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Powdered mixtures reactivity by thermal analysis

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Abstract

Two less common methods of thermal analysis, namely amperometric and emanation thermal analysis (ATA and ETA, respectively), were used to evaluate the reactivity of various Fe_2O_3 materials The reactivity was measured using the onset temperature (t_p) of the reaction Fe_2O_3 and ZnO

The ATA method described here can be connected to a personal computer to give the exact determination of t_p values The possible applications of the ATA and ETA methods are demonstrated by means of several examples (the reactivities of various iron oxide samples or $Fe_2O_3 + ZnO$ reaction mixtures treated with milling). Both methods are suitable for use in cases where the studied processes proceed separately without any overlapping

INTRODUCTION

When reactions between compounds in the solid phase are to be carried out, the method of preparation or modification of the reaction components is important and often determines the final properties of the product. This effect may be expressed as the "reactivity" of one reactant with respect to the others present in the reaction mixture [1–3].

In the present study we looked at spinel ceramic pigments (stains). Thermostable spinel compounds are prepared by calcination of, for example, a mixture of iron, chromium and zinc oxides (the simpler type marked as K 507). The product obtained is a mixed spinel compound containing the cations Fe^{3+} and Cr^{3+} in a ratio determined by the reactivities of the iron or chromium oxides towards zinc oxide. This mixed spinel compound is soluble, as are the iron or chromium oxides; this gives rise to some point defects [1,4]. Therefore the reactivities of the reactants can influence the colour of the resulting product (pigment).

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We were interested in the reactivity of iron oxide because, if it was found to be suitable, it could be used instead of the imported Fe_2O_3 Bayferox 130B. The evaluation of reactivity can be done using thermal analysis methods. When differential thermal analysis (DTA) is used, the reaction $Fe_2O_3 + ZnO$ proceeds as a slightly exothermic one. The ease of this reaction and, therefore, the high reactivity of Fe_2O_3, is connected with the onset temperature t_0 of the exothermic effect [5]: i.e. the more easily the reaction proceeds, the lower the onset temperature.

The conductance (amperometric) and emanation thermal analysis methods (ATA and ETA, respectively) both indicate the onset temperature of reaction sooner than DTA and, therefore, are also more sensitive than DTA. In this paper we present some examples of the use of these methods.

EXPERIMENTAL

The reactivity of various commercial or specially prepared samples of iron oxide towards zinc oxide was evaluated by means of three methods: DTA, ATA and ETA.

The DTA method was done using Robert's crucibles (the temperature was measured inside the sample and the reference material) with a temperature increase of 5 K min^{-1}. The equipment used was a Derivatograph Q 1500 (MOM, Hungary).

The equipment used for the conductance thermal analysis (amperometric TA-ATA) [6,7] is shown in Fig. 1. The measured sample, e.g. a reaction

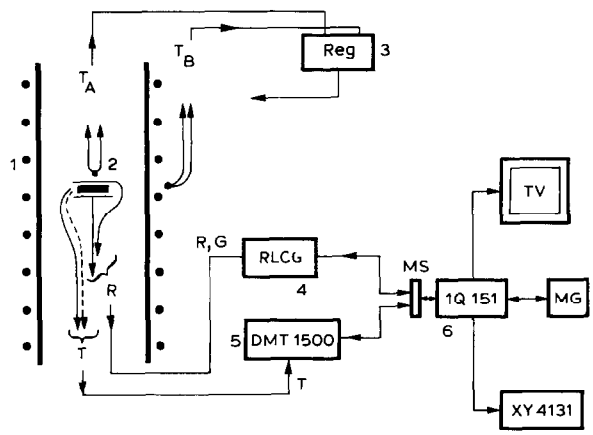


Fig 1 The apparatus used for the conductance thermal analysis (ATA): (1) vertical electric furnace, (2) pastille of measured sample, (3) programmed temperature regulator; (4) digital R, σ meter (Tesla BM 591), (5) digital thermometer (DMT 1550), (6) personal computer and interface

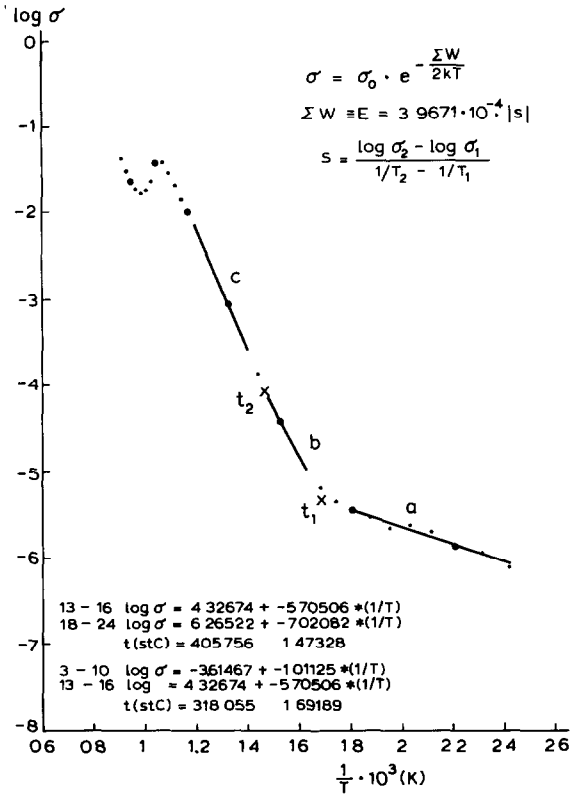


Fig 2 Measured values of log σ and $1/T$ for the reaction mixture $ZnO + Fe_2O_3$ (a) Region of extrinsic conductivity, (b) region of intrinsic conductivity of the reaction mixture, (c) region of partially reacted mixture, $t_2 \equiv t_p$, $E(b) = 2.26$ eV.

mixture of $Fe_2O_3 + ZnO$, was in the form of a pressed pastille (12 mm in diameter and usually 2 mm thick) with thin Pt plates pressed on it. The sample was placed in a special holder between two platinum electrodes. (This method was found to be the best because it eliminates transient resistance between the electrodes and sample pastille.) The resistance was measured by using an automatic LCRG meter (Tesla BM 591 with automatic adjustment of measuring resistivity or conductivity range and digital output of measured values), connected to a personal computer. The LCRG meter works on an alternating current of frequency 1000 Hz and a voltage of 50 mV. The measuring range was from 1 nS to 20 S, the error being $\pm 0.25\%$.

The computer program enabled us to print out all the measured values and to change the temperature from increasing to decreasing. When the measurements were finished, complete data on the diameter and thickness of the pastille have been obtained. The results were then displayed graphically as plots of log σ vs. $1/T$ for selected ranges of data (see Fig. 2). The onset temperature t_0 was calculated as the point of intersection of two regression

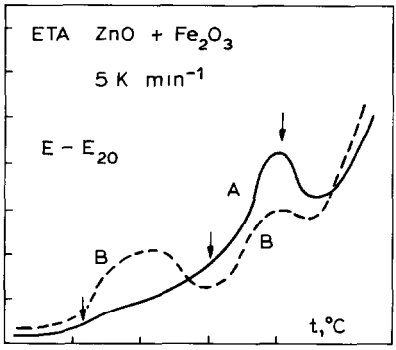


Fig 3 Plot of the emanation release rate E vs t (in °C) for the system $ZnO + Fe_2O_3$. (A) The whole sample was labelled with ^{228}Th; (B) only one component (ZnO) was labelled with ^{228}Th

lines for the selected region of experimental points. The slopes of regression lines were used to calculate the activation energy of the electrical conductivity (E, ΣW; see the equation in Fig. 2).

The temperature of the sample being measured was followed using a thermocouple situated at the edge of the sample. The digital output of the DMT 1550 meter (SVÚM, Brno) was also fed into the computer. The linear increase or decrease in temperature was controlled by means of a Chinotherm LP 849 (Hungary), the rate used was usually 5 K min^{-1}.

Emanation thermal analysis (ETA) was done in the same way as described by Balek and coworkers [8,9]. The emanation release rate was measured by means of a scintillation detector (Tesla NS 9501) situated in a special through-flow chamber and the measuring set NZ Q 717 T connected to a two-channel recorder. Sample labelling was carried out by wetting the powder reaction mixture or ZnO alone with a solution of ^{228}Th nitrate. The samples were left for 6–8 weeks to reach radioactivity equilibrium. The measurements were then made. An example of an emanation thermogram is shown in Fig. 3.

RESULTS

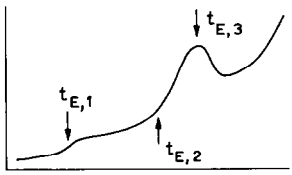
The use of the DTA and ATA methods for evaluating the reactivities of various commercial iron oxides towards zinc oxide has been described previously [5,6]. The previously measured values and the new values ($t_{p,2}$) measured with the equipment described in this paper are listed in Table 1. The results show that the conductance method (ATA) is more sensitive than the DTA method.

The reaction mixture of Fe_2O_3 (fepren DR) and ZnO was homogenized in two ways: (A) dry milled in a porcelain ball mill for 15 h; and (B) rotated in

TABLE 1

Temperature (°C) of the onset of reaction ($ZnO + Fe_2O_3$, 1:1) for various samples of Fe_2O_3

Iron oxide	DTA	ATA [a]			ETA [b]		
	t_0	$t_{p,1}$	$t_{p,2}$	$t_0 - t_p$	$t_{E,1}$	$t_{E,2}$	$t_{E,3}$
Bayferox 130B	790	746	745	45	520	600	850
Fepren 202TD	750	632	634	117	300	530	840
Fepren 303TP	710	600	600	110	300	510	760
Fe_2O_3 for hard ferrites	695	590	591	105	300	480	730
Fepren DR 63	690	580	580	110	240	470	695
Fepren Y (yellow)	665	585	580	83			
Fepren B (black)	660	527	526	133			



[a] $t_{p,1}$, refs. 5 and 6; $t_{p,2}$, this work.
[b] Temperatures of increased emanation release (see figure at bottom of table)

a cylinder without mill balls for 5 h. Both mixtures were then milled for various times in a vibrating dry ball mill (LE 102, Hungary). The measured temperatures of the onset of the reaction Fe_2O_3 + ZnO are listed in Table 2. It can be seen from Table 2 that the reactivity of Fe_2O_3 is increased when the reaction mixture is milled. This increase in reactivity is due to the formation of structural defects by milling. However, when milling was carried out for a long time, the amount of defects decreased, probably due to annealing. The results of the classical DTA method in this case show only a small and inconclusive difference between the onset temperatures (10–12 °C) for samples A and B.

Similarly, measurements of the reactivity of the pre-calcinates of iron yellow or iron black pigments were made. The previously reported DTA measurements [10] were completed by the ATA values measured here. The onset temperatures found by ATA were, again, about 90–100 °C lower than the DTA ones.

TABLE 2

Temperature (t_p in °C) of the onset of reaction ($Fe_2O_3 + ZnO$, 1:1) related to the milling time for the two reaction mixtures A and B

Sample	Length of time of milling (h)							
	0	0.25	0.5	0.75	1	2	4.5	5
A	545	530	495	520	550	560	545	
B	615	–	517	–	520	545	–	590

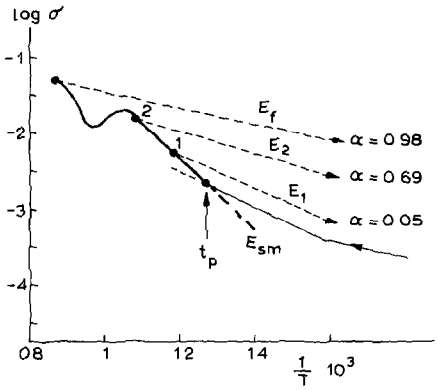


Fig. 4 The conductance thermogram (ATA) of the $ZnO + Fe_2O_3$ system E_f (ferrite) < E_2 < E_1 .. < E_{sm} (starting reaction mixture).

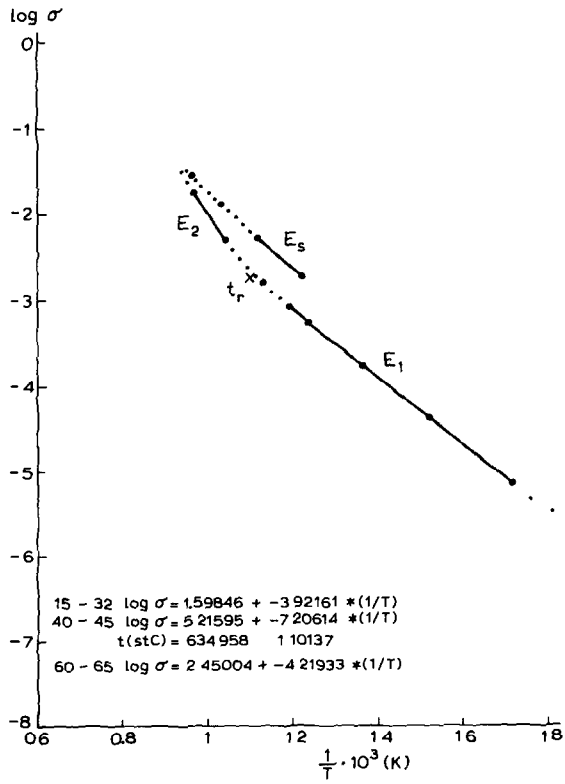


Fig 5 Conductance thermogram of the pigment K 507 + Fe_2O_3 (2 mol%) system. (X) The point of intersection indicates the start of solution formation ($t_p = 635.64 \approx 636\,^\circ C$) The activation energies of the conductance of a mixture and that of a solution are $E_1 = 1\,6$ eV and $E_s = 1\,7$ eV, respectively.

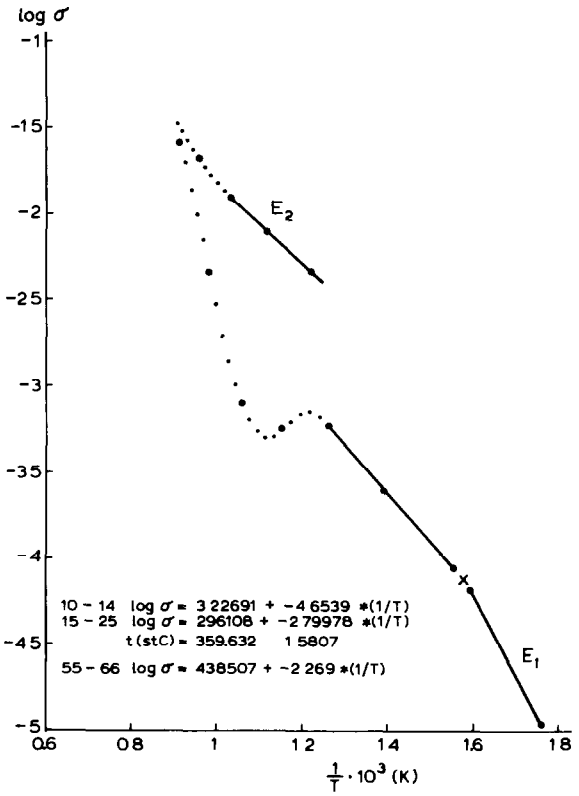


Fig 6 Conductance thermogram of the $ZnO + Cr_2O_3$ system. $t_p = 359.632 \approx 360\,^\circ C$, $E_1 = 1.8$ eV, $E_2 = 0.9$ eV

The linear relationship of log σ vs. $1/T$ enabled the exact onset temperature t_p to be determined. Figure 4 shows that taking t_p as the onset of reaction is correct. Activation energies were found to change in the range of E_s to E_f only; in this range the degree of reaction (α) is $\alpha \in (0, 1)$. The α values were obtained by analytical determination of unreacted ZnO after leaching with a solution of NH_4OH and NH_4Cl.

The relationship log σ vs. $1/T$ may take other forms. For example, when iron oxide is added to the pigment K 507 (a mixed spinel $Zn/Fe_{1+x}Cr_{1-x}/O_4$), its dissolution is seen as a change in the slope of the log σ vs. $1/T$ straight line plot (Fig. 5). The calculated activation energies ($E_1 = 1.6$ eV and $E_s = 1.7$ eV) agree with the wavelength of the absorption edge.

A further example, a conductance thermogram (ATA) of the $Cr_2O_3 + ZnO$ system, is shown in Fig. 6. Discontinuous changes before reaching the temperature t_p are probably caused by the formation of an intermediate product. The reaction mechanism proposed in refs. 11 and 12 for the preparation of $MgCr_2O_4$ is

$$2MgO + Cr_2O_3 + \tfrac{3}{2}O_2 \rightarrow 2MgCrO_4 \rightarrow Mg_2Cr_2O_5 + \tfrac{3}{2}O_2$$

The decomposition of $Mg_2Cr_2O_5$ then occurs according to two reactions

$$Mg_2Cr_2O_5 \rightarrow MgCr_2O_4 + MgO$$

or

$$Mg_2Cr_2O_5 + Cr_2O_3 \rightarrow 2MgCr_2O_4$$

Zinc oxide reacts in a similar way. When calcining the reaction mixture $ZnO + Cr_2O_3$, a yellow extract is obtained in the temperature range 250–350 °C which has a non-negligible Cr(VI) content. The X-ray patterns show that the spinel structure of $ZnCr_2O_4$ is present until the temperature goes above 500 °C.

CONCLUSION

The two methods (ATA and ETA) described were found to be useful in providing further information about the measured sample. The methods enabled us to indicate the onset of reaction more sensitively and, therefore, more exactly than the traditional DTA and TG methods.

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