

THERMOANALYTICAL STUDY ON SOME FILM-FORMING QUICK-DRYING AND WATERPROOF PRODUCTS

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ABSTRACT

The paper deals with the thermal behaviour of the copolymer vinyl chloride : vinyl acetate = 85:15 (mass percentage)(resin) and dimethyl phthalate (plasticizer) as compared to their thermal behaviour in the matrix of some film-forming, quick-drying and waterproof products.

For some ink type film-forming products used in the markers with fibre tip, the evaporation rate of the solvents was determined in the following systems: methyl-ethyl ketone : cyclohexanone = 2:1 (in volume); toluene : acetic acid = 66:34; toluene : pyridine = 78:22; toluene : butyl formate = 70:30 (mass %), the last three systems correspond to azeotropic compositions.

Due to the constant evaporation rate of the solvents from the systems having azeotropic compositions, the ratio between the component solvents is preserved constant with time and consequently also the marking quality of the ink is preserved.

EXPERIMENTAL

The thermal analyses were carried out for the vinyl chloride-vinyl acetate copolymer (85:15) with and without maleic anhydride, dimethyl phthalate (DMP), pigmented materials consisting of ZnO + DMP (70 % in pigment), yellow pigment 1-11680 + DMP (50 %) and two paints white and yellow, respectively with the above compounds.

A thermal analysis apparatus with Paulik-Paulik-Erdey system was used.

The experimental determinations were conducted on a 500-1000 mg sample displayed on 6 platinum trays; the sensitivities were TG 500 and 1000, DTG 1/5 and DTA 1/10; the inert thermal material Al_2O_3 , the heating rate of $10^\circ C/minute$ and maximum heating temperature of $800^\circ C$.

RESULTS AND DISCUSSIONS

We have obtained and characterized six film-forming, quick-drying and water-proof products to be used for marking the quality and size characteristics on the metal, plastic and glass products /1-4/.

In the composition of such products, film-forming materials such as polystyrene and vinyl chloride - vinyl acetate copolymer (85:15) were used, the latter being with and without maleic anhydride.

A good adhesion to the metal, glass and polyethylene surfaces was obtained with the vinyl chloride - vinyl acetate copolymer containing in its composition maleic anhydride, maybe due to the numerous acetate polar groups in its composition.

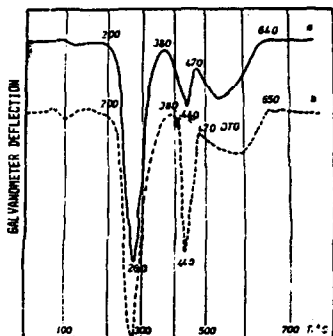


Fig. 1. DTG curves of vinyl chloride -vinyl acetate copolymer (85:15) with (1) or without (2) maleic anhydride

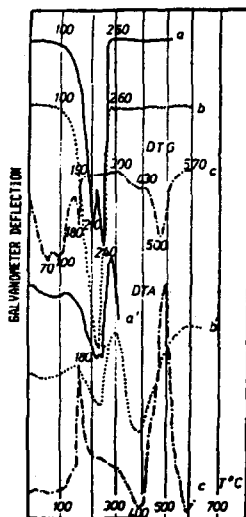


Fig. 2. DTG and DTA curves of DMP (a and a', respectively), ZnO-DMP prefabricated (b and b') and of a white paint (c and c')

Fig.1 illustrates the DTG curve of the copolymer (a) and the copolymer with maleic anhydride (b). The loss of the acetate groups by heating occurs in the temperature range 330-470°C, with maximum speed at 440°C.

In all the compositions as plasticizer was used dimethyl phthalate (DMP) because due to its volatility it provides a short time for drying (some minutes) for the non-absorbing supports.

The thermal behaviour of DMP is different depending on the matrix within which it exists. Thus, fig.2 shows the DTG and DTA curves of DMP (a), of the white pigmented material (ZnO and DMP prefabricate)(b) and of a white paint (c).

Within the temperature range 100° to 260°C DMP undergoes two transformations (Fig.2, a and a'). The first transformation has the maximum speed at 210°C and is endothermal being accompanied by a 60 % mass loss, maybe due to the splitting of molecule and loss of esterified acid groups, fact which was also found from the quantitative interpretation of the TG curve.

The second transformation has a maximum speed at 240°C, it is exothermal and is accompanied by 40 % mass loss corresponding to the ignition of the aromatic nuclei.

In the pigmented material (ZnO + DMP) (Fig.2, b and b') the two stages are differentiated on the DTA curve but not also on the DTG curve.

Above 200°C, ZnO undergoes only a colour reversible modification from white to yellow /5-6/ due to the appearance of some network defects called thermal gaps. This transformation does not appear on the thermal curves.

Fig. 2, c and c' presents the thermal behaviour of the white paint. The first stage of endothermal decomposition of DMP is overlapped on the solvent evaporation and the ignition of the aromatic nuclei occurs at lower temperature, with maximum speed at 180°C.

Fig. 3 shows the DTG curves for DMP (a), for the vinyl chloride - vinyl acetate copolymer with maleic anhydride, for the yellow pigmented material (Yellow 1-11680 and DMP prefabricate, 50 % in pigment) (c) and for a yellow paint containing all the components mentioned above.

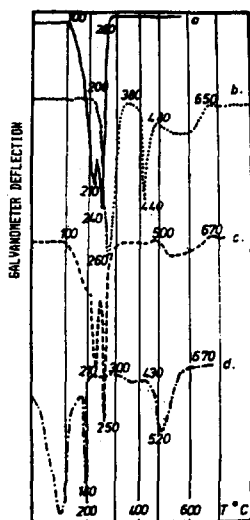


Fig. 3. DTG curves of DMP (a), vinyl chloride-vinyl acetate copolymer with maleic anhydride (b), yellow organic pigment-DMP prefabricated (c) and of a yellow paint(d)

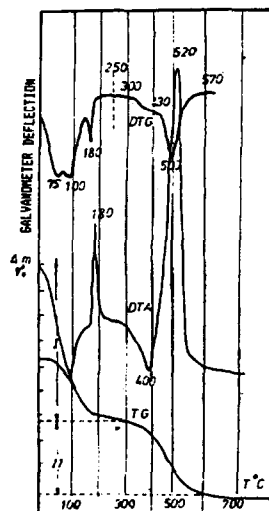


Fig. 4. DTG (a), DTA (b) and TG (c) curves of a paint based on ZnO

It is found from Fig. 3 that in the pigmented material DMP preserves its thermal individuality decomposing itself into two well differentiated stages, while in the matrix of the yellow paint the behaviour is similar to that in the matrix of the white paint.

From the DTG curve of the copolymer (b) it is found a high mass loss from 200 to 380°C which according to TG curve would correspond to the loss of chlorine /7/. The effect does no longer appear on the DTG curve of the paint (d) within the same temperature range but from 300 to 400°C.

The other effects of the resin, i.e. the loss of acetate groups (380-480°C) and the burning of the organic remainder rich in carbon (480-650°C) appear also on the DTG curve of the paint.

Knowing the individual thermal behaviour of the components the DTG, DTA and TG curves of a film-forming material such as the paint from Fig. 4 may give useful information on their modifications with time and at high temperature. Thus, the films of hardened paint obtained by us may be used up to a temperature

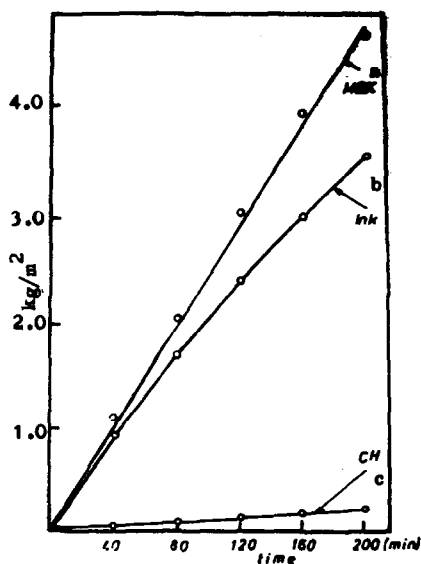


Fig. 5. Specific evaporation depending on time for MEK (a), cyclohexane (b) and the ink containing them (c)

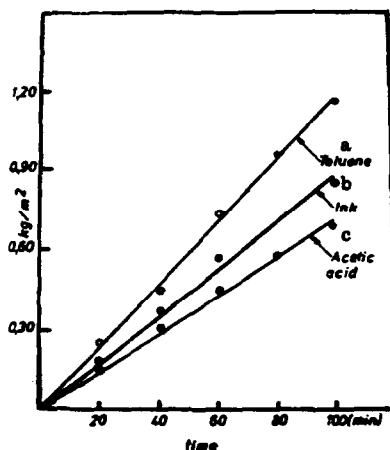


Fig. 6. Specific evaporation depending on time for toluene (a), acetic acid (b) and the ink containing them (c)

of maximum 250°C.

In the case of the ink type film-forming materials with quick-drying and water resistance used in the markers with fibre tip, it is very important to study the evaporation rate of the solvents involved in their composition.

Each component solvent plays the part of dissolving or gelifying the resin and/or dissolving the dyestuff which usually is an organic one.

We have obtained and characterized such products /1-4/ in which the two solvents do not form (Fig. 5) or form azeotropic compositions (Figs. 6-8).

We have experimentally established a conventional method for the determination of the evaporation rate of the solvents in various materials by using the thermal gravimetry method /8/. This method was applied in the determination of the evaporation rate of the solvents in the ink.

The evaporation rate influences the drying time of the film and a sudden evaporation microcracks the film and causes the precipitation of the resin and/or dyestuff in the marker tip.

The solvent system consisting of methyl-ethyl ketone (MEK)

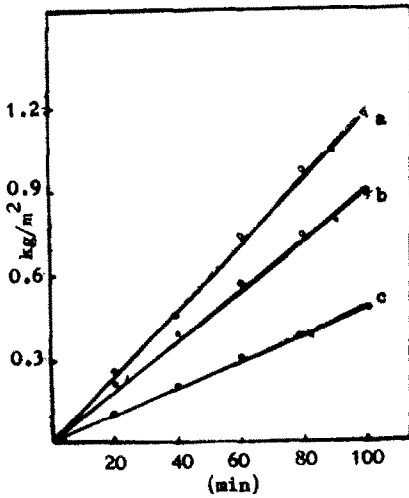


Fig. 7. Specific evaporation depending on time for toluene (a), pyridine (b) and the ink containing them (c)

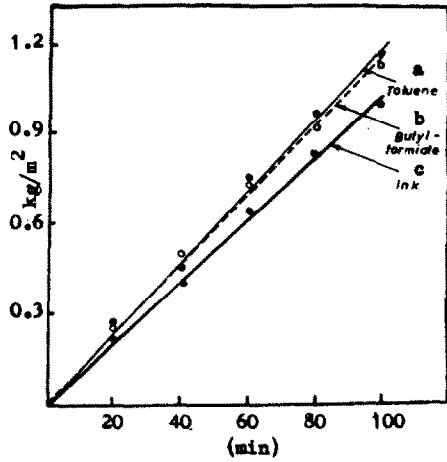


Fig. 8. Specific evaporation depending on time for toluene (a), butyl formiate (b) and the ink containing them (c)

and cyclohexanone (CH) (2:1 in volume) in Fig. 5 shows a decrease with time of the evaporation rate of the solvents in ink due to MEK evaporation. After three-months storage, MEK volatilizes totally from the ink. Therefore, if the initial ink might have been used for marking several plastic supports with a type B drying time of 5 seconds, after three months storage the ink may be used only for the PVC supports on which it is dried by filtration for 120 seconds.

In the case of the azeotropic solvents systems: toluene : acetic acid = 66:34 (Fig. 6); toluene : pyridine = 78:22 (Fig. 7) and toluene : butyl formiate = 70:30 (Fig. 8)(mass %), the evaporation rate of the solvents involved in the ink composition is constant with time. In this way the ratio between the component solvents is maintained during ink conservation, fact which has important consequences in preserving the marking qualities of the ink.

APPLICATIONS

The information provided by the thermal analysis method applied on the film-forming materials are numerous. The most re-

presentative data are obtained when in the composition of the film-forming material is introduced an inorganic pigment which does not thermally decompose up to 800°C.

For instance, within range I of temperature 20 -300°C of the TG curve (Fig. 4), quantitative information are obtained regarding the solvents in the composition, in this case being a mixture of toluene and butyl acetate and as plasticizer in this case being DMP and within range II of temperature 300 -600°C quantitative information are obtained regarding the thermal behaviour of the resin. The residue which remains after burning represents the quantity of pigment.

CONCLUSIONS

The information provided by the thermal analysis method applied on the film-forming materials are numerous. Besides the orientative amounts of solvent-plasticizer, resin and pigment, information on the evaporation rate of the component solvents, on the interactions between the components in the matrix of the film-forming materials as well as on some transformations of the components with time may also be obtained.

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