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ISOTHERMAL PYROLYSIS OF A FIRE RETARDANT COATING HEATED BY FREE CONVECTION IN AIR

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Pyrolysis studies of a fire retardant coating were conducted under isothermal conditions by taking into account the kinetic data of the overall reaction and the heat transfer process. The coating was made of polyurethane and chlorinated paraffin. A 160 μm thick film was heated by free convection from heated air, and conduction through the coating. Profiles of temperature developed through the coating were obtained by calculation, as well as those of loss in weight due to the thermal decomposition. The thermal conduction did not vary because of the formation of a porous char resulting from the coating decomposition.

This work deals with the pyrolysis of a fire retardant coating by taking into consideration the effect of several heat transfer processes taking place normally. An attempt has been made to explain the mechanism of thermal degradation of the coating when it is exposed to heated air, by the following steps:

(i) Heat transfer by convection from the heat source to the coating, through the air-coating interface. This convection can be free when there is no air flow, and forced when a stream of air is blown during experiments. Furthermore this convection rate can be laminar or turbulent type, depending upon the values of some dimensionless numbers such as Grashof and Prandtl.

(ii) Heat transfer by radiation from the heated source to the coating surface.

(iii) Heat transfer through the coating by conduction followed by an internal reaction of pyrolysis.

(iv) Matter transfer of non-flammable gases from the coating to the heated air responsible for a hindered diffusion of oxygen to the flame source.

The last step in our model was especially studied [1, 2] by making the following assumptions: the fluid is steady, laminar and non-radiative, the matter transfer is governed by Fick s laws.

The main purpose of this work is to study the first two steps, combined together, for a fire retardant coating exposed to heated air or nitrogen without motion. It was found that the behavior of a polyurethane film was the same when it is exposed to air or nitrogen at temperature below 350° [3]. As the heat transfer by radiation is not found to be substantial compared with that by convection [1, 2], the heat transfer is obtained in our case by free convection through the air-coating interface and by conduction through the coating.

Very often, the problem can be more complicated, because of the change in the thermal properties of the coating due to pyrolysis. We did not encounter any such complication due to the fact that the thermal properties did not vary to a considerable extent during the pyrolysis. This might have been due to several reasons e.g. the degradation of the coating leaves a porous and crusty char having a thickness and thermal properties comparable to these of the coating; the temperature for the coating was below the ignition temperature of the char in our experiments; the heat transfer by free convection through the air-coating interface being very low with regard to that by conduction through the coating, a change in the thermal conductivity of the coating is not of great importance for our investigation.

The coating is comprised of polyurethane and chlorinated paraffin; upon heating, it intumesces and leaves a crusty and porous char [3–5]. These coatings deposited on wood panels were subjected to heated air in isothermal conditions. The profile of the temperature and loss in weight developed through the coating were evaluated using an explicit numerical analysis method [6, 7]. An important parameter such as the gas temperature was especially investigated.

Experimental

Preparation of the fire retardant coating

Polyurethane coating in this work consisted of a reaction product of tenth-second butyrate (Eastman Kodak Chemicals) and Desmodur-N (Mobay Chemicals). The fire retardant coating contained Chlorowax-70 as fire retardant ingredients [5, 6]. These components were blended together in the solvent. The following example of coating composition was used:

Cellulose acetate butyrate	41.4
Desmodur-N	30
Chlorowax-70	28
Mar and slip additives	0.6

The coating was applied to asbestos panels.

Pyrolysis experiments

Experiments were carried out under nitrogen or air in a furnace by using asbestos panels covered with coatings of different thicknesses. The gas on contact with the coating face was kept motionless and at a constant temperature.

The temperature at the coating-asbestos interface was registered, as well as the loss in weight.

Kinetic parameters

The kinetic parameters of the overall reaction of pyrolysis were determined by thermogravimetry under isothermal conditions [3], and the following equation stands for this overall reaction

$$\frac{d(\Delta P)}{dt} = K_0(62 - \Delta P)\ \exp - \frac{E}{RT} \tag{1}$$

Theoretical

Theoretical studies were conducted on both convection and conduction as successive stages. The heat transfer is given by the following equations:

Free convection:
$$\mathrm{Gr} = \frac{\alpha g \rho^2 L^3}{\mu^2}\, \Delta T \tag{2}$$

$$\mathrm{Pr} = \frac{\mu c}{\lambda} \tag{3}$$

$$\mathrm{Nu} = \frac{hL}{\lambda} = a.\ (\mathrm{Gr} \cdot \mathrm{Pr})^n \tag{4}$$

Conduction:
$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c}\, \frac{\partial^2 T}{\partial x^2} \tag{5}$$

The equation 5 is transcendent and might be transformed for computer as follows: A detailed figure for the mathematical treatment of heated nitrogen-coating is presented in Fig. 1. Several possible equations for this treatment were investigated and those reported below were found to coincide well with experimental results obtained with the vulcanization of thin and thick rubber sheets [6, 7].

The first equation for the gas-coating interface is given as follows:

$$T_{i+1,\mathrm{int}} = \frac{1}{M}\left[N T_{i,\mathrm{gas}} + (M - 1 - N)\, T_{i,\mathrm{int}} \neq T_{i,1}\right] \tag{6}$$

while for coating the following expression was found suitable

$$T_{i+1,m} = \frac{1}{M}\left[T_{i,m-1} + (M - 2)\, T_{i,m} + T_{i,m+1}\right] \tag{7}$$

where moduli M and N are equal to

$$M = \frac{(\Delta x)^2}{\Delta t}\, \frac{\rho c}{\lambda} \tag{8}$$

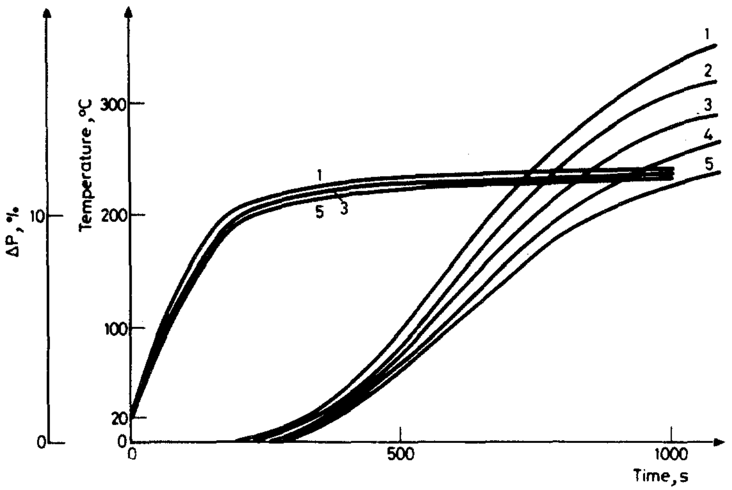

Fig. 1 Temperature and weight loss as a function of time. Gas temperature 329°. Initial temperature of coating: 20°. Coating thickness: 160 μm. 1: coating face, 3: coating midplane, 5: panel-coating interface

$$N = \frac{h\Delta x}{\lambda} \tag{9}$$

h	stands for the surface coefficient of heat transfer;
λ	thermal conductivity;
g	acceleration owing to gravity;
ρ	density and
μ	viscosity;
ΔT	temperature potential;
α	coefficient of volumetric expansion of gas;
c	specific heat;

Δx and Δt are the increments of space and time.

Results and discussion

The numerical values for heat transfer and kinetics of reaction are in Table 1 and Table 2.

As in our study, $\mathrm{Gr} \cdot \mathrm{Pr} = 2 \cdot 10^5 \Delta T$, the free covection is in laminar range, and for a vertical plane the Nusselt's number is given as follows [8]:

$$\mathrm{Nu} = 0.56\,(\mathrm{Gr} \cdot \mathrm{Pr})^{0.25} \tag{10}$$

Two experiments were carried out at two different temperatures for the gas phase (329 and 424°), while the initial temperature of the coating and asbestos panel was equal to 20°.

Table 1 Numerical values for heat transfer

$h = 2 \cdot 10^{-4}$ cal/cm^2 · s · deg	$N = 10^{-2}$ $M = 4$	
$\Delta x = 40$ μm	$\Delta t = 4 \cdot 10^{-3}$ s	
$\lambda = 5.5 \cdot 10^{-4}$ cal/cm · s · deg		coating
$c = 0.4$ cal/g · deg	$\rho = 1.25$	
$\lambda = 58 \cdot 10^{-6}$ cal/cm · s · deg	$\mu = 175 \cdot 10^{-6}$ cgs	air
$\alpha = 1.29 \cdot 10^{-3}$ g/cm^3	$c = 0.17$ cal/g · deg	

Table 2 Kinetic data for the overall reaction of pyrolysis

$k_0 = 2.4 \cdot 10^{17}$	$E = 50$ kcal/mole

Temperatures were calculated at three positions: on the coating face, at the midplane of the coating, and at the asbestos-coating interface. Temperature measurements were done at the asbestos-coating interface, and they were found to be in agreement with the calculated ones.

The values of loss in weight were calculated for different positions taken through the coating:

1: on the coating face; 3: at the midplane; 5: on the asbestos-coating interface; 2 and 4 being at two intermediate positions. The total loss in weight was recorded, and it was found to follow the mean value of the calculated losses in weight.

From data expressed in Fig. 2 at 329° and Fig. 3 at 424°, several results are worth mentioning.

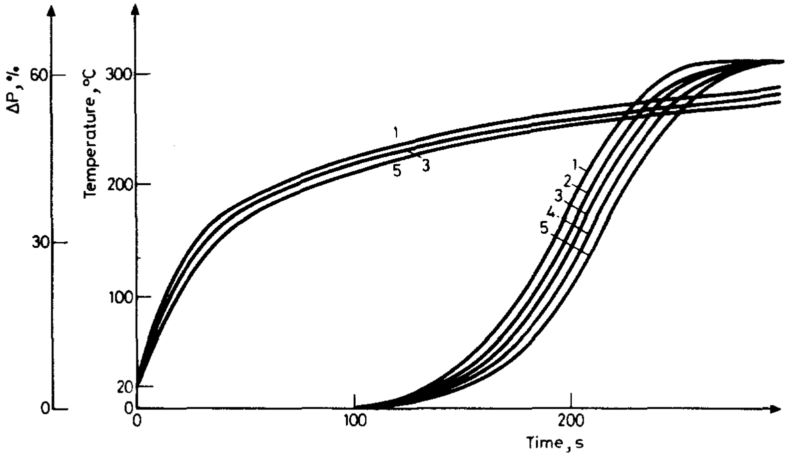

Fig. 2 Temperature and weight loss as a function of time. Gas temperature: 424°. Initial temperature of coating: 20°. Coating thickness: 160 μm. 1: coating face, 3: coating midplane, 5: panel-coating interface

(i) The free convection through the gas-coating interface is a limitation for the heat transfer process.

(ii) A gradient of temperature is developed through the coating (about 100°/mm at 424°) and kept about constant for several minutes.

(iii) It takes the coating a definite time to start decomposing: about 100 s at 424° and 250 s at 329°.

(iv) The rate at which the decomposition takes place is not the same through the coating, as well as the corresponding loss in weight. Of course, the loss in weight is constantly higher at the face where the temperature is higher.

The calculation was done by keeping constant the value of the thermal conductivity during the coating decomposition. The results proved that this assumption is available. Two reasons may explain this fact:

The convection through the gas-coating interface is very important and a variation in the heat transfer by conduction through the coating is not very sensible with regard to the heat transfer process. The other reason is concerned with the intumescence of the coating. At the end of the reaction about 38% of the material remained. During the thermal decomposition an expanded foam is formed, composed of carbon char. This char plays the role of another insulating barrier.

Conclusions

A scheme describing the behavior of a fire retardant coating during pyrolysis allowed us to find results concerned with the temperature and loss in weight. Profiles of temperature were proved to be developed through the coating, as well as profiles of loss in weight.

The heterogeneity characterizing the temperature and loss in weight was not negligeable, while the coating was heated through a free convection by a gas under isothermal conditions. The free convection was proved to be a limitation for the heat transfer and for the pyrolysis of the coating.

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Zusammenfassung — Untersuchungen der Pyrolyse eines feuerretardierenden Überzuges wurden unter isothermen Bedingungen ausgeführt, wobei die Kinetik des Gesamtprozesses und der Prozeß der Wärmeübertragung Berücksichtung fanden. Der Überzug bestand aus Polyurethan und chloriertem Paraffin. Ein 160 μm dicker Film wurde durch freie Konvektion mit erhitzter Luft aufgeheizt. Die sich im Überzug ausbildenden Temperaturprofile und die durch thermische Zersetzung verursachten Gewichtsverluste wurden berechnet. Veränderungen in der Wärmeleitfähigkeit treten nicht auf, da als Zersetzungsprodukt eine poröse Kohle gebildet wird.

Резюме — Исследования пиролиза огнестойких покрытий были проведены в изотермических условиях, учитывая кинетические данные общей реакции и процесс переноса тепла. Покрытия были изготовлены из полиуретана и хлорированного парафина. Пленка толщиной 160 ммк нагревалась естественной конвекцией горячего воздуха и проводимостью его через покрытие. Вычислены температурные профили, возникающие через покрытие, а также температура потери веса, обусловленного термическим разложением. Теплопроводность не изменялась, вследствие образования пористого обугленного остатка, образующегося при разложения покрытий.