GLOBAL SCIENTIFIC INC.
ISSN(PRINT) : 2320 -1967
ISSN(ONLINE) : 2320 -1975
ChemXpress

ORIGINAL ARTICLE

CHEMXPRESS 8(3), 225-229, (2015)

Use of CyDTA for Fe^{3+} mask to improve the purity of TiO_2 product

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Abstract : Impurities removal and hydrolysis of TiO^{2+} aqueous solutions are core techniques in sulfuric acid method for titania industry, wherein, removal of Fe^{3+} from titanium solution is a puzzle in industry because $Fe(OH)_3$ yields during hydrolysis process, leading that subsequent formed Fe_2O_3 affects variable properties of titanium white. In order to solve the problem, cyclohexane diamine-tetracetic acid (CyDTA), an organic complex, was added in titanium solution to incorporate Fe^{3+} in this paper in case of hydrolysis of Fe^{3+} into $Fe(OH)_3$ dispersing into hydrolysis products of TiO^{2+} and debasing properties of the latter. Single factor experiment employing CyDTA as a complex to incorporate Fe^{3+} presents that: purity of TiO_2 increases with mole ratio of CyDTA to Fe^{3+}, reaching 99.56% when the ratio is 3. The content of Fe_2O_3 reduces to be 0.43% in final product. Anatase TiO_2 product was prepared according to XRD diagram result following the above conditions. TiO_2 production flow sheet will be optimized if the addition of CyDTA is considered based on the current titanium slag technology.

Keywords : TiO^{2+}; Hydrolysis; CyDTA; Fe^{3+}; Impurity removal.

INTRODUCTION

Titanium white is best white pigment so far due to its non-toxicity, strong shelter ability, high white degree and lightness, and used comprehensively in pigment, porcelain enamel, plastic[1], paper making, rubber, electronics industries. Therefore, high-quality titanium white is a preference.

Sulfuric acid method in the next period of time will still be used for a long time[2-5]. A technique problem in titanium white industry in sulfuric acid method is to avoid the formation of $Fe(OH)_3$ during the hydrolysis process of TiO^{2+}[6].

Presently, Ti^{3+} is used to reduce Fe^{3+} into Fe^{2+}, whereas, Fe^{2+} hydrolyzes at higher pH of 6, stands in filtrate during TiO^{2+} hydrolysis process. Therefore, Fe^{3+} does not exist in TiO_2 product. However, further puzzle is that Ti^{3+} is easily oxidized by O_2 in air in the same time, so, the concentration of Ti^{3+} is difficult to control, leading to low TiO_2 content product and lengthy afterwards treatment units and much more waste acid. In order to solve the above problems, an organic complex compound, cyclo hexane diaminaacentic acid (CyDTA) was employed in this paper to chelate Fe^{3+} into soluble ion during TiO^{2+} hydrolysis process and the soluble ion was filtrated out, and then high purity TiO_2 product can be derived. CyDTA can be considered in the preparation of titanium dioxide from titanium slag with sulfuric acid because adding CyDTA can save much rinsed H_2SO_4 due to scarce Fe^{3+}.

EXPERIMENTAL

Figure 1 presents hydrolysis reaction apparatus, which include heating system, temperature controlling system, agitating system and reactor. 40.00 ml 0.411 mol/l $TiOSO_4$ solution[7] and 40.00 ml 0.0401 mol/l $NH_4Fe(SO_4)_2$ were transferred precisely into a tri-neck flask with 250 ml in volume, corresponding quantitive CyDTA powder was added into the fore-mentioned vessel. 2 wt% NaOH was then put into the solution dropwise to adjust pH of the solution into 2 after the electric agitator (JJ-1) was triggered. The pH value was monitored by a pH measurer (PHBJ-260).

Electric-heated sheath was started to heat the foresaid solution boiled, hot water was given timely to maintain the liquid level. Time was measured on boiling, 2.5 h was regarded as available hydrolysis time according to our previous investigation[8-10]. After that, the hot suspending solution was filtrated out. The filter cake, hydrous metatitanic acid, was rinsed using deioned water until there is no existing Fe^{3+} in the filtrate, detected through 40 wt% KSCN solution, and no SO_4^{2-}, detected through 5 wt% $BaCl_2$ solution. The washed filter cake was subsequently shifted into ceramic crucible, followed by calcination at different temperatures. A portion of washed filter cake was employed for thermalgravimetric analysis via TGA 4000 (Perkin Elmer). TiO_2 contents of calcined samples are analyzed via titration method using 0.0401 mol/l $NH_4Fe(SO_4)_2$ standard solution subsequent to the complete dissolution of a certain amount of TiO_2 specimen by 90% H_2SO_4 solution at 180°C X-ray differaction analysis was conducted by a Philips X-ray diffreactometer employing Cu kα radiation and a step size of 0.02°in the range of 10-90°.

RESULTS AND DISCUSSION

Selection of calcining temperature for metatitanic acid

In a bid to convert H_2TiO_3 into pure TiO_2 and eliminate impurityÿthe hydrous precipitate adsorbing large amount of water and slight sulfuric acid, though rinsed via deioned water, has to be calcined. In the stage, the following chemical reactions occur:

$$TiO_2 \bullet xH_2O \bullet ySO_3(s) \overset{\Delta}{=} TiO_2(s) + xH_2O\uparrow(g) + ySO_3\uparrow(g)$$

And the process can be characterized by TG

a: electric heater; b: three flask; c: agitator; d: controller; e: thermal couple

Figure 1 : Hydrolysis reaction apparatus

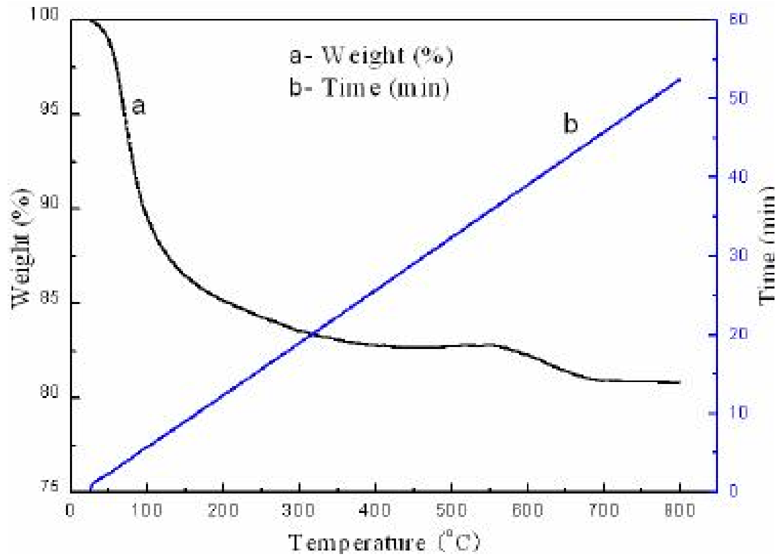


Figure 2 : Curve of TGA of sample 1: derived from TiO^{2+} solution without CyDTA and Fe^{3+}

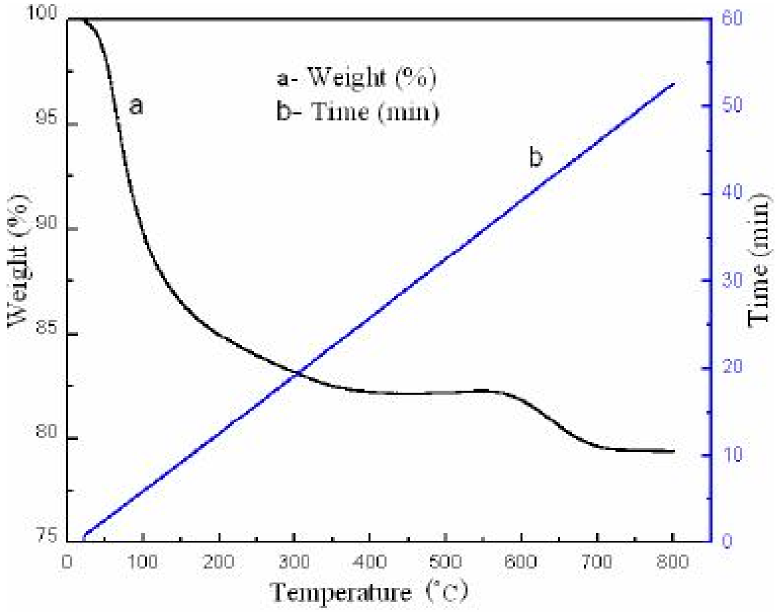


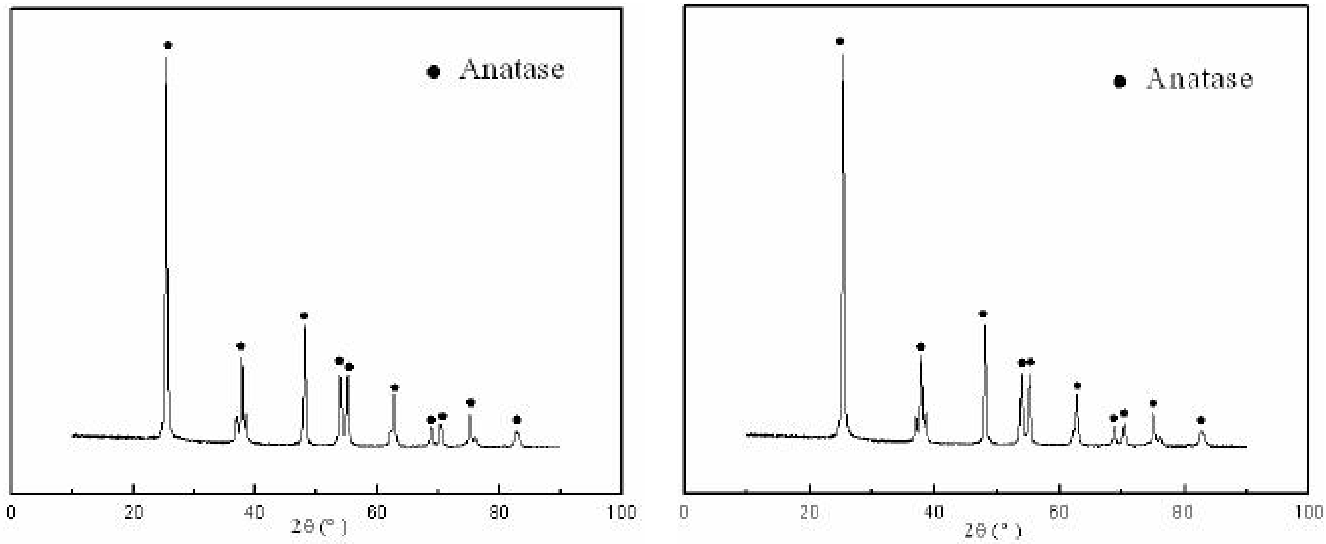
Figure 3 : Curve of TGA of sample 2: derived from TiO^{2+} containing CyDTA and Fe^{3+} with mole ratio of 3 to 1

curves, as depicted in Figure 2 and Figure 3.

The adsorbed water adhering on the H_2TiO_3 exterior surface or carried among particles, can fundamentally evaporate under 150°C, and the water of hydration within inner H_2TiO_3 molecule can be eliminated tardily at the temperature range 150-400°C[11]. The mass of specimens is essentially invariable with temperature increase at 400-550!, subsequently drops slightly, and then becomes stable until 700°C, indicating that residue sulfide is removed completely. At a later time, the mass has no variableness even at high temperature up to 800°C.

TG curve in Figure 3 dropped more than that in Figure 2 at 750 °C range, which may be caused by carrying more SO_4^{2-} in specimens derived from TiO^{2+} solution added with CyDTA and Fe^{3+}, while the crystalline of products is shown in Figure 4. Even in the presence of $Fe(OH)_3$, it can decompose into Fe_2O_3 under 500°C.

Figure 4 shows XRD spectra of sample 1 and 2. Both of them are calcined at 700 °C for 1.5 hour. The XRD diagrams show anatase crystalline, indicating CyDTA has no impact on TiO_2 crystalline. No impurity is found in curve d compared with curve c in Figure 4. The low calcining temperature is ben-



c: sample 1

d: sample 2

Figure 4 : XRD patterns presenting crystal structures

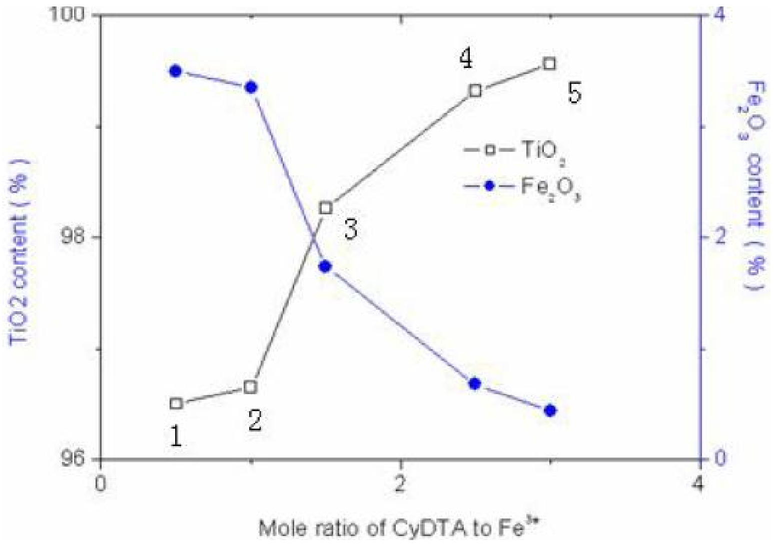


Figure 5 : Effect of mole ratio of CyDTA to Fe^{3+} on TiO_2 purity of the specimens

eficial to anatase crystalline.

Effect of mole ratio of CyDTA to Fe^{3+} on TiO_2 content

From Figure 5, it can be seen that TiO_2 content of the final product increases with the increasing mole ratio of CyDTA to Fe^{3+}, reaching 99.5% at most. Correspondingly, Fe_2O_3 content drops sharply from 3.63% to 0.43%.

White degree variation of TiO_2 appearance with mole ratio of CyDTA to Fe^{3+}

According to the reference[12], complex constant of CyDTA with Fe^{3+} is large (lgk=30.1). However, complex constant of OH- with Fe^{3+} is much larger than the foresaid (lgk=38). And some subsidiary reactions with impurity ions still exist. Therefore, the fundamental requirement quantity of CyDTA is more than the theoretical. Additionally, H_2TiO_3 precipitate can adsorb adjacent Fe^{3+}, resulting some $Fe(OH)_3$ presents in hydrolysis products. The specimen number is corresponding to the number in Figure 5. White degree increases with adding CyDTA/Fe^{3+} mole ratio in turn, namely TiO_2 purity. White degree of number 5 is almost same as that of number 6. Number 6 is made by TiO_2 company, which is incompact and white. Due to the strong complexation of CyDTA and large volume, resulting in TiO_2 was dispersed completely, so the calcined TiO_2 is loose powder in small particle

Figure 6 : White degree variation of specimens due to different adding amount of CyDTA

size (sample 5 in Figure 6), the property is very favorable for titanium dioxide pigment. Maybe it is a better way to add CyDTA based on the current TiO_2 production technology.

CONCLUSIONS

Adding CyDTA can effectively inhibit the hydrolysis of Fe^{3+} impurities in the hydrolysis of titanium ion process, improve the product purity in case of existing Fe^{3+} in titanium solution. TiO_2 content increases from 96.4% to 99.5% via using CyDTA as a complex of Fe^{3+}, while white degree of the product adds much and the crystalline of the TiO_2 specimen prepared is anatase after calcined under 700 °C for 1.5 hour. Due to the strong complexation of CyDTA and large volume, resulting in TiO_2 was dispersed completely, so the calcined TiO_2 is loose powder in small particle size and the property is very favorable for titanium dioxide pigment.

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