

ON THE FORMATION OF DOUBLE OXIDES OF COBALT  
AND TITANIUM BY THE THERMAL DECOMPOSITION  
OF CERTAIN COPRECIPITATES

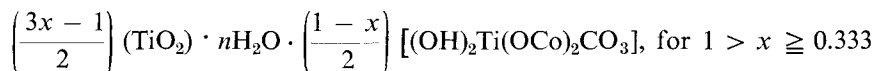
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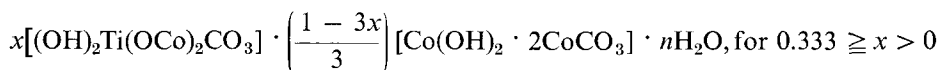
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A series of coprecipitates of basic cobalt carbonate and hydrated titanium oxide were investigated by TG and DTA up to 1000°. In the absence of water and CO<sub>2</sub>, an oxide system is obtained consisting of Co<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub>, from which cobalt metatitanate is first formed; from the latter, depending on the presence of TiO<sub>2</sub> or Co<sub>3</sub>O<sub>4</sub> in the system, the dititanate or the orthotitanate is formed. IR absorption and X-ray spectra and TG and DTA curves prove that the double oxides of cobalt and titanium are obtained in this manner at temperatures lower than in other methods; this gives them useful properties for practical applications.

The chemical composition of the coprecipitates obtained by addition of ammonium carbonate to aqueous solutions of CoCl<sub>2</sub> and TiCl<sub>4</sub> can be described by one of the following two formulas:



or



where  $x$  is the fraction of the titanium atoms and  $1 - x$  the fraction of the cobalt atoms among the total metal atoms in a certain coprecipitate.

The coprecipitates obtained in this manner consist of a basic cobalt titanium carbonate [1], uniformly distributed in a matrix of hydrated titanium dioxide (for  $1 > x \geq 0.333$ ) or of basic cobalt carbonate (for  $0.333 \geq x > 0$ ).

The double oxides of cobalt and titanium were obtained by thermal decomposition of the coprecipitates in the compositions of which  $x$  is replaced by the values 1; 0.903; 0.8; 0.666; 0.623; 0.5; 0.4; 0.357; 0.208; 0.133; and 0, in the corresponding formulas given above. (In the Figures, these compositions are designated accordingly as 0<sub>p</sub>, 1<sub>c</sub> - 9<sub>c</sub> and 10<sub>p</sub>, the letters  $c$  and  $p$  meaning coprecipitate and precipitate, respectively.

### Experimental

The processes of thermal decomposition were investigated by thermogravimetry (TG) and differential thermal analysis (DTA), using an apparatus without automatic recording [2], over a temperature range between room temperature and 1000°. The heating rate was 6°/minute. The progress of the thermal decomposition was followed by taking samples at regular temperature intervals and by analysing the products by means of chemical analysis, infrared absorption spectrophotometry and X-ray diffraction analysis.

### Results and discussion

#### A model example

The TG and DTA curves of the coprecipitate 8c, with  $x = 0.208$ , whose thermal decomposition process involves practically all the types of decomposition steps

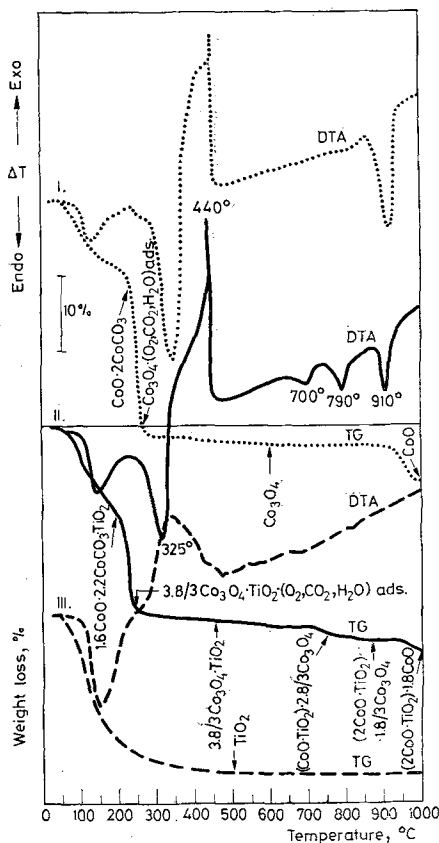


Fig. 1. TG and DTA curves of I: basic cobalt carbonate ( $[\text{Co}(\text{OH})_2 \cdot 2\text{CoCO}_3] \cdot (\text{H}_2\text{O})_{1.6}$ ), II: coprecipitate 8c ( $x = 0.208$ );  $[(\text{HO})_2\text{Ti}(\text{OC}_2\text{CO}_3)_2] \cdot [\text{Co}(\text{OH})_2 \cdot 2\text{CoCO}_3]_{0.6}[\text{H}_2\text{O}]_{1.6}$ , III: hydrated titanium dioxide ( $\text{TiO}_2 \cdot 1.2\text{H}_2\text{O}$ )

that may occur in the case of the coprecipitates studied, are given in Fig. 1 (curves II). The loss of water from the coprecipitate takes place from 25 to 192° and causes an endothermic peak at 140°. From 200 to 250°, the decomposition of the carbonate takes place. This stage of decomposition is associated with a strong endothermic effect, with the peak at 325°. The exothermic peak at 440° indicates the formation of the first oxide system. The discrepancies between the actual temperature range of decomposition of the cobalt carbonate (TG curve I, 200–250°) and the range calculated from TG curve II (192–455°), and also the position of the corresponding endothermic effect (the peak at 325°), are due to the interference from several chemical and physical processes over the temperature range 25–455°. These processes are dehydration, decomposition of the carbonate, chemisorption and physical adsorption of molecules of O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O, followed by the gradual desorption of the latter, and the formation of the crystalline lattices of the oxides of cobalt and titanium [3].

After the formation of the first oxide system, which is either a mixture or a double oxide [3] of Co<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub> (250°), with physically-trapped O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O molecules, at 440° only the pure oxide system is present. On the thermo-analytical curves of the hydrated titanium dioxide (curve III, Fig. 1), over the temperature range 440–1000° no significant change is recorded. In the case of the basic cobalt carbonate (curve I, Fig. 1), a weight loss is recorded between 890 and 1000°, correlated with an endothermic effect on the DTA curve, caused by the decomposition of Co<sub>3</sub>O<sub>4</sub> to CoO.

For the coprecipitate 8c a weight loss in three steps was found at 650–750°, 750–870° and 870–1000°, correlated with three exothermic peaks at 700°, 790° and 910°, respectively, which indicate solid-state reactions between Co<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub>.

### General considerations

The mechanism of thermal decomposition of the coprecipitates is given in Fig. 2 and Table 1.

*Dehydration and decomposition processes.* The coprecipitates having one of the two possible compositions lose the water of constitution and the water of hydration over the temperature range from room temperature up to 155–500° (Fig. 2 areas A and B). The cobalt carbonate which is a constituent of the systems from the previous process decomposes over the temperature range 155–600° (Fig. 2 areas C and D). In fact, this process takes place between 200° and 225–260°, depending on the chemical composition of the coprecipitate. For the reasons shown in the case of coprecipitate 8c, the data estimated from the TG curves and the processes recorded in the DTA curves, the upper limit of the temperature range in which this step of thermal decomposition takes place extends up to 370–600°. The steps of the dehydration and of the decomposition of the carbonate are superimposed in the TG curves for coprecipitates whose chemical composition corresponds to  $x$  values of 1–0.5. This is the case with the two corresponding endo-

thermic effects too. The stages are separated for the coprecipitates whose chemical composition corresponds to  $x$  values of 0.5–0.

*Formation of the first oxide system.* After the decomposition of the carbonate, oxide systems consisting of  $\text{Co}_3\text{O}_4$  and  $\text{TiO}_2$  remain, the cobalt being in a higher oxidation state. These systems contain  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as chemisorbed or physically-adsorbed molecules. The formation of the oxide systems is also confirmed by characteristic bands in the range  $1000-400\text{ cm}^{-1}$  [4–6] in the infrared absorption spectra of the  $350^\circ$  samples (Fig. 3).

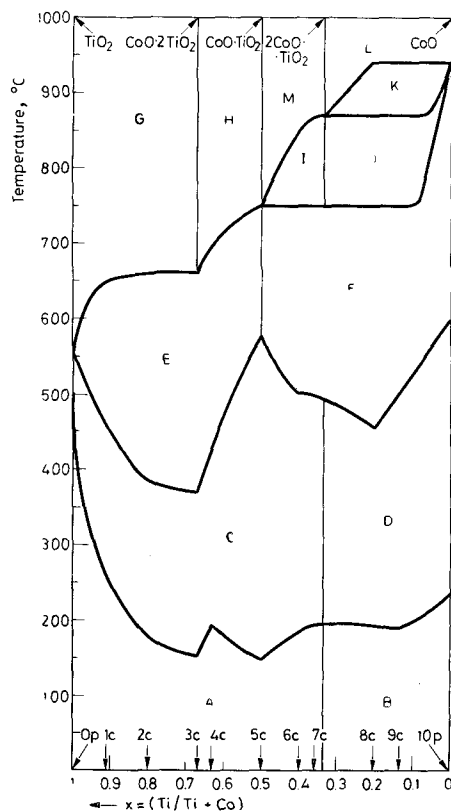


Fig. 2. Diagram of the thermal decomposition of the coprecipitates and the precipitates

Up to at most  $600^\circ$ , the chemically bound and physically-adsorbed molecules are removed and the oxide systems consist of  $\text{Co}_3\text{O}_4$  and  $\text{TiO}_2$  only. The experimental evidence [3] does not allow a decision as to whether these systems are physical mixtures, non-equilibrium solid solutions or double oxides of  $\text{Co}_3\text{O}_4$  and  $\text{TiO}_2$ .

Table 1  
Co-existent phases in the areas of Fig. 2

Area in Fig. 2	Co-existent phases
A	$\left(\frac{3x-1}{2}\right) \text{TiO}_2 \cdot n\text{H}_2\text{O} \cdot \left(\frac{1-x}{2}\right) \cdot [(\text{OH})_2\text{Ti}(\text{OCo})_2\text{CO}_3] +$ $+ x\text{TiO}_2 \cdot \left(\frac{1-x}{2}\right) \cdot (\text{CoO} \cdot \text{CoCO}_3)$
B	$x[(\text{OH})_2\text{Ti}(\text{OCo})_2\text{CO}_3] \cdot \left(\frac{1-3x}{3}\right) [\text{Co}(\text{OH})_2 \cdot 2\text{CoCO}_3] \cdot n\text{H}_2\text{O} +$ $+ x\text{TiO}_2 \cdot 1/3\text{CoO} \cdot \left(\frac{2-3x}{3}\right) \text{CoCO}_3$
C	$x\text{TiO}_2 \cdot \left(\frac{1-x}{2}\right) (\text{CoO} \cdot \text{CoCO}_3) + x\text{TiO}_2 \cdot \left(\frac{1-x}{3}\right) (\text{Co}_3\text{O}_4) \cdot m\text{O}_{2(\text{ads.})}$
D	$x\text{TiO}_2 \cdot 1/3\text{CoO} \cdot \left(\frac{2-3x}{3}\right) \text{CoCO}_3 + x\text{TiO}_2 \cdot \left(\frac{1-x}{3}\right) (\text{Co}_3\text{O}_4) \cdot m\text{O}_{2(\text{ads.})}$
E	$x\text{TiO}_2 \cdot \left(\frac{1-x}{3}\right) (\text{Co}_3\text{O}_4) \cdot m\text{O}_{2(\text{ads.})} + (2x-1)\text{TiO}_2 \cdot (1-x)(\text{CoO} \cdot \text{TiO}_2)$
F	$x\text{TiO}_2 \cdot \left(\frac{1-x}{3}\right) (\text{Co}_3\text{O}_4) \cdot m\text{O}_{2(\text{ads.})} + x(\text{CoO} \cdot \text{TiO}_2) \cdot \left(\frac{1-2x}{3}\right) \text{Co}_3\text{O}_4$
G	$(2x-1)\text{TiO}_2 \cdot (1-x)(\text{CoO} \cdot \text{TiO}_2) + (3x-2)\text{TiO}_2 \cdot (1-x)(\text{CoO} \cdot 2\text{TiO}_2)$
H	$(2x-1)\text{TiO}_2 \cdot (1-x)(\text{CoO} \cdot \text{TiO}_2) + (2-3x)(\text{CoO} \cdot \text{TiO}_2) +$ $+ (2x-1)(\text{CoO} \cdot 2\text{TiO}_2)$
I	$x(\text{CoO} \cdot \text{TiO}_2) \cdot \left(\frac{1-2x}{3}\right) \text{Co}_3\text{O}_4 + (3x-1)(\text{CoO} \cdot \text{TiO}_2) +$ $+ (1-2x)(2\text{CoO} \cdot \text{TiO}_2)$
J	$x(\text{CoO} \cdot \text{TiO}_2) \cdot \left(\frac{1-2x}{3}\right) \text{Co}_3\text{O}_4 + x(2\text{CoO} \cdot \text{TiO}_2) \cdot \left(\frac{1-3x}{3}\right) \text{Co}_3\text{O}_4$
K	$x(2\text{CoO} \cdot \text{TiO}_2) \cdot \left(\frac{1-3x}{3}\right) \text{Co}_3\text{O}_4 + x(2\text{CoO} \cdot \text{TiO}_2) + (1-3x)\text{CoO}$
L	$x(2\text{CoO} \cdot \text{TiO}_2) + (1-3x)\text{CoO}$
M	$(3x-1)(\text{CoO} \cdot \text{TiO}_2) + (1-2x)(2\text{CoO} \cdot \text{TiO}_2)$

However, it is obvious that in the oxide systems obtained in this way the reaction of the two constituent oxides, and therefore the formation of the double oxides of cobalt and titanium, is extremely favoured. Thus, the TG curves of the coprecipitates show one step for the compositions corresponding to  $x = 1 - 0.5$ , two steps for the compositions corresponding to  $x = 0.5 - 0.333$  and three steps for the compositions corresponding to  $x = 0.333 - 0$ , in which oxygen is lost

owing to the reaction between  $\text{Co}_3\text{O}_4$  and  $\text{TiO}_2$  which results in double oxides of  $\text{CoO}$  and  $\text{TiO}_2$ . These steps are correlated with the same number of endothermic effects on the DTA curves.

*Formation of the metatitanate.* For each coprecipitate the first visible step in which oxygen is lost by the decomposition of  $\text{Co}_3\text{O}_4$  to  $\text{CoO}$  is to be found in the temperature range  $370-940^\circ$ , depending on the oxide composition of the system. In this step cobalt metatitanate ( $\text{CoO} \cdot \text{TiO}_2$ ) is always formed, independently of

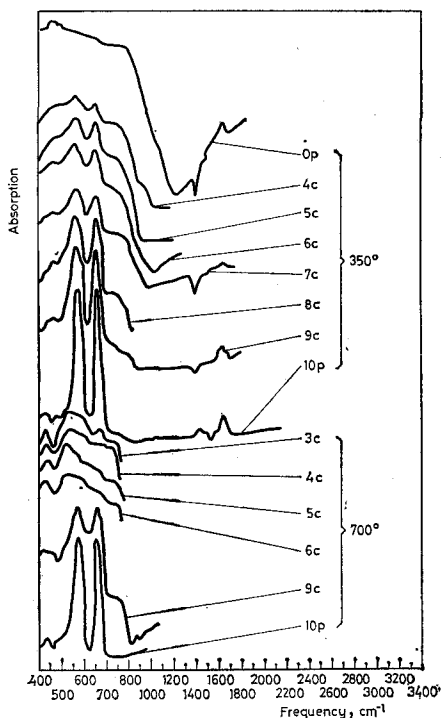


Fig. 3. IR absorption spectra of certain products of the thermal decomposition of the coprecipitates and precipitates, obtained at  $350^\circ$  and  $700^\circ$

the oxide composition. The domain of existence and co-existence of the reactant oxides and of the first double oxide is given in Fig. 2 by areas E and F. The existence of the double oxides in the  $700^\circ$  samples is confirmed by the characteristic bands of the IR absorption spectra (Fig. 3) in the  $800-400\text{ cm}^{-1}$  region [6]. In Fig. 3 one may observe that, while the characteristic bands of  $\text{Co}_3\text{O}_4$  (spectrum 10p) are found in the  $350^\circ$  thermal decomposition products, these are no longer present in the spectra of the  $700^\circ$  samples (spectra 3c, 4c, 5c and 6c), except for those in which there is a high excess of cobalt oxide in comparison with that

corresponding to the metatitanate (spectrum 9c). In the X-ray diffraction spectra the lines of the metatitanate may be discerned although they are very weak. Cobalt metatitanate has an ilmenite type structure [7–10] and  $\text{Co}_3\text{O}_4$  a spinel structure [11].

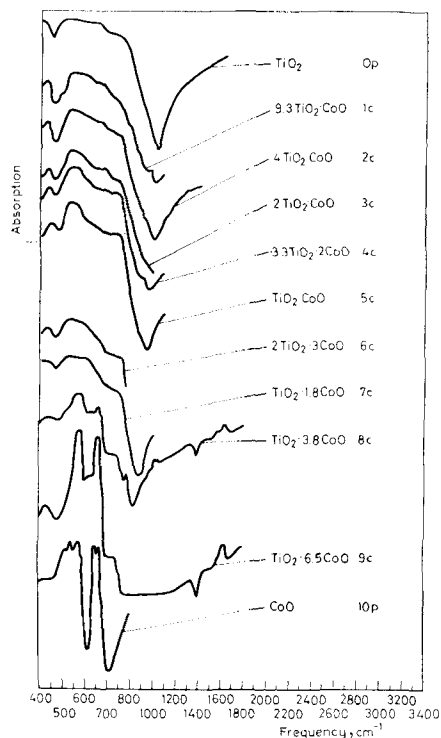


Fig. 4. IR absorption spectra of the products of the thermal decomposition of certain coprecipitates and precipitates, obtained at  $1000^\circ$

Further, with the rise of temperature, the oxide systems that have metatitanate in their composition change in different ways, depending on their chemical composition, i.e. depending on whether the metatitanate is present along with  $\text{TiO}_2$  or  $\text{Co}_3\text{O}_4$ , or not.

*Formation of the dititanate.* In the case of the oxide systems consisting of metatitanate and  $\text{TiO}_2$ , no significant change is recorded on the thermal curves up to  $1000^\circ$ . The infrared absorption spectra of the  $1000^\circ$  samples (Fig. 4, spectra 1c, 2c, 3c and 4c) show that over the temperature range  $550-750^\circ$  to  $1000^\circ$  (Fig. 2, areas G and H) another double oxide is formed, namely cobalt dititanate ( $\text{CoO} \cdot 2\text{TiO}_2$ ), as a result of the solid-state reaction between the metatitanate and  $\text{TiO}_2$ . The

infrared absorption spectra and the X-ray diffraction spectra of the samples in which  $1 > x > 0.666$  (Fig. 4, spectrum 1c, and Fig. 5, spectra 1c and 2c) are superimposed on those of rutile (Fig. 4 and 5, spectra 0<sub>p</sub>), which indicates the co-existence of the dititanate (Fig. 4 and 5, spectra 3c) and of rutile over this domain of composition (Fig. 2, area G). The cobalt dititanate has a pseudobrucite structure [12–14] and the TiO<sub>2</sub> that of rutile [12]. The oxide systems obtained from 660 to 1000° (Fig. 2, area H), in which  $0.666 > x > 0.5$ , are composed of

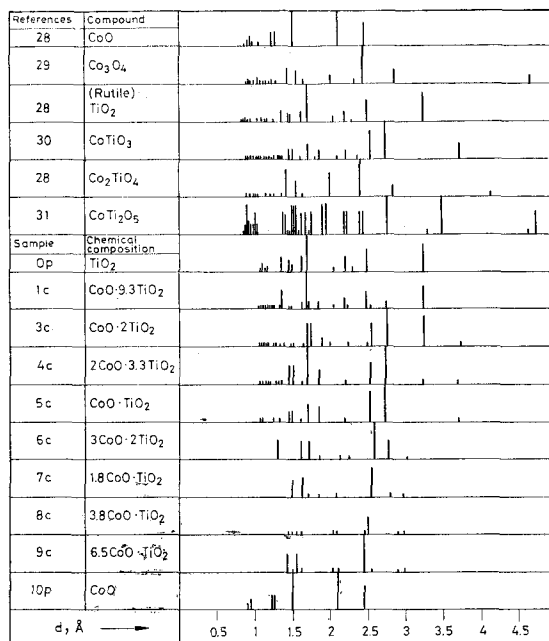


Fig. 5. X-ray diffraction spectra of the thermal decomposition products of certain coprecipitates and precipitates, obtained at 1000°

meta- and dititanate, as follows from the IR spectrum (Fig. 4) and X-ray spectrum (Fig. 5) of the oxide system 4c, that has  $x = 0.623$  and a composition corresponding to  $1.3(\text{CoO} \cdot 2\text{TiO}_2) \cdot 0.7(\text{CoO} \cdot \text{TiO}_2)$ . Its spectra show the absorption bands and the diffraction lines of the dititanate (spectra 3c) and of the metatitanate (spectra 5c). It is understood that in the oxide systems with  $x = 0.666$  (Fig. 2, 3c) at 1000° there is only cobalt dititanate ( $\text{CoO} \cdot 2\text{TiO}_2$ ) and in the oxide system 5c (Fig. 2) with  $x = 0.5$  from 750 to 1000° there is only cobalt metatitanate ( $\text{CoO} \cdot \text{TiO}_2$ ).

*Formation of the orthotitanate.* After the formation of the metatitanate in the oxide systems in which, along with the latter, there is also  $\text{Co}_3\text{O}_4$ , from 750 to 940° (Fig. 2, areas I and J) the formation of cobalt orthotitanate takes place by the solid-



state reaction of cobalt metatitanate and  $\text{Co}_3\text{O}_4$ . Over area I (Fig. 2), i.e. for the composition having  $0.5 > x > 0.333$ , the metatitanate, orthotitanate ( $2\text{CoO} \cdot \text{TiO}_2$ ) and  $\text{Co}_3\text{O}_4$  co-exist. At a temperature of  $750^\circ$  and at most  $870^\circ$ , depending on the oxide composition, only meta- and orthotitanate remain in the systems (Fig. 2, area M) since the total amount of  $\text{Co}_3\text{O}_4$  existing at  $750^\circ$  reacts with the corresponding amount of metatitanate to give orthotitanate. In area J (Fig. 2), i.e. for the compositions corresponding to  $0.333 > x > 0$ , over the temperature interval from  $750$  to  $870^\circ$ , or at most  $940^\circ$ , meta- and orthotitanate co-exist with  $\text{Co}_3\text{O}_4$ , with the difference compared to area I that there is more  $\text{Co}_3\text{O}_4$  than necessary to consume the total amount of the metatitanate for the formation of cobalt orthotitanate. The formation of the orthotitanate by the reaction between metatitanate and  $\text{Co}_3\text{O}_4$  which is decomposed to  $\text{CoO}$  causes the second step on the TG curves in which oxygen is lost, and a corresponding endothermic effect on the DTA curves.

It is obvious (Fig. 2) that in the system for which  $x = 0.333$ , the pure orthotitanate is formed from metatitanate and  $\text{Co}_3\text{O}_4$ . This exists as such from  $870$  to  $1000^\circ$ . The IR spectrum (Fig. 4, spectrum 7c) and the X-ray diffraction spectrum (Fig. 5, spectrum 7c) reveal an oxide system that has a composition close to that of the orthotitanate, viz.  $1.8\text{CoO} \cdot \text{TiO}_2$ . The cobalt orthotitanate has an inverse spinel structure [15–17].  $\text{CoO}$  has a face-centered NaCl type structure [11], and the IR and X-ray spectra are shown by 10p in Figs 4 and 5. In these Figures, the IR and X-ray spectra of certain other oxide compounds having compositions corresponding to  $0.333 > x > 0$ , viz. 6c:  $3\text{CoO} \cdot 2\text{TiO}_2$ ; 8c:  $3.8\text{CoO} \cdot \text{TiO}_2$ ; and 9c:  $6.5\text{CoO} \cdot \text{TiO}_2$ , are also given.

*Decomposition of the excess  $\text{Co}_3\text{O}_4$ .* In area K (Fig. 2), the decomposition of the last portion of  $\text{Co}_3\text{O}_4$  to  $\text{CoO}$  takes place, so that here orthotitanate co-exists with  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$ . For this process the TG curves show another loss of weight and the DTA curves a corresponding endothermic effect. Above  $870^\circ$  or at most  $940^\circ$ , depending on the oxide composition of the systems having  $0.333 > x > 0$ , the cobalt orthotitanate co-exists with  $\text{CoO}$  (Fig. 2, area L).

*Remarks.* In general the infrared absorption spectra and the X-ray diffraction spectra of the oxide masses obtained at  $1000^\circ$ , exhibiting only a few weak absorption bands and, diffraction lines, the latter placed on a dark background, permit determination of the oxide composition only with great difficulty. This feature of the IR and X-ray spectra is due to the structural characteristics of these oxides. They are very weakly-ordered, and have many defects and anomalies in comparison with the stoichiometries of the known double oxides of cobalt and titanium. This last fact is correlated with the permanent changes which take place in the oxide systems over this temperature range, from their formation ( $370$ – $600^\circ$ ) up to  $1000^\circ$ . The state of high dispersion of the constituents of the oxide systems, as well as their structural features, draw attention to certain possibilities of their practical application as catalysts, pigments and ceramic colouring agents, or materials with particular electrical and magnetic properties [18–20]. The oxide composition and the structural characteristics of the oxide systems obtained by thermal

decomposition of the coprecipitates of basic cobalt carbonate + hydrated titanium dioxide are also complicated by the fact that the double oxides of cobalt and titanium, particularly the orthotitanate, can either form solid solutions with  $\text{Co}_3\text{O}_4$  and  $\text{CoO}$ , or maintain the crystalline structure in the event of insufficient cobalt oxide compared with that stoichiometrically existing in titanates, over quite large composition intervals [13, 24]. Moreover, we must take into account the possibility of non-equilibrium solid solutions or physical mixtures of double and simple oxides.

### Conclusions

Consequently, independently of the oxide composition, i.e. of the  $\text{Co}_3\text{O}_4/\text{TiO}_2$  ratio in the oxide systems at  $370-600^\circ$ , the first double oxide formed by the subsequent rise of temperature is cobalt metatitanate,  $\text{CoO} \cdot \text{TiO}_2$ . With the rise of the temperature and also depending on the total cobalt oxides to titanium dioxide ratio, the metatitanate is transformed to dititanate or orthotitanate or remains as such. This finding agrees with those of other authors [21-23].

The double oxide with the formula  $2\text{CoO} \cdot 3\text{TiO}_2$ , prepared by Joubert and Durif [25], could not even be obtained by the thermal decomposition of this type of coprecipitate of cobalt and titanium, although there were very propitious conditions for the solid-state reactions due to the high dispersion and homogeneity of the reactants. This oxide could not be obtained either by the thermal decomposition of a mixed complex, hexamine cobalt(III)titanyl oxalate [26, 27].

It is obvious that the preparation of the double oxides of cobalt and titanium by the thermal decomposition of the coprecipitates of basic cobalt carbonate + hydrated titanium dioxide is more advantageous than other methods because it requires temperatures from  $370^\circ$  up to at most  $1000^\circ$ , the double oxides thus obtained having useful properties for practical applications.

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ZUSAMMENFASSUNG — Eine Reihe gemeinsamer Niederschläge basischer Kobaltkarbonate und hydratisierter Titanoxide wurde mittels TG und DTA bis zu 1000°C untersucht. In Abwesenheit von Wasser und CO<sub>2</sub> wird ein aus Co<sub>3</sub>O<sub>4</sub> und TiO<sub>2</sub> bestehendes Oxidsystem erhalten. Aus diesem wird zuerst Kobaltmetatitanat gebildet und daraus in Abhängigkeit von der Gegenwart an TiO<sub>2</sub> oder Co<sub>3</sub>O<sub>4</sub> im System, das Dititanat oder das Orthotitanat. Die IR-Absorptions-, sowie die Röntgenspektren und die DTA-Kurven zeigen, daß die Doppel-Oxide von Kobalt und Titan auf diese Weise bei niedrigeren Temperaturen entstehen, als bei dem Einsatz anderer Methoden. Diese Tatsache verleiht obigen Verbindungen merkwürdige Eigenschaften in bezug auf ihre Anwendung.

RÉSUMÉ — On a étudié par TG et ATD jusqu'à 1000°C une série de co-précipités de carbonates basiques de cobalt et d'oxydes de titane. En l'absence d'eau et de CO<sub>2</sub> il se forme un système d'oxydes qui consiste en Co<sub>3</sub>O<sub>4</sub> et TiO<sub>2</sub>. A partir de celui-ci, on obtient d'abord le métatitanate de cobalt puis le bititanate ou l'ortho-titanate suivant la présence dans le système de TiO<sub>2</sub> ou de Co<sub>3</sub>O<sub>4</sub>. Les spectres de rayons X et d'absorption infrarouge ainsi que les courbes TG et ATD montrent que les oxydes doubles de cobalt et de titane se forment alors à des températures plus basses que par les autres méthodes. Ce fait confère à ces composés des qualités remarquables quant à leurs applications.

Резюме — Ряд соосажденных вместе основного углекислого кобальта и гидроокиси титана был исследован с помощью ТГ и ДТА при температурах до 1000°C. В отсутствии воды и углекислого газа получается окисная система, состоящая из Co<sub>3</sub>O<sub>4</sub> и TiO<sub>2</sub>, из которых сначала образуется метатитанат и из которого затем, в зависимости от наличия TiO<sub>2</sub> или Co<sub>3</sub>O<sub>4</sub> в системе, образуется дититанат или ортотитанат. Инфракрасные и рентгеновские спектры, кривые ТГ и ДТА показывают, что двойные окислы кобальта и титана получают таким путем при более низких температурах, чем при других методах. Этот факт является замечательным свойством для практического использования.