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A SIMPLE THEORETICAL DESCRIPTION OF THE BEHAVIOUR OF INTUMESCENT
PAINTS.

ABSTRACT

A simple theoretical description is given of the behaviour of a layer of intumescent paint under the action of a constant heat input at one surface. The physical model of Buckmaster, Anderson and Nachman is used and several new results are derived. In particular a relationship is derived between the time it takes for the temperature at the inner surface of the layer to rise to a given value and the parameters characterising the layer of paint. Other results depend upon the assumption that the front at which intumescence takes place moves through the layer slowly compared with decay times of thermal transients within the layer.

1. INTRODUCTION

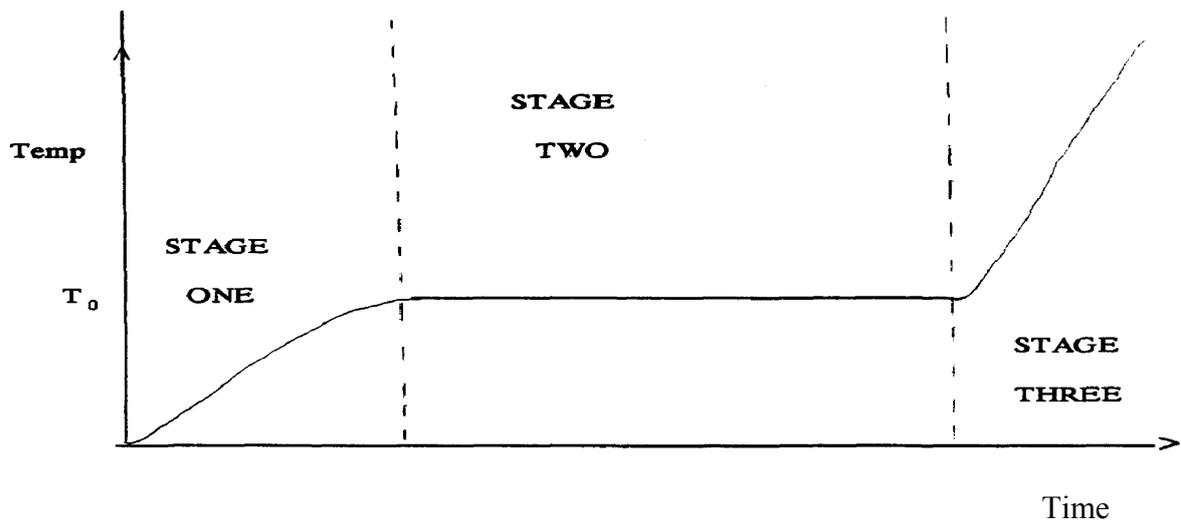
When heat is externally applied to an object coated with an intumescent paint, the presence of the paint has a delaying effect upon the increase in temperature of the object. The usefulness of such paints has been apparent to the United States Navy for some years. The disastrous fire aboard the aircraft carrier USS Forrester (1967) which resulted in the deaths of 133 men and 72 million dollars worth of damage, and the more recent fire on the flight deck of USS Nimitz (1981) with immediate deaths of 14 men and 60 million dollars damage, demonstrated the importance of delaying the detonation of weapons when subjected to heat. Two other contexts in which the paint proves useful are the protection of structures from rocket exhausts, and in the delaying of the collapse of the metal superstructure of large buildings when a fire occurs

To provide the required delay the paint must possess several properties. Here we give a simplified version of the paint's behaviour but one adequate to describe the delaying mechanism. The interested reader is referred to [1] [2]. When the paint is heated and reaches a specific temperature (T_0), an endothermic reaction takes place with the evaporation of one component of the paint. At this temperature the remaining components are in a viscoelastic state and expand to form an open foam-like structure. The volume of the paint may have increased by as much as 400% and the gaseous component, which may make up as much as 50% of the mass of the paint, subsequently diffuses to the surface and escapes.

Following Buckmaster, Anderson and Nachman [1] we assume that when the paint is heated through one surface the liberation of gas begins at this surface when it reaches the temperature T_0 . Subsequently a thin front, at which the reaction is taking place, moves slowly through the layer of paint. The temperature at this front is firmly clamped at the value T_0 and behind the front the paint takes on its expanded form. When the front reaches the inner surface we are left with a homogeneous expanded layer. To discuss the full development of the process it is convenient to divide it into three stages: stage one before the maximum temperature of the paint reaches T_0 and normal thermal conduction is taking place; stage two during which the front is moving through the paint and; stage three, a return to normal conduction but with new thermal parameters characterising the layer of paint.

The experiments that have been performed with these paints usually consist of applying a constant supply of heat to the outer surface of the paint layer and measuring the temperature at the inner surface as a function of time. The existence of three stages of development is frequently displayed by the presence of a plateau in the observed graph (see Figure). Some paints even display two such plateaus clearly separated from each other. Measurements of mass loss by the layer indicate that it takes place not only during stage two but well into stage three

In this report the assumption is made that the continuous variation of the thermal properties of the paint with gas density can be ignored. The only variation that is taken into account is a discrete jump in the values of the parameters at the advancing front. Buckmaster et al view this as a major limitation on the usefulness of this model.



Figure

2. NOTATION

The subscripts 1 and 2 apply to the thermal properties of the paint in its virgin state and after expansion respectively.

k : coefficient of thermal conductivity

c : specific heat per unit length

$D = k/c$

L_0 : initial thickness of layer.

L_1 : final thickness of layer

and $L_1 = (1+R)L_0$

ρ : mass density.

E : energy influx at outer surface.

N : heat of reaction per unit length.

3. ENERGY CONSERVATION

The effectiveness of a particular layer of paint is measured by the time (τ) it takes for the temperature at the inner surface to rise from room temperature to some temperature (T_d) that would be considered dangerous. We now derive an expression for τ by applying the principle of energy conservation to this full period. The more detailed model described in later sections consists almost entirely of local statements of energy conservation and an expression for τ could be derived from the results obtained there; however, a direct derivation shows that the resulting form is independent of many of the approximations used in the detailed model.

During the time τ the energy input to the paint layer is $E \tau$. This energy does three things. Firstly it provides energy $c_1 L_0 T_0$ to raise the temperature of the whole layer to T_0 , secondly it provides the full heat of reaction $N L_0$ and thirdly it provides energy

$$(T_d - T_0) c_z (1+R) L_0 + \frac{E c_2 (1+R)^2 L_0^2}{6k_2}$$

to the expanded layer. In deriving this final expression we assume the transients have decayed away leaving the temperature profile

$$T(x) = T_d + \frac{E x^2}{2k_2(1+R)L_0} .$$

Hence

$$\begin{aligned} \tau = & \frac{N L_0}{E} + \frac{T_0 c_1 L_0}{E} - \frac{T_0 c_2 (1+R) L_0}{E} \\ & + \frac{T_d c_2 (1+R) L_0}{E} + \frac{c_2}{6k_2} (1-R)^2 L_0^2 \end{aligned} \quad (1)$$

This expression leads us to some simple conclusions.

(a) τ is independent of k_1 the paint's initial thermal conductivity.

(b) τ 's dependence on L_0 is of the form

$$\tau = AL_0 + BL_0^2$$

where A and B are positive constants, so increasing the thickness of the layer will increase τ by more than a proportionate amount.

(c) τ 's dependence on E is of the form

$$\tau = \frac{A}{E} + B$$

where A and B are again positive constants. For a low input of energy τ becomes very large but for a high input τ has a lower limit of

$$\frac{C_2 (1+R)^2 L^2}{6k_2}$$

This is explained by the fact that when the inner surface reaches the temperature T_d the outer surface is at temperature

$$\frac{E(1+R)L_0}{2k_2}$$

In the event of a very fierce conflagration this lower bound for τ may give a good indication of the delay time with its quadratic dependence on the final thickness of the layer.

(d) τ depends on N through the term NL_0/E . This could well be dominant if N is large compared to both $T_0(c_1 - c_2(1+R))$ and $T_d c_2(1+R)$.

(e) Intuitively one expects τ to depend upon the temperatures T_0 and T_d through the combination $T_0 + T_d$ but in fact they occur in the form

$$c_1 T_0 + c_2 (1+R) (T_d - T_0) .$$

If $c_2(1+R) > c_1$ then τ can be increased by having T_0 as close to room temperature as possible whilst if $c_2(1+R) < c_1$ a temperature close to T_d is beneficial.

(f) The dependance of τ upon the extent to which the layer expands ($(1+R)$) is not clear because both c_2 and k_2 depend on this factor in unknown fashions.

4. GENERALISATION OF (1)

The expression for τ (1) can be very easily generalised to the case of paint which liberates several gases at various temperatures and with various heats of reaction. To do this let these components of the paint be labelled by the variable α so that their contribution to the specific heat per unit length of the unswollen paint is $c(\alpha)$ and

$$c_1 = \sum_{\alpha} c(\alpha) + c_2$$

Also component α outgases at temperature $T(\alpha)$, with heat of reaction per unit length of the unswollen paint $N(\alpha)$. Then

$$\begin{aligned} \tau = & \frac{L_0}{E} \sum_{\alpha} N(\alpha) + \frac{L_0}{E} \sum_{\alpha} c(\alpha) T(\alpha) \\ & + \frac{T_d c_2 (1+R) L_0}{E} + \frac{c_2 (1+R)^2 L_0^2}{6k_2} \end{aligned}$$

Many of the comments about (1) apply equally well to this expression.

5. STAGE ONE

During this stage the equation to be solved is

$$\frac{\partial T}{\partial t} = \frac{k_1}{c_1} \frac{\partial^2 T}{\partial x^2} \quad 0 < x < L_0$$

subject to the conditions

$$\frac{\partial T}{\partial x} = 0 \quad \text{at } x = 0, t > 0.$$

$$\frac{\partial T}{\partial x} = \frac{E}{k} \quad \text{at } x = L_0, t > 0$$

and $T = 0, t = 0$.

The solution is

$$T(x, t) = \frac{E}{2k_1 L_0} \left(x^2 + \frac{k_1}{c_1} t \right) - \frac{EL_0}{6k_1} + \frac{2EL_0}{k_1 \pi^2} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n^2} \exp \left[-n^2 \frac{k_1 \pi^2 t}{c_1 L_0^2} \right] \cos \left[\frac{n \pi x}{L_0} \right]$$

The transient terms decay away leaving a steadily rising parabolic temperature profile. This stage finishes when the temperature at the outside surface reaches the value T_0 . If we ignore the contribution from the transients this takes a time

$$\frac{c_1 L_0 T_0}{E} - \frac{c_1 L_0^2}{3k_1}$$

At the inner surface the temperature rises linearly with slope $E/c_1 L_0$. Observation of this rising temperature can be used to decide whether we are justified in ignoring the transient terms. Using the data of reference [1] we find that in this particular case the rise time is 2.5s and the decay times of the transient terms are $0.1/n^2$ s.

6. STAGE TWO

During this stage the equations to be solved are

$$\frac{\partial T}{\partial t} = \frac{k_1}{c_1} \frac{\partial^2 T}{\partial x^2} \quad 0 < x < s$$

$$\frac{\partial T}{\partial t} = -u \frac{\partial T}{\partial x} + \frac{k_2}{c_2} \frac{\partial^2 T}{\partial x^2} \quad s < x < L$$

where $L(t)$ is the co-ordinate of the outer surface, $u = dL/dt$, and the front is situated at $x = s(t)$. The boundary conditions are at

$$x = L \quad k_2 \frac{\partial T}{\partial x} = E$$

and at $x = s$. $T = 0$,

$$\text{and} \quad k_1 \left[\frac{\partial T}{\partial x} \right]_1 - k_2 \left[\frac{\partial T}{\partial x} \right]_2 = N \frac{ds}{dt} .$$

For convenience we have chosen the temperature at which the reaction takes place to be zero. The initial conditions are determined by the temperature profile at the end of stage one.

The speeds with which the expanded paint and the front move are related in a simple way. If the densities of the paint either side of the front are ρ_1 and ρ_2 and the final thickness of the layer is L_1 then mass conservation tells us that

$$\rho_1 L_0 = \rho_2 s + \rho_2 (L - s) = \rho_2 L_1$$

$$\text{Then} \quad \frac{dL}{dt} = -R \frac{ds}{dt}$$

$$\text{and} \quad L_1 = (1 + R) L_0$$

$$\text{where} \quad R = \frac{\rho_1 - \rho_2}{\rho_2}$$

The change of variable

$$y = x \quad 0 < x < s$$

$$y = \frac{1}{1+R} x + \frac{R}{1+R} s \quad s < x < L$$

brings the outer surface to rest and yields

$$\frac{\partial T}{\partial t} = \frac{k_2}{c_2 (1+R)^2} \frac{\partial^2 T}{\partial y^2} \quad s < y < L$$

At $y = L_0$

$$\frac{k_2}{(1+R)} \frac{\partial T}{\partial y} = E .$$

and at $y = s$

$$T = 0$$

and

$$k_1 \left[\frac{\partial T}{\partial x} \right]_1 - \frac{k_2}{(1+R)} \left[\frac{\partial T}{\partial y} \right]_2 = N \frac{ds}{dt}$$

The diffusion equation and most of the boundary conditions are expressions of energy conservation at particular points. We can obtain a more useful expression of this conservation law if we consider the total energy of the system. The thermal energy contained in the region $s < x < L$ is $U(t)$ where

$$\begin{aligned} U(t) &= c_2 \int_s^L T \, dx . \\ &= \frac{c_2}{(1+R)} \int_s^{L_0} T \, dy . \end{aligned}$$

and

$$\frac{dU}{dt} = \frac{c_2}{(1+R)} \int_s^{L_0} \frac{\partial T}{\partial t} \, dy - \frac{c_2}{(1+R)} \left[\frac{\partial T}{\partial t} \right]_s \frac{ds}{dt} .$$

After some manipulation this yields

$$(1+R)^2 \frac{dU}{dt} = E + N \frac{ds}{dt} - k_1 \left[\frac{\partial T}{\partial y} \right]_1 .$$

If the k_1 term is ignored then integrating

$$(1+R)^2 U = Et + N(s-L_0) . \quad (2)$$

Two times characterise the equations above, a lower bound for the transit time of the front

$$\tau_c = \frac{NL_0}{E}$$

and the diffusive relaxation time behind the advancing front

$$\tau_d = \frac{c_2 (1+R)^2 L_0^2}{k_2} .$$

One assumption we make in what follows is that

$$\tau_c \gg \tau_d .$$

An assumption which holds in the case of the figures quoted in section 9. The diffusive relaxation time ahead of the front is considerably shorter than τ_d which supports our last step in the deriving of (2).

Following Goodman [3] we introduce a parabolic temperature profile behind the front

$$T = A(y-s) + B(y-s)^2$$

where A and B are possibly functions of time. Then

$$U = \frac{c_2}{1+R} \left[\frac{A}{2} (L_0 - s) + \frac{B}{3} (L_0 - s)^3 \right]$$

and (2) becomes

$$t = \tau_c p + \frac{\tau_d k_2}{(1+R)E} \left[\frac{A}{2} p^2 + \frac{B}{3} L_0 p^3 \right] . \quad (3)$$

where $p = \frac{L_0 - s}{L_0}$.

The boundary condition at $y = L_0$ gives

$$A + 2BL_0 p = (1+R) E/k_2 \quad (4)$$

Substituting the parabolic profile into the diffusion equation we find that A and B must obey

$$\frac{dB}{dt} = 0$$

$$\frac{dA}{dt} + 2BL_0 \frac{dp}{dt} = 0$$

and

$$A \frac{dA}{dt} = \frac{2BL_0}{\tau_d} \quad (5)$$

If the first of these three equations is obeyed then the second equation follows from (4). Whilst

$$\frac{dp}{dt} < \frac{1}{\tau_c}$$

intimates that $A \gg BL_0$.

Expanding A, B and t in powers of p and substituting in the equations (3), (4) and (5) yields the results

$$t = \tau_c p + \tau_d \frac{p^2}{2} - \frac{2}{3} \frac{\tau_d^2}{\tau_c} p^3 + - \dots$$

$$A = (1+R) \frac{E}{k_2} \left[1 - \frac{\tau_d}{\tau_c} p + 4 \left[\frac{\tau_d}{\tau_c} \right]^2 p^2 + - \dots \right]$$

$$B = \frac{(1+R)}{2} \frac{E}{k_2 L_0} \left[\frac{\tau_d}{\tau_c} - 4 \left[\frac{\tau_d}{\tau_c} \right]^2 p + 10 \left[\frac{\tau_d}{\tau_c} \right]^3 p^2 + - \dots \right]$$

These series are also in rising powers of $\frac{\tau_d}{\tau_c}$, the ratio we can take to be

very much less than unity. The series for t describes how the front

commences with a speed of $\frac{L_0}{\tau_c}$ but slows slightly to a speed of about

$\frac{L_0}{\tau_c + \tau_d}$ by the time it has reached the inner surface. The transit time of

the front is given by the expression

$$\tau + \frac{\tau_d}{2} - \frac{2}{3} \frac{\tau_d^2}{\tau_c} + - \dots$$

7. STAGE THREE

This stage resembles the first, the primary differences being that the layer has expanded to width $(1+R)L_0$ and the specific heat and thermal conductivities have reduced values. When the transients have died away the temperature profile has the form

$$T(x, t) \sim \frac{E}{2k_2 (1+R)L_0} \left[x^2 + 2 \frac{k_2}{c_2} t \right].$$

The temperature at the inner surface now rises at a rate

$$\frac{E}{c_2 (1+R)L_0}.$$

This is faster than the rise during stage one because c_2 is less than c_1 on two scores, the expansion of the layer (a factor $(1+R)^{-1}$), and the loss of mass due to escaped gas. Using the data of section 9 the increase can be of the order 50%. It is worth noting that this final paint layer is a poorer insulating layer than the initial unswollen layer. The transients during this final stage have decay periods given by the expressions

$$\frac{c_2 (1+R)^2 L_0^2}{k_2 \pi^2 n^2}$$

This shown an increase over the decay periods during stage one, using section 9 data, by a factor of 5 and 10. On the other hand the initial temperature is parabolic leading one to expect the transients to have much smaller amplitudes.

8. COMPARISON WITH EXPERIMENT

The model presented in this report provides at least a qualitatively correct description of the head conduction process through a layer of intumescent paint. In this section we answer the question, what quantitative information about the layer can be extracted from an accurate graph of the temperature at the inner surface versus time?

(a) The stage one rate of rise of temperature yields a value of

$$\frac{E}{c_1 L_0} .$$

(b) Similarly the stage three rate of rise yields

$$\frac{E}{c_2 L_1} = \frac{E}{c_2(1+R)L_0} .$$

(c) For some layers during stage three the rate of rise of temperature gently decreases with rising temperature. This is probably due to the fact that the outer surface is reaching temperatures at which heat loss to the environment should be taken into account. This can be done by including an extra term into the boundary condition at $x = L$,

$$k_2 \frac{\partial T}{\partial x} - E - mT .$$

It can easily be shown that the curvature of the graph reveals information about m/E .

(d) If stage two has a clearly defined plateau then it tells us T_0 , the temperature at which the endothermic reaction takes place.

(e) The transient behaviour of the temperature at the commencement of stage two, if distinct enough, can yield a value for the principle decay time

$$\frac{\pi^2}{4} \frac{c_1}{K_t L_0^2}$$

(f) If the movement of the front is dominated by the heat of reaction N then the duration of stage two (τ_0) gives us a value for

$$\frac{NL_0}{E}$$

However, if the more complicated expressions for τ_0 derived in section 6 needs to be used we obtained a value of

$$\frac{NL_0}{E} + \frac{c_2(1+R)^2 L_0^2}{2K_2}$$

9. NUMERICAL VALUES

By way of illustration, numerical values are substituted for the various parameters describing the properties of the layer of paint, and the input energy flux. Care must be taken in drawing detailed conclusions from these calculations because the values of the parameters are open to considerable uncertainty and E and L_0 can be varied. The values used are taken from reference [1] and are listed below.

$$T_0 \sim 130 \text{ c .}$$

$$L_0 = 0.1 \text{ cm.}$$

$$E = 2.7 \text{ cal cm}^{-2} \text{ s}^{-1}$$

$$1+R = 4.5$$

$$k_1 = 5.5 \times 10^{-3} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ deg}^{-1}$$

$$k_2 = 2.0 \times 10^{-3} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ deg}^{-1}$$

$$c_1 = 0.6 \text{ cal cm}^{-3} \text{ deg}$$

$$c_2 = 0.12 - 0.06 \text{ cal cm}^{-3} \text{ deg}$$

$$N \sim 30 - 80 \text{ cal cm}^{-3} \cdot$$

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2. Anderson C. and Wauters D. Int. J. Engng. Sci. 22 (7), 881 (1984).
3. Goodman T.R. (1964) Advances in Heat Transfer (Eds. T.F. Ervin and J.P. Hartness) Vol 1 p.51, Academic Press, New York.

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