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DIFFERENTIAL THERMAL ANALYSIS OF TITANIUM ENAMELS

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Over 30 white and coloured titanium enamels of different origin were tested with a derivatograph. Thermoceram crucibles were used, which enabled the tests to be interrupted when a change was indicated by the DTA curve. The crucible was removed from the derivatograph, and the sample pulverized and studied by X-ray diffraction method. A major difference compared to previous observations was the fact that the exothermic peak indicating the anatase-rutile transformation was also found on the DTA curves of certain anatase-type enamels. With these enamels the temperature relating to the start of the transformation peak was regarded as the critical temperature, as at a temperature below this the enamel was stable, but above it unstable.

Some time ago, stannic oxide and antimony oxide were used for opacifying enamels. These opacifying agents were partly melted and partly batched to the system. During melting a part of these oxides dissolved in the enamel, while another part formed a crystalline suspension and produced an opacifying effect. As there is a relatively small difference between the refractive indices of transparent enamels and of these oxides, this type of enamel resulted in a suitable covering only if applied as a thick layer. As a consequence, researchers tried to develop enamels which ensured a perfect covering even in the form of relatively thin layers. This problem was solved by the development of the titanium enamels, containing titanium dioxide of a much higher refractive index.

Titanium enamels are called "recrystallization enamels". In contrast to stannic and antimony enamels the total amount of titanium dioxide is melted in the enamel in which it dissolves completely. In the course of firing, the titanium dioxide which was present in solution separates out in small crystals; thus the titanium dioxide recrystallizes from the melt.

Three modifications of titanium dioxide are known: brookite, anatase and rutile. Of these rutile is the most stable and brookite the least. According to the literature of these three modifications only anatase and rutile can be detected in the enamel.

The modification of the titanium dioxide in the enamel plays an important role from the point of view of the colour shade of white enamel.

Anatase-containing enamels have a bluish hue, those containing rutile a yellowish one. It should be mentioned that in addition to their yellowish colour rutile-

type enamels also have a tendency to discoloration due to traces of heavy metals present. This tendency can hardly be noticed in anatase-type enamels.

The bluish hue of anatase-type enamels and the yellowish one of the rutile-type is primarily due to the fact that rutile crystals absorb a greater amount of blue rays of short wavelength from the white light than do anatase crystals [1]. Fig. 1 illustrates clearly the remission difference of rutile and anatase at short wavelengths.

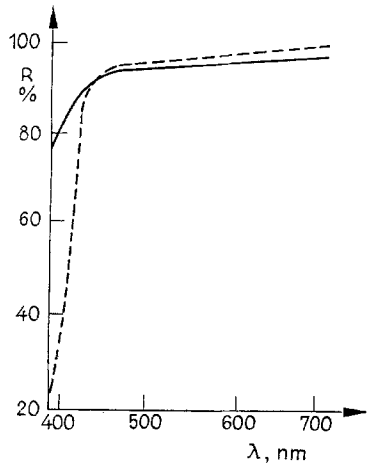

Fig. 1. The remission curve of anatase and rutile, —— anatase; - - - - - rutile

As reported by Eppler and McLeran [2] three reactions occur during the firing of a TiO_2-opacified enamel:

1. crystallization of anatase,
2. crystallization of rutile,
3. conversion of anatase to rutile.

Which of the three reactions plays the predominant role during firing depends on the composition of the enamel. With a suitable composition the transformation occurs only at a temperature higher than the firing temperature and in this case the enamel will be stable.

However, with an unsuitable composition when anatase and rutile occur simultaneously, by increasing the time or temperature of firing the amount of rutile increases at the expense of anatase, and the firing colour stability of the enamel will not be satisfactory.

The crystallization processes during firing, the nucleation, the growth of anatase crystals and the anatase to rutile transformation, produce enthalpy changes. Several researchers have tried to follow these changes and determine their temperatures by differential thermal analysis (DTA).

Sullivan and Cole [3] reported that an exothermic peak can be observed on the DTA curve of anatase between 700° and 950°, indicating the anatase to rutile transformation. It was presumed that in the course of differential thermal analysis of titanium enamels the transformation would be indicated in the DTA curves in the form of such an exothermic peak.

In contrast, neither Olympia [4], nor Imoto and Hirao [5] could detect the transformation of anatase to rutile.

Experimental

The DTA curves were taken with a Paulik – Paulik – Erdey type derivatograph [6]. In this instrument the thermoelement does not come into direct contact with the sample and thus the investigations can be carried out above the softening temperature of the sample without any danger of sticking. The recording conditions were as follows: weight of sample 1.5 g; heating rate 10°/min.

Platinum and corundum crucibles were used as sample holders.

The X-ray tests were carried out with a Rigakut – Denki diffractometer. Recording data: Cu K_α radiation, Ni filter, 32 kV, 24 mA, entire width 1000 c/s.

Results

Over 30 white and coloured titanium enamels of different origin were tested. As already mentioned, platinum crucibles were used at the start. In this way, however, it was not possible to make an X-ray test on the same heat-treated sample, and this had to be carried out therefore on a separate sample. In this case, of course, it was impossibe to guarantee an entirely similar heat treatment. A remarkable difference compared to earlier observations [2, 3, 7] was the fact that the exothermic peak indicating the anatase to rutile transformation was found on the DTA curve of certain anatase-type enamels. Then we changed over to using corundum crucibles. This enabled us to interrupt the tests when changes were observed on the DTA curves, take out the crucible, pulverize the sample and then make X-ray tests on the sample itself. By this method we succeeded in establishing the nature of crystallization processes indicated by the DTA peaks.

From their DTA curves, the enamels could be divided into two groups according to whether or not a thermal peak indicating the anatase to rutile transformation could be observed. The first group contains the enamels the DTA curve of which indicated the anatase to rutile transformation by an exothermic peak. With these enamels the temperature at the start of the transformation peak was regarded as the critical temperature, as at a temperature below this the enamel was colour-stable during firing, whereas above it (the anatase to rutile transformation occurred on increasing the temperature or time of firing) the enamel was not colour-stable.

The second group contains the enamels the DTA curves of which do not indicate the anatase to rutile transformation. This group includes anatase-type enamels where the anatase to rutile transformation occurs so slowly that the DTA curve cannot indicate it. However, enamels are also to be found in this group from which rutile separates directly.

In the following section four enamel tests will be discussed in detail.

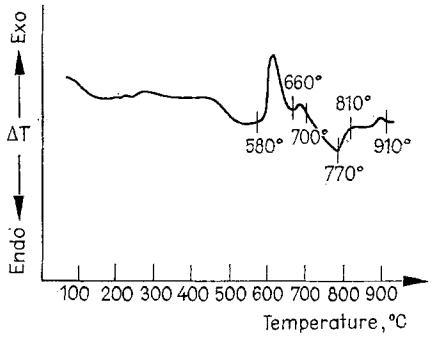

Fig. 2. The DTA curve of enamel "A"

The titania-opacified white enamel "A" belongs to the first group and is characterized by the fact that it is highly colour stable. Its DTA curve (Fig. 2) indicates a highly protracted endothermic peak between 480° and 580°, a double exothermic peak between 580° and 700°, another endothermic one between 700° and 800°, and a smaller exothermic one above 860°. It should be mentioned that not all the enamels belonging to this group produce the first exothermic peak as a doublet, and not all show a second endothermic peak at all. This enamel exhibits all the characteristics of the enamels belonging to this type.

The DTA-tests of the enamel were interrupted at 580°, 660°, 700°, 770°, 810° and 910°. The heat-treated samples were pulverized and studied with an X-ray diffractometer.

The X-ray diffractometer results of heat-treated enamel "A" are as follows:

	580°	660°	700°	770°	810°	910°
$I_{3.52}$ (anatase)	0	27	27	24	18	0
$I_{3.24}$ (rutile)	0	0	0	0	0	17

I is the relative intensity.

We succeeded in proving with the aid of X-ray tests that the doublet exothermic peak indicates the growth of anatase crystals. As no crystalline phase could be

indicated at 580°, it may be presumed that the endothermic peak below it is a sign of the glass transformation and softening.

The second endothermic peak can be presumed to be due to the partial dissolution of anatase crystals as in this thermal interval the anatase reflection intensity decreases and no rutile reflection can be observed.

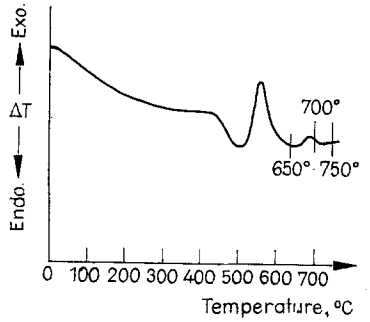

Fig. 3. The DTA curve of enamel "B"

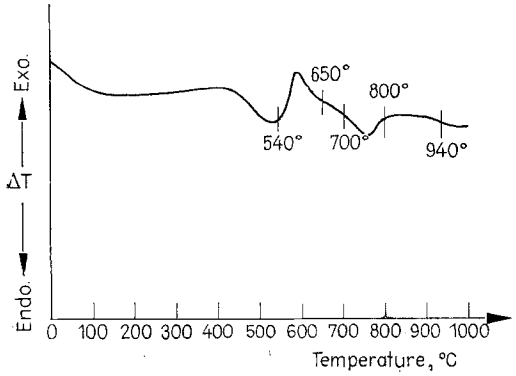

Fig. 4. The DTA curve of enamel "C"

The second, smaller exothermic peak undoubtedly indicates the anatase to rutile transformation as below it only anatase and above it only rutile can be detected. The enamel is stable because this peak, and the "critical temperature" relating to its starting stage, are well above the firing temperature.

Enamel "B", another less stable member of this group was also studied in detail (Fig. 3). The first exothermic peak of this enamel (due to the growth of anatase) was not doubled and the second exothermic peak was observed well below the firing temperature. We intended to study this enamel over a thermal interval involving the second exothermic peak, to prove that this peak appeared in this case too as a consequence of the anatase to rutile transformation.

As already mentioned, the second group contains the enamels for which no anatase to rutile transformation peak can be observed on the DTA curve, and thus there is no "critical temperature" to be recorded.

The DTA curve of enamel "C" (Fig. 4) showed an endothermic peak between 460° and 540°, an exothermic one corresponding to the crystal growth between 540° and 650°, and another endothermic one between 650° and 800°. No more peaks were observed on the curve, but the curve did assume an endothermic character above 950°.

The first DTA test was interrupted at 540°, before the start of the anatase crystal growth. The X-ray test indicated no crystalline phase in this case. The next measurement was carried out at 620°, and here the X-ray test detected only ana-

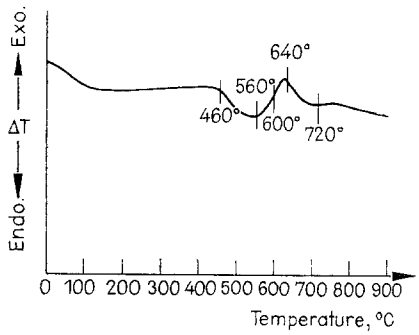

Fig. 5. The DTA curve of enamel "D"

tase. With a test at 700° still only anatase could be detected; repeating the test, however, after keeping the sample for half an hour at 700°, the reflection of rutile could also be detected, although with about half the intensity of anatase. (It should be mentioned that the control-test carried out for enamel "A" did not indicate rutile.) At a temperature of 800° rutile appeared with a somewhat higher intensity than anatase, at 940° the entire amount of anatase was transformed into rutile, and at 1000° due to the dissolution of rutile, its reflection intensity started to diminish.

These tests proved our assumption that, although with this enamel the anatase to rutile transformation started at a relatively low temperature, the reaction velocity was very low, the transformation proceeded very slowly and the DTA instrument could not record such a slow transformation.

Fig. 5 shows the rutile type enamel "D".

The DTA curve of this enamel showed an endothermic peak between 460° and 600°, and between 600° and 720° a blunt exothermic peak, in a form differing from the former one. No crystalline phase could be detected in the sample heat-treated at 560°, and in the sample heat-treated at the temperature of the maximum of the exothermic peak, 640°, only rutile could be detected. Thus in this case the

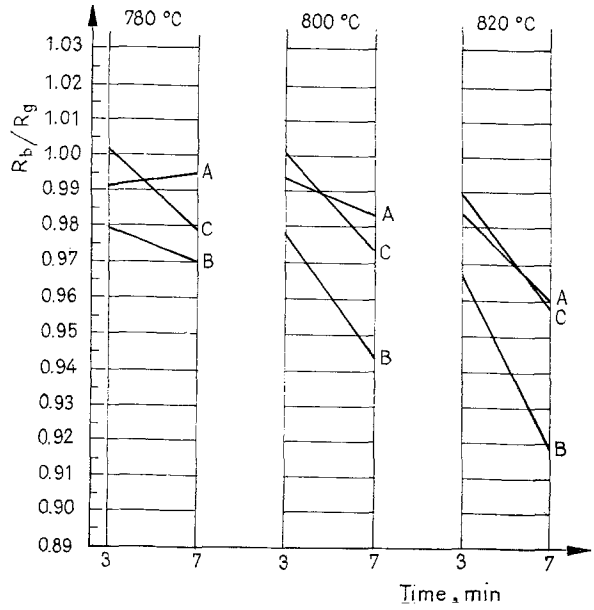

Fig. 6. The change in remission quotients measured with blue and green filters as a function of firing time and temperature

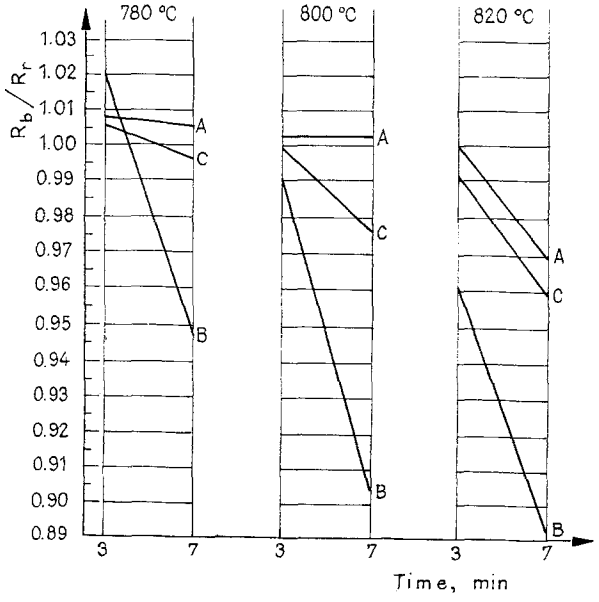

Fig. 7. The change in remission quotients measured with blue and red filters, as a function of firing time and temperature

exothermic peak did not indicate the growth of anatase but of rutile, which means that rutile separated directly from the enamel.

Further tests were carried out to prove the existence of a correlation between the firing colour stability of the enamels under examination and the DTA peaks. We therefore enamelled sample plates in a similar layer with the three anatase type enamels and fired them at 780°, 800° and 820° for 3 and 7 minutes. The remissions of these enamel layers were measured with a leucometer with blue, green and red filters. The remission values measured with a blue filter were divided by those obtained with a green and red filter, respectively, and these values were plotted graphically.

In Fig. 6 the firing times are shown on the horizontal axis, and the remission quotient measured with a blue and a green filter (R_b/R_g) on the vertical one. Enamel "A" is highly stable at 780° and 800°, while it is less so at 820° (about the same as the enamel "C" at 780°). The stability of enamel "B" at 780° is satisfactory, but diminishes proportionally with temperature increase. The stability of enamel "C" is medium and is reduced by temperature increase only slightly.

In Fig. 7 the remission quotients measured with a blue and a red filter (R_b/R_r) are indicated on the vertical axis. The firing colour stability of enamel "A" is excellent at 780° and 800°, but much less so at 820°. The stability of enamel "B' was rather poor already at 780°, and of course the same could be observed at higher temperatures. The stability of enamel "C" is medium in this case too.

Thus those enamels are colour stable in which the peaks indicating the anatase to rutile transformation and "critical temperature", respectively, are above the technological firing temperature. On the other hand, those with a "critical temperature" below the technological firing temperature are not stable. The anatase-type enamel, the "critical temperature" of which cannot be determined by the DTA method, is of an intermediate character, and its firing colour stability is medium.

Conclusions

1. The "critical temperature", above which the anatase-type enamel is no longer stable during the firing, can be determined from the DTA curve.

2. If the anatase-type enamel has no "critical temperature" detectable by the DTA method, its firing colour stability is medium.

3. There are also titanium enamels from which rutile separates directly. The exothermic peak on their DTA curve indicating the crystal increase is not as sharp as with anatase-type enamels.

From the DTA curves, titanium enamels can be classified into the following groups:

I. Enamels which have a "critical temperature" detectable by the DTA method.

a) Anatase-type colour-stable titanium enamel, for which the "critical temperature" detected by DTA is above the firing temperature,

b) Anatase-type, non-colour-stable enamel, for which the "critical temperature" indicated by the DTA curve is below the firing temperature.

II. Enamels for which no "critical temperature" can be detected with DTA.

a) Anatase-type titanium enamel with a medium firing colour stability.

b) Rutile-type titanium enamel.

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RÉSUMÉ — On a examiné plus de 30 émaux au titane, de différentes origines, blancs et colorés, à l'aide du "Derivatograph". L'emploi de creusets en thermoceram a permis d'interrompre l'essai au moment où l'on observe un changement sur les courbes d'ATD, de sortir le creuset, de pulvériser l'échantillon et d'en faire l'examen aux rayons X. Une différence importante par rapport aux observations précédentes consiste en ce que le pic exothermique indiquant la transformation anatase-rutile apparaît sur les enregistrements d'ATD de certains émaux de type anatase. Pour ceux-ci, la température correspondant au début du pic de transformation a été considérée comme température critique puisqu'au-dessous de celle-ci l'émail est stable, tandis qu'au-delà il ne l'est plus.

ZUSAMMENFASSUNG. — Mehr als 30 weiße und gefärbte Titanenemails verschiedener Herkunft wurden mit dem Derivatographen untersucht. Die Prüfung erfolgte in Korund-Tiegeln, die eine Unterbrechung der Untersuchungen bei Änderungen in der DTA-Kurve ermöglichten, um die pulverisierte Probe einer röntgenographischen Analyse zu unterwerfen. Es gelang, die durch die Anatase-Rutil Umwandlung hervorgerufene Spitze in der DTA-Kurve verschiedener Emails vom Anatase-Typ zu beobachten. Bei diesen Emails ist der Anfang der Umwandlungsspitze als die kritische Temperatur zu betrachten, unter welcher das Emaii stabil und über welcher es unstabil ist.

Резюме — Более 30 белых и цветных титанистых эмалей проверены на дериватографе. Измерения проводились в термокерамических тиглях, что дало возможность прерывать проверку, когда на кривой ДТА наблюдалось изменение. Тигель вынимали, образец размельчали и подвергали проверке с помощью рентгеновских лучей. Основным отличием от результатов, полученных до сих пор, является тот факт, что в случае некоторых эмалей типа анатаза на кривой ДТА наблюдался экзотермический пик, соответствующий анатаз-рутил превращению. Температура, при которой начинается превращение для этих эмалей, считается критической: при более низкой температуре эмаль не стабильна и становится стабильной только при температуре, выше критической.