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THERMOELECTROMETRY AS A METHOD FOR REACTIVITY ESTIMATION OF SOLID POWDERY MATERIALS

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ABSTRACT

A ceramic spinel pigment of Zn-Fe-Cr type has been used for demonstration of application of thermoelectrometry to evaluation of suitability of the Fe_2O_3 raw material. Conductometrical thermal analysis very sensitively indicates the beginning of the reaction between the oxides; the temperatures found by this method for the beginning of the reaction Fe_2O_3+ZnO are lower than those found by DTA by as much as 120°C. The measurements of admittance and of phase angle or dielectric loss factor $tg\delta$ in dependence on frequency of the measuring voltage and on temperature enable - if a suitable equivalent circuit is chosen - interpretation of surface changes of the powdery material during its heating or during the course of its reaction with another substance.

INTRODUCTION

Reproducible preparation of pigments (especially the high-temperature ones) is difficult because of sensitivity of their final properties to negligible changes in the starting materials - usually oxides. Refs.1,2 show the dependence between properties (particularly the colour hue) of pigments of the spinel type - in particular the pigment $Zn/Fe_{1+x}Cr_{1-x}/O_4$ - and reactivity of the starting oxides. In our country production of these pigments starts from Fe_2O_3 made by Bayer, and it would be interesting to replace this raw material by cheaper Czechoslovak oxide. Therefore, considerable attention was paid to comparison and evaluation of reactivity of inland Fe_2O_3 (ref.3). This reactivity of Fe_2O_3 towards ZnO represents a complex picture of properties of the oxide as a raw material, and it is given by a number of factors, especially the situation in the crystal lattice and its disturbances.

During the reaction course a product layer (the spinel compound) is formed at the interphase surface; kinetics of this reaction is controlled either by diffusion of ions or - in the case of powdery oxides - by diffusion of Zn^{++} ions and electrons (ref.4). The labelling experiments carried out with compressed tablets of ZnO and Fe_2O_3 showed that the product is formed at the side of Fe_2O_3. Ref.5 points at a possibility of partial transfer of ZnO in vapours. These facts indicate that the reaction course can make

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itself felt just by electric and dielectric properties.

MEASURING METHODS

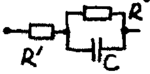
The measurements were carried out with the following types of Fe_2O_3: Bayferox 130 B (Bayer, West Germany); Thermal Red TP 303 (Přerov) with no surface modifications, finely ground; Thermal Red TD 202 (Přerov), surface-modified, dispersed;Precipitated Red Fepren DR 63 (Přerov); Oxide for Hard Ferrites (Further denoted as FT) (Hrušov); Ferric Yellow Fepren Y (Přerov); Ferric Black Fepren B (Přerov); the other substances used: ZnO (Košeca) and Cr_2O_3 (Bayer).

The calcination mixtures of Fe_2O_3+ZnO were prepared in molar ratio of 1:1 by wet grinding in a ball mill (20 h). For the measurements the samples of ferric oxides or their reaction mixtures with ZnO were compressed into tablets. For the measurements of electric conductivity the pastille (ø 12 mm) was placed between gilden platinum electrodes in an oven whose heating or cooling was linear at a rate of 5 K min^{-1}. The electric resistance, impedance, was measured either by means of a RLC bridge Tesla BM 509 (frequency f = 1 kHz) or by means of an indicator of impedance Z or phase angle φ Tesla BM 507 (f in the range from 5 Hz to 500 kHz). The oven was heated by direct current. The results of the measurements were in the form of the dependence of conductance σ or admittance (in log scale) on 1/T.

The dielectric properties were measured either non-isothermally with the Z and φ indicator (BM 507) or isothermally with the Q meter Tesla BM 560. In the latter case the pastilles (ø 32 mm) were clamped between gilden electrodes in a metal chamber temperated at 50°C. The measurement is described in more detail in ref.2.

RESULTS AND DISCUSSION

Refs.2,3 show that the temperature of the beginning of reaction of ZnO with various types of Fe_2O_3 (determined by the method of conductometric thermal analysis) correlates best with the changes in colour hues of the resulting pigments. Particularly, comparison of this method with the classic differential thermal analysis (DTA) confirms its much higher sensitivity, because the temperatures of the reaction start are lower by as much as 120°C than those found by DTA. Figure 1 gives the typical shape of the dependence log σ vs. 1/T. With the ZnO+Fe_2O_3 systems, a slight increase in σ is observed from t_p temperature followed by formation of a "peak". Slopes of the linear sections can be used for determination of activation energy of conductivity ($\mathcal{E}$). With $ZnO+Cr_2O_3$, on the contrary, the conductivity is slightly decreased from t_p. The presumption that the t_p temperature can be considered the reaction start is supported by chemical analyses of the conversion degree α and by the fact that e.g. the $\mathcal{E}'$ energy lies between the values $\mathcal{E}$ (for the starting mixture) and $\mathcal{E}_F$ (for the product). Sensitivity of the method would be documented by the results given in poster. During the grinding process the reactivity of the raw materials slightly increases. When using prefired ferric yellow FeOOH as a reaction component the reactivity with the temperature of prefiring decreases.

The measurements of complex admittance Y in dependence on temperature (whose increase was programmed) have similar character as $\sigma(T)$. Figure 2 shows the dependence of phase angle φ or dielectric loss factor $tg\delta$ for the system Fe_2O_3+ZnO. Fig.3 represents the same dependence for pure Fe_2O_3. The curves obtained can be interpreted by means of a suitably chosen electric equivalent circuit, the best seamed (B):  $\omega_{min.} = \sqrt{\frac{R+R'}{R'R^2C^2}} \doteq \frac{1}{C\sqrt{RR'}}$, $tg\delta_{min} = 2\frac{\sqrt{R'(R'+R}}{R} \doteq 2\sqrt{\frac{R'}{R}}$

The $tg\delta$ function shows a minimum for scheme (B), the values of its ω_{min} and $(tg\delta)_{min}$ are determined by the given formulas, the symbol $\doteq$ being valid for R> 5R'. Figure 2 shows a distinct shift of the minimum $tg\delta$, which means a decrease in the C,R,R' values. This phenomenon can be explained by formation of a defective and, hence, more conducting layer of the product Zn-ferrite on Fe_2O_3 particles. Figure 3 (pure Fe_2O_3) shows a shift of the minimum $tg\delta$ towards lower ω with increasing temperature and, moreover, a lowering of $(tg\delta)_{min}$. These two facts - with respect to the relations-mean an increase in C,R,R' and simultaneous decrease in R'/R. A likely explanation can be seen in decreased concentration of the defects during temperation of the oxide.

The measurements carried out show that the equivalent scheme (B) is suitable, the resistance R' being interpreted as resistance of the mass of the particle, the values R and C being connected with properties of the surface layer and/or of the remaining interlayer cavities.

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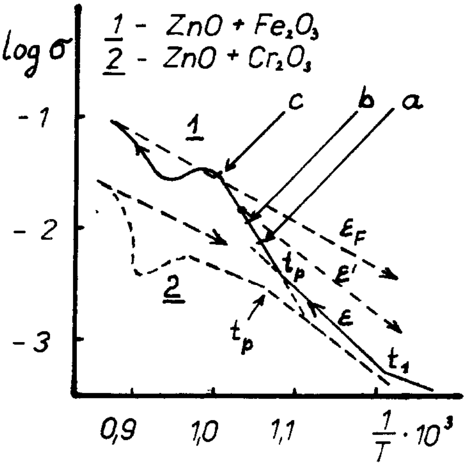

Fig.1. Temperature dependence of the conductivity σ, reacted fraction α=0,05(a), 0,08(b), 0,37(c), t_p=632°C, ε=3,4, ε_F=2,5eV, $\varepsilon < \varepsilon' < \varepsilon_F$

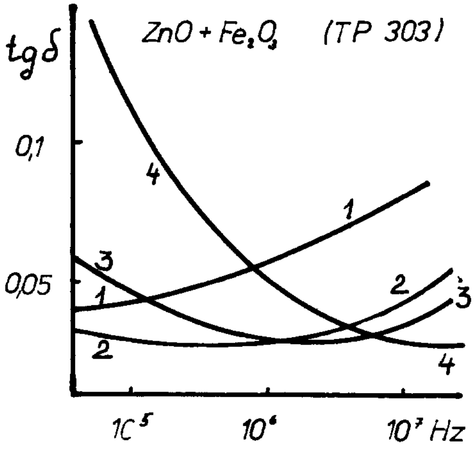

Fig.2. Frequence dependence of the loss factor tgδ, measured by Q-meter, α=0,01(1), 0,06(2), 0,15(3), 0,80(4).

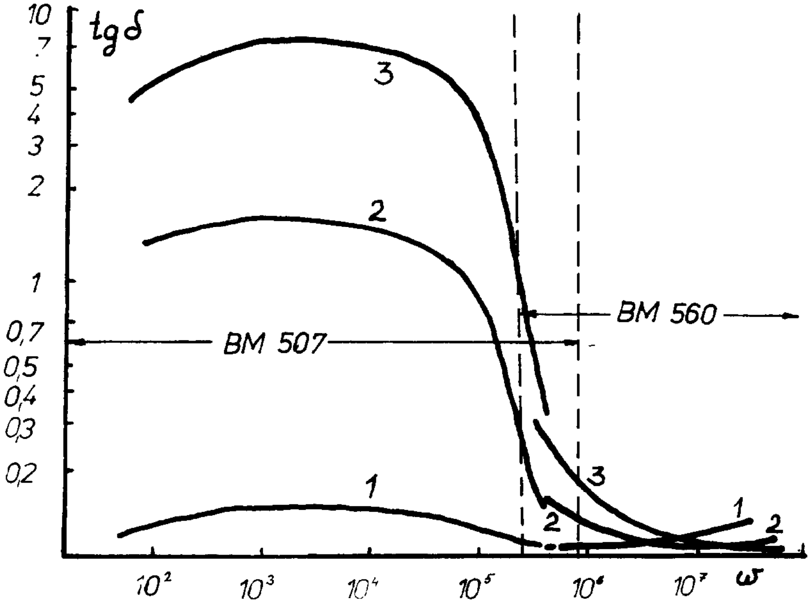

Fig.3. Frequence and temperature dependence of tgδ, ferric oxide TP 303. The temperature of heating (or preheating) of the oxide is 50°(1), 400°(2), 600°C(3).