Journal of Thermal Analysis, Vol. 36 (1990) 2131-2134

THERMAL TRANSFORMATIONS OF HYDROUS TITANIUM DIOXIDE

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During heating hydrous titanium dioxide with a general empirical formula $TiO_2 \cdot xH_2O \cdot ySO_3$ prepared by hydrolysis of titanium sulphate solution drying, dehydration, desulphurization and anatase - rutile transformation proceed. The studies applying the DTA, TG, DTG methods have been carried out. To separate the particular effects damp samples, dried up to constant mass samples as well as samples after removing sulphur compounds have been used.

Among titanium compounds, which due to their particular physico-chemical properties focus constantly increasing attention of researchers, the most important is unquestionably titanium dioxide applied widely to obtain titanium white. In the broad range of single processes and operations involved in the sulphate method, the one of a great importance is a calcination of hydrous titanium dioxide derived from titanium sulphate solution hydrolysis [1-3].

A hydrous titanium dioxide paste subjects to the calcination in a rotary drum furnace forms the TiO_2 - SO_3 - H_2O system. The system involves also some compounds as rutile crystal seeds, and K_2O, P_2O_5, ZnO - that modify the calcination and affect the optical properties of the product such as a color tint, its brightness and intensity.

The principle of the calcination is to remove unbounded and bounded water as well as sulphur compounds from hydrous titanium dioxide and to process TiO_2 into the required crystal form. So, in a calcinator some various physico-chemical processes as drying, dehydration, desulphurization, polymorphic transformation of anatase to rutile proceed.

Introductory studies have been made to investigate qualitative transformations of the process while heating hydrous titanium dioxide.

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Experimental

The damp samples of hydrous titanium dioxide obtained from industrial sources consisted of TiO_2 (36%) and H_2SO_4 (2.8%).

Drying in the temperature of 105° up to constant mass resulted in removing about 95% of water and 16% of H_2SO_4. Dried samples of hydrous titanium dioxide consisted of TiO_2 (87%) and H_2SO_4 (5.9%) in average with the empirical formula $TiO_2 \cdot 0.362\ H_2O \cdot 0.055\ SO_3$.

After a chemical treatment to remove sulphates and drying at 105° up to constant mass finally gave samples included 92% of TiO_2 in average with the empirical formula $TiO_2 \cdot 0.386\ H_2O$.

To carry out simultaneous DTA, TG and DTG researches a 1500 D derivatograph (MOM Budapest) was used. A thermal analysis in the temperature range of 20-1000° was conducted. The samples (1000 mg damp, 500 mg dried) at the heating rate of 5 deg/min in ceramic crucibles were heated.

Results

In Fig. 1 the DTA, TG, DTG curves of damp hydrous titanium dioxide are shown. On the DTA curve the distinct endothermic peak lies between 20° and 250° with minimum at 100° and the plain endothermic peak between 440° and 800° with minimum at 570°. The first of them indicates the loss of water, the second the loss of sulphur compounds. On the TG curve the loss of mass is shown: up to 100° – 47%, to 250° – 58%; the total loss of mass – 62%.

To separate drying and dehydration effects, damp samples of hydrous titanium dioxide were purposely dried to remove unbounded water. The DTA, TG, DTG curves of dried hydrous titanium dioxide samples are shown in the Fig. 2. On the DTA curve the lower endothermic peak lies in the range of 100-250° with minimum at 150° probably referring to dehydration, the second endothermic peak between 440° and 800° with minimum at 570° that is likely to indicate desulphurization and the small exothermic peak with maximum at 900°, that illustrates polymorphic anatase – rutile transformation. The TG curve shows the two-stage loss of mass: the first stage the range of 20-500° referring to the loss of mass of 10.4% and the second one in the range of 500-1000° indicating the 5.4% loss of mass.

Further thermal tests were performed to separate dehydration and desulphurization effects. DTA, TG and DTG curves of the samples of hydrous

titanium dioxide after removing sulphates and drying up to the constant mass at 106° are shown in the Fig. 3. There is a small exothermic peak with the maximum at 900° referring to the polymorphic anatase - rutile transformation. The loss of mass reaching 8% up to temperature of about 500° and referring to the dehydration of titanium dioxide is seen on the TG curve.

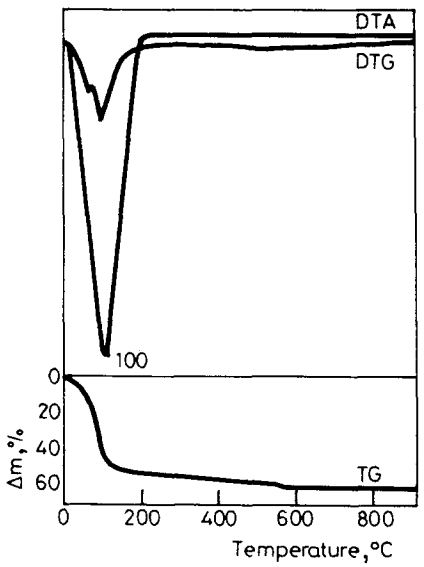

Fig. 1 DTA, TG, DTG curves of damp hydrous titanium dioxide

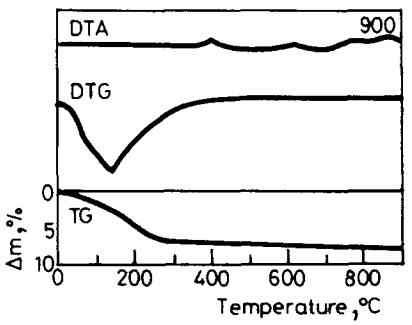

Fig. 2 DTA, TG, DTG curves of $TiO_2 \cdot 0.362\ H_2O \cdot 0.055\ SO_3$.

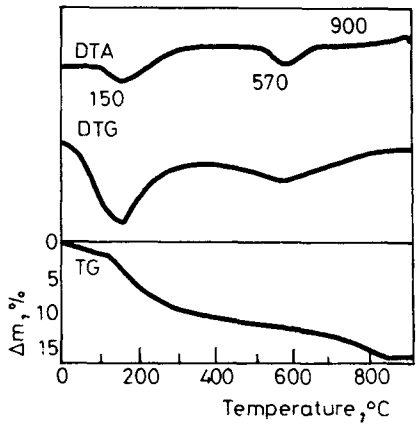

Fig. 3 DTA, TG, DTG curves of $TiO_2 \cdot 0.368\ H_2O$

Conclusions

The results of initial studies completed prove that during a heat treatment of hydrous titanium dioxide a lot of complicated phenomena take place. The phenomena proceed in the wide range of temperatures and effects of them overlap one another during sequent and parallel changes. The proceeding of the processes concerned depends on a constitution of the samples, which varies in a quiet wide range in industrial conditions.

Initial preparations applied for hydrous titanium dioxide enabled to separate drying, dehydration, desulphurization and polymorphic transformation effects. To describe kinetics of the changes further experiments and analytic tests will be carried out.

References

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Zusammenfassung — Während des Erhitzens von wasserhaltigem Titandioxid der allgemeinen Formel $TiO_2 \cdot xH_2O \cdot ySO_3$, hergestellt durch Hydrolyse von Titansulfatlösung, verlaufen Trocknung, Dehydratation, Desulfurisation und eine Anatas - Rutil Umwandlung. Die Untersuchungen wurden unter Anwendung von DTA, TG und DTG durchgeführt. Zur Unterscheidung der einzelnen Effekte wurden feuchte, bis zur Massekonstantheit getrocknete als auch entschwefelte Proben verwendet.