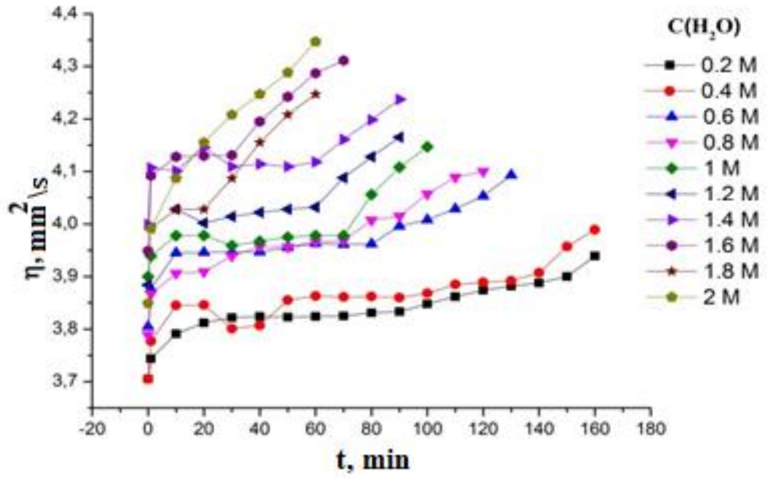

Figure 1. Change in the kinematic viscosity of film-forming solutions with different concentrations of H_2O

Water actively enters into hydrolysis with tetrabutoxytitanium. The resulting hydroxy derivatives of tetrabutoxytitanium are then condensed; $C_4H_9OH_2^+$ ions serve as catalysts of this process in a butanol medium. As a result of dissociation, the concentration of $C_4H_9OH_2^+$ ions in the solution increases, which is confirmed by a gradual decrease in the pH of the freshly prepared solution (Table 1). As a result, the molecular weight of the forming polymers increases, and the viscosity of the solution increases rapidly.

Table 1. PH values of film-forming solutions depending on time.

C (H_2O) in solution	**PH value**			
	1 min.	**5 min.**	**10 min.**	**20 min.**
0.2 M	7.71	6.42	5.22	4.65
0.4 M	7.67	6.39	5.31	4.58
0.6 M	7.61	6.31	5.18	4.52
0.8 M	7.56	6.26	5.15	4.54
1 M	7.49	6.20	5.07	4.59
1.2 M	7.52	6.36	5.16	4.62
1.4 M	7.50	6.24	5.28	4.51
1.6 M	7.47	6.18	5.25	4.55
1.8 M	7.55	6.29	5.12	4.58
2 M	7.59	6.31	5.23	4.57

It is known that in an acidic medium, the hydrolysis of tetrabutoxytitanium occurs at a higher rate, which leads to an increase in the aggregative stability of sols and the stability of film-forming solutions [8, 9]. Considering this fact, it was decided to introduce nitric acid into the composition of film-forming solutions.

The study of the influence of the concentration of nitric acid on the stability of film-forming solutions revealed that with an increase in the concentration of HNO_3 in them from 0.01 to 0.06 M, their viscosity almost halved. This is because hydrolysis is faster than condensation, and the resulting particles have a small size due to their low-branched structure.

The addition of nitric acid in the range from 0.01 to 0.04 M leads to rapid gel formation, as a result of which the solution is unsuitable for producing film coatings. It was found that when the concentration of nitric acid is more than 0.05 M, the viscosity of the investigated colloidal systems is stabilized. For a solution with a nitric acid concentration of 0.06 M, viscosity stabilization is observed after 6 hours and reaches 5.52-5.64 mm/s^2; this is accompanied by an increase in the solution stability interval for more than 48 hours.

Further measurement of the viscosity in time of film-forming solutions with concentrations of nitric acid from 0.01 to 0.06 M made it possible to establish the period of their suitability for producing films (Table 2).

Table 2. Stability of film-forming solutions over time.

C (HNO_3)	Stabilization time, h	Expiration date, days
0.01 M	More 24	Unsuitable
0.02 M	More 24	Unsuitable
0.03 M	More 24	Unsuitable
0.04 M	More 24	27
0.05 M	10	34
0.06 M	6	42

The addition of tetraethoxysilane to the system is due to the effect on the parameters of the resulting coatings. A decrease in the thickness of films containing SiO_2 was shown, as well as an increase in their uniformity in thickness was noted.

An increase in the concentration of tetraethoxysilane in film-forming solutions is accompanied by a smoother increase in viscosity and faster stabilization of solutions (Figure 2).

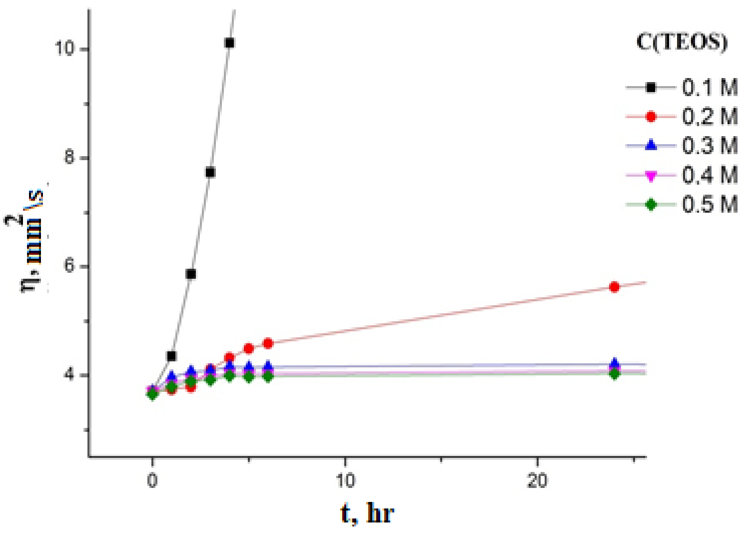

Figure 2. Change in the kinematic viscosity of film-forming solutions with different concentrations of HNO_3

The addition of silver nitrate to the system is due to the effect of silver ions on the band gap of titanium dioxide. The presence of silver ions makes it possible to reduce the energy of the band gap of the final material, which makes it possible to expand its photocatalytic capabilities. The introduction of silver nitrate into the film-forming solution in the selected concentration range (0.001 - 0.006 M) practically does not affect the nature of the change in viscosity and the stability of the film-forming solutions.

4. Conclusion

As a result of the work carried out, it was found that the processes occurring during the preparation of film-forming solutions are significantly affected by the concentration of water and nitric acid (in the studied concentration ranges). The most stable in time turned out to be film-forming solutions with concentration ratios of water 0.2 - 0.4 M and nitric acid 0.05 - 0.06 M. The studies carried out will optimize the composition of solutions to obtain stable TiO_2 sols.

Acknowledgments
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