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THERMO-INDICATING PAINT FOR DAMAGE WARNING

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Abstract

Thermal analysis coupled with the measurement of temperatures at which colour changes are observed in situ was used to test various inorganic pigments with the aim of introducing them into the compositions of thermo-indicating paints. Through a reversible or irreversible modification of the colour these can indicate an undesired increase in temperature of a fluid in a metallic enclosure. Three such pigments are described, which indicate temperatures of 110, 300 and 400°C. The paint contains the thermo-indicator pigment, soluble glass as binder and either ultrafine silica or silica gel, or a mixture of Na_2SiF_6 and finely-ground sand as hardener. Such paints are used for damage warning.

Keywords: thermo-indicating paints

Introduction

The paper discusses the use of thermal analysis to study film-forming materials of paint type, whose compositions were established so that the materials change colour at a certain temperature. This colour modification indicates an undesired increase in temperature of a fluid circulating through pipes and/or metal process vessels.

The compositions of some thermo-indicating paints for temperatures of 110, 300 and 400°C were established, tested and applied. The first two of these compositions undergo an irreversible colour modification of the pigments in the composition [1]; the third undergoes a reversible colour modification due to an increase in the lattice defect number on temperature increase following oxygen loss from the pigment composition (ZnO) [2].

We use thermal analysis extensively in the study of film-forming materials, due to the multiple information obtained: the amounts of solvent-plastifier, resin and pigment, the rates of evaporation of volatile components, interactions between matrix components, their transformations in time [3, 4], and in the present paper physical and chemical modifications in the pigment in response to elevated temperature, which result in a colour modification of the paint.

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Experimental

A Paulik-Paulik Erdey 2895 thermal analyser and a PU 110 immersion thermocouple were used.

Thermal analyses were carried out on several pigments; results on three are presented here: iron yellow, basic cupric carbonate and zinc white. For the paints containing such pigments, applied to a metal support (in situ), we measured the temperatures at which colour modifications were noted.

Results and discussion

The paints used are polycomponent systems consisting of soluble glass (sodium silicate) as binder, thermo-indicating pigments and ultra-fine silica (UFS), silica gel or a mixture of Na_2SiF_6+finely-ground sand as hardeners [5–8]. The preparation of such products is of current interest [9–11].

The binder used in the composition is sodium silicate, a commercial product, in a concentration of 40% (percentage expressed on an anhydrous basis) and with φ=1.4 g/cm^3.

The hardening of such binders results from complex physical and chemical processes that have not yet been completely clarified; we earlier studied the influence of different hardeners [12]. The hardening is mainly influenced by temperature and hardener type. Our tests were carried out at a constant operation temperature of 100°C and with the above-mentioned hardeners.

The aim of the hardening process was to achieve a special polycondensation of the orthosilicic acid so that the hardened paint film should not be degraded by rainwater dissolution. Similar processes may be attained by using either 2.5% silica gel or 10–15% UFS or a mixture of 10% sand (Ø<0.125 mm) with 5% Na_2SiF_6 in the composition; the percentages are mass percentages expressed versus 100 ml sodium silicate solution.

The essential problem in the establishment of the compositions of such products is to find suitable thermo-indicating pigments. In our products, we used three pigments: iron yellow, cupric basic carbonate and zinc white.

Many analogous pigments either do not modify their colour following thermal decomposition or modify their colour within different temperatures ranges depending on the matrix and crystallinity [13, 14]. Therefore, to find a suitable pigment basically requires thermal analysis complemented with temperature measurements when a paint applied to a metallic test bar in situ undergoes a colour modification. The latter measurements were carried out with a PU 110 immersion thermocouple immersed in a low-melting alloy, applied to the test bar surface.

Thermal analysis reveals the probable physical-chemical modifications in certain temperature intervals and the immersion thermocouple indicates the temperature at which the colour modification is visible.

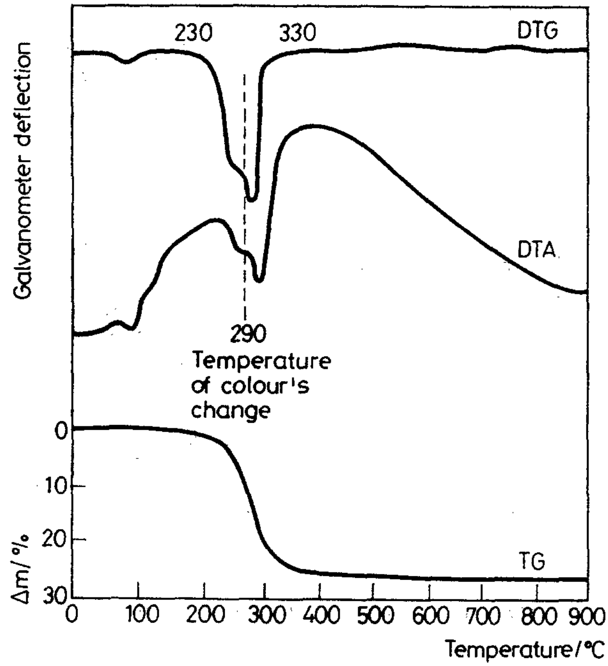

Fig. 1 Thermal behaviour of iron yellow up to 400°C; heating rate 4 deg·min^{-1}

As an irreversible indicator for the temperature of 300°C, the natural pigment iron yellow was used; this contains goethite (α-FeO(OH)), lepidocrocite (γ-FeO(OH)) and about 10% H_2O.

The thermal analysis curves (Fig. 1) show that the loss of differently linked water takes place in two distinct steps, the first (230–290°C) probably corresponding to gelic water and the second (290–330°C) to $Fe(OH)_3$. The second dehydration is accompanied by the colour modification (yellow→brick-red), due to the conversion to hematite (α-Fe_2O_3). On further temperature elevation, the colour is intensified, possibly due to the exothermal conversion of γ-Fe_2O_3 from lepidocrocite to α-Fe_2O_3 between 400 and 500°C (Fig. 2) [1]. An amount of 25% pigment was introduced into the paint.

As an irreversible indicator for a temperature of 110°C, a commercial artificial pigment, basic cupric carbonate, was used. This was introduced in a ratio of 65% into the paint composition.

Thermal analysis revealed that the pigment mainly contains malachite $\{Cu_2(CO_3)(OH)_2\}$ [1] (Fig. 3). A water loss was followed by a CO_2 loss. The water loss at 110°C was accompanied by a colour modification of the product from light-green to black, a quite visible modification. On continuation of the heating, following CO_2 loss, a visible degradation of the paint film and support adherence took place, owing to the high mass loss of about 30% (Fig. 3).

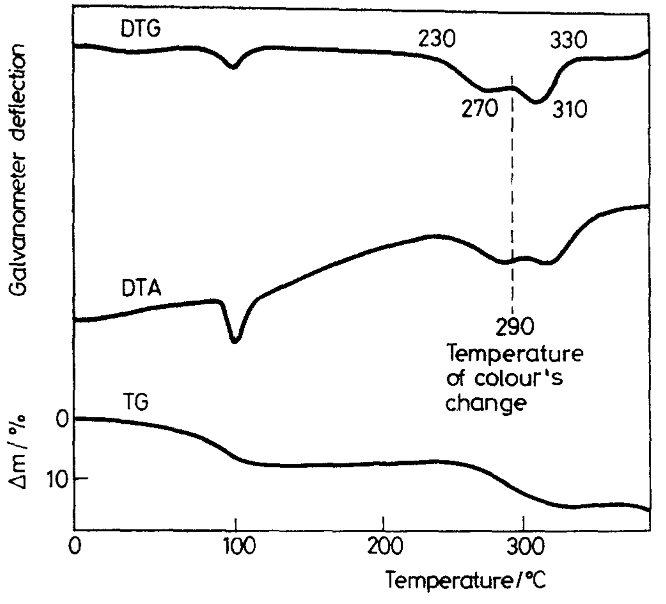

Fig. 2 Thermal behaviour of iron yellow up to 1000°C; heating rate 10 deg·min^{-1}

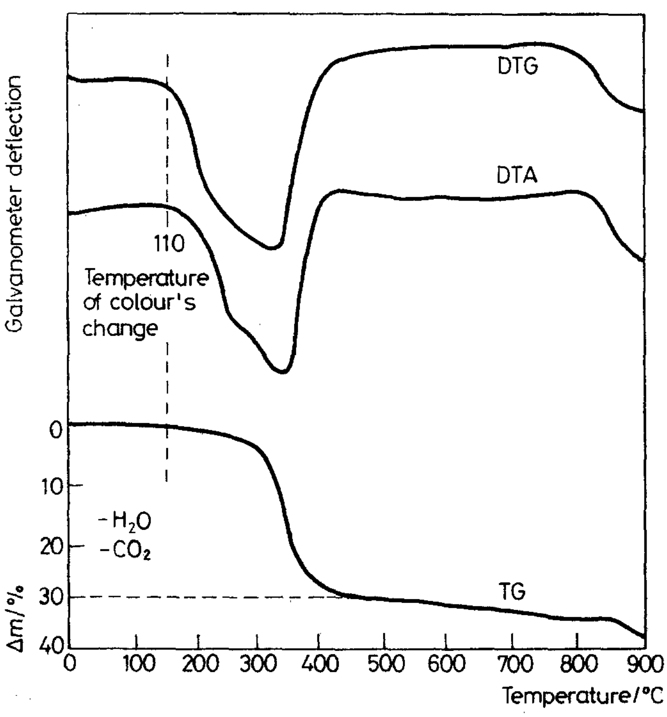

Fig. 3 Thermal behaviour of basic cupric carbonate; heating rate 10 deg·min^{-1}

As reversible indicator for a temperature of 400°C, a commercial zinc white introduced in a ratio of 50% into the paint composition was used. Zinc white contains finely-ground ZnO of white, green or red range type.

The colour modification is white ⇄ yellow as a result of compositional-structural modifications, created by reversible migration in the oxygen structure modifying the number of lattice defects (thermal gaps), this modification being accompanied by the colour change [2].

It was noted that the yellow colour occurred at 400°C and it became more prominent with increase of the defect number caused by the temperature increase.

Applications

By choosing a suitable pigment, we may obtain thermo-indicating paints applicable to metal supports used in the open air and at high temperature; by changing their colour, these may warn of the occurrence of damages.

Conclusions

Thermal analysis, together with the in situ determination of the temperature at which colour modification takes place, was applied to inorganic pigments used in the compositions of thermo-indicating paints.

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