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BRIEF COMMUNICATIONS

On the Condition of Rising the Content of the TiO_2 Rutile Form during a Vapor-Phase Hydrolysis

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Abstract—On the basis of the examination of the data on the process of producing titanium dioxide by the vapor-phase hydrolysis the temperature dependence of obtaining the contents of the rutile form of titanium dioxide and chlorine in the finished product was studied.

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The practical application of TiO_2 produced by the vapor-phase hydrolysis from $TiCl_4$ [1] in the industry of plastics and in the production of some types of paper depends on the TiO_2 form, rutile or anatase. Technical specifications normalize the rutile form content in a finished product to be no less than 90%, and in some special cases even more: up to 95–97%. Theoretical reasons point to the fact that rising the rutile form content in the finished product is connected with an increase in the process temperature, as anatase and brookite irreversibly turn to rutile on heating at 400–1000 and ~750°C, respectively [2]. An examination of concrete data on the process of titanium dioxide production has shown that the process temperature is the main factor of reaching the required quality of the finished product.

The vapor-phase hydrolysis proceeds at 550–1400°C and higher by the reaction

$$TiCl_4\ (\text{vapor}) + 2H_2O\ (\text{vapor}) = TiO_2 + 4HCl.$$

Fine particles of titanium dioxide subside under own gravity and leave the plant, whereas waste gases together with HCl are removed to a gas-cleaning units. The complete an engineering scheme of the process is given in [1].

The main data on the process of titanium dioxide production are given in [1] where the effect of the addition of the lowest titanium chlorides and silicon tetrachloride on the process characteristics is described (see the table).

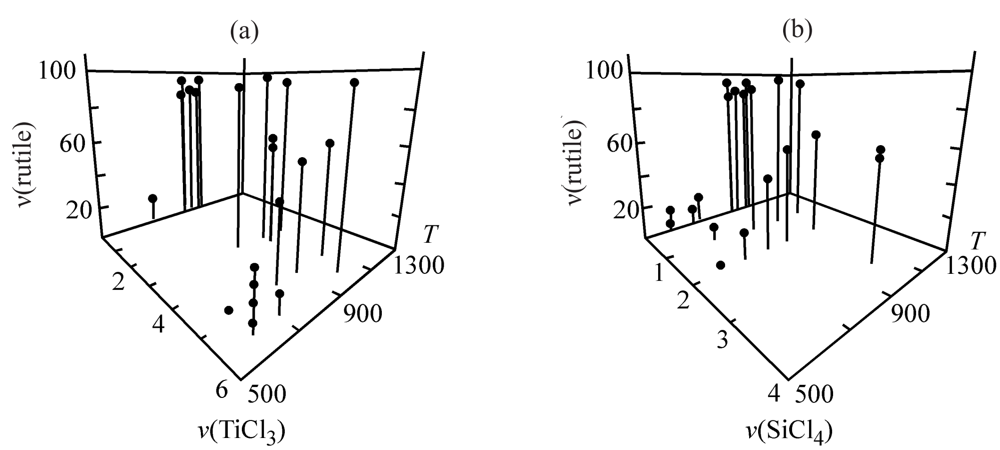

Fig. 1. Three-dimensional drawing of the effects of (a) $TiCl_3$, (b) $SiCl_4$, and temperature on the content of the rutile TiO_2 form according to the data of [1]. (ν) a component content, wt %; (*T*) temperature, C.

Certain data on the process [1]

Content of additions, %		Temperature in a reaction zone, °C	TiO_2 form, wt %		Content in a product, wt %	
$TiCl_3$	$SiCl_4$[a]		rutile	anatase	Cl^-	TiO_2
5.55	0.02	1000	92.8	7.2	0.17	97.0
5.55	0.02	700	10.6	89.4	1.07	97.0
5.55	0.02	600	4.6	95.4	1.24	96.0
5.55	0.02	600	13.8	86.2	1.10	95.5
4.88	1.90	800	42.1	57.9	0.25	97.0
4.88	1.90	900	57.5	42.5	0.20	97.0
4.88	1.90	1050	63.3	36.8	0.12	97.0
4.88	0.90	700	7.3	92.7	0.60	97.0
4.88	1.90	700	15.2	84.8	0.55	97.0
4.88	1.90	600	1.7	98.3	0.97	95.0
3.11	1.10	860	90.8	9.2	0.15	97.0
3.11	1.10	1000	95.8	4.2	0.06	97.0
3.11	1.10	1120	93.1	6.9	0.14	97.0
3.40	3.40	1000	58.5	41.5	0.12	95.0
3.40	3.40	1000	62.3	37.7	0.11	98.0
0.02	0.02	980	86.4	13.6	0.36	98.0
0.02	0.02	900	85.7	14.3	0.33	97.2
0.02	0.02	940	88.5	11.5	0.29	97.8
0.02	0.02	730	17.4	82.6	0.63	98.0
0.02	0.02	1000	94.7	5.3	0.17	98.1
0.02	0.02	900	94.1	5.9	0.2	97.1

[a] Low-boiling distillate containing about 80% of $SiCl_4$, the remaining $TiCl_4$.

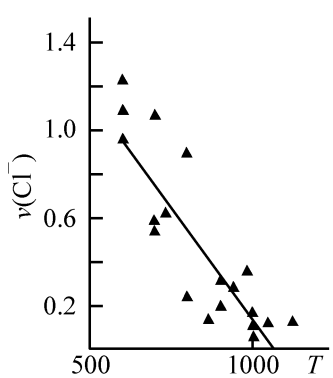

Fig. 2. Dependence of Cl^- content $\nu(Cl^-)$ (wt %) in the target product on the process temperature T (°C).

The data of the table point to a correlation between the process temperature, introduced additions, and the content of the rutile TiO_2 form. The obtained dependences are presented in Fig. 1. Greater rutile contents correspond to high temperatures. The correlation coefficients corr[T, ν(rutile)] = 0.89 and corr[T, ν(anatase)] = –0.89 were obtained for a linear regression model. Against such a background the effect of additions on the rutile (anatase) content is very poorly significant. Furthermore, these additions only reduce the rutile content as the correlation coefficients are negative:

$$\mathrm{corr}[\nu(\text{rutile}), \nu(TiCl_3)] = -0.56,$$

$$\mathrm{corr}[\nu(\text{rutile}), \nu(SiCl_4)] = -0.099,$$

which is clearly seen in the three-dimensional diagrams (Figs. 1a and 1b).

Conclusions drawn in [1] on the effect of additions on the rutile content in a product are insufficiently justified in view of the nonzero correlation between the contents of components and the process temperature (mainly determining the product quality),

$$\mathrm{corr}[\nu(TiCl_3), T] = -0.63,$$

$$\mathrm{corr}[\nu(SiCl_4), T] = 0.39,$$

i.e. in view of insufficiently accurate experimental data processing.

Furthermore, at a process temperature higher than 1000°C the Cl^- content in the product is lower by an order of magnitude than at 600–700°C (Fig. 2), $\mathrm{corr}[T, \nu(Cl^-)] = -0.889$ (irrespective of the effect of additions). Hence, the high-temperature process conditions are preferable for obtaining a product with the minimal Cl^- content. The effect of additions on the Cl^- content is of a small significance level relative to the main dependence.

The recommended process temperature determined as a result of the data examination by the method of principal components [3] for obtaining a product of a specified quality with a probability $p > 0,95$ exceeds 1250°C (Fig. 3).

The presence of one principal parameter of the product quality (rutile content) and one principal parameter of the control (temperature of the process), which also affect the minor quality parameter (Cl^- content), allows an application of the state-space method to the process control (obtaining a product of a specified quality at the minimization of costs). This method is applicable to various types of chemical engineering processes [4].

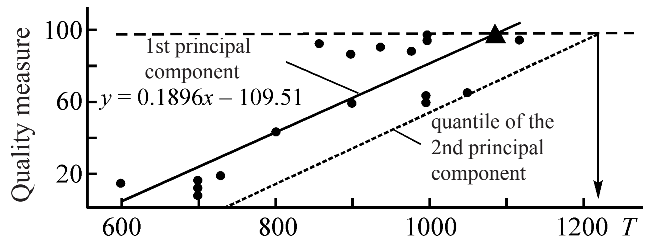

Fig. 3. Determination of the recommended temperature T(°C) of the process by the method of principal components. (*1*) 1st principal components; (*2*) $p = 0.95$, quantile of the 2nd principal component.

CONCLUSIONS

(1) It was shown that the high-temperature process mode provides conditions for the obtaining of the rutile TiO_2 form with more than 90% rutile content, i.e. of the commercial quality product. The recommended process temperature is higher than 1250°C.

(2) According to the obtained data examination, the technique of producing titanium dioxide from $TiCl_4$ in an arc of an electric discharge (at an arc temperature higher than 2500°C) is promising and has a simpler manufacturing scheme.

REFERENCES

1. Teterin, V.V., Kudryavskii, Yu.P., Laukart, N.F., et al., *Tsvet. Metall.*, 2002, no. 2, pp. 29–31.
2. *Khimicheskaya entsiklopediya* (Chemical Encyclopedia), Knunyants, I.L., Ed., Moscow: BRE, 1995, vol. 4.
3. Aivazyan, S.A., Ardavichus, V.G., and Kolbasina, O.V., *Teoriya veroyatnostei i prikladnaya statistika* (Probability Theory and Applied Statistics), Moscow: YuNITI, 2001, vol. 1.
4. Chechulin, V.L., Ardavichus, V.G., and Kolbasina, O.V., *Khim. Prom.*, 2008, vol. 85, no. 1, pp. 39–44.