Production of fine-dispersed tungstic acid

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The paper presents the results of studies of fine-grained tungstic acid synthesis and research of tungsten trioxide obtained from it. A literature analysis was performed and the direction of the study was formulated. A method of precipitation of tungstic acid from sodium tungstate solutions by hydrochloric acid solution has been proposed. To produce tungstic acid, a continuous operation unit that provided the required draining rates of sodium tungstate and hydrochloric acid solutions, the temperature of draining solutions and their concentrations, was created. The dependence of the specific surface of the obtained tungstic acid on the concentration of the used hydrochloric acid was investigated, and the optimum concentration of hydrochloric acid at 430 grams per liter was determined. Using the mathematical method of simplex-planning experiments, the effect of three parameters on the specific surface area of tungstic acid — the concentration of sodium tungstate solution, the ratio of volume rates of drained solutions, and the temperature of drained solutions, was investigated. The following, close to optimum parameters have been received: concentration of sodium tungstate solution of 35–40 grams per liter, ratio of concentrated (430 g/l) hydrochloric acid to the volume of sodium tungstate solution is (1.9–2.0):1, temperature of solutions is 15–20 °C. Tungstic acid with a specific surface area of 60 m^2/gram was obtained. It is determined that for the preparation of tungsten trioxide with a high specific surface area, the heating rate of tungsten acid in its drying must be 40–50 degrees per hour and the final drying temperature must be equal to 400 °C. Figures illustrating the dependence of the specific surface of the obtained tungstic acid on the concentration of sodium tungstate solution, the ratio of the volume velocities of the drained solutions and the temperature of the drained solutions are presented.

Key words: tungstic acid, tungsten trioxide, specific surface area, synthesis, precipitation, tungsten carbide.

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Introduction

One of the applications of tungstic acid H_2WO_4 is the preparation of composite materials (composites (CM)) [1, 2] and in particular structural and hard alloys [3–6]. There are a great number of literary sources on composites by the present time. For example, composite materials are very detailed covered by the professor of the Russian Chemical-Technological University M. L. Kerber [1] as well as by N. V. Klyuchnikova [2]. CMs consist of a relatively plastic base or matrix and hard and strong filler components. According to the purpose composites are divided into general-structural, heat-resistant, friction and antifriction. As matrixes for manufacturing of metal structural composites are used: light metals on the basis of magnesium and aluminum; alloys on the basis of titanium and copper; heat resistant alloys on the basis of iron, nickel and cobalt; refractory alloys on the basis of tungsten, molybdenum, niobium and their carbides [7].

The most important properties of metal carbides are durability, heat resistance, chemical stability, which have tungsten monocarbide WC and semi-tungsten carbide W_2C, carbides of tantalum TaC, titanium TiC, molybdenum MoC, zirconium ZrC, silicon SiC, vanadium VC. Their hardness is comparable to that of corundum, they do not decompose at high temperatures and are insoluble in the most corrosive acid environments. Some of the hardest carbides are tungsten carbides with a hardness of 9 out of 10 on the Mohs scale. Melting point of WC is 2720 °C, density 15.6 g/cm^3, microhardness 17.16 GPa. The above carbides are used in metallurgical industries, particularly in powder metallurgy [8, 9].

WC and W_2C tungsten carbides are the most significant from a practical point of view. WC tungsten monocarbide compared with W_2C is more stable and has greater hardness, W_2C semi-carbide is more heat-resistant and penetrates into solid solutions with iron, cobalt and other metals faster. The set of physical-chemical properties of WC and W_2C is determined by their dispersibility, i.e. fineness of grain, as well as by their degree of purity, and depends on the production technology. WC particle size in tungsten-carbide alloys used for metal-cutting tools varies from 0.1 to 16 micrometers. At that, an increase in WC grit leads to a decrease in hardness, elasticity, and resistance to abrasive wear. Special fine-grained grades of tungsten-carbide alloys are used to process heat- and corrosion-

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resistant alloys. In addition, tungsten carbide is used as a catalyst in gas-phase reactions [10−14], for a hydrogen electrode in fuel cells (electrochemical generators) [15], as a catalyst in petrochemistry [16].

In connection with the above, the preparation of fine-grained tungsten carbide as a catalyst for various chemical processes and dispersion-strengthening phases for the synthesis of composite materials is a very relevant task.

To produce tungsten carbides the following methods are used:

1. Method of carbon saturation of calcined carbon black with tungsten powder obtained from tungsten trioxide. Saturation temperature 1350−1650 °C, with process duration of 1.5−2.5 hours in hydrogen medium;

2. Method of carbon reduction of tungsten trioxide with carbon black accompanied by carbidization. The reduction reaction of tungsten trioxide is carried out through the gas phase in the presence of CO and H_2;

3. Tungstic acid and tungsten trioxide mixture heating in a methane-hydrogen medium at 860−1100 °C;

4. Electrolysis of salt melts.

Most tungsten carbide production methods use tungsten acid with a specific surface area of 1−2 m^2/gram and the tungsten trioxide WO_3 derived from it. According to the literature [17], tungstic acid H_2WO_4 or tungsten trioxide monohydrate $WO_3 \cdot H_2O$ can be precipitated from alkali metallic tungstates solutions under the influence of strong acids, such as sulfuric, hydrochloric and nitric acids.

Tungstic acid exists in two modifications: white and yellow. White modification is produced by the interaction of alkali metallic tungstates with dilute acids; yellow is produced by the use of more concentrated acids. Under normal conditions, the white modification of poorly-filterable hydrated tungstic acid $H_2WO_4 \cdot H_2O$ falls out, which when heated to 70-100 °C loses a water molecule and turns into the yellow modification. When heated to a temperature of 188 to 500 °C, tungstic acid completely loses water and turns into tungsten trioxide WO_3 [18], which is the main reagent for the preparation of tungsten carbide powders WC and W_2C.

Research methods

For the preparation of tungsten carbide of the required quality, we took as a basis the second and third methods (described above). The aim of the research was to increase the fineness of grain, that is, to reduce the particle diameter (which corresponds to an increase in the specific surface area) of the resulting material. We used the precipitation of tungstic acid H_2WO_4 from sodium tungstate solution by its interaction with hydrochloric acid according to the reaction:

$$Na_2WO_4 + 2HCl = H_2WO_4 + 2NaCl \qquad (1)$$

Diluted solutions of sodium tungstate and an excess of concentrated hydrochloric acid solutions were used to receive tungstic acid with an increased specific surface area.

The residual content of sodium tungstate after the reaction (completeness of tungstic acid precipitation) was checked by the procedure given in [19]. The resulting diluted pulp was thickened during sedimentation, decanted, then the thick pulp was centrifuged or filtered on a Büchner funnel to produce tungstic acid paste. Tungstic acid paste was dried to form granules with a diameter of 1−2 mm, then the granules were milled to a particle size of 0.044 mm in order to obtain good accessibility of carbon monoxide to tungstic acid molecules during further carbidation, the resulting powder was analyzed to determine the dispersion of tungstic acid.

To obtain tungsten carbide, we heated tungsten powder in a carbon monoxide atmosphere and kept it under certain conditions. In this process, tungstic acid is carbidized to produce tungsten carbide in the following steps:

$$H_2WO_4 - WO_3 - WO_{2.9} - WO_{2.72} - W_2C - WC \quad (2)$$
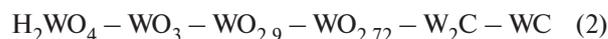
To obtain tungsten carbide with a small grain size it is necessary to use the initial material — fine-grained H_2WO_4, which was the task of this stage of research.

The dispersion of tungsten acid and the products obtained from it — tungsten trioxide, carbidization intermediate phases and tungsten carbide — was determined indirectly by measuring the specific surface of powders. For this purpose, there are several methods, for example, by low-temperature adsorption of krypton on the Brunauer-Emmett-Teller installation or by low-temperature adsorption of nitrogen on the Klyachko-Gurvich installation.

Study of the phase composition was carried out on an automated diffractometer DRON-3 with Cu K_α — radiation and β-filter. X-ray phase analysis was performed on powder sample diffractograms using the method of equal weights of artificial mixtures. Identification of phases is carried out according to the known reference books.

Results and discussion

To carry out experiments on obtaining fine-grained tungstic acid, we created an installation including the main unit (Fig. 1) and auxiliary devices: a vessel for the preparation of sodium tungstate solution of a certain concentration and temperature, a vessel for thickening the tungstic acid pulp, decantator, centrifuge, Büchner funnel, Bunsen flask, vacuum pump, drying cabinet with programmable drying mode, grinding device, such as a mill, installation to determine the specific surface of powders.

A sketch of the main block of the continuous unit for tungstic acid synthesis is shown in Fig. 1. On the magnetic stirrer 1 there is a reactor 2 for interaction of tungstate solution with hydrochloric acid. The temperature of solutions in the reactor is measured by thermometer 3. Tungstate solution is poured into the tank 4, and hydrochloric acid — into the tank 5. The volume of drained solutions is regulated by dosing taps 6. The amount of solutions is controlled by the degree of opening of the dosing cocks, calibrated in advance for certain solution flow rates. Tungstic acid slurry is discharged into the collecting
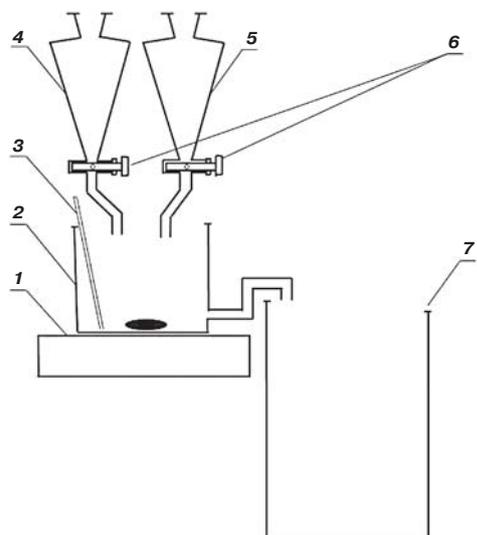
Fig. 1. Tungstic acid synthesis unit:
1 — magnetic stirrer; *2* — reactor; *3* — thermometer; *4* — sodium tungstate solution tank; *5* — hydrochloric acid tank; *6* — dosing taps; *7* — tungstate acid collecting tank

tank *7*.

The unit works as follows. Solutions of sodium tungstate and hydrochloric acid are prepared in separate containers with required concentrations and temperatures. Solutions are poured into the appropriate tanks *4* and *5*. The magnetic stirrer *1* is switched on, the dosing cocks *6* at required solution flow rates are opened and then the solutions are fed to the reactor *2*. During intensive stirring of the solutions with a magnetic stirrer, tungstate reacts with hydrochloric acid to produce tungstic acid, after which the pulp of tungstic acid is poured into tank *7*. Then the tungstic acid pulp is thickened and the condensed part is separated from the solution by centrifugation and filtration. Since the resulting tungstic acid is very fine-grained, the thickening proceeds slowly.

If the units are used in continuous mode, pre-prepared solutions of tungstate and hydrochloric acid are topped up in the corresponding tanks *4* and *5*. The volumetric velocities of sodium tungstate and hydrochloric acid solutions ranged from 20 to 800 ml/min. The tungstic acid pulp obtained as a result of reaction (1) contains NaCl, so after thickening the pulp and separating the thickened part from the solution by decantation an intensive washing of the thickened part of tungstic acid from sodium chloride was performed.

For precipitation of tungstic acid can be used solutions of ammonium tungstate $(NH_4)_2WO_4$ or sodium tungstate Na_2WO_4, we used the most common reagent — sodium tungstate Na_2WO_4 with "ХЧ" grade of purity (reagent grade) and hydrochloric acid with "ХЧ" grade of purity (reagent grade).

The concentration of hydrochloric acid C_{HCl} and sodium tungstate C_{Na2WO4} solutions, the temperature of interaction between the components, as well as the ratio of volume rates of the drained solutions $V_{HCl}/V_{Na_2WO_4}$ (one

liter of Na_2WO_4 solution consumes from 1.56 to 2.12 liters of HCl) can affect the dispersity of tungstate acid (the value of its specific surface area S_{sa}).

At the initial stage, search experiments were carried out to determine the effect of hydrochloric acid concentration on the dispersity of tungstic acid **(Table 1)**. In these experiments the concentration of sodium tungstate solution was 50 g/l, the ratio of the volume of hydrochloric acid to the volume of sodium tungstate solution was 2, the temperature of the drained solutions was chosen to be 40 °C. The concentration of hydrochloric acid was varied from 300 g/l to 430 g/l.

According to **Table 1**, the concentration of hydrochloric acid has little effect on the specific surface area of tungstic acid, but in order to reduce the volume of solutions, it is preferable to take concentrated hydrochloric acid (430 g/l).

Further research and processing of the results were carried out using the mathematical method of simplex planning experiments [19–22]. During the process of tungstic acid precipitation the following variables were taken: concentration of sodium tungstate solution CNa_2WO_4, ratio of volume velocities of drained solutions $V_{HCl}/V_{Na_2WO_4}$, temperature of initial solutions τ, °C, which were prepared in advance in appropriate containers (see **Fig. 1**). The specific surface area of the obtained tungstic acid is given in the last column of **Table 2**.

The deposition parameters of experiments 7 and 8 lead the research to an almost stationary region of maximum specific surfaces of tungstic acid. To confirm this, the ninth experiment was carried out. In this case, tungstic acid with a specific surface of 55 m^2/g was obtained. According to **Table 2**, the extremum of optimality was reached in the

Table 1
Dependence of specific surface area of the obtained tungstic acid on the concentration of hydrochloric acid

Exp. No.	HCl concentration, g/l	Specific surface area, m^2/g
1	300	36.95
2	350	37.60
3	400	37.91
4	430	38.06

Table 2
Optimization of the tungstic acid precipitation process

Exp./ No.	$C_{Na_2WO_4}$, g/l	$V_{HCl}/V_{Na_2WO_4}$	τ, °C	S_{sa}. H_2WO_4, m^2/g
1	55	2.12	44	29.36
2	45	2.12	44	39.39
3	50	1.80	44	34.90
4	50	2.00	28	48.51
5	42	1.83	33	59.36
6	41	2.15	26	57.15
7	44	1.85	14	60.54
8	35	1.89	22	60.34
9	40	1.56	20	55.01

seventh and eighth experiments.

It is not possible to illustrate the conducted research with a single figure, since the output parameter Ssa depends on three variables. Therefore, some experiments (**Table 2**) are illustrated by **Fig. 2, a-c**, in each of which S_{sa} depends on two variables. **Fig. 2, a** shows experiments 1–3, conducted at a temperature of 44 °C. The figure clearly shows that to increase S_{sa}. of tungstic acid it is necessary
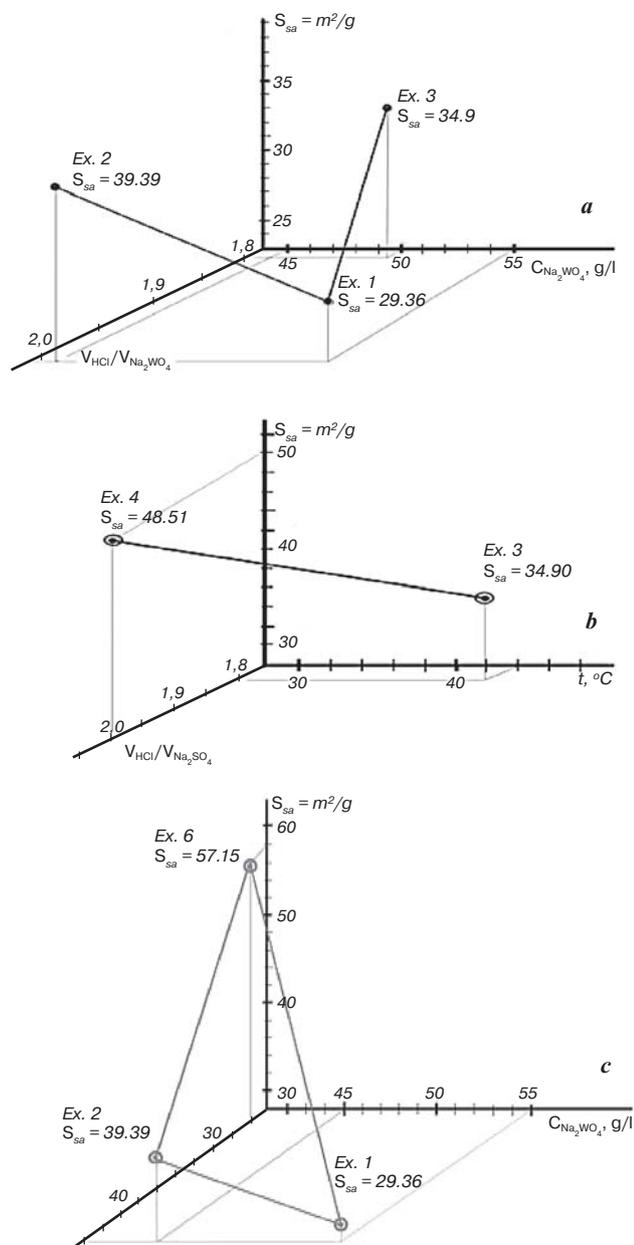
Fig. 2. Dependence of the specific surface area of tungstic acid S_{sa}:
a – Dependence of specific surface area S_{sa} on concentration of sodium tungstate solution $C_{Na_2WO_4}$ and ratio of hydrochloric acid volume to volume of sodium tungstate solution $V_{HCl}/V_{Na_2WO_4}$;
b – Dependence of specific surface area of tungstic acid Ssa on temperature of drained solutions t,°C and ratio of hydrochloric acid volume to sodium tungstate solution volume $V_{HCl}/V_{Na_2WO_4}$
c – Dependence of specific surface area of tungstic acid S_{sa} on concentration of sodium tungstate solution C_{Na2WO4} and temperature t, °C

to decrease concentration of sodium tungstate solution and to decrease the ratio of hydrochloric acid volume to sodium tungstic acid solution volume from 2.12 to ≈ 1.8.

Fig. 2, c shows experiments 1, 2, 6, where the concentration of sodium tungstate and temperature of solutions are variables. In this case the ratios $V_{HCl}/V_{Na_2WO_4}$ are very close to each other and are equal to 2.12–2.15. The figure shows that in order to increase Ssa it is necessary to reduce the concentration of sodium tungstate and the temperature of solutions in the reactor. A very high specific surface area of tungstic acid was obtained, which wes 57.15 m²/g. Maximum Ssa was obtained in experiments 7 and 8 (60.54 and 60.34 m²/g), where all three variables are close to optimal values.

Thus, using the simplex-planning method of experiments [19–22], with only nine experiments it was possible to achieve a nearly stationary region and obtain tungstic acid with a specific surface area of 60.34-60.54 m²/g.

According to data of **Table 2** and **Fig. 2** we can find the convenient parameters of tungstic acid precipitation, which are within the range: $C_{Na_2WO_4}$ = 35–40 g/l, $V_{HCl}/V_{Na_2WO_4}$ = 1.9–2.0, the temperature of draining solutions 15–20 °C. In these conditions the specific surface of tungstic acid will be 60–64 m²/gram.

Using parameters received as a result of the experiment 8 presented in the **Table 2**, experiments on definition of influence of speed of draining of solutions of sodium tungstate and hydrochloric acid on a specific surface of tungstic acid were carried out. The rate of draining the solutions ranged from 20 to 800 milliliters per minute and had no significant effect on the S_{sa} H_2WO_4. Deviations of the values of the specific surface area of tungsten acid were equal to ≈ 3% and S_{sa} in five parallel experiments ranged from 58.52 to 62.13 m²/g.

For further experiments, a significant batch of tungstic acid was prepared according to the precipitation regime given in experiment 8 **(Table 2)**. Deviations of values of specific surface of the samples obtained in all experiments were 0.82 m²/g, which is 1.36% of 60.34 m²/g.

Tungstic acid drying

In experiments on the preparation of tungstic acid a slurry of hydrated tungstic acid with the formula $H_2WO_4 \cdot H_2O$ was obtained. This acid, due to its grain fineness, thickened for a long time and after filtration and centrifugation it turned into a pasty state. Further, to remove sodium chloride the tungstic acid paste was washed with a large excess of distilled water, then placed in a thin layer in a Petri dish and dried in a desiccator at a certain temperature and heating rate until constant weight is reached. Under these conditions, hydrated tungstic acid lost its water molecule and transformed into anhydrous H_2WO_4. At temperatures above 188 °C, H_2WO_4 (or $WO_3 \cdot H_2O$) loses the water molecule and converts to tungsten trioxide WO_3 through the stages:

$$WO_3 \cdot H_2O \rightarrow WO_3 \cdot 0.5H_2O + 0.5H_2O \rightarrow WO_3 + H_2O \quad (3)$$
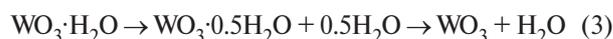
In this case, if the heating rate is high, the particles of

tungstic acid and tungsten trioxide obtained from it stick together and become larger, resulting in a decrease in the specific surface area of tungsten trioxide. If the heating rate is low, there is no adhesion of the particles. The calculation, which takes into account tungstic acid and tungsten trioxide molecular weight ($H_2WO_4 - 249.86$; $WO_3 - 231.85$) and their density ($H_2WO_4 - 5.5$; $WO_3 - 7.16$) shows that the specific surface of resulting WO_3 should be 1.2 times less than the original tungstic acid, due to changes in molecular weight and density of the material. To reduce particle coarsening, the suitable heating rate of tungstic acid during its drying process was determined.

For the experiments on H_2WO_4 drying, tungstic acid with a specific surface area of 60.00 m^2/g was taken. The heating rate of the desiccator was from 40 to 140 °C per hour. The results of the experiments are shown in **Table 3**.

There is practically no decrease in the specific surface area during slow heating, and it may even increase slightly (experiments 4 and 5). Probably, the removal of water from tungstic acid causes the splitting of its particles, which leads to an increase in the specific surface area of the resulting tungsten trioxide.

Powder of dried tungsten trioxide was grinded on an "ИД65" grinder to a particle size of 0.044 mm. It was found experimentally that such a particle size is achieved in 10 minutes of the grinder's work.

Literature review showed that powdered tungsten carbide is widely used as a catalyst in the chemical and petroleum industries, in the creation of composite materials with a metal matrix for the manufacture of metalworking products and drilling tools. At the same time, the more fine-grained tungsten carbide powders are, the higher their performance properties are. Thus, obtaining fine-grained tungsten carbide is an actual task.

The synthesis of highly dispersed tungsten carbide powder also requires highly dispersed tungstic acid, as well as the tungsten trioxide obtained from it. In order to prepare them, the authors chose the method of precipitation of tungstic acid from sodium tungstate solution with hydrochloric acid. A tungstic acid production unit has been developed, the basic unit of which includes a magnetic stirrer, a reactor, a thermometer, tanks for sodium tungstate solution and hydrochloric acid with dosing cocks and a collecting tank. The unit provides the required parameters of tungstic acid precipitation.

The authors showed that it is necessary to take concentrated hydrochloric acid to precipitate tungstic acid from sodium tungstate solution. The authors applied a mathematical method of simplex-planning of experiments that allows to achieve the maximum output parameter, i.e. the specific surface of tungstic acid, with a minimum number of experiments. Using the method of simplex-planning experiments, the effect of three parameters on the specific surface area of tungstic acid was investigated: the concentration of sodium tungstate solution, the ratio of volume velocities of drained solutions, and the temperature of drained solutions. Nine experiments found near-

Table 3

Dependence of the specific surface area of tungsten trioxide on the heating rate of tungstic acid

Exp. No.	Final temperature, °C	Heating rate, °C/hour	Final S_{sa}, m^2/g
1	380	140	45.34
2	290	100	51.21
3	360	70	56.38
4	400	50	59.93
5	400	40	60.57

optimal conditions for producing tungstic acid with a specific surface area of 60 m^2/g. These conditions are as follows: concentration of sodium tungstate solution of 35−40 grams per liter, ratio of concentrated (430 g/l) hydrochloric acid to tungstate solution volume (1.9-2.0):1, temperature of solutions 15−20 °C. The obtained results are illustrated by figures.

It was found that for the preparation of tungsten trioxide with a high specific surface area, the heating rate of tungstic acid in its drying should be 40−50 degrees per hour and the final drying temperature should be equal to 400 °C.

Conclusion

1. An installation that provides the necessary parameters for tungstic acid deposition has been created.

2. Using the mathematical method of simplex-planning experiments, the effect of three parameters on the specific surface area of tungstic acid was studied: the concentration of sodium tungstate solution, the ratio of volume velocities of drained solutions, and the temperature of drained solutions. Nine experiments found near-optimal conditions for producing tungstic acid with a specific surface area of 60 m^2/g. These conditions are as follows: concentration of sodium tungstate solution of 35−40 grams per liter, ratio of concentrated (430 grams/liter) hydrochloric acid to tungstate solution volume (1.9−2.0):1, temperature of solutions 15−20 °C.

3. It was found that for the preparation of tungsten trioxide with a high specific surface area, the heating rate of tungsten acid in its drying should be 40−50 degrees per hour and the final drying temperature should be equal to 400 °C.

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