Formation of polymeric powder coatings

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Abstract. The initial stage of the formation of polymeric powder coatings is considered. The equations for estimating the convergence velocity of the particles and the obstacle at impact, as well as other characteristics were obtained when depositing the particles on the body surface. Using fictitious bubble and the ideal model of the porous medium we found dependencies that describe the coalescence dynamics of the deposited softened powder particles, determined at the time of their full agglutination.

1. Introduction

In general, during the formation of the polymeric coating the initial stage of particles deposition on the body surface, then their agglutination, coalescence, spreading over the surface (sintering, melting) and also curing and polymerization are distinguished [1, 2]. Each of these stages can be the subject for a separate research. In this paper we consider without going into details the first of these stages largely determining the quality of the polymeric coatings.

2. Deposition of polymeric particles on the treated body surface

Among the large number of technologies, methods and techniques of application of polymeric powder coatings we focus on the jet spraying [2-5]. For this method it is characteristic that powder particles moving in a stream of air, flue gases or their mixture under the influence of the inertial forces, fields of the body forces fall on the treated body [6-11].

In order to simplify the modeling of the sprayed polymeric particles we assume that in the unit volume V, adjacent to the unit area S_m of the treated body the particles are of the same average diameter d, fly with the same velocity $\vec{v}_d$. At that the total number of impacts of all particles with the surface S_m over the time τ will be:

$$N_m = \tau \sum_{d} (N_d v_{dn})/\ell,$$

where v_{dn} – projection of the vector $\vec{v}_d$ on the normal to the body surface, N_d – number of particles with the diameter d, which are situated in the considered unit volume V, V_d – the total amount of particles with the diameter d, quantitatively V_d is equal to the concentration of particles with the size d; ℓ – unit length.

IOP Conf. Series: Materials Science and Engineering **240** (2017) 012014 doi:10.1088/1757-899X/240/1/012014

At low impact velocity of a single particle in the quasi-stationary mode in accordance with Newton's second law [9]

$$\int_0^s P(s)ds = (4\pi\rho_p \; r_p^3/3) \int_v^{v_p} vdv, \tag{1}$$

where r_p, ρ_p, v_p – radius, material density, particle impact velocity, respectively; $P = P(s)$– impact force; s, v– current convergence, velocity of the colliding particles and obstacle.

Assuming that $P(s) \sim 2P_* \,(s/s_0)(1 - s/2s_0)$, from (1) we find:

$$v = v(s) = (v_p^2 - (3s^2P_*/4\pi s_0\rho_p r_p^3)(1 - S/3s_0))^{1/2} \,, \tag{2}$$

Here, according to the condition $v(s_0) = 0$, the maximum convergence of the particles and obstacle

$$s_0 = 2\pi\rho_p r_p^3 v_p^2 / P_*. \tag{3}$$

The maximum force on impact P_* is determined by the formula [10]:

$$P_* = \delta_{pm}^{2/5}(5m_p v_p^2/4)^{3/5} \,,$$

where m_p – particle mass, $\delta_{pm} = 4(r_p)^{1/2}/(3\pi(\kappa_p + \kappa_m)), \kappa_p = (1 - v_p^2)/\pi E_p$, $\kappa_m = (1 - v_m^2)/\pi E_m$; $E_p, E_m; v_p, v_m$ – Young's modulus, Poisson's ratio of the particle and obstacle material, respectively.

If it is necessary having the dependency (2) from the equation

$$\int_0^s ds/v(s) = \tau$$

you can find the convergence law of the particle and obstacle at impact $s = s(\tau)$ and knowing s_0 (3), to assess the impact time τ_0 and other parameters characterizing the impact.

3. Particle agglutination

When depositing powder particles they subsequently stick together before their liquefaction. Correspondingly, the porosity of the sprayed layer decreases. In order to describe this process mathematically the sprayed powder layer is represented as a bubble porous medium [12]. When laying particles close to the sphere in shape rhombohedrally the equivalent diameter of these pores will be

$$d_\Pi = d_p \,(6\sin^2\vartheta\,\sqrt{1 + \cos\vartheta}/(\pi(1 + \cos\vartheta) - 1)^{1/3} \,, \tag{4}$$

where d_p – particle diameter, ϑ – angle characterizing the laying of particles ($\pi/3 \le \vartheta \le \pi/2$). At that, approximately, the initial porosity of the medium

$$m_0 \sim 0.5 - 0.33\cos\vartheta. \tag{5}$$

According to [1] when particles stick together the equivalent radius of the spherical pores $a = a(\tau)$ satisfies the equation:

$$da/d\tau = -3\kappa\sigma/(4\eta). \tag{6}$$

Here, κ – correction factor, basically, caused by the difference of the pores shape of the real material from spherical shape in the model of the fictitious medium, influence of gas pressure on the agglutination process, σ – surface tension coefficient at the bubble boundary, η – polymeric material viscosity.

Integrating the given equation we find

$$a = a(\tau) = a_0 - K_0\tau,$$

где a_0 – initial equivalent radius of the pores ($a_0 = 0.5d_\Pi$), $K_0 = 3\kappa\sigma_0/(4\eta_0)$;
σ_0, η_0 – average values of the surface tension coefficient and viscosity.

Hence, at initially rhombohedral laying of spherical powder particles of the sprayed layer the time of their full agglutination will be:

$$\tau_{C\Pi} \approx 1.33\,(1 - 0.22\cos\vartheta)\eta_0 r_p/(\kappa\sigma_0).$$

If you use the ideal model of a porous medium [13] then at the initial time the radius of the channels cross-sections of this medium is determined by the relationship:

IOP Conf. Series: Materials Science and Engineering **240** (2017) 012014 doi:10.1088/1757-899X/240/1/012014

$$r_{\Pi 0} = 2m_0 r_p/(3(1-m_0)).$$

Assuming that at agglutination the radius of the pores channels r_Π changes over time in accordance with (6) we find:

$$r_\Pi = r_\Pi(\tau) = r_{\Pi 0} - K_0 r.$$

Approximately, taking into account (5) time of full agglutination of particles

$$\tau_{C\Pi} \approx 0.89(1-0.66\cos\vartheta)^2\,\eta_0\,r_p/(\kappa\sigma_0).$$

Comparing the ratio for $\tau_{C\Pi}$ we make sure that in the case of a model of the ideal porous medium the time of the pores collapse is less than that when using the model of the bubble medium.

4. Coalescence and spreading of particles material over the body surface

When analyzing the coalescence of the fluid particles of the polymeric powder we consider only the behavior of particles in a layer adjacent to the solid surface of the treated body.

If the body surface is wettable then the initial (τ = 0) shape of the half section of the separated particle and transformation of the cross-section over time are shown in figure 1 *a*, *b*, respectively. Here, *Ox* axis is directed along the body surface, *AB* – part of the upper boundary of the particle, *A'B'* – its average position, *PQ* – interphase boundary, h_k – average particle height equal to $2r_p$ in the initial position, θ – limiting wetting angle ($\cos\theta = \zeta$), *BQ* – interface surface of the adjacent particles, *QQ'* – conventional boundary parallel to the *Ox* axis.

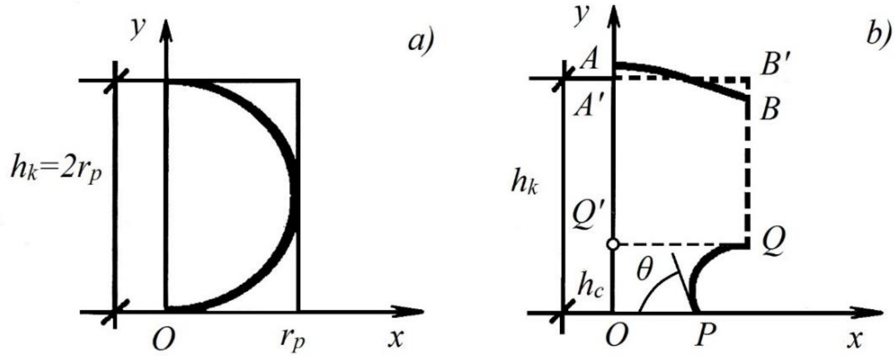

Figure 1. Half of the cross-section of the separated fluid particle: at the initial (a) and intermediate (b) time points.

Further we use the provisions of the capillary hydrodynamics [13-19] to solve the problem of the particles coalescence. Let's present the transformation of the cross-section (fig. 1) over time as a settling of the rectangle $A'B'QQ'$ with constant area as a result of spreading of the fluid located in *OPQQ'*, accompanied by a displacement of the points *P*, *Q* and reduction of gas cavity area up to its collapses. In this case, we assume that near *PQ* boundary the fluid moves along *Ox* axis in the horizontal direction under the action of the pressure difference and surface tension forces.

It is known [20] that at plane-parallel flow of a viscous fluid in the channel one of the walls of which is moving with a velocity v_0 at constant longitudinal pressure gradient $\partial p/\partial x = p_x < 0$ the fluid velocity

$$v = v(y) = v_0 y/h_c + p_x/2\eta\,(y^2 - yh_c),$$

where h_c– remoteness of the conventional interface of the areas *QQ'* from the axis *Ox* (fig. 1)

If $p_x \approx -\Delta p/\tilde{x}_p$, where Δp – pressure difference at length $\tilde{x}_p(\Delta p > 0)$, then the average velocity of the fluid flow

$$\bar{v} = 0.5v_0 + \Delta p h_c^3/(12\eta S).$$

Here S – *OPQQ'* area, equal to $\tilde{x}_p h_c$. Provided that the fluid is incompressible its flow through the conventional boundary *QQ'* is small, $S \approx const$.

h_c and v_0 remain so far undetermined values in relationships, characterizing the fluid flow along the solid surface. When determining them we take into consideration that

IOP Conf. Series: Materials Science and Engineering **240** (2017) 012014 doi:10.1088/1757-899X/240/1/012014

$$\overline{v} = \frac{d\tilde{x}_p}{d\tau} = -S(dh_c/d\tau)\,/h_c^2 = 0.5v_0 + \Delta p h_c^3/(12\eta S), \qquad (7)$$

the shear stress (specific friction force) at the conventional boundary *QQ'*:

$$\tau_{xy} = \eta\left.\frac{dv(y)}{dy}\right|_{y=h_c} = \eta v_0/h_c + 0.5h_c p_x.$$

Assuming that $\tau_{xy} \sim 0$, replacing p_x on the $-\Delta p/\widetilde{x_p}$, we find:

$$v_0 \approx \Delta p h_c^3/(2\eta S).$$

Substituting this value $\mathrm{v_0}$in (7), relative to $\mathrm{h_c}$ we obtain the differential equation:

$$dh_c/h_c^5 = -7(\Delta p/(12\eta S^2))d\tau.$$

Integrating it on condition that at the initial time $\tau = 0$ the height $h_c = h_{\mathrm{co}}$ is known the pressure drop $\Delta p = \Delta p_0 = const$, we determine

$$h_c = h_c(\tau) = 1/((1/h_{co}^4) + (\tau\Delta p_0/3\eta S^2))^{1/4}. \qquad (8)$$

Hence the time of complete layer deposition when gas cavity disappears, will be

$$\tau_k = \left(\left(r_p h_{co}\right)^4 - S^4\right)(3\eta/(h_{co}^4 S^2 \Delta p_0)).$$

The presented solutions at the given parameters $\sigma, \eta;$, the initial values $\widetilde{x_p} = \widetilde{x_{po}}$, $h_c = h_{\mathrm{co}}$, the constant pressure difference $\Delta p = \Delta p_0$ allow you to find the area S, to assess the movement of the boundaries *PQ*, *QQ'*; the time of complete deposition of the particles layer, spreading of the polymeric material over the treated body surface.

At the capillary flow of the fluid in the channel in the absence of mass forces the average difference in pressure is evaluated by the dependency [13-15]:

$$\Delta p = p_\sigma - p_g + p_p.$$

Here p_g, p_p – pressure in the cavity and the particle material, $p_\sigma = \sigma/R$ – capillary pressure, σ – surface tension coefficient at the fluid-gas interface, $R = r/\cos\theta$ – curvature radius of this interface, r– half of the channel width. Pressure p_σ is the sum of two specific forces $\sigma\cos\theta/d$, acting in the direction of the channel axis and applied to the ends of the meniscus.

Let's assume that when particles coalesce (see fig. 1) the force $\sigma\cos\theta/h_c$, applied at the point *P* and the force σ/h_c – at point *Q* are acting on the *PQ*. The total specific tension force directed towards *Ox* axis,

$$p_\sigma = (1+\zeta)\sigma/h_c\,.$$

Consequently, the average difference in pressure causing the displacement of the PQ interface

$$\Delta p = \Delta p(\zeta) = (1+\zeta)\sigma/h_c - \Delta p_g(\Delta p > 0),$$

where $\Delta p_g = p_g - p_p$.

Hence the motion of *PQ* boundary will be directed towards the *Ox* axis, if

$$(1+\zeta)\sigma/h_c > \Delta p_g.$$

In the case when at the *PQ* interface the average pressure drop $\overline{\Delta p_{go}} = const$, the average curvature radius of the *PQ* interface in accordance with the Laplace equation will be:

$$\bar{R} = \sigma/\overline{\Delta p_{go}} = R_0 = const.$$

When this condition is satisfied the *PQ* interface surface displacement at the three characteristic points in time is shown in fig. 2. It should be noted that if at the initial time $\theta \sim \pi/2\,(\zeta \sim 0)$, then as cavity sizes decrease the limiting wetting angle increases (fig. 2 *b*, *c*) tending to $\pi(\zeta = -1)$. It is known that the values $\theta > \pi/2$ are typical for nonwettable surfaces of the solid body.

Since $\zeta = \cos\theta < 0$, the tension force $\sigma\cos\theta/h_c$ at the point P is directed oppositely to the movement of the interface, however, at the point Q it still acts in the *Ox* axis direction.

In the considered case when the cavity radius R_0 is constant from its geometry it follows that

$$h_c = (1+\zeta)R_0.$$

Thus, in contrast to (8), at a given value of h_{co} the radius $R_0 \approx h_{\mathrm{co}}$ ($\zeta \approx 0$), the cavity height h_c depends on $\zeta = \zeta(\tau)$, the pressure difference

$$\Delta p = \sigma/R_0 - \Delta p_g.$$

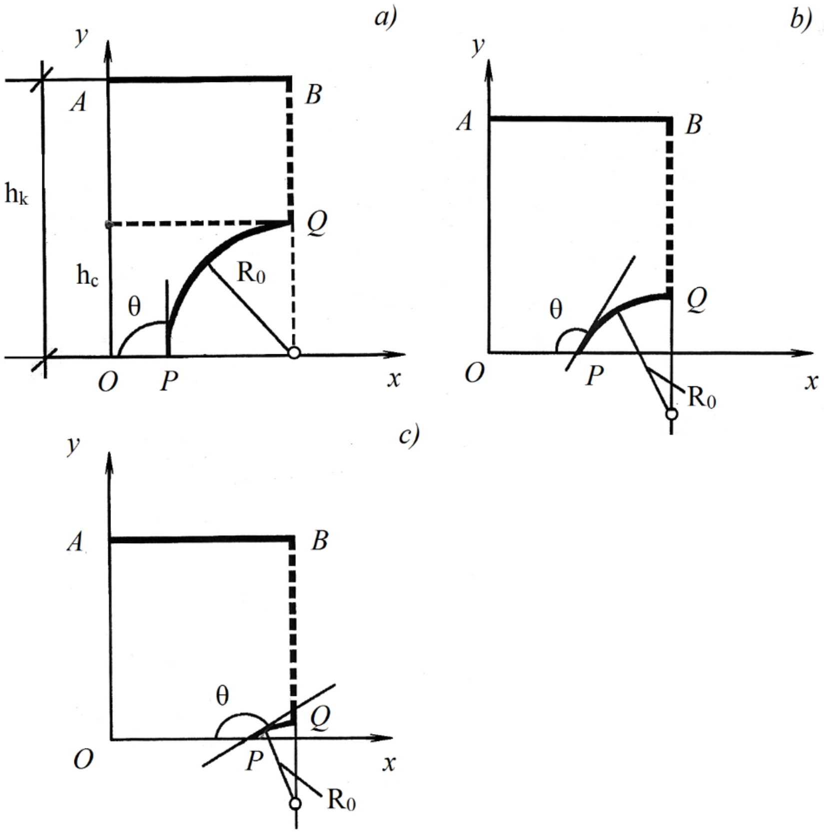

Figure 2. Transformation of fluid particle cross-section over time.

Hence, *PQ* interface will move in the direction of *Ox* axis, if the following condition is satisfied

$$\Delta p_g < \sigma / R_0.$$

Here the pressure drop Δp_g can be interpreted as a control parameter when it changes both the velocity of interface movement and direction of movement also change.

5. Conclusions

In conclusion, note that the obtained solutions can be used to calculate the appropriate characteristics taking into account the changes of the governing parameters depending on the temperature.

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This work was performed with financial support from Ministry of Education and Science of the Russian Federation in the framework of the Federal Target Program “Research and development in priority development fields of science and technology sector of Russia for 2014-2020” the agreement No. 14.583.21.0057 on 28th of July 2016 (Project ID RFMEFI58316X0057).