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PYROLYSIS OF A FIRE RETARDANT COATING MADE OF POLYURETHANE AND CHLOROWAX HEATED BY FREE CONVECTION IN AIR

M. ABDUL, V.M. BHATNAGAR, J.C. DAVID and J.M. VERGNAUD

Laboratory of Materials and Chemical Engineering, U.E.R. of Sciences, University of St. Etienne, 23, Dr. P. Michelon, St. Etienne, 42100 (France)

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ABSTRACT

Pyrolysis studies of a fire retardant coating were achieved in a real situation by using the kinetic data of the overall reaction of pyrolysis and of all the heat transferences. The coating was made of polyurethane and chlorinated paraffin. The heat was transferred from heated air to the coating deposited on a wood panel by free convection, and by conduction through the coating. The increase in the air temperature vs. time followed a logarithmic law resulting from real experiments on fires. The profiles of the temperature and loss in weight caused by the decomposition were determined at different times and positions through the coating. The effect of the thickness of coatings on these profiles is especially noted.

INTRODUCTION

It is well known that an intumescent fire retardant coating can effectively control fire spread [1]. It will provide sufficient time for evacuation of personnel from buildings and allow for the arrival and efficient use of fire-fighting equipment. The dual purpose of a fire retardant coating is to confine spread of the flames along the coated surface to the source of the fire, and to retard penetration of heat and flame through the coated surface. The efficiency of fire retardant coatings can be tested by several fire tests, and the best-known for laboratory preliminary testing is the two-foot tunnel test [2]. Any complete model of fire development must be able to answer the questions: what is the extent of the fire growth with time [3] and what is the extent of spread of non-flammable gases from the fire retardant coating as a function of time [4]?

A general model for the behavior of a fire retardant coating exposed to a flame or to heating has already been presented [5]. Several successive or simultaneous steps should be considered: (i) Heat transfer by convection through air from the fire to the coating face and through the air–coating interface. (ii) Heat transfer by conduction through the coating, followed by

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pyrolysis. As the temperature increases through the coating, the pyrolysis takes place progressively from the heated face to the protected material. The pyrolysis is responsible for giving off non-flammable gases. (iii) A matter transfer of these non-flammable gases hinders the diffusion of oxygen, decreasing the fire spread.

The third step in our model was especially considered [6] by making the following assumptions; the fluid flow is steady, laminar and non-radiative and that matter transfer is governed by Fick's law.

The purpose of this work is to study the first two steps for a fire retardant coating exposed to heating. The heat transfer is obtained by free convection through the air–coating interface and by conduction through the coating and the coated wood. The assumption of free convection derives from the above assumptions made by several authors [6,7]. The study was carried out using control of air temperature obeying a logarithmic law vs. time. The fire retardant clear coating composition was formed by combining an organic polyisocyanate and a highly chlorinated hydrocarbon. The chlorinated hydrocarbon is trapped within the cells of the coating, and with further heating non-flammable gases are emitted and an expanded char formation providing an excellent heat barrier is developed. The coating was applied in a variety of thicknesses throughout the 80–600 micron range. To further enhance our work, theoretical studies were conducted on both the heat transfer and the pyrolysis stages, applying a mathematical treatment previously used for investigating vulcanization taking place through a rubber mass [8].

THEORETICAL

A fire retardant coating was subjected to heat treatment through air at a logarithmic heating rate

$$T_t = T_0 + \log_{10}(8t + 1) \qquad (1)$$

where T is the temperature at time t and 0, respectively, expressed in degrees Celsius and t is the time in minutes. This relation is very often accepted as the rate of heating during the spread of a fire.

We believe that the coating deposited on a wood panel allows heat transference as follows:

(i) The heat flow is conducted as convection heat from the air to the coating face. This convection is free in this case as there is no air flow [6].

(ii) The heat is transferred by conduction through the coating. The thermal properties of the coating are assumed to be constant while the heat transfer and pyrolysis are taking place. This assumption is well founded as swelling of the coating developes during pyrolysis. Hence, within the range of temperature studied in this paper (260°C or below) no combustion takes place and the thermal properties of the coating do not vary appreciably.

Mathematical treatment of heat transfer

Theoretical studies were conducted on both convection and conduction stages and are given by the following equations.

Heat transfer by free convection

Heat transfer by natural (or free) convection between air and the coating surface was dealt with by use of dimensionless Prandtl and Grashof moduli, Pr and Gr. The heat transferred by radiation was not found to be substantial compared with that by convection. The 15 × 15 coated panel was vertical. As in our study

$$Gr \times Pr < 10^9 \tag{2}$$

the free convection is conducted in laminar range and the dimensionless Nusselt modulus is given as follows [11]

$$Nu = 0.56(Gr.Pr)^{0.25} \tag{3}$$

Heat transfer through the coating by conduction

The heat flow is unidirectional along the x axis, through the coating thickness

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \tag{4}$$

α is the thermal diffusivity of the coating.

Computing evaluation

A detailed figure for the mathematical treatment of the air–coating interface is presented in Fig. 1. The coating is divided into a number of equal finite slices of thickness Δx by temperature-reference planes. Several possible equations for this treatment were investigated and those reported below were found to coincide well with our results.

For the air–coating interface, the following equation gave the best results

$$T_{i+1,0} = \frac{1}{M}\left[2T_{i,1} + (M - 2 - 2Nu)T_{i,0} + 2NuT_{\mathrm{a}}\right] \tag{5}$$

where $T_{i,0}$ is the temperature at time $i\Delta t$ at the coating face, T_{a} is the temperature of air and $T_{i,1}$ is the temperature at the first slice in the coating.

The modulus M is equal to

$$M = \frac{(\Delta x)^2}{\Delta t}\frac{1}{\alpha} \tag{6}$$

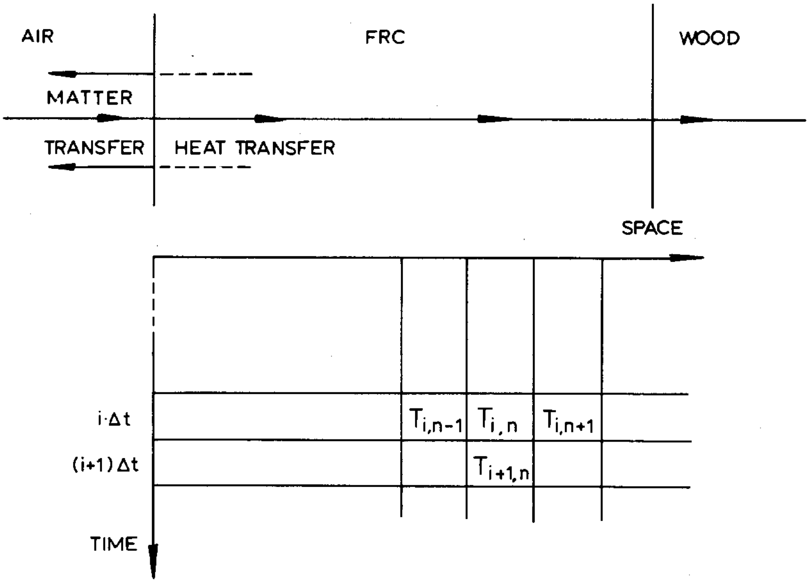

Fig. 1. Scheme of the pyrolysis process.

In the equation above Δx represents the incremental space and Δt is the incremental time.

The Nusselt number is

$$Nu = \frac{h \Delta x}{\lambda} \tag{7}$$

where h is the heat transfer coefficient at the interface.

For the coating the following expression was found suitable

$$T_{i+1,n} = \frac{1}{M}\left[T_{i,m-1} + (M-2)T_{i,m} + T_{i,m+1}\right] \tag{8}$$

Kinetics of pyrolysis of the coating

Pyrolysis studies of the coating were conducted using isothermal thermogravimetry under air at selected temperatures. After introduction into the furnace, the samples were quickly heated from room temperature to the constant temperature of pyrolysis. For temperatures ranging from 150 to 270°C, the loss in weight resulting from the pyrolysis was found [9] to follow a single law

$$\frac{\mathrm{d}(\Delta P)}{\mathrm{d}t} = 2.2 \times 10^{22}(62 - \Delta P) \exp - \frac{30400}{T} \tag{9}$$

where t is expressed in seconds.

EXPERIMENTAL

Preparation of the fire retardant coating

The main ingredients of the coating were [1,10] cellulose acetate butyrate and hexamethylene diisocyanate (Desmodur N, Bayer) for polyurethane, chlorowax 70 (Diamond–Shamrock Chemical) as chlorinated paraffin, and methyl isobutyl ketone as solvent. These components were blended together in the solvent. The following coating composition was used in this work: cellulose acetate butyrate, 41.4%; desmodur N 30%; chlorowax 70 28%; mar and slip additive 0.6%.

The coating was applied to red oak panels previously conditioned for four weeks at 20°C. The coating dried tack free within 30 min to 1 h and required 2 days to reach maximum hardness.

Pyrolysis experiments

Measurements were carried out under air in a furnace by using wood panels covered with coatings of different thicknesses. The air was allowed to reach higher temperatures according to the logarithmic law by using a system of heating regulation. The air in contact with the coating face was kept motionless. The temperatures at various positions in the air and at the coating–wood interface were registered by thermocouples. The loss in weight was measured at various times.

RESULTS

The calculated and experimental results concerned with the development of the temperature and loss in weight were in good agreement. There was no noticeable displacement of the surface of coatings during the pyrolysis. In fact, for low temperatures (250°C or below) the volatilization of chlorowax took place with a low degradation of polyurethane, leaving a char crust [9]. The thermal properties of the coating were not modified during pyrolysis, and the thermal barrier of the coating remained very low with regard to the thermal barrier due to the natural convection of heat through the air–coating interface.

Data on heat transfer by natural convection from motionless air to vertical planes were obtained [11], and a low heat transfer coefficient was found with a resulting low value for Nusselt's number.
$h = 2 \times 10^{-4}$ cal cm^{-2} s K
$Nu = 10^{-2}$
$M = 4$
$\Delta x = 40$ microns
$\Delta t = 4 \times 10^{-3}$ s
$\lambda = 5.5 \times 10^{-4}$ cal cm^{-1} s K
$\alpha = 10^{-3}$ cm^2 s^{-1}

Study of the degradation of a 320 micron coating

A coating of this thickness is very useful for protecting wooden furniture.

Temperature–time curves

Figure 2 provides an excellent idea of temperature variation at different parts of the coating (on both faces, the one exposed to air, the other close to the wood). A high temperature gradient at the air–coating interface was found, due to the low value of heat transfer coefficient in natural convection.

Loss in weight–time curves

The types of weight loss–time curves obtained upon exposing the coating to heated air without motion are shown in Fig. 3. As previously reported [9], a perceptible volatilization of chlorowax takes place at 120°C.

The loss in weight depends on both time and position in the coating. The three curves shown in Fig. 3 were obtained for both faces of the coating and

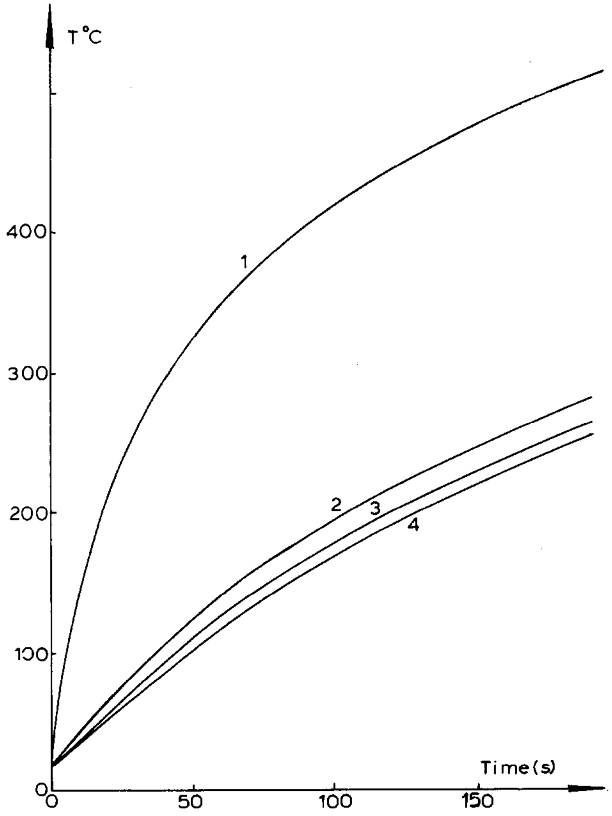

Fig. 2. Temperature–time curves for a 320 micron thick coating. 1, air; 2, coating face; 3, coating–wood interface; 4, within the wood at 160 microns from the coating–wood interface.

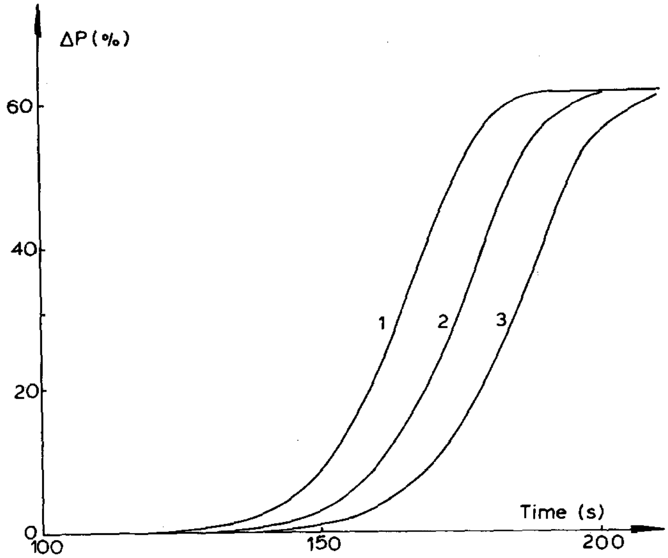

Fig. 3. Loss in weight–time curves for a 320 micron thick coating. 1, coating face; 2, coating midplane; 3, coating–wood interface.

the midplane. All these curves have the same shape and asymptotical value of 62%. They can be derived, one to the next, by a translation along the time abscissa with a translation time of 20 s for the 320 micron thick coating. The loss in weight reaches 31%, half its asymptotical value at about 176 s as shown in Table 1.

Effect of coating thickness

The thickness of coatings can be controlled and this parameter is of interest. The effect of thickness on heat transfer was studied by using coatings of different thicknesses [2]; 80, 160, 320 and 600 microns.

Temperature–time curves

These curves are shown in Figs. 4, 6 and 8 for the different coatings. The temperature remained the same in the heated air, as well as at the coating face exposed to air.

TABLE I

Variation of time of heat retardation and time for weight loss with coating thickness

Coating thickness (microns)	80	160	320	600
Time retardation (s)	5	10	20	37
Time for $P = 31\%$ (s)	167	169	175	183

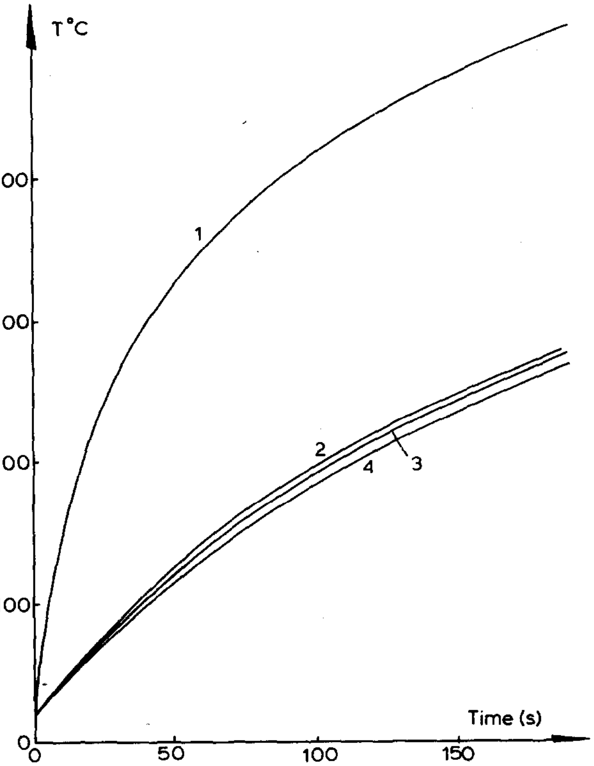

Fig. 4. Temperature–time curves for an 80 micron thick coating. 1, air; 2, coating face; 3, coating–wood interface; 4, within the wood at 160 microns from the coating–wood interface.

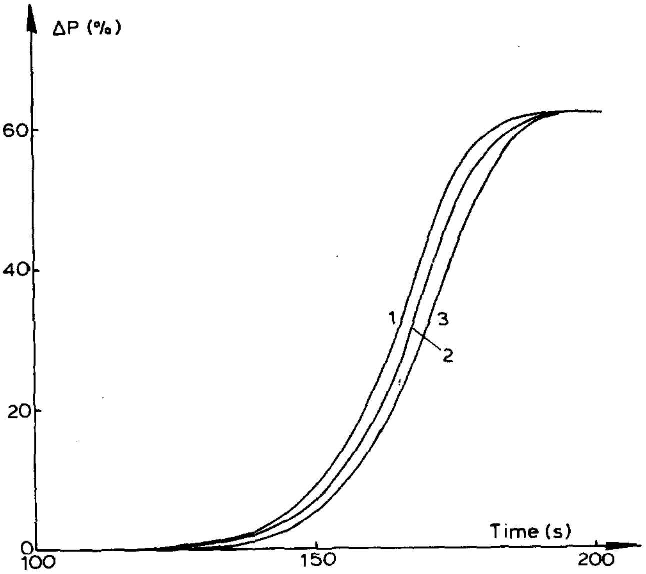

Fig. 5. Loss in weight–time curves for an 80 micron thick coating. 1, coating face; 2, coating midplane; 3, coating–wood interface.

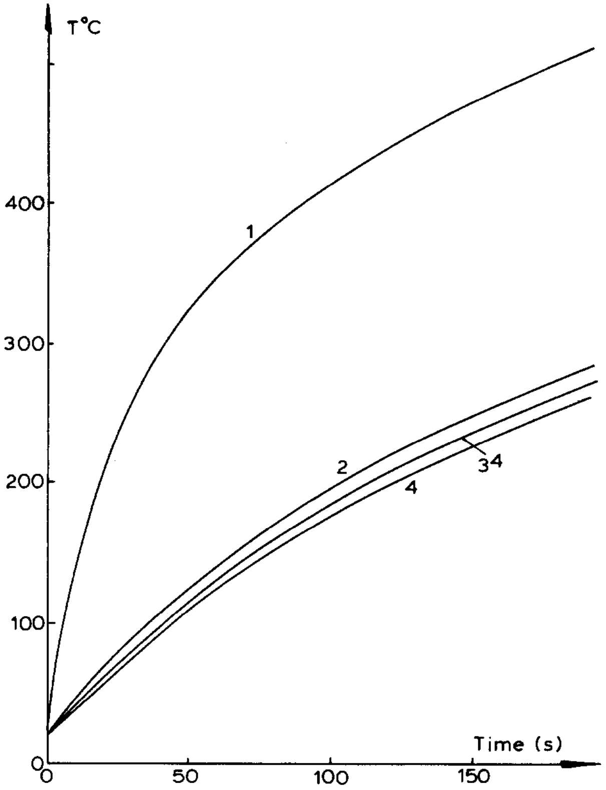

Fig. 6. Temperature–time curves for a 160 micron thick coating. 1, air; 2, coating face; 3, coating–wood interface; 4, within the wood at 160 microns from the coating–wood interface.

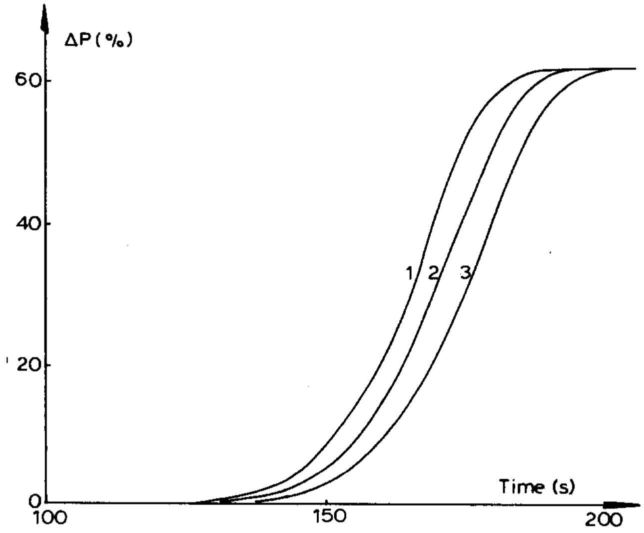

Fig. 7. Loss in weight–time curves for a 160 micron thick coating. 1, coating face; 2, coating midplane; 3, coating–wood interface.

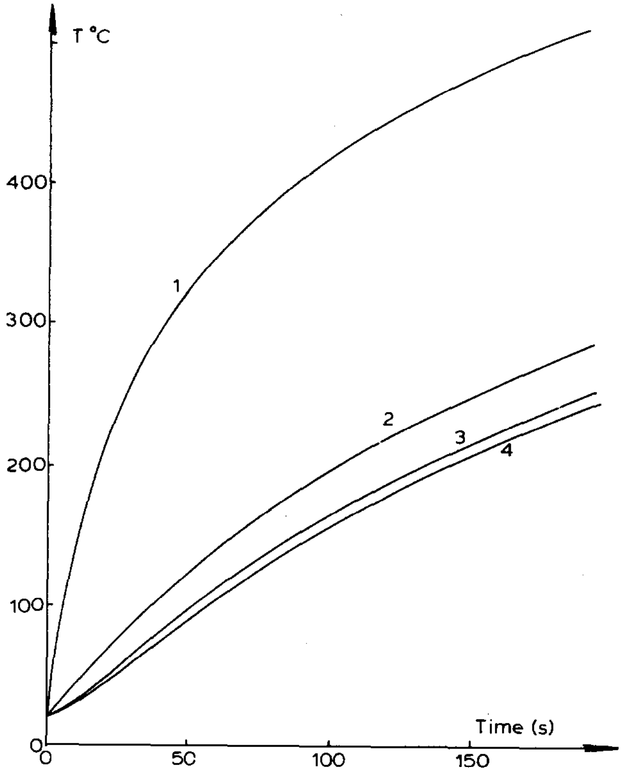

Fig. 8. Temperature–time curves for a 600 micron thick coating. 1, air; 2, coating face; 3, coating–wood interface; 4, within the wood at 160 microns from the coating–wood interface.

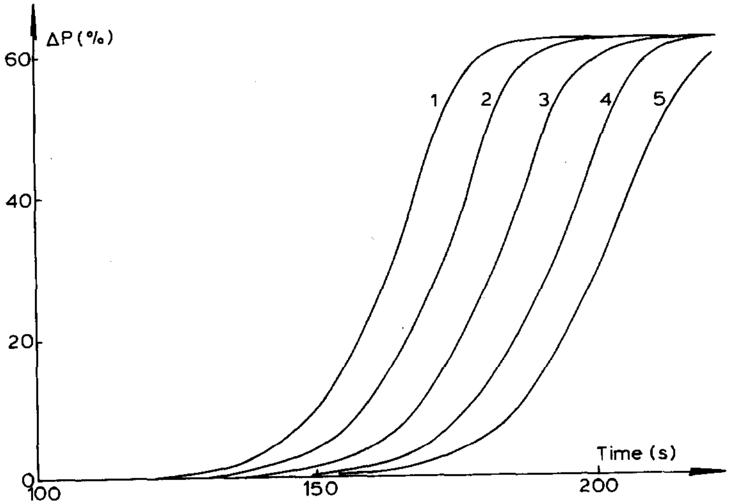

Fig. 9. Loss in weight–time curves for a 600 micron thick coating. 1, coating face; 2, within the coating at 150 microns from the face; 3, coating midplane; 4, within the coating at 450 microns from the face; 5, at the wood face.

The retardation in the advancement of heat through the thickness of all the coatings was found to be proportional to the thickness, as shown in Table 1.

Weight loss–time curves

The degradation starts at the same time and temperature for all the coatings (Figs. 5, 7 and 9). The weight loss–time curves are the same for the face exposed to air; the curves at the midplane and at the coating–wood interface are obtained by a translation along the time abscissa, this translation being proportional to the thickness as shown in Table 1.

The time at which the weight loss reaches half its asymptotical value was found to increase only slightly with the coating thickness.

CONCLUSIONS

Heat conduction through a fire retardant coating and heat convection from heated air to the coating surface provide a study on the extent of decomposition in a real situation. Kinetic parameters of the overall reaction of decomposition were investigated by thermogravimetry. The profiles of temperatures developed through the coating determined by a numerical method were in good agreement with experimental values. It was found that profiles of decomposition can be obtained by calculation if the kinetic data and heat transfer parameters were known. A logarithmic law for the increase in the temperature of heated air, as well as a natural convection from air to the coating were used. The effect of the thickness of coatings was shown to be of interest, and the loss in weight–time curves at different places in the coating were correlated by a time translation proportional to the thickness.

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