

# SOLUBILITY OF TITANIUM DIOXIDE IN COSMETIC FORMULATIONS

Agata Flis, Joanna Glówczyk-Zubek, Stanislaw Kus, Sergiusz Dzierzgowski

Department of Chemistry, University of Technology, Warsaw, Poland

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## Summary

Titanium dioxide was found to be unstable, i.e. soluble, in the presence of  $\alpha$ -hydroxycarboxylic acids in o/w emulsions or in cosmetic formulations.

The amount of dissolved titanium(IV) was determined and/or monitored using UV spectroscopic method.

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## Riassunto

Attraverso questo studio è stato dimostrato come il biossido di titanio sia instabile in presenza degli acidi  $\alpha$ -idrossicarbossilici, nelle emulsioni o/w o nelle formulazioni cosmetiche.

La quantità di titanio (IV) dissolto è stata determinata e monitorata usando il metodo della spettroscopia a UV.

## INTRODUCTION

Anatase, rutile and brookite – three minerals found in nature - represent three crystalline forms of the titanium dioxide. Anatase and rutile have found numerous practical applications. For many years these two  $\text{TiO}_2$  forms gained a widespread interest due to their chemical and physical properties, i.e. very high reflectivity and photocatalytic and surface reactivity with various organic compounds. Titanium dioxide is a high-melting, non-toxic compound, resistant to popular chemical reagents<sup>1</sup>. The high refraction coefficients: 2.7 for rutile and 2.5 for anatase result in their most popular applications as a white pigments in various industries including cosmetic industry<sup>2,3</sup>. Particles of titanium dioxide smaller than 100 nm are practically transparent to visible light due to the low particle size/incident radiation wavelength ratio; however, they can reflect, scatter and/or absorb UV radiation. Therefore titanium dioxide in its microfine form is applied in UV protection cosmetic products.

The studies of durability of cosmetic o/w emulsions have been carried out at the Department of Chemistry, Warsaw University of Technology. Relatively fast pH changes have been observed in preparations containing titanium dioxide on addition of lactic or citric acid. As no significant information concerning reactions of titanium dioxide with diluted  $\alpha$ -hydroxycarboxylic acids have been found in the literature, the studies have been undertaken with the goal to clarify the observed phenomenon.

## MATERIALS

Titanium dioxide rutile (Kronoss) and titanium dioxide P25 (Degussa) were used. Cosmetic raw materials for emulsion preparation have been obtained from Cognis company. All solutions

have been prepared using analytical grade chemical reagents and distilled water.

## METHODS

pH changes in titanium dioxide suspensions in  $\alpha$ -hydroxycarboxylic acids solutions as well as pH changes in emulsions containing titanium dioxide were followed. The concentration of titanium(IV) ions dissolved in  $\alpha$ -hydroxycarboxylic acid solution and in emulsion water phase has been determined by the derivative spectrophotometry and hydrogen peroxide spectrophotometric method. Every several days a 5  $\text{cm}^3$  sample has been taken out from the examined suspensions or emulsions. Titanium dioxide has been centrifuged off or filtered off carefully and the concentration of titanium ions in the filtrates has been determined. In case of emulsions water phase has been separated by incubation, freezing and finally centrifuging the sample.

### *Method of derivative spectrophotometry*<sup>4</sup>

Concentration of titanium ions in solutions was determined using their complexes with  $\alpha$ -hydroxycarboxylic acids. In order to establish dependence between the titanium ions concentration in the examined solution and the absorbancy of UV radiation, a calibration curve for titanium(IV) with appropriate  $\alpha$ -hydroxycarboxylic acid has been prepared. Spectra were recorded for the range 220 – 360 nm using HITACHI U-3300 spectrophotometer. The spectrum points have been collected with 1 nm step. A 1cm cuvette has been used. From the dependence of the solutions' curve shape on pH, the location of isosbestic point (radiation wavelength at which pH does not influence the value of the second derivative of absorbancy) has been determined. Fig. 1 shows that for citric acid solution the isosbestic point occurs at 309 nm.

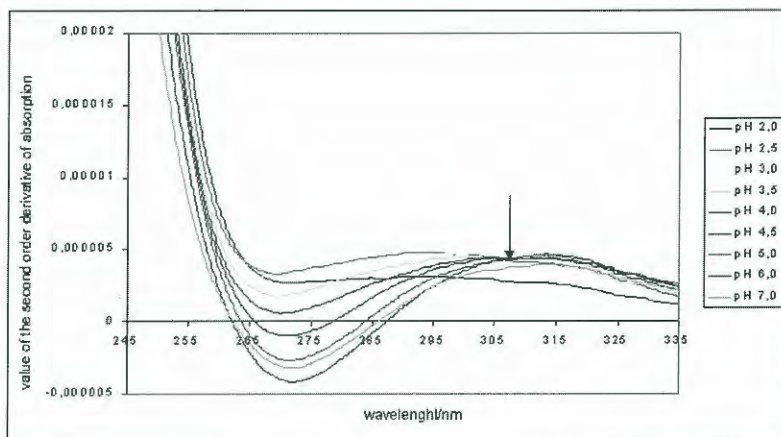


Fig. 1 Second order derivative of the UV absorption spectra of the titanium(IV) complexes with citric acid at various pH values. Isosbestic point at 309 nm.

Titanium(IV) concentration in the analysed samples was determined using the second order derivative of the calibration spectrum (calculated with Savitzky – Golay’s algorithm with 51 points). This procedure eliminated the adverse effect of the samples turbidity.

The second order derivative of the UV absorption spectra of the titanium(IV) complexes with citric acid at various concentrations are shown in Fig. 2.

The following equation of the calibration curve

has been derived from the second order derivative of the spectra at the wavelength of 309 nm:

$$y = 5,47553E-05x+5,61133E-06$$

Similarly the equation of the calibration curve for the second order derivative of the absorption spectra of titanium(IV) and malic acid complexes has been derived for the wave length of 314 nm:

$$y=2,74486E-05x+7,227334E-0$$

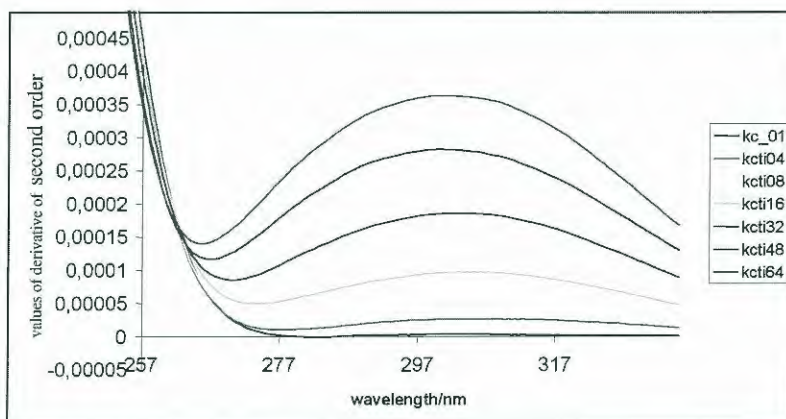


Fig. 2 The second order derivative of the UV absorption spectra of the titanium(IV) complexes with citric acid at various titanium(IV) concentrations.

## Spectrophotometric method with hydrogen peroxide<sup>5</sup>

In order to compare the results obtained by the method of derivative spectrophotometry, samples have been analysed by the spectrophotometric method with hydrogen peroxide after 68 days of incubation. The peroxide method of the titanium(IV) determination is based on the formation in the acidic medium the orange coloured complex  $[\text{TiO} \cdot \text{H}_2\text{O}_2]^{2+}$ .

The calibration curve for titanium(IV) with hydrogen peroxide has been prepared. The samples have been submitted to mineralisation and then the absorbance of their solutions has been measured using SPECORD M40 spectrophotometer at the wave-length 410 nm. 5 cm<sup>3</sup> cuvette were used.

pH was measured with a digital pH-meter.

## RESULTS

### pH examination of ready cosmetic preparations containing $\text{TiO}_2$ <sup>6</sup>

The examination was started by checking the

behaviour of a ready cosmetic preparations – o/w emulsions of the type of the liquid face powder – marked as e1 and e2. These preparations contained, among others, titanium dioxide and small amount of citric acid added before an emulgation process. Various amounts of citric acid were added to the samples and the pH changes were recorded (Table I).

Sample symbol	Volume of 1% citric acid [cm <sup>3</sup> ]
e101, e201	0
e102, e202	6.25
e103, e203	8.75
e104, e204	12.50

The observed pH changes in e1 samples are shown in Fig. 3. The changes for the e2 samples were almost the same.

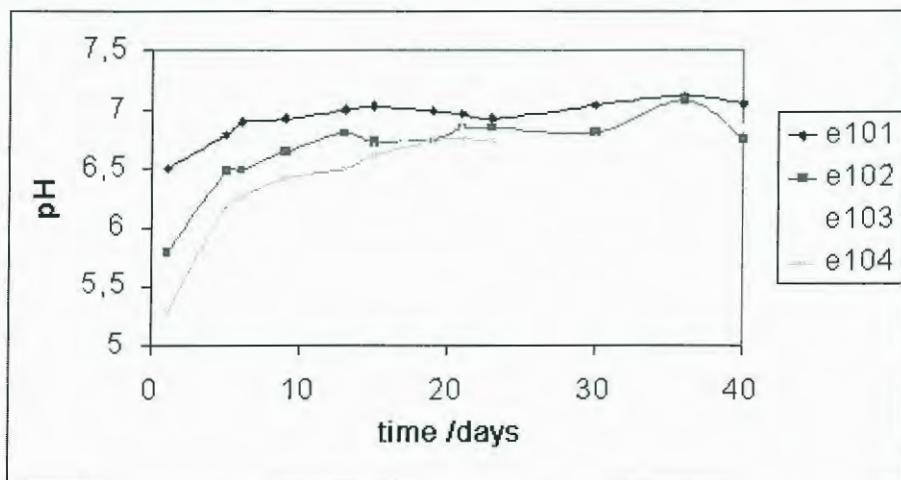


Fig. 3 pH changes in e1 emulsions.

In both preparations pH had been rising up to the almost neutral value. Separate studies of the model systems shown the existence of the strong interactions between titanium dioxide and  $\alpha$ -hydroxycarboxylic acid. Therefore the investigations of the suspensions containing different concentrations of titanium dioxide and  $\alpha$ -hydroxycarboxylic acid were undertaken.

***TiO<sub>2</sub> suspensions in diluted  $\alpha$ -hydroxycarboxylic acid***

pH changes and changes of the concentrations of dissolved titanium(IV) in titanium dioxide suspensions in diluted solutions of citric, malic and lactic acids have been examined. Titanium dioxide suspended in diluted acid has been placed in a closed flask equipped with a magnetic stirrer. The composition of the samples is shown in Table II.

The examined samples of highly diluted citric and malic acid solutions showed a slow pH

increase similarly as in the case of cosmetic emulsions e1 and e2. For solutions containing 0.3 – 0.4 % acid, pH remained stable or only slightly changed (Figs. 4 and 5).

Sample symbol	Sample composition (per 100g emulsion)
kctiz1	1g TiO <sub>2</sub> , 0.03g citric acid
kctiz2	4g TiO <sub>2</sub> , 0.38g citric acid
kjtiz1	1g TiO <sub>2</sub> , 0.04g malic acid
kjtiz2	4g TiO <sub>2</sub> , 0.27g malic acid

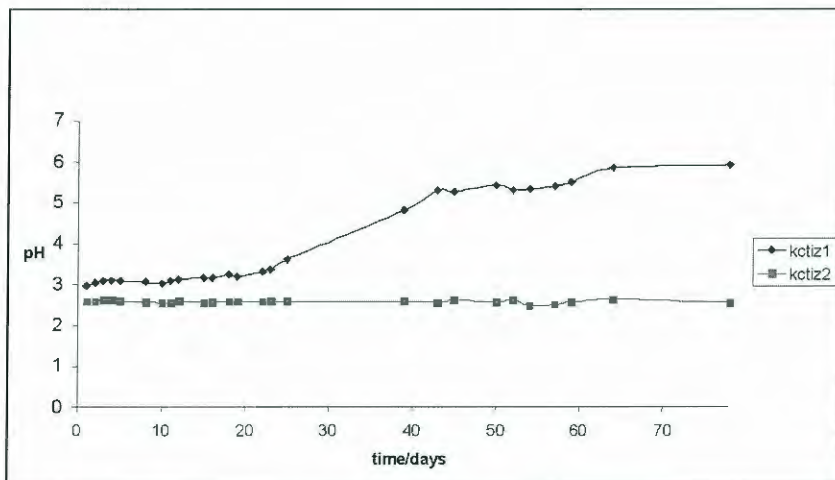


Fig. 4 pH changes in suspensions containing titanium dioxide and various amounts of citric acid.

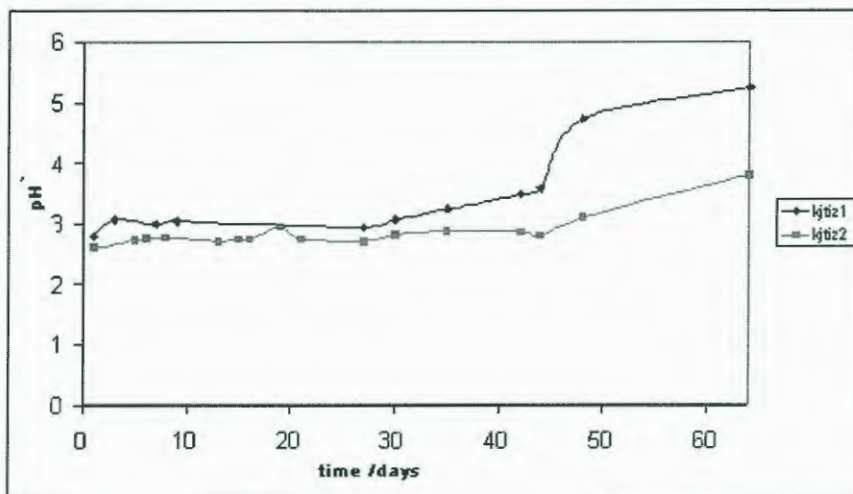


Fig. 5 pH changes in suspensions containing titanium dioxide and various amounts of malic acid.

UV absorption spectra of the collected samples after precise separation of the undissolved titanium dioxide, very similar to the calibration spectra, were used for the determination of the concentration of the titanium(IV) ions. The observed changes in concentration of titanium(IV) ions in examined suspensions

determined by the derivative spectrophotometry method are presented in Figs. 6 and 7.

In all four experiments, irrespective of the initial concentration of the  $\alpha$ -hydroxycarboxylic acid and the content of the titanium dioxide, an increase of concentration of titanium dissolved in water has been noted.

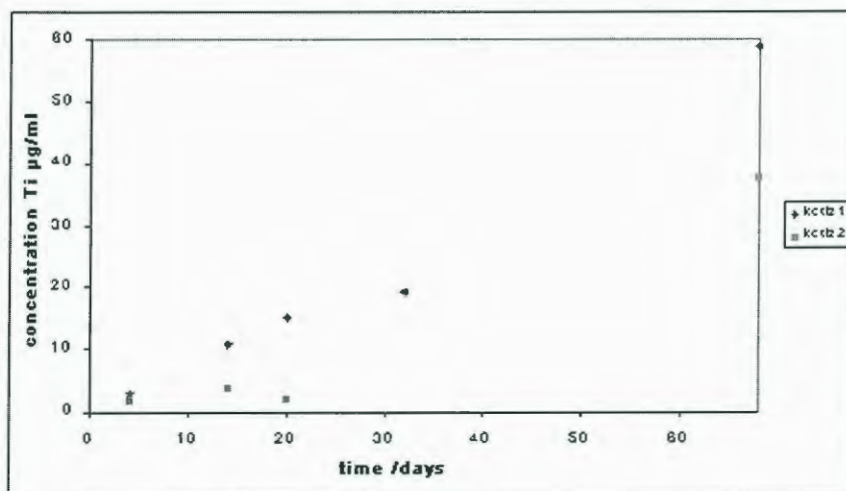


Fig. 6 Changes of the titanium(IV) concentration for the titanium dioxide suspensions in malic acid.

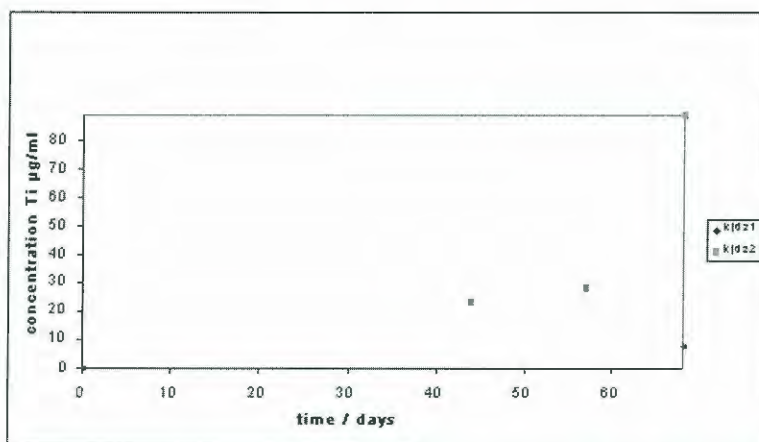


Fig. 7 Changes of titanium concentrations in suspensions of titanium dioxide in malic acid.

	Trade name	INCI Name	Amount [g]
oil phase	Cutina MD	Glyceryl Stearate	8
	Eumulgin B1	Ceteareth-12	1
	Eutanol G	Octyldodecanol	4
	Isopropyl Myristate	Isopropyl Myristate	4
	Paraffin Oil	Paraffin Oil	4
aqueous phase	aqueous phase	Water	Water 77

### **Emulsions containing $TiO_2$**

Similar measurements have been carried out for cosmetic emulsion. The o/w emulsion was prepared according to the formulation shown in Table III.

The same as before amounts of the titanium dioxide and citric acid were added to the above mentioned emulsion yielding four samples marked as kctie1, kctie2, kjtie1, kjtie2 (Table IV).

Sample symbol	Sample composition per 100g emulsion
kctie1	1g $TiO_2$ ,
	0.03g citric acid
kctie2	4g $TiO_2$ ,
	0.38g citric acid
kjtie1	1g $TiO_2$ ,
	0.04g malic acid
kjtie2	4g $TiO_2$ ,
	0.27g malic acid

Time dependent pH changes in the examined o/w emulsions containing titanium dioxide and citric acid are shown in Fig. 8. Emulsion marked as e0 contained neither the titanium dioxide nor the acid. Its pH decreased with time significantly. Thus the only slight pH increase observed for the samples containing titanium dioxide and citric acid most probably reflects the significantly larger pH increase when corrected for the blind sample behaviour. The similar changes have been observed for samples with the added  $\text{TiO}_2$ /malic acid.

The concentration of the titanium(IV) ions dissolved in water phase of the emulsions has been determined by the derivative spectrophotometry method. The results are shown in Figs. 9 and 10. The amount of the titanium(IV) dissolved in

samples collected after 68 days of the experiment has been determined spectrophotometrically by hydrogen peroxide method.

## CONCLUSIONS

The above described experiments have shown that titanium dioxide suspended in diluted solutions of citric, malic or lactic acid (for lactic acid a similar series of measurements has been done, reported elsewhere) dissolves via the acids water soluble complexes. The similar effect is taking place in the o/w emulsions upon the above listed acids addition. The concentrations of titanium(IV) measured in samples kept for 68 days vary from several to tens of mg/ml (Table V).

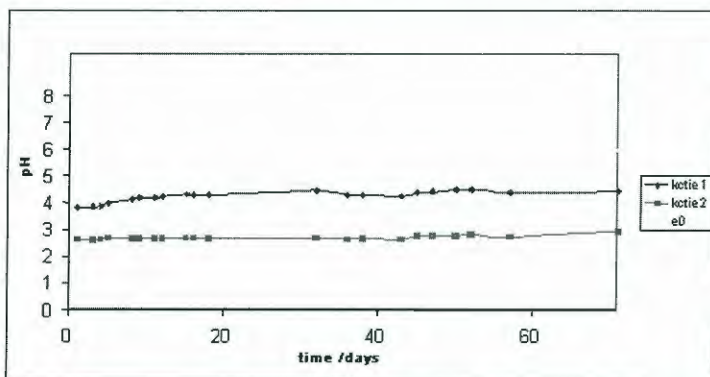


Fig. 8 The pH changes in time in emulsions containing titanium dioxide and citric acid.

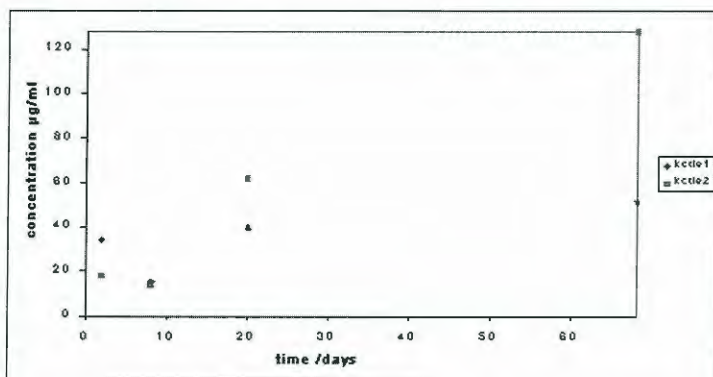


Fig. 9 Changes in the titanium(IV) concentration in aqueous phase of emulsion containing titanium dioxide and citric acid.



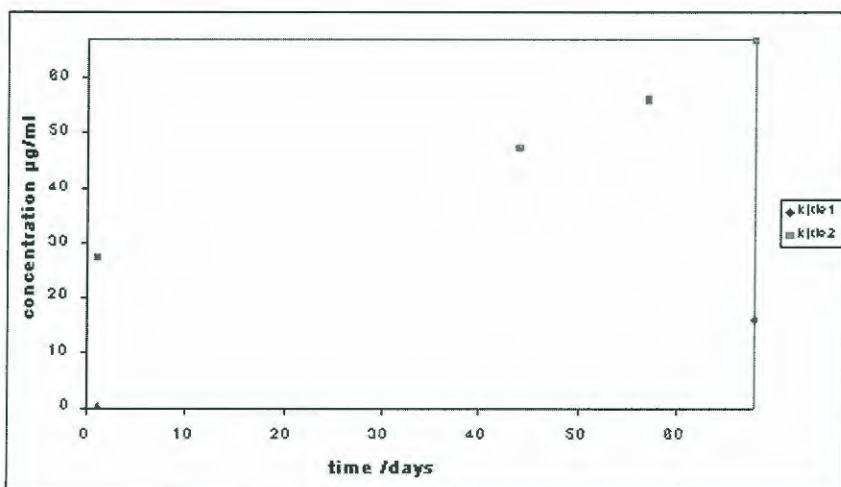


Fig. 10 Changes in the titanium(IV) concentration in aqueous phase of emulsion containing titanium dioxide and malic acid.

Sample symbol		68th day, conc. of TiIV [µg/ml]
Citric acid	kctiz1	40.99
	kctie1	51.39
	kctiz2	37.57
	kctie2	84.68
Malic acid	kjtiz1	8.10
	kjtie1	15.97
	kjtiz2	88.99
	kjtie2	61.02

In the case of added citric acid, titanium(IV) concentrations determined for 0.03% acid solution (kctiz1) and for 0.38% acid solution (kctiz2) were quite close to each other. For malic acid (kjtiz1 and kjtiz2) an increase in acid concentration by one order of magnitude resulted in an increase of concentration of dissolved titanium also by one order of magnitude.

In three out of four cases the measured concentration of the titanium(IV) dissolved in aqueous

phase of the o/w emulsion was even higher than in a model suspension of the titanium dioxide in an acidic aqueous solutions.

The studies confirmed that titanium dioxide reacts with a diluted  $\alpha$ -hydroxycarboxylic acid both in model aqueous  $\text{TiO}_2/\alpha$ -hydroxy acid suspensions and in o/w emulsions. Similar reactions, when occurring in a cosmetic preparation, might destabilise ready products formulated with the above said components.

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### Author Address:

Joanna Glowczyk-Zubek  
Warsaw University of Technology  
Department of Chemistry  
ul. Noakowskiego 3  
00-664 Warszawa  
Poland  
e-mail: jmzubek@ch.pw.edu.pl