DETERMINATION OF THE PRIMARY THERMAL-RADIATION CHARACTERISTICS OF SEMITRANSPARENT FILLED POLYMER COATINGS

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Equations are derived for calculating the primary thermal-radiation constants of a heterogeneous semitransparent material. These constants are determined for the case of a filled epoxy coating.

Questions associated with the transfer of thermal radiation play a leading part in many fields of modern technology [1, 13]. The study of radiant heat transfer in heterogeneous media is especially complicated. When radiation interacts with such a medium, scattering occurs at local inhomogeneities. The scattering effects greatly complicate the analysis of radiation transfer in scattering media. Many papers have been published in relation to these problems, but the majority of these have been mainly concerned with mathematical procedures for solving the transfer equation. At the same time experimental methods of determining the primary thermal-radiation characteristics and establishing the radiant-transfer singularities in a semitransparent heterogeneous material are not entirely satisfactory. The main reason for this is that there are no convenient methods of obtaining these coefficients from measurements of the external thermal-radiation characteristics (R_λ, T_λ). Among existing methods we may indicate fairly simple phenomenological models relating the hemispherical transmission and reflecting powers to the primary coefficients of the material. The best known of these is the two-flux Gurevich — Kubelka — Munk approximation [2, 3]. A shortcoming of these methods is the fact that the proposed transcendental equations are not analytically soluble for the unknown constants. A number of methods were developed in [4, 5], but these cannot be used for the situations of present interest, in which reflection of the incident radiation occurs at the interface between the ambient and the continuous phase containing the dispersed scattering centers.

We attempted to develop an experimental — analytical method of determining the primary spectral thermal-radiation characteristics of an absorbing and scattering material, allowing for the effects of reflection at the interface, and on this basis to determine the characteristics in question for a filled polymer material of the ÉKM type. From the point of view of transferring thermal radiation, this material is, on the one hand, semitransparent, and, on the other hand, a strongly scattering and absorbing medium. On the basis of these physical considerations it is clear that, for such materials, in addition to determining the external thermal-radiation characteristics (R_λ, T_λ, ε_λ), it is very important to know the primary coefficients of the elementary volume or layer which would characterize the properties of the actual material [4, 6].

A compound polymer coating may be approximated by the following physical model. Let the object of investigation be a substance (polymerized resin) with optically smooth surfaces of thickness d and with a refractive index of $m_\lambda = n_\lambda - i\varkappa_\lambda$. For our own particular case we may put $m_\lambda = n_\lambda$ to a fair degree of accuracy, since in the case of dielectrics the influence of the absorption coefficient $\varkappa_\lambda$ on the reflecting and refracting properties of the radiation is very slight ($n_\lambda \gg \varkappa_\lambda$) [11]. We shall consider the substance with refractive index n_λ as an optically homogeneous

TABLE 1. Value of $\bar{n}_\lambda$, $\bar{\varkappa}_\lambda$

Sample thickness, μ		Spectral range, μ	$\bar{n}_\lambda$	$\bar{\varkappa}_\lambda$
d_1	d_2			
1200	1770	0,9—2,2	1,62	$0{,}23\cdot10^{-4}$

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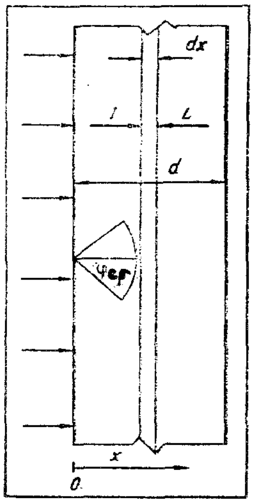

Fig. 1

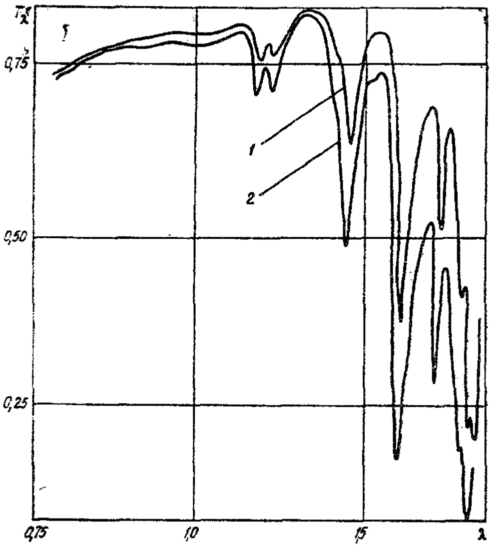

Fig. 2

Fig. 1. Analytical model of radiation transfer in a layer of scattering and absorbing material.

Fig. 2. Spectral transmission coefficient of the base of the compound EKM: 1) d = 1200 μ; 2) d = 1770 μ; λ, μ.

(not radiation scattering) matrix containing scattering particles (for example, the inorganic filler and pigment) with a refractive index differing from that of the matrix. Owing to the jump in refractive index at the phase interface these particles scatter the incident thermal radiation. Thus, this model of the compound coating represents the most complicated case encountered when considering radiation transfer, in which allowance has to be made for the influence of the reflecting and refracting interface between the ambient (air) and the matrix. The existence of this boundary should have a major effect on the reflecting and absorbing properties of the layer.

Let us give some more detailed consideration to the propagation of radiation in a model of this kind. If directional radiation falls on a plane-parallel layer (Fig. 1), the transmission of the interface may easily be calculated by means of the Fresnel reflection and refraction laws. In the case of homogeneous and diffuse incident radiation of intensity I, the reflecting power of the surface may be found by integrating the expressions for the reflected and incident fluxes over the whole solid angle 2π:

$$\rho_{\text{dif}} = \frac{E_{\text{refl}}}{E_{\text{inc}}} = \frac{\int_{\omega=2\pi} I\rho_{\varphi}\cos\psi d\omega}{\int_{\omega=2\pi} I\cos\psi d\omega}. \quad (1)$$

After passing through the medium—air interface the radiation undergoes multiple scattering at optical inhomogeneities. This has the effect that inside the material the radiation changes its angular structure very considerably, and the initially directional radiation may be converted into radiation almost diffuse as regards its angular distribution. Let us now consider the reflection of the interface on receiving radiation directed outward from inside the sample. The reflecting power of this flux will be far higher than that of the former. This is because radiation takes place through the interface from a dense into a less dense medium. The important factor which distinguishes the internal incidence of the radiation from the external is the fact that not all the radiation incident upon the interface is refracted into the ambient, because of the phenomenon of total internal reflection. If the radiation is incident at an angle φ greater than the critical angle φ_{cr}, the energy will be totally reflected (the value of the critical angle depends on the refractive index of the material and may be calculated from Snell's law).

Let us calculate how much of the total flux incident upon the interface within the material will be reflected with a reflection coefficient equal to 1 (as before, the incident radiation is assumed homogeneous

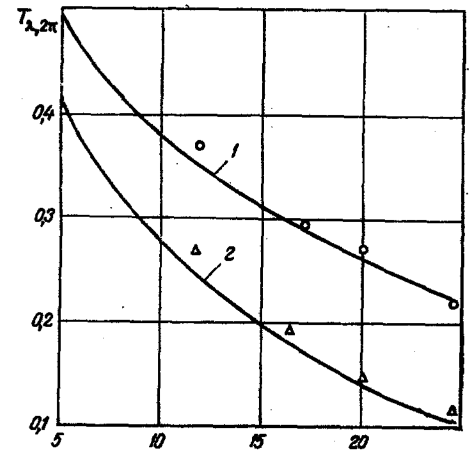

Fig. 3. Hemispherical transmission coefficient of the compound EKM as a function of the layer thickness d, mm: 1) $\lambda = 1.05\,\mu$; 2) $\lambda = 1.28\,\mu$.

and diffuse, with an intensity I). The flux of radiation E_1 falling within the solid angle $\omega_1 = \int_0^{2\pi} \int_{\arcsin\frac{1}{n}}^{\frac{\pi}{2}} \sin\varphi d\varphi d\psi$ is equal to

$$E_1 = \int_0^{2\pi} d\psi \int_{\arcsin\frac{1}{n}}^{\frac{\pi}{2}} I \cos\varphi \sin\varphi d\varphi, \tag{2}$$

where $\arcsin 1/n = \varphi_{cr}$ (this follows from Snell's law).

The total flux E falling in the whole solid angle $\omega = 2\pi$,

$$E = \int_0^{2\pi} d\psi \int_0^{\frac{\pi}{2}} I \cos\varphi \sin\varphi d\varphi. \tag{3}$$

The proportion of the total radiation falling on the interface at an angle exceeding the critical value equals $E_1/E = 1 - 1/n^2$. If in order to be specific we put $n = 1.6$ (this is the right order of magnitude for n in the present case), the contribution to the reflecting power of the interface simply arising from total internal reflection is about 0.6. The second part of the flux falling in a cone of solid angle $2\varphi_{cr}$ is divided into two components. One component is reflected in accordance with the Fresnel law, the other passes through the interface. At the same time the reflecting power for the incidence of radiation from outside is 0.09 in the case of a diffuse flux and 0.05 in that of directional radiation [9].

Thus, after considering the transfer of radiation in a scattering layer it is easy to understand the importance of allowing for reflection at the boundary surfaces. A high value of the reflecting power for internal incidence of the radiation reduces the probability of its leaving the layer, so that the neglect of boundary effects creates serious errors. The absorbing power of the layer calculated without allowing for reflections at the boundary may be too low, in some cases by a factor of several times [7].

The two-flux approximation was used in [6] to obtain equations relating the internal optical constants of an elementary layer to the experimentally measured hemispherical thermal-radiation characteristics ($T_{\lambda,2\pi}$ or $R_{\lambda,2\pi}$), without allowing for the boundary reflections. A consideration of the propagation of radiation in a plane-parallel layer consisting of a continuous, optically homogeneous substance containing uniformly distributed scattering centers leads to the conclusion that this problem ought really to be solved with new boundary conditions. The analytical model employed is shown in Fig. 1. The general solution of the well-known system of equations in the two-flux method of [4] may be written [8]

$$I = B_1(1-\beta)\exp(\sigma x) + B_2(1+\beta)\exp(-\sigma x),$$
$$L = B_1(1+\beta)\exp(\sigma x) + B_2(1-\beta)\exp(-\sigma x) \tag{4}$$

for the following boundary conditions:

$$I^0 = I_i' + r'L^0, \qquad L^d = r'I^d, \tag{5}$$

where I_i is the intensity of the flux incident upon the outer surface; r' is the reflecting power of the surfaces with coordinates $x = 0$ and $x = d$ for the incidence of radiation inside the layer. As already indicated, the order of magnitude of the reflecting power of the radiation I_i from the surface $x = 0$ is extremely small (~5%) and need not be considered in the boundary conditions.

As indicated in [8, 6], the primary thermal-radiation constants β and σ are uniquely related to the absorption coefficient k and the scattering coefficient s of the elementary layer by the following relationships:

$$\beta = \sqrt{\frac{k}{k+2s}} \text{ and } \sigma = \sqrt{k(k+2s)}.$$

After solving the system of equations (4) with boundary conditions (5) we obtain an expression for the hemispherical transmission of a layer of thickness d:

TABLE 2. Values of σ_λ, β_λ

λ, μ	T_1	T_2	n	d_1, mm	d_2, mm	r	r'	σ_λ, mm	β_λ
1,28	0,32	0,43	1,62	0,14	0,07	0,056	0,64	6,5	0,062
1,05	0,21	0,35	1,62	0,14	0,07	0,056	0,64	0,56	0,103

$$T_{2\pi} = \frac{I^d(1-r')}{I_i} = \frac{4\beta}{\left[1-r'+\beta^2\frac{(1+r')^2}{1-r'}\right]\sqrt{A^2-4}+2\beta(1+r')A}, \tag{6}$$

where

$$A \equiv \exp(\sigma d) + \exp(-\sigma d). \tag{7}$$

Writing down expressions of type (6) for $T_{1.2\pi}$ and $T_{2.2\pi}$ and taking their ratio, after certain transformations we arrive at the equation

$$A_2 = T_{2.2\pi}\left(1+r'+\frac{1}{T_{1,2\pi}}\right), \tag{8}$$

where $T_{2.2\pi}$ and $T_{1.2\pi}$ are the hemispherical transmission coefficients of samples of thicknesses d_2 and d_1, respectively, in which $d_1 = 2d_2$.

Solving the system of equations (7) and (8) we obtain an expression for the constant σ:

$$\sigma = \frac{1}{d_2}\ln\frac{A_2+\sqrt{A_2^2-4}}{2}. \tag{9}$$

The solution of (6) for the other constant gives the following expression for β:

$$\beta = \frac{-ac+\sqrt{(ac)^2-b}}{b}, \tag{10}$$

where

$$a = A_2 - \frac{2}{T_{2.2\pi}(1+r')}; \qquad b = \frac{1+r'}{1-r'}; \qquad c = \sqrt{\frac{1}{A_2^2-4}}.$$

Equations (9) and (10) give an explicit analytical relationship between the unknown primary coefficients and the experimentally measured hemispherical transmission coefficients of two layers of scattering material with different thicknesses d_1 and d_2.

We may show that the constant σ equals the attenuation coefficient of the incident radiation in a layer of heterogeneous material. Usings Eqs. (4) and (5) we find the values of the integration constants B_1 and B_2 for a layer of infinite thickness ($d = \infty$):

$$B_1 = 0, \quad B_2 = \frac{I_i[\beta(1+r')+1-r']}{2\beta(1-r'^2)+\beta^2(1+r')^2+(1-r')^2}. \tag{11}$$

From Eq. (4) we then obtain the following equation for the flux of radiation at a depth x:

$$I(x) = I_i\left\{\frac{[\beta(1+r')+1-r'](1+\beta)}{\beta^2(1+r')^2+(1-r)^2+2\beta(1-r'^2)}\right\}e^{-\sigma x}. \tag{12}$$

The expression in the curly brackets is equal to a constant quantity, and we may rewrite (12) in the form

$$I(x) = KI_i e^{-\sigma x}. \tag{13}$$

The latter relationship may be considered as the attenuation law of radiation propagating in a scattering and absorbing medium. Equation (13) differs from the well-known Bouguer law in that, firstly, it is applicable to a layer with a zero transmission (infinitely dense layer) and, secondly, the attenuation is a function of the two constants σ_λ and β_λ.

In order to determine the constants σ_λ and β_λ from Eqs. (9) and (10) we must know the parameter r', the reflecting power of the sample — air interface for the internal incidence of the radiation. This quantity cannot be measured experimentally. However, the value of r'_λ may be calculated if we assume that the flux of radiation falling on the boundary surface from inside the sample is diffuse. This approximation will be the more accurate, the greater the scattering power of the material under test. In this case the parameter r'_λ is calculated by the Gershun equation [9]:

$$r'_\lambda = 1 - \frac{1}{n_\lambda^2} + \frac{r_\lambda}{n_\lambda^2}. \tag{14}$$

The problem of the angular distribution of the incident radiation deserves attention, since one of the assumptions of the two-flux approximation is that the flux falling on the sample is diffuse. Measuring the hemispherical $R_{\lambda,2\pi}$ and $T_{\lambda,2\pi}$ with diffusely incident radiation is, nevertheless, a very difficult problem. All modern spectrophotometers have collimated incidence of the radiation on the sample. The question arises as to how justifiable it is to use the two-flux approximation in such an experimental situation. This question has been studied on a number of occasions [10, 11] and it has been concluded that the diffuse radiation may be replaced by directional radiation without introducing any serious errors. This assertion is valid for large optical thicknesses and high concentrations of the scattering particles [10]. These requirements are satisfied by the majority of filled polymer coatings.

As already indicated, our subject for studying the thermal-radiation characteristics was a compound coating of the ÉKM type. In its physical structure this material corresponds to the model which we have been considering in connection with the two-flux method (one requiring due allowance for boundary reflections). The values of r_λ were calculated from the well-known Fresnel formula for directional radiation, using existing data as to the spectral refractive index of the binder. The refractive index was determined by the method proposed in [12]. The underlying idea of this method lies in the fact that, instead of the accurate but very complicated method of calculating the constants n_λ and $\varkappa_\lambda$ forming the complex refractive index m_λ with full allowance for the selectivity of the absorption spectrum, an approximate method (which still preserves the selective character of the absorption spectrum of the test material) is used. For this purpose the spectrum of the transmission coefficient (T_λ) is divided into several regions, and it is assumed that in each of these regions, bounded by wavelengths λ_1 and λ_2, the optical constants remain independent of the wavelength. The coefficients n_λ and $\varkappa_\lambda$ are calculated by means of formulas in which the original data are the experimentally obtained transmissions T_1 and T_2 of two samples with thicknesses d_1 and d_2.

The binding component of the material under consideration was the hardened base of the compound ÉKM (main ingredients epoxy resin ED-5 and maleic anhydride).

The average refractive index was determined for the spectral range 0.9-2.2 μ. Figure 2 shows the spectral transmission coefficients of the material in question for two different thicknesses of the layer. Table 1 shows the main experimental parameters and the calculated average values $\bar{n}_\lambda$ and $\bar{\varkappa}_\lambda$ for the base of the compound ÉKM. The samples were treated so as to produce the maximum degree of hardening, which was monitored by a spectral method involving the combined absorption band of the epoxy groups (4520 cm^{-1}). The primary thermal-radiation characteristics of the compound ÉKM were determined for two wavelengths and calculated by means of Eqs. (9) and (10). The resultant values of σ_λ and β_λ and also the original experimental data, are presented in Table 2.

The attenuation coefficient at a wavelength of 1.28 μ was considerably greater than that at a wavelength of 1.05 μ. This fact may be explained by remembering that the wavelength of 1.28 μ lies in the neighborhood of the absorption band (Fig. 2) of the binding substance, and a considerable proportion of the attenuation coefficient arises from the absorption of the radiation.

Figure 3 shows the directional hemispherical transmission coefficient of the compound ÉKM as a function of the thickness of the layer for wavelengths of 1.05 and 1.28 μ, calculated by means of Eq. (6), and the experimentally measured values of $T_{\lambda,2\pi}$ for sample thicknesses of 0.12, 0.16, 0.20, and 0.25 mm. We see from Fig. 3 that the experimental points $T_{\lambda,2\pi}$ are close to the calculated values, the difference between these values being the smaller, the greater the optical thickness of the sample, in agreement with the basic principles of the two-flux approximation.

Let us apply Eq. (13) to an infinitely dense layer in order to determine the depth of penetration of monochromatic radiation at a wavelength of 1.28 μ. The calculated value of the coefficient K for the resultant value of the coefficient β_λ (Table 2) equals 2.30. Putting $x = 2/\sigma$ in (13) we find that at a depth of d = 0.31 mm in an infinitely dense layer of the compound EKM an incident flux of density I_i is weakened by a factor of 3.22.

Thus, the proposed method of determining the primary thermal-radiation characteristics allowing for surface reflection may be used when studying the transfer of thermal radiation in heterogeneous semitransparent dielectric materials.

NOTATION

R_λ, T_λ, spectral reflection and transmission coefficients of a layer of thickness d; ε_λ, spectral emissivity; n_λ, spectral refractive index of the material; $\varkappa_\lambda$, spectral absorption coefficient; ρ_φ, reflection coefficient of the surface for a ray incident at an angle φ; ψ, azimuthal angle of incidence of the ray; σ_λ and β_λ, primary thermal-radiation constants of the transparent material; r_λ, reflection coefficient for radiation incident on the sample from the ambient; r'_λ, reflection coefficient for radiation incident on the interface from inside the sample.

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