# MODELING FOAM COKE FORMATION .

A.M. Lipanov, E.N. Bajenova, V.I. Kodolov, I.N. Efimov ,
Izhevsk State Technical University

ABSTRACT.

In this paper the designing of a mathematical model of processes in the intumescent material based on the epoxy resin modified by ammonia polyphospate as a foaming agent and as a carbonization agent is discussed.The modeling of foamcoke formation processes which take place during polymer pyrolysis is carried out allowing a liquid phase formation and assuming that polymeric materials contain active and passive components . Active components contain a foaming agent and a polymeric matrix. Chemical reactions of a foaming agent destruction , reactions in a bubble volume and on an inner surface of a bubble ( the boundary of foaming agent residues and a polymeric matrix ) are considered. The system of differential equations proposed will be solved by a net method. As a result the relations of density , porosity , thermal conductivity and heat capacity in dependence on the composition of a polymeric composite are determined . The mathematical model designed corresponds to the tendency of parameter changes.

## NOMENCLATURE.

$\rho$ - the density ;

$T$ - the temperature;

$a$ - the heat transfer coefficient;

$W$ - the bubble volume;

$H$ - the intumescent layer hight ;

$h$ - the distance between the centres of foaming agent particles;

$\lambda$ - the thermal conductivity;

$m$ - the mass;

$u$ - the rate of gas formation on the inner surface of the bubble;

$t$ - the duration .

$P$ - the pressure ;

$\alpha$ - the mass concentration;

$E$ - the activation energy;

$R$ - the gaseous constant;

$D$ - the diffusion coefficient;

$Q$ - the reaction heat;

$S$ - the surface area;

$r$ - the bubble radius;

$c_p, c_v$ - isobaric and isochoric heat capacities;

$v$ - the rate of swelling bubble wals due to pressure;

INDEXES:

$g$ - gas;  $fa$ - foaming agent;

$p$ - particle;  $b$ - bubble;

$cl$ - cross-linked polymer;  $s$ - surface;

$d$ - destruction;  $eq$ - equilibrium;

$f$ - forward;  $rev$ - reverse;

## INTRODUCTION.

The effective method of decreasing combustion of polymeric materials is the application of intumescent coatings or the modification of material surface layers for rendering them intumescense properties. Many papers are devoted to this scientific trend. In spite of this the intumescense mechanism for different polymeric systems was studied insufficiently , and the regulation of intumescense processes requires the designing of a process mathematical model.

This paper is devoted to designing the mathematical model of processes proceeding in the intumescent layer .

## SHORT INFORMATION ABOUT THE INTUMESCENT POLYMERIC COMPOSITION BEING INVESTIGATED.

The composition of a coating (or an outer layer of polymeric composite ) usually contains the following types of components :

a) the carbonization agent which has the greatest coke number , a parameter of viscosity and also the greatest value of surface tension when the liquid phase forms ;

b) the carbonization catalyst ;

c) the foaming agent .

As the carbonization agent the carboamide-formaldehyde resin is used , in the above composition . The foaming agent is the ammonia polyphosphate which is decomposed in ammonia , water vapour and polyphosphoric acid . In turn the polyphosphoric acid is a carbonization catalyst . The choice of ammonia polyphosphate as the foaming agent is explained by a high yield of gaseous products . We can assume that gaseous substances ( water vapours and ammonia ) fill the volume of a bubble , and the condesated polyphosphoric acid is formed on its inner walls participating in the carbonisation process of epoxyresin .

## PHYSICO - CHEMICAL PATTERN .

The initial material is found in a solid state . The material contains the proportionally distributed foaming agent particles which have the same sizes .

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During the heating the material is transformed into a liquid state. The foaming agent (ammonia polyphosphate) is decomposed with the formation of water vapours and ammonia and with the bubble formation when a definite temperature is achieved (a destructtion temperature). Simultaneously the carbonization process proceeds. At the same time the melt viscosity is increased because the destruction process starts from the very beginning. These processes promote the system transformation from a melt to a solid state which is usually a carbon net preventing the evolving of gaseous substances into the surroundings.

Let us consider the following reactions which can be divided into three groups:

1) destruction reactions on the foaming agent surface

$$HO-[-NH_4PO_3-]-_m H \Leftrightarrow HO-[-NH_4PO_3-]-_{2m} H + \\ + H_2O - Q_1 \qquad \text{(a)}$$
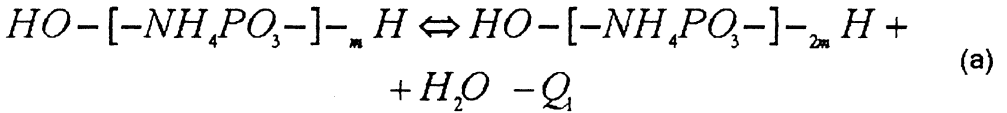
(This is a dehydratation reaction. For this reaction the constant $K_1$ corresponds to the the Arrhenius's function).

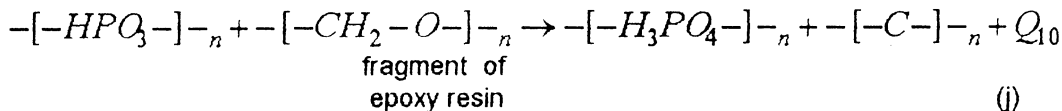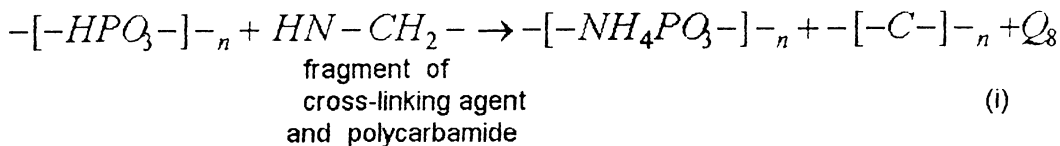$$-[-NH_4PO_3-]-_n \Leftrightarrow -[-HPO_3-]-_n + nNH_3 \quad -Q_2 \qquad \text{(b)}$$
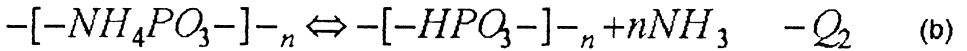
(This reaction is a deaminiation. Here the constants of forward and reverse reactions are analogous).

2) condensation reaction proceeding in the bubble volume:

$$NH_3 + H_2O \Leftrightarrow NH_4OH \qquad + Q_3 \qquad \text{(c)}$$
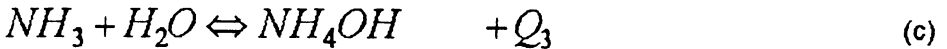
3) interaction reactions proceeding on the inner surface of the bubble or interaction reactions between the polyphosphoric acid ( or its intermediate substances) and the functional groups of epoxypolymer composition :

$$HO-[-NH_4PO_3-]-_m H \Leftrightarrow HO-[-NH_4PO_3-]-_{2m} H + \\ + H_2O - Q_1 \qquad \text{(d)}$$

$$-[-NH_4PO_3-]-_n \Leftrightarrow -[-HPO_3-]-_n + nNH_3 \quad -Q_2 \qquad \text{(e)}$$

$$-[-HPO_3-]-_n + n[-CH_2-]- \rightarrow -[-H_3PO_3-]-_n + -[-C'-]-_n + Q_5$$

fragment of
epoxyresin or
cross-linking
agent

(f)

$$-[-H_3PO_4-]-_n \Leftrightarrow -[-HPO_2-]-_n + nH_2O \qquad -Q_6 \quad \text{(g)}$$

$$-[-H_3PO_4-]-_n \Leftrightarrow -[-HPO_3-]-_n + nH_2O \qquad -Q_7 \qquad \text{(h)}$$

$$-[-HPO_3-]-_n + HN-CH_2- \rightarrow -[-NH_4PO_3-]-_n + -[-C-]-_n + Q_8$$

fragment of
cross-linking agent
and polycarbamide

(i)

$$-[-HPO_3-]-_n + -[-CH_2-O-]-_n \rightarrow -[-H_3PO_4-]-_n + -[-C-]-_n + Q_{10}$$

fragment of
epoxy resin

(j)
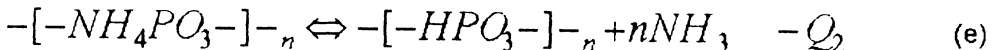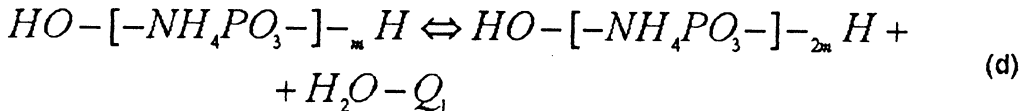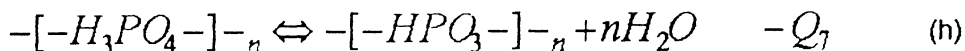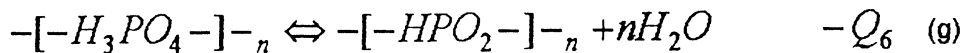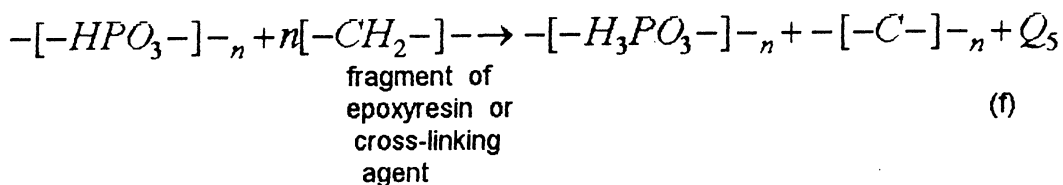
It is noted that the quantity of cross-linking agent fragments is 10 times less than the quantity of epoxy resin fragments.

## THE DESIGNING OF MATHEMATICAL MODEL.

Let us assume that particles have equal sizes, a spheric form and they are proportionally distributed in the material volume, and are found in vertices of a cube, in other words the particles form equal cubes (fig.1).
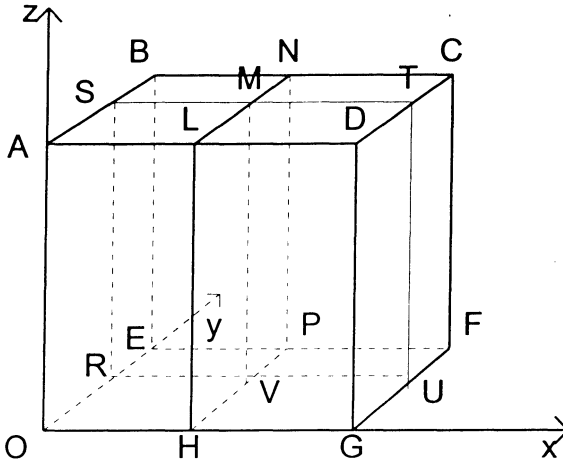
Fig.1 . Scheme of particle disposition in volume of
intumescent coating .

According to fig. 1 two layers of particles in plane $ABCD$ and $OEFG$ contain particles in vertices of the cube $OABEFCDG$ . The distance between planes or the initial thickness of the intumescent coating $(AO)$ is known . The intumescent coating is glued to the substrate . The material heating takes place on the normal to its outer surface .

We consider a plane case . Coordinate system is chosen so that axes $OX$ and $OY$ are in the plane parallel to its outer surface , and axis $OZ$ is directed on the normal to plane $XOY$ . At a uniform heating the symmetry planes of temperature fields $HLNP$ and $RSTU$ are formed outside due to the difference of properties of the foaming agent and a binder in cube

$OABEFCDG$ . In this case the equality corresponding to $\dfrac{\partial T}{\partial x} = 0$ will hold

on the normal to plane $HLNP$ and the equality $\dfrac{\partial T}{\partial y} = 0$ on the normal to

$RSTU$ . It enables to choose as an integration volume a cylinder of a rectangular section whose sides are the prolongation of planes $OALH$ ,$OASR$ , $RSMV$ and $HLMV$ from an outer surface of the intumescent coating to the substrate and further inside it . Here the following conditions are realized :

$$\frac{\partial T}{\partial z} = 0 \quad \text{at} \quad z \to -\infty.$$

In this case the condition

$$-\lambda_{cl}\frac{\partial T_{cl}}{\partial z} = a\left(T_g - T_s\right) \qquad (1)$$

can hold on the material surface $(z = 0)$. Here $a$ is the heat transfer coefficient corresponding to the conditions of a uniform heating of the material throughout its surface.

It is necessary to distinguish four stages of a material heating process. First when foaming agent particles and the binder are heated as inert bodies, the heating of foaming agent particles obeys the following relations:

$$T_p = T_{cl}$$

$$(2)$$

$$-\lambda_p\frac{\partial T_p}{\partial z} = -\lambda_{cl}\frac{\partial T_{cl}}{\partial z}$$

However in fact the clearance will be formed between particles and the binder which is explained by the difference of values $a$ (coefficients of linear thermal

expansion $(a_p < a_{cl})$. For the simplification of calculation it is assumed that the

clearance increases by jumps when $T = T_\partial$, where $T_\partial$ - the destruction temperature.

At the moment of destruction the equations (2) are substituted for the following condition:

$$-\lambda_p\frac{\partial T_p}{\partial z} = -\lambda_b\frac{\partial T_b}{\partial r} - q_\partial \qquad (3)$$

where $q_\partial$ - the heat quantity spent in a time unit during the destruction of foaming agent material mass unit.

$$-\lambda_b\frac{\partial T_b}{\partial r} = -h_b\left(T_b - T_s\right) \qquad \text{-the heat flow from the clearance}$$

between particles of the foaming agent and polymeric matrix.

This clearance is supposed to be an initial bubble volume . At the same time the pressure in the clearance equals the ambient pressure , and the temperature is the binder temperature value . When the relation (3) takes place the preliminry stage finishes . The transition stage (from preliminary to the main stage ) begins until the wave satisfying the condition $T = T_{\partial}$ comes to the substrate . After that the main stage begins . During this stage the bubbles increase and the intumescense of the coating is observed .

The horizontal section of the volume considered which passes through the bubble will be as it is shown in fig. 2 because the destruction products of the foaming agent are evolved only from 1/4 of the surface of particles located along axis $OZ$ .
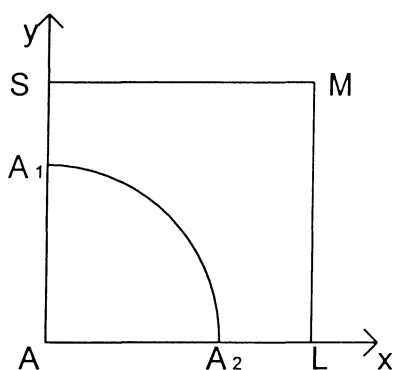


Fig. 2 . Scheme of bubble change .

For this stage the one- dimensional processes will be true in the bubble .

Let us assume that the destruction process of the foaming agent proceeds as a result of reversible reactions (a) and (b) in which reverse reactions proceed as heterogeneous ones , proportionally to a gaseous reagent concentration .

It is supposed that the metaphosphoric acid $HPO_3$ with gaseous substances ( ammonia $NH_3$ vapour of water $H_2O$ ) is carried over from the foaming agent particle surface to the bubble inner surface where the acid is transformed in the polyphosphoric acid .

On the inner surface of the bubble irreversible reactions ( f ), ( i ),( j ) of the polyphosphoric acid interaction with functional groups of the polymeric matrix are considered . These reactions lead to the carbon formation . At the same time the reversible reactions ( d ) , ( e ), ( h ) , ( g ) of same acid result in gaseous substances . Here the reactions ( f ), ( i ) ,( j ) are heterogeneous as well as the reverse reactions for processes ( d ) , ( e ) , ( h ) , ( g ) regarded . As for forward reactions their equations are written as the equations for corresponding destruction processes .

In addition one reversible reaction ( c ) proceeding in the bubble volume is taken into consideration . The values of constants for its forward and reverse reactions depend on the concentrations of reactants and the temperature . The temperature dependence for the forward reaction is :

$$K_f(T) = BT^\beta e^{-\frac{E}{RT}} \qquad (4)$$

ããå $B, \beta, E, R$ - constants . The function of temperature dependence for the reverse reaction is determined using the equilibrium constant

$$\frac{K_f(T)}{K_{rev}(T)} = K_{eq}(T) \qquad (5)$$

where $K_{eq}(T)$ - the thermodynamic function corresponding to equilibrium conditions

As a result we can write necessary expressions for the mass increase during the reaction proceeding on the foaming agent particle surface and on the bubble surface and also in the bubble volume . Then let us write the equation for the calculation of the mass and energy for gaseous substances in the bubble volume :

$$\frac{dm}{dt} = S_s \sum_i \dot{m}_{si} + S_b \sum_j \dot{m}_{bj} \qquad (6)$$

$$\frac{d}{dt} mc_v T = S_s \sum_i \dot{m}_{si} Q_{si} + S_b \sum_j \dot{m}_{bj} Q_{bj} + \dot{m}_w Q_w^f - \dot{m}_w Q_w^{rev} - S_b P_b V_b$$

$$(7)$$

where forward and reverse reactions which proceed on the surface of the foaming agent and heats corresponding to them are designated by index i , and analogous processes related to the bubble surface - by index j ; index  w corresponds to the reaction in the volume .

The work of pressure forces directed to the increasing of the bubble size with

the rate $V_b$ is taken into account in the last summand of the energy equation . Another reason for the increasing of the bubble size is the proceeding of heterogeneous

reactions . The radius of the bubble increases with the rate $u_b$ determined by the following expression :

$$u_b = \frac{1}{\rho_{cl}} \sum_j \dot{m}_{bj} \qquad (8)$$

Here there is the decomposition of the binder material but the intumescense does not occur .

If in every $\upsilon$ - layer the increasing of the distance $h$ between the particle centres of the foaming agent along coordinate $Z$ takes place with the following rate -

$$\frac{dh_\upsilon}{dt} = \pi \left(\frac{r_{b\upsilon}}{h_0}\right)^2 v_\upsilon \qquad (9)$$

then the rate throughout the whole thickness of the coating will equal -

$$\frac{dH}{dt} = \frac{\pi}{h_0^2} \sum_{\upsilon=1}^{N} r_{b\upsilon}^2 v_\upsilon \qquad (10)$$

where $N$ - the number of foaming agent particle layers in the coating . In this case to increase the bubble volume in any layer the following expression is used -

$$\frac{dW_{b\upsilon}}{dt} = \pi r_{b\upsilon}^2 \left(u_{b\upsilon} + v_\upsilon\right) \qquad (11)$$

In turn for the calculation of rate $v_{b\upsilon}$ the Real's equation is applied:

$$r_b \frac{dv_b}{dt} = -\frac{3}{2} v_b^2 + \frac{P_{cl} - P_\infty}{\rho_{cl}} \qquad (12)$$

$$\frac{dr_b}{dt} = u_b + v_b \qquad (13)$$

$$P_{cl} = P_b - \frac{2\sigma}{r_b} \qquad (14)$$

Here $P_{cl}$ -the pressure in the binder on the boundary with the bubble ;

$\rho_{cl}$ - the density of the binder material ;

$P_{\infty}$ - the pressure in the binder far from the bubble ;

$\sigma$ - the value of the bubble surface tension .

Values of pressure , temperature and density in the bubble volume are averaged .

Then from equations (6),(7) the mass and the energy of gaseous substances in the bubble are determined , and then the density is found -

$$\rho_b = \frac{m_b}{W_b} \qquad (15)$$

If the energy is known it is prossible to find the temperature and then using the Clapeyron - Mendeleev equation the pressure is defined :

$$P_b = \rho_b R T_b \qquad (16)$$

However it is necessary to calculate the heat capacity $C_v$ and the gaseous constant $R$ for the mixture of gaseous substances found in the bubble volume .

For this purpose let us apply the approximate relations :

$$c_v = \sum_{i=1}^{4} c_{vi} \alpha_i \qquad (17)$$

$$R = \sum_{i=1}^{4} R_i \alpha_i \qquad (18)$$

In the bubble volume there are the vapours of water , the ammonia , the metaphosphoric acid and the ammonia hydroxide .

For the calculation of these concentrations the one - dimensional equation of diffusion is used -

$$\frac{\partial \alpha_i \rho_b}{\partial t} = \frac{1}{r_b^2} \frac{\partial}{\partial r_b} r_b^2 D_i r_b \frac{\partial \alpha_i}{\partial r_b} - \frac{\rho_b}{r_b^2} \frac{\partial}{\partial r_b} r_b^2 \alpha_i v_g + \dot{m}_i \qquad (19)$$

$$\left( i = 1,2,3,4 \right)$$

While writing the diffusion equations the convective transfer with the rate $v_g$ is taken into account when the foaming agent destructs . From its agent surface gaseous substances flow with the rate $v_f$ and further move to the bubble inner

surface where they have the rate $v_b$. The rate value $v_g$ is obtained as a parabolic equation by the approximation

$$v_g = v_f - \left(v_f - v_b\right)\left(\frac{r - r_p}{r_b - r_p}\right)^2 \qquad (20)$$

It is assumed that the rate of a gaseous substances movement $v_g$ is small and it does not influence the changes of the pressure , the density and the temperature .

The summand $\dot{m}_i$ for $HPO_3$ equals zero , and for other terms of equation (19) there are the following expressions :

$$\dot{m}_{NH_4OH} = -f_f\left(\alpha_{NH_3},\alpha_{H_2O}\right)K_f\left(T\right) + $$
$$+ f_{rev}\left(\alpha_{NH_3},\alpha_{H_2O}\right)K_{rev}\left(T\right) \qquad (21)$$

$$\dot{m}_{NH_3} = \dot{m}_{NH_4OH}\left(1 + \frac{\mu_{H_2O}}{\mu_{NH_3}}\right)^{-1} \qquad (22)$$

$$\dot{m}_{H_2O} = \dot{m}_{NH_4OH}\left(1 + \frac{\mu_{NH_3}}{\mu_{H_2O}}\right)^{-1} \qquad (23)$$

For the solution of equetions (19) it is necessary to set the initial and boundary conditions .

The values of concentrations $\alpha_i$ for vapours of water , the polyphosphoric ammonia acid and the ammonia at the moment of the foaming agent destruction are defined as equal parts . The concentration of $NH_4OH$ is assumed as the value equaled to zero .

For the calculation of gradients $\dfrac{\partial \alpha_i}{\partial r}$ on the surfaces of foaming agent particles and the bubble the following equalities are obtained:

$$-D_i\,\frac{\partial \alpha_i \rho_g}{\partial r} = \alpha_{ig}\sum_i \dot{m}_{ig} - \dot{m}_{ig}$$

$$-D_i\,\frac{\partial \alpha_i \rho_g}{\partial r} = \alpha_{ib}\rho_{cl}u_b - \dot{m}_{ib}$$

The expressions for the calculation of values $\dot{m}_{ig}$ and $\dot{m}_{ib}$ are not witten here

As a result set of equations required for the calculation of parameters within bubble and for the increasing of its size is obtained. These relations allow to calculate the increasing of a carbon mass.

The third stage of the coating intumescense process is finished when the "equator" of the bubble reaches points $H$ and $R$ (fig. 1,3). At this moment the radius of the bubble will be equaled to $R_b = OH = OR$. The line $RH$ (a circumference) is the result of the intersection of a spheric surface with the plane $ROH$.

After that the process of interaction of bubbles with each other with the formation of planes $RSMV$ and $HLMV$ (fig. 1) begins. It is shown in fig.4 in the axinometry by the planes $RR_1V_1$ and $HH_1V_2$, where the line $V_1V_2$ corresponds to the place of intersection of the sphere with the plane $ROH$. In this case the radius of the bubble equals $OV_1 = OV_2$. The process of intersection of bubbles which are found, for instans, in points $O$ and $A$ (fig.1) begins with some delay. In the direction of axis $OZ$ the coating will be intumescent and the distance $OA$ will increase quicker when the layer considered is closer to the surface.
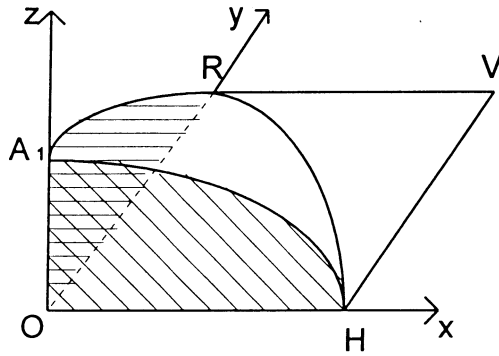
fig.3 .The  scheme of bubble increase.

The  plane  of  the  interaction  of  two  bubbles  along  $OZ$  will  correspond  to  their intersection  with  the  horizontal  plane . The  bubbles  will  have  different  sizes, and  the plane  of  intersection  with  the  sphere  will  form  the  circumference . Its  projection  on the  plane  will  at  first  gradually  approach  points $R$ and $H$  and  then  it  will  move along  lines $RV$ and $HV$  until  the  residue  of  spheric  surface  reaches  the  point which  is  found  in  the  middle  brtween  points  $V$  and  $M$ (fig.1) . This  point  moves along  the  coordinate $Z$ , and  the  value  of  radius  is  determined  after  the  solution  of the  problem  on  the  whole . The  one - dimensional  processes  are  finished  with  the completing  of  the  third  stage .
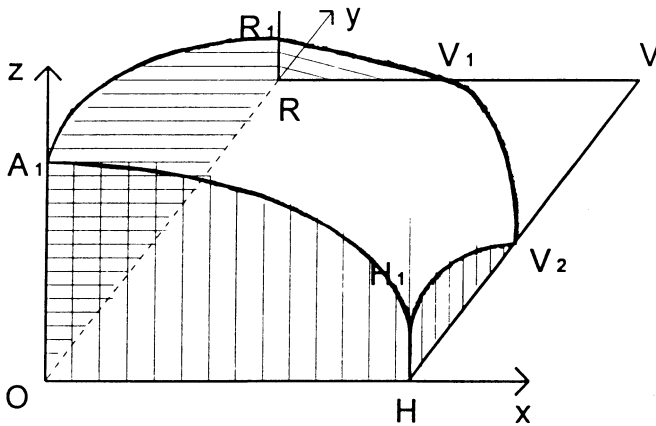


fig.4 . The  scheme  of  bubbles  intersection.

However  for  the  final  fourth  stage  the  equations  (6)  and  (7)  are  used , where

$S_b$  should  be  calculated  using  additional  relations . The  three - dimensional equations  of  diffusion  at  this  stage  of  coating  intumescense  will  be  used  instead of  equation (19) .

Here it is necessary to solve of three - dimensional equations of thermal conductivity with the jump of thermophysical properties on the boundary with the substrate

REFERENCES :

1. Isakov G. N. , Nesmelov V. V. Physics of combustion and explosion . 1994 , N2 , p 57-63 .

2. Bulgakov V. K. , Kodolov V. I. , Lipanov A. M. Modeling polymeric materiel combustion . M.: Chimia , 1990 , 238 p .