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Theoretical Study on Radiative Properties of an Optically
Thick Painted Layer Containing Spherical Pigment*
(Case of Normal Incidence)

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An analysis is presented for the radiative transfer in the semi-infinite medium of an absorbing vehicle containing the absorbing and anisotropically scattering particles of the pigment to predict the reflection properties of an optically thick painted layer in the wavelength range of 0.35-20 μ m. The effects of the volume concentration ($v=0.005-0.55$) and the optical property of the pigments (TiO_2 , Fe_2O_3) on the bidirectional and hemispherical reflectances are examined. A generalized relation between the hemispherical reflectance and the scattering albedo is obtained. The procedure of expressing the bidirectional reflection intensity as a continuous function of cosine of polar angle and the interpolation method to obtain the hemispherical reflectance at the intermediate optical thickness between the small and the infinitive ones are presented.

1. Introduction

The analyses of the radiative transfer within a semi-infinite scattering medium were carried out by several investigators (1-8). Also, experimental studies (9-11) were carried out on the radiative properties of an optically thick layer of a scattering medium. However, these studies, either analytical or experimental, did not deal so much with the practical engineering application of the optically infinitely thick painted layer, and were limited to the simple cases including isotropic scattering, weakly absorbing or purely scattering medium and non-reflecting boundaries.

A previous theoretical study (12) was carried out on the radiative properties of a painted layer of finite optical thickness τ_1 . The radiative transfer was analysed and treated by Chandrasekhar's theory. The Gaussian quadrature formula was adopted and the Gaussian elimination procedure was applied to obtain the constants of the numerical solution. However, in the calculation procedure for obtaining the constants of the numerical solution for the homogeneous system of the transfer equation, an overflow problem exists as a result of increasing the exponent products for the exponential functions in the expressions for the elements of the matrix to which the Gaussian elimination procedure is applied. Therefore, the calculation in the visible and near infrared regions was limited to small pigment volume concentrations and thin layers.

The present study extends the analysis to include the most practical applications

of thick layers and large pigment volume concentrations keeping in mind the same approximation made by neglecting the effect of the interference between the scattered fields of the pigment particles. A painted layer of infinite optical thickness ($\tau_1=\infty$) which expresses the asymptotic case for optically thick painted layers is investigated. The painted layer in this case is considered an absorbing and anisotropically scattering semi-infinite medium with its upper boundary specularly reflecting. The same pigments (12) (TiO_2 , Fe_2O_3) of spherical particles are selected for the present study. A trial for the generalized curve of the hemispherical reflectance for the case of $\tau_1=\infty$ is discussed. An interpolation method is investigated also to obtain the results for a painted layer of finite τ_1 larger than the limit ($\tau_1 \approx 9$) due to the overflow problem. A new and more accurate method (13) is adopted for expressing the intensity of the diffuse radiation $I(\tau, \mu)$ within the painted layer as a continuous function of τ and μ in terms of the constants of the numerical solution $I(\tau, \mu_i)$.

Nomenclature

- b_{i0} : constant
- c_k : directional distribution coefficient
- d : diameter of the pigment particle, μm
- $d\Omega$: element of solid angle
- F : net flux of monochromatic radiation
- g_α : constant
- I : monochromatic intensity of the diffuse radiation field
- K_{av} : absorption coefficient of the vehicle, μm^{-1}
- K_{sp} , K_{ep} : scattering and extinction coefficients of the pigment for a single particle, μm^{-1}
- L : thickness of the painted layer, μm
- n_v : real refractive index of the vehicle
- $p(\cos\theta)$: phase function
- P_n : Legendre polynomial of order n

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R, r : reflectances
 $S(\tau, \mu)$: source function for direction μ at level τ
 s_i, t_i : constants
 v : pigment volume concentration
 W_j : Gaussian weight
 γ_α : constant
 Θ : angle between directions (μ, ϕ) and (μ', ϕ')
 θ : polar angle measured from the outward normal to the painted layer
 λ : wavelength in the vacuum, μm
 μ : $\cos \theta$
 μ_i : Gaussian divisions of the interval $(-1, 1)$ according to the zeros of Legendre polynomial $P_{2n}(\mu)$
 ρ_D : hemispherical reflectance of the perfect diffuse substrate
 ρ_1 : normal reflectivity at the upper boundary (air-coating)
 ρ_2 : normal reflectivity at the lower boundary (coating-specular substrate)
 τ : normal optical depth from the upper boundary
 τ_1 : total normal optical depth
 ϕ : azimuthal angle
 $\tilde{\omega}$: scattering albedo of the painted layer for single scattering

2. Formulation of the problem

2.1 Theoretical model

The painted layer of infinite optical thickness ($\tau_1 = \infty$) can be treated as a semi-infinite medium of the absorbing and anisotropically scattering particles of the pigment dispersed in the absorbing vehicle. Fig.1 shows a model of the painted layer system with the upper boundary which is represented by the specular interface between air and vehicle. The layer is irradiated by a normally incident unpolarized light of unit flux ($I_0 \mu_0 d\Omega_0 = 1$).

2.2 Basic equations

The equation of the radiative transfer within the layer is expressed by

$$\mu \frac{dI(\tau, \mu)}{d\tau} = I(\tau, \mu) - \frac{\tilde{\omega}}{4\pi} \int_{4\pi} p(\cos \Theta) I(\tau, \mu') d\Omega' - (1 - \rho_1) \exp(-\tau) \cdot \frac{\tilde{\omega}}{4\pi} \int_0^{2\pi} p(\cos \Theta_0) \frac{d\phi}{2\pi}, \quad (1)$$

where Θ_0 is the angle between the direction of $\mu = -1$ and that of μ . The third term in R.H.S. of Eq.(1) corresponds to the contribution of scatter to the beam intensity $I(\tau, \mu)$ out of the attenuated incident flux $(1 - \rho_1) \cdot \exp(-\tau)$ which penetrates to the level τ . In

Fig.1 Painted layer system for the case of $\tau_1 = \infty$

Eq.(1) the scattering albedo $\tilde{\omega}$ of the painted layer for single scattering, and the phase function $p(\cos \Theta)$ are expressed by the same equations presented in Ref.[12]. ρ_1 is the normal reflectivity at the upper boundary. The upper boundary condition associated with Eq.(1) is given by

$$I(0, -\mu) = \rho_1 \cdot I(0, \mu) \quad \text{for } \mu > 0. \quad (2)$$

2.3 Numerical analysis

Eq.(1) can be solved numerically by applying the Gaussian quadrature formula in the n th approximation. Thus, Eq.(1) is replaced by the following $2n$ linear differential equations

$$\begin{aligned} \mu_i \frac{dI(\tau, \mu_i)}{d\tau} &= I(\tau, \mu_i) \\ &- \frac{\tilde{\omega}}{2} \sum_{j=1}^{2n} w_j I(\tau, \mu_j) \sum_{k=0}^m c_k P_k(\mu_i) P_k(\mu_j) \\ &- (1 - \rho_1) \exp(-\tau) \frac{\tilde{\omega}}{4\pi} \sum_{k=0}^m c_k P_k(\mu_i) (-1)^k, \end{aligned} \quad (i=1, 2, \dots, 2n). \quad (3)$$

Let the solution of the associated homogeneous system

$$\begin{aligned} \mu_i \frac{dI(\tau, \mu_i)}{d\tau} &= I(\tau, \mu_i) \\ &- \frac{\tilde{\omega}}{2} \sum_{j=1}^{2n} w_j I(\tau, \mu_j) \sum_{k=0}^{2n} c_k P_k(\mu_i) P_k(\mu_j), \end{aligned} \quad (i=1, 2, \dots, 2n), \quad (4)$$

$$\text{be } I(\tau, \mu_i) = b_i \exp(\gamma \tau), \quad (i=1, 2, \dots, 2n). \quad (5)$$

Substituting Eq.(5) in Eq.(4) we obtain

$$b_i = \frac{1}{(1 - \mu_i \gamma)} \sum_{j=1}^{2n} \frac{\tilde{\omega}}{2} w_j b_j \sum_{k=0}^m c_k P_k(\mu_i) P_k(\mu_j) \quad (6)$$

or in the matrix form

$$(A + \gamma I)(b_i) = (0), \quad (7)$$

where A is $2n \times 2n$ matrix whose elements are defined by Eq.(6) and I is $2n \times 2n$ unit matrix. Eq.(6) is the characteristic equation for γ and it is of the order n in γ^2 only [14]. Thus $2n$ eigenvalues of the matrix A must occur in pairs as $\pm \gamma_\beta$ ($\beta=1, 2, \dots, n$) and γ_β 's are the positive values of the exponent γ .

The particular integral $t_i \exp(-\tau)$ of the non-homogeneous system Eq.(3) combined with the possible linearly independent solutions of the homogeneous system Eq.(4) gives a general solution. Considering the boundedness of the intensity $I(\tau, \mu)$ as $\tau \rightarrow \infty$, the general solution is expressed in the form

$$I(\tau, \mu_i) = \sum_{\alpha=1}^n g_\alpha b_{i\alpha} \exp(\gamma_\alpha \tau) + t_i \exp(-\tau), \quad (i=1, 2, \dots, n), \quad (8)$$

where α stands only for the orders corresponding to the negative values of γ_α , and $b_{i\alpha}$ are the related eigenvectors. The n constants of integration, g_α 's are determined from the boundary condition Eq.(2) in the numerical form

$$I(0, \mu_i) = \rho_{(2n+1-i)} \cdot I(0, \mu_{(2n+1-i)}), \quad (i=n+1, \dots, 2n). \quad (9)$$

3. The approximate closed form for the intensity $I(0, \mu)$

The final calculations for the bidirectional relative diffuse reflectance r_D for the case of a painted layer of $\tau_1 = \infty$ are carried out using the approximate closed form $I(0, \mu)$ in terms of the constants obtained for the numerical solution $I(\tau, \mu_1)$. For the sake of comparative study, the case of a painted layer of finite optical thickness τ_1 on specular or diffuse substrate is considered as well as the present case of $\tau_1 = \infty$ in deriving the closed form $I(0, \mu)$.

(a) Case of finite τ_1 with specular substrate

The outward and the inward intensities at the level t inside the painted layer, respectively, can be expressed in the integral form:

$$I(\tau, \mu) = I(\tau_1, \mu) \exp[-(\tau_1 - \tau)/\mu] + \int_{\tau}^{\tau_1} S(t, \mu) \exp[-(t - \tau)/\mu] dt / \mu, \quad (10)$$

$$I(\tau, -\mu) = I(0, -\mu) \exp(-\tau/\mu) + \int_0^{\tau} S(t, -\mu) \exp[-(t - \tau)/\mu] dt / \mu, \quad (11)$$

where $1 \geq \mu > 0$. The source function $S(t, \mu)$ is expressed by

$$S(t, \mu) = \frac{\tilde{\omega}}{4\pi} \int_{4\pi} P(\cos \Theta) I(t, \mu') d\Omega' + \frac{(1 - \rho_1) \exp(-t)}{1 - \rho_1 \rho_2 \exp(-2\tau_1)} \frac{\tilde{\omega}}{4\pi} \int_0^{2\pi} P(\cos \Theta_0) \frac{d\phi}{2\pi} + \frac{\rho_2 (1 - \rho_1) \exp[-(2\tau_1 - t)]}{1 - \rho_1 \rho_2 \exp(-2\tau_1)} \frac{\tilde{\omega}}{4\pi} \int_0^{2\pi} P(\cos \Theta_0') \frac{d\phi}{2\pi}, \quad (12)$$

where Θ_0' is the angle between the direction of $\mu=1$ and that of μ . Applying the Gaussian quadrature formula to Eq.(12) we obtain

$$S(t, \mu) = \frac{\tilde{\omega}}{2} \sum_{j=1}^{2n} w_j I(t, \mu_j) \sum_{k=0}^m c_k P_k(\mu) P_k(\mu_j) + \frac{(1 - \rho_1) \exp(-t)}{1 - \rho_1 \rho_2 \exp(-2\tau_1)} \frac{\tilde{\omega}}{4\pi} \sum_{k=0}^m c_k P_k(\mu) (-1)^k + \frac{\rho_2 (1 - \rho_1) \exp[-(2\tau_1 - t)]}{1 - \rho_1 \rho_2 \exp(-2\tau_1)} \frac{\tilde{\omega}}{4\pi} \sum_{k=0}^m c_k P_k(\mu). \quad (13)$$

The equations resulting from the substitution of $\tau=0$ in Eq.(10) and $\tau=\tau_1$ in Eq.(11) can be reduced for the outward intensities $I(0, \mu)$ by eliminating the other intensities $I(\tau_1, \mu)$, $I(\tau_1, -\mu)$ and $I(0, -\mu)$ through the application of the boundary conditions

$$I(0, -\mu) = \rho_{\mu} \cdot I(0, \mu) \quad (14a)$$

and

$$I(\tau_1, \mu) = \rho_{-\mu} \cdot I(\tau_1, -\mu), \quad (14b)$$

where $1 \geq \mu > 0$.

The numerical solution for the case of finite τ_1 with specular substrate is given by (12)

$$I(\tau, \mu_1) = \sum_{\alpha=1}^{2n} g_{\alpha} b_{i\alpha} \exp(\gamma_{\alpha} \tau) + s_i \exp(\tau) + t_i \exp(-\tau), \quad (i=1, 2, \dots, 2n). \quad (15)$$

Introducing the solution $I(\tau, \mu_1)$ of Eq.(15) for $\tau=t$ into Eq.(13) and then substituting

the resulting expression for $S(t, \mu)$ in the corresponding form of $I(0, \mu)$ after elimination of the other intensities and integrating over t , we obtain finally

$$I(0, \mu) = \frac{1}{[1 - \rho_{\mu} \rho_{-\mu} \exp(-2\tau_1/\mu)]} \cdot \left\{ \sum_{\alpha=1}^{2n} g_{\alpha} (A_{\alpha} \psi_{\alpha} + B_{\alpha} \phi_{\alpha}) + A_0 \psi_0 + B_0 \phi_0 + C_0 \chi_0 + D_0 \eta_0 \right\}, \quad (16)$$

where A_{α} , B_{α} , A_0 , B_0 , C_0 and D_0 are functions of μ only and can be determined in terms of ρ_1 , ρ_2 , γ_{α} , $b_{i\alpha}$, s_j , t_j , c_k and the Legendre polynomials $P_k(\mu_j)$, using the summation over the Gaussian divisions μ_j with the corresponding weights w_j , ($j=1, 2, \dots, 2n$). ψ_{α} , ϕ_{α} , ψ_0 , ϕ_0 , χ_0 and η_0 are functions of μ and τ_1 (See Appendix A). The reflectivities ρ_{μ} and $\rho_{-\mu}$ are calculated at the upper and the lower boundaries, respectively.

(b) Case of finite τ_1 with diffuse substrate

The intensity $I(0, \mu)$ is expressed by Eq.(10) directly. The source function $S(t, \mu)$ is expressed by Eq.(12) for $\rho_2=0$. The numerical solution in this case is given by (12)

$$I(\tau, \mu_1) = \sum_{\alpha=1}^{2n} g_{\alpha} b_{i\alpha} \exp(\gamma_{\alpha} \tau) + t_i \exp(-\tau), \quad (i=1, 2, \dots, 2n). \quad (17)$$

The corresponding boundary conditions are

$$I(0, -\mu) = \rho_{\mu} I(0, \mu), \quad (18a)$$

$$I(\tau_1, \mu) = 2\rho_D \sum_{j=n+1}^{2n} w_j |\mu_j| I(\tau_1, \mu_j) + \frac{\rho_D}{\pi} (1 - \rho_1) \exp(-\tau_1), \quad (18b)$$

where $1 \geq \mu > 0$. Proceeding as in the case of specular substrate we can obtain

$$I(0, \mu) = \sum_{\alpha=1}^{2n} g_{\alpha} [C_{\alpha} \exp[\tau_1 \gamma_{\alpha} - (\tau_1/\mu)] - A'_{\alpha}] + C'_0 \exp[-\tau_1 - (\tau_1/\mu)] + A'_0, \quad (19)$$

where C_{α} , A'_{α} , C'_0 and A'_0 are functions of μ only and can be determined similarly to the functions of Eq.(16). (Appendix A).

(c) Case of $\tau_1 = \infty$

The intensity $I(0, \mu)$ can be expressed simply by

$$I(0, \mu) = \int_0^{\infty} S(t, \mu) \exp(-t/\mu) dt / \mu, \quad (1 \geq \mu > 0). \quad (20)$$

The source function $S(t, \mu)$ is expressed also by Eq.(12) for $\rho_2=0$. Proceeding as in the cases of finite τ_1 , we can obtain

$$I(0, \mu) = \sum_{\alpha=1}^n g_{\alpha} E_{\alpha} / (1 - \mu \gamma_{\alpha}) + E_0 / (1 + \mu), \quad (1 \geq \mu > 0) \quad (21)$$

where E_{α} and E_0 are functions of μ only which are determined in a manner similar to the cases (a) and (b). (Appendix A). In the above we considered only the intensity $I(0, \mu)$ which is related to the diffuse reflective properties at the upper boundary of the painted layer ($\tau=0$). For a better understanding of the radiative transfer mechanism inside the optically thick layer ($\tau_1 = \infty$), an example is given in Appendix B for the effect

Fig.2 Bidirectional relative diffuse reflectance for the case of $\tau_1=\infty$ (effect of v) Fig.3 Hemispherical reflectance of TiO_2 system ($\tau_1=\infty$), (effect of v) Fig.6 Generalized relation between R_h and $\tilde{\omega}$ for the case of $\tau_1=\infty$ Fig.4 Hemispherical reflectance of Fe_2O_3 system ($\tau_1=\infty$), (effect of v) Fig.5 Diffuse ratio R_D/R_h (effect of v and optical properties of the pigment)

of the scattering albedo $\tilde{\omega}$ and the scattering phase function on the spatial distribution of the intensities $I(\tau, \pm 1)$ and the net flux $F(\tau)$.

4. Analysis of the results

The approximate closed form for the bi-directional relative diffuse reflectance $r_D(\mu')$ in the direction μ' out of the painted layer at the upper boundary is defined by

$$r_D(\mu') = \pi I_e(0, \mu'), \quad (22)$$

where the emergent intensity $I_e(0, \mu')$ is related to the outward intensity $I(0, \mu)$ in the direction μ by

$$I_e(0, \mu') = (1 - \rho_\mu) I(0, \mu) / n_V^2, \quad (1 \geq \mu > 0), \quad (23)$$

where μ' and μ satisfy Snell's law. The hemispherical diffuse reflectance R_D is determined by numerical integration of the bi-directional relative diffuse reflectance $r_D(\mu')$ over the hemisphere, and is given by

$$R_D = 2\pi \sum_{j=1}^n w_j \mu_j (1 - \rho_{\mu_j}) \cdot I(0, \mu_j). \quad (24)$$

The specular reflectance R_S in the case of finite τ_1 with specular substrate is given by (for the other cases $R_S = \rho_1$)

$$R_S = \rho_1 + \rho_2 (1 - \rho_1)^2 \exp(-2\tau_1) / \{1 - \rho_1 \rho_2 \exp(-2\tau_1)\} \quad (25)$$

Fig. 7 τ_1 dependence of R_h and R_D/R_h in visible region (effect of the reflection properties of the substrate)

Fig. 8 τ_1 dependence of R_h and R_D/R_h in visible region (effect of v)

Fig. 9 τ_1 dependence of R_h and R_D/R_h in near infrared region (effect of v)

The total hemispherical reflectance R_h (for any case) is given by

$$R_h = R_D + R_S \quad (26)$$

5. Results and discussions

In the calculation the r_D values are obtained at fixed and regular divisions of $\sin^2\theta'$; 0.03, 0.1-0.9 with an interval of 0.1 and 0.92-0.98 with an interval of 0.02, where θ' is the reflection angle. These divisions are selected to enable easy plotting of the r_D curves. In the previous study, the irregularity and the limited number of the corresponding values of $\sin^2\theta'$ led to a dissatisfactory result of plotting the same curves. The average of the two cases of the Gaussian divisions of $2n=26$ and 28 is adopted as the final results. The same data as in reference[12] on the vehicle, specular substrate (Al) and the pigments (TiO_2 , Fe_2O_3) are used in calculations.

The results for the present case of $\tau_1 = \infty$ are shown in Figs. 2 to 6. The effect of the pigment volume concentration v (including the wavelength dependence, the absorption by the pigment and the absorption by the vehicle) on r_D is shown in Figs. 2(a) and 2(c). In the case of $\lambda=0.45\mu\text{m}$ of Fig. 2(a) the curves of r_D for TiO_2 are directed predominantly towards the normal direction due to the directional characteristics of the phase function $p(\cos\theta)$ and r_D increases with v . The value of r_D for Fe_2O_3 is much smaller than that for TiO_2 due to the large absorption of Fe_2O_3 , which also leads to a smaller effect of v . Fig. 2(b) and 2(c) show the results at longer wavelength ($\lambda=1.0$ and $2.2\mu\text{m}$) where still a considerable scattering exists. Since the vehicle exhibits noticeable absorption at $\lambda=2.2\mu\text{m}$, r_D for TiO_2 is small for all values of v in comparison with the results at $\lambda=1.0\mu\text{m}$. The effect of the vehicle absorption becomes stronger in the case of the smaller pigment volume concentration. Quantitative account of the effect of the vehicle absorption is clear in view of the indicated values of the scattering albedo ω for TiO_2 . Comparison of the results for

Fe_2O_3 at $\lambda=1.0\mu\text{m}$ with those at $\lambda=2.2\mu\text{m}$ shows a clear difference between the effects of the absorption by the pigment and the absorption by the vehicle. The total absorption by the pigment is strongly related to v while the total absorption by the vehicle is strongly related to $(1-v)$. In Fig. 2 and the following discussion, the pigment volume concentration v is limited to a maximum value of 0.55 which corresponds to the critical value of pigment volume concentration[15]. It must be emphasized that in considering such large concentrations, we neglect the effect of the interference between the scattered fields of pigment particles[12]. However, we consider the results for large values of v in the comparison with the exact experimental results of optically thick painted layers which may be available in the future to investigate the interference effect accurately. The wavelength dependence of R_h is shown in Figs. 3 and 4. The results for TiO_2 in Fig. 3 indicate the following: (a) The curves of R_h coincide with each other at $R_h=1$ in the range of $\lambda=0.65-0.70\mu\text{m}$ where neither the pigment nor the vehicle absorbs. (b) R_h decreases to a large extent due to the absorption by TiO_2 in the range of $\lambda=0.35-0.40\mu\text{m}$. (c) The difference between R_h and ρ_1 (the specular reflectance), representing R_D , is affected mainly by scattering by the pigment and the absorption by the vehicle in the near infrared region. In the infrared region of $\lambda>7.0\mu\text{m}$ the scattering by the particles is less or negligible and the absorption by the vehicle and the pigment becomes dominant. Thus R_h is limited to the specular reflectance ρ_1 for all values of v . Similar discussion can be made on the results of Fe_2O_3 in Fig. 4, except the strong absorption by the pigment in the visible region which leads to a small effect of v .

Fig. 5 shows the wavelength dependence of the diffuse ratio as defined by R_D/R_h . Since the specular reflectance ρ_1 is small compared with R_D in the visible and near infrared regions, R_D/R_h is slightly affected by the variation of v . On the contrary, since ρ_1 is comparable to R_D due to the ve-

Fig.10 $1/\tau_1$ dependence of R_h in visible region (effects of v , optical properties of the pigment and reflection properties of the substrate)

Fig.11 $1/\tau_1$ dependence of R_h in near infrared region (effect of v and reflection properties of the substrate)

hicle absorption in the infrared region, a clear effect of v is recognized.

Shown in Fig.6 is a trial to generalize the effects of v , the optical properties of the pigment and the wavelength on R_h for a painted layer of $\tau_1 = \infty$. The scattering albedo $\tilde{\omega}$ is selected to combine these parameters. The plots shown include the results for the whole range of wavelength λ in the present study (0.35–20 μm) with v varying from 0.005 to 0.55. From the plot of ρ_1 vs λ shown in Fig.3 one can consider the reflectivities ρ_u to be nearly independent of λ . Consequently the solution of the transfer equation Eq.(1) (with the boundary condition Eq.(2)) in the case of isotropic scattering ($p(\cos\theta)=1$) leads to the relation of

$$R_h = R_h(\tilde{\omega}) \quad (27)$$

Thus the point $\circ$ and $\bullet$ denoting nearly isotropic scattering ($1.2\mu\text{m} < \lambda < 2.2\mu\text{m}$) can be plotted in a single solid line which expresses Eq.(27). For $\lambda < 1.2\mu\text{m}$ the scattering by single particle is anisotropic and predominantly directed forward. Then the amount of the absorption by either the pigment or the vehicle becomes larger than that for the

isotropic scattering, which results in smaller R_h . Thus the corresponding points Δ and $\blacktriangle$ lie below the solid line. On the other hand, for $\lambda > 2.2\mu\text{m}$ the anisotropy of the scattering is slightly directed backward. This causes a smaller amount of the absorption by the pigment and/or the vehicle, compared with the case of isotropic scattering. Thus R_h shows a little increase compared with that of the isotropic case for the same value of $\tilde{\omega}$. Hence, the points $\square$ and $\blacksquare$ lie above but near the solid line.

Fig.7~9 show dependence of R_h and R_D/R_h on τ_1 . The results for the effect of the reflection properties of the substrate are shown in Fig.7. At the wavelength of $\lambda = 0.7\mu\text{m}$, neither the pigment (TiO_2) nor the vehicle absorbs, the only absorption being by the substrate which is influenced by the scattering characteristics of the pigment particles in the layer. In the case of specular substrate (Al), beginning from $\tau_1 = 0$, R_h decreases at first with an increase of τ_1 . This is due to the combined effect of the scattering by the pigment particles and the total reflection at the air-vehicle interface, which increases the absorption by the substrate. But further increase in τ_1 which corresponds to an increase of the scattering centers (accordingly an increase of the contribution to the back scatter) decreases the absorption by the specular substrate and R_h increases continuously. In the case of diffuse substrate ($\rho_D = 0.1$), a continuous increase of R_h with an increase in τ_1 from $\tau_1 = 0$ can be explained by the diffuse reflection at the substrate together with the total reflection at the air-vehicle interface which increases the absorption by the diffuse substrate. The effect of diffuse reflection is always offset by the back scatter produced by an increase of the scattering centers as τ_1 increases. The ratio R_D/R_h increases with an increase in τ_1 for both specular and diffuse substrates. The constant values of $R_h = 1$ and $R_D/R_h = 0.958$ for $\rho_D = 1$ represent the asymptotic values as $\tau_1 \rightarrow \infty$ for both the specular substrate and the diffuse substrate with $\rho_D < 1$. For quantitative comparison between specular and diffuse substrate cases, the results for $\rho_D = \rho_2 = 0.813$ are shown, where the specular hemispherical reflectance of Al metal substrate is approximated by the normal specular reflectivity ρ_2 . The results for two cases come close to each other as τ_1 increases and they nearly coincide at $\tau_1 > 6$. Figs.8 and 9 show the effect of the pigment volume concentration v . At the same wavelength the variation in $\tilde{\omega}$ is only related to the variation in v by the relation⁽¹²⁾

$$\tilde{\omega} = vK_{sp} / \{vK_{ep} + (1-v)K_{av}\}, \quad (28)$$

while the variation in τ_1 results from both the variations in v and in the thickness L of the layer by the relation

$$\tau_1 = L\{vK_{ep} + (1-v)K_{av}\}. \quad (29)$$

The results for $\lambda = 0.45\mu\text{m}$ are summarized in Fig.8. At this wavelength a considerable scattering exists while there is no absorption by the pigment but a weak absorption by the vehicle. For small values of v (0.005, 0.01), R_h decreases continuously with τ_1 from

the initial value at $\tau_1=0$ and approaches the corresponding asymptotic value $R_h(\tau_1=\infty)$ as $\tau_1 \rightarrow \infty$. On the other hand for large values of $v(0.03, 0.4)$ R_h decreases with τ_1 to a minimum and then increases continuously to the asymptotic values as $\tau_1 \rightarrow \infty$. These characteristics of the dependence of R_h on τ_1 are due to the combined effects of (a) the absorption by the metallic substrate (Al) which decreases at large τ_1 ; (b) the absorption by vehicle which increases with τ_1 and decreases with v ; and (c) the back-scatter by the pigment particles which increases with both v and τ_1 . The broken line represents the substrate effect at $\lambda=0.65\mu\text{m}$ (with nearly the same scattering characteristics as for $\lambda=0.45\mu\text{m}$) where $\tilde{\omega}=1$ for all values of v . Similar discussion can be made for the results at $\lambda=2.2\mu\text{m}$ in Fig.9, except for a considerable absorption by vehicle represented by smaller values of $\tilde{\omega}$ compared with those at $\lambda=0.45\mu\text{m}$. Correspondingly R_h for smaller values of $v(0.005, 0.01)$ reaches the asymptotic value below $\tau_1=9$. Negligible effect of v is recognized on the dependence of R_D/R_h on τ_1 at $\lambda=0.45\mu\text{m}$ while at $\lambda=2.2\mu\text{m}$, a considerable effect of v is recognized.

In Figs.10 and 11 the results for R_h are plotted against $(1/\tau_1)$ to include the case of $\tau_1=\infty$ ($1/\tau_1=0$). The limit of $\tau_1=9$ due to the overflow problem is indicated by the vertical line. The curves shown are ones interpolated between $\tau_1=9$ ($1/\tau_1=0.11$) and $\tau_1=\infty$ ($1/\tau_1=0$) following the tendency shown by the available results for $\tau_1<9$. This procedure provides us with the values of R_h for $\tau_1>9$ which could not be obtained previously due to the overflow problem⁽¹²⁾ in the calculation procedure. It must be noticed that the rate of the approach to the asymptotic value depends mainly on the scattering albedo $\tilde{\omega}$. Also the increasing or decreasing tendency of R_h depends on the reflection properties of the substrate as indicated by Al for the specular substrate, or $\rho_D=0, 0.5$ and 1.0 for the diffuse substrate.

6. Conclusions

The reflection properties of an optically thick painted layer have been studied theoretically. The summary of the results is given below.

- (1) The pigment volume concentration v affects significantly the bidirectional and hemispherical reflectances for the case of $\tau_1=\infty$. The absorption by the vehicle enhances this effect of v for the case of $\tau_1=\infty$ and the absorption by the pigment on the other hand decreases or diminishes this effect.
- (2) The hemispherical reflectance R_h for $\tau_1=\infty$ can be obtained as a function of the scattering albedo $\tilde{\omega}$ in the region of the wavelength corresponding to nearly isotropic scattering by the pigment particles.
- (3) For a painted layer on specular substrate the hemispherical reflectance R_h is affected by the absorption by the substrate. The effect of the absorption by the substrate increases at first and then decreases till it vanishes as the total optical thickness τ_1 increases to ∞ . In the case of the diffuse substrate, a continuous decrease of the effect of the absorption by the substrate can be

seen as τ_1 increases from 0 to ∞ .

- (4) The combined effect of the absorption by the pigment or the vehicle (as expressed by the scattering albedo $\tilde{\omega}$) and the predominance of the forward scattering by a single particle of the pigment together with the effect of the absorption by the substrate determines the limit of τ_1 at which the layer can be regarded as infinitely optically thick, and R_h can be obtained by calculations for the case of $\tau_1=\infty$.

- (5) The values of R_h for a painted layer of finite τ_1 larger than the limit value caused by the overflow problem in the computer calculations can be obtained by the interpolation procedure between the result for the limit value and that for $\tau_1=\infty$.

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Appendix A: The functions in the expression for the intensity $I(0, \mu)$

The source function $S(t, \pm\mu)$ in the case of a painted layer with specular substrate can be written as

$$S(t, \pm\mu) = \frac{\tilde{\omega}}{2} \sum_{j=1}^{2n} w_j q(\pm\mu, \mu_j) I(t, \mu_j) + H_1(\pm\mu) \exp(-t) + H_2(\pm\mu) \exp(-t), \quad (A1)$$

$$q(\pm\mu, \mu_j) = \frac{\tilde{\omega}}{2} \sum_{k=0}^m c_k P_k(\pm\mu) P_k(\mu_j) \quad (A2)$$

$$H_1(\pm\mu) = \frac{1-\rho_1}{1-\rho_1\rho_2\exp(-2\tau_1)} \frac{\tilde{\omega}}{4\pi} \sum_{k=0}^m c_k P_k(\pm\mu) \cdot (-1)^k \quad (A3)$$

$$H_2(\pm\mu) = \frac{\rho_2(1-\rho_1)\exp(-2\tau_1)}{1-\rho_1\rho_2\exp(-2\tau_1)} \frac{\tilde{\omega}}{4\pi} \sum_{k=0}^m c_k P_k(\pm\mu) \quad (A4)$$

Accordingly the functions appearing in the expression for $I(0, \pm\mu)$ in this case can be defined by

$$A_\alpha = \sum_{j=1}^{2n} w_j b_{j\alpha} q(-\mu, \mu_j) \quad (A5)$$

$$B_\alpha = \sum_{j=1}^{2n} w_j b_{j\alpha} q(+\mu, \mu_j) \quad (A6)$$

$$A_0 = H_2(-\mu) + \sum_{j=1}^{2n} w_j s_j q(-\mu, \mu_j) \quad (A7)$$

$$B_0 = H_1(-\mu) + \sum_{j=1}^{2n} w_j t_j q(-\mu, \mu_j) \quad (A8)$$

$$C_0 = H_2(+\mu) + \sum_{j=1}^{2n} w_j s_j q(+\mu, \mu_j) \quad (A9)$$

$$D_0 = H_1(+\mu) + \sum_{j=1}^{2n} w_j t_j q(+\mu, \mu_j) \quad (A10)$$

$$\psi_\alpha = \frac{\rho_\alpha - \mu}{1 + \mu \gamma_\alpha} [\exp\{\gamma_\alpha \tau_1 - (\tau_1/\mu)\} - \exp(-2\tau_1/\mu)] \quad (A11)$$

$$\phi_\alpha = \{1/(1 - \mu \gamma_\alpha)\} [1 - \exp\{\gamma_\alpha \tau_1 - (\tau_1/\mu)\}] \quad (A12)$$

$$\psi_0 = \frac{\rho_0 - \mu}{1 + \mu} [\exp\{\tau_1 - (\tau_1/\mu)\} - \exp(-2\tau_1/\mu)] \quad (A13)$$

$$\phi_0 = \frac{\rho_0 - \mu}{1 - \mu} [\exp\{-\tau_1 - (\tau_1/\mu)\} - \exp(-2\tau_1/\mu)] \quad (A14)$$

$$\chi_0 = \{1/(1 - \mu)\} [1 - \exp\{-(\tau_1/\mu) + \tau_1\}] \quad (A15)$$

$$\eta_0 = \{1/(1 + \mu)\} [1 - \exp\{-(\tau_1/\mu) - \tau_1\}] \quad (A16)$$

Similarly the functions for $I(0, +\mu)$ in the case of a painted layer with the diffuse substrate ($\rho_2=0$) can be defined by

$$A'_\alpha = \{1/(\mu \gamma_\alpha - 1)\} \sum_{j=1}^{2n} w_j b_{j\alpha} q(+\mu, \mu_j) \quad (A17)$$

$$C'_\alpha = A'_\alpha + 2\rho_D \sum_{j=n+1}^{2n} w_j |\mu_j| b_{j\alpha} \quad (A18)$$

$$A'_0 = \frac{H_1(+\mu)}{1 + \mu} + \frac{1}{1 + \mu} \sum_{j=1}^{2n} w_j t_j q(+\mu, \mu_j) \quad (A19)$$

$$C'_0 = 2\rho_D \sum_{j=n+1}^{2n} w_j |\mu_j| t_j + \frac{\rho_D}{\pi} (1 - \rho_1) - A'_0 \quad (A20)$$

The functions for $I(0, +\mu)$ in the case of $\tau_1 = \infty$ ($\rho_2=0$) can be defined by

$$E_\alpha = \sum_{j=1}^{2n} w_j b_{j\alpha} q(+\mu, \mu_j) \quad (A21)$$

$$E_0 = H_1(+\mu) + \sum_{j=1}^{2n} w_j t_j q(+\mu, \mu_j) \quad (A22)$$

Appendix B: Spatial distribution of the intensities $I(\tau, \pm 1)$ and the net flux $F(\tau)$ inside an optically thick layer

The expressions for the outward normal and inward normal intensities $I(\tau, +1)$ and $I(\tau, -1)$, respectively, are derived by substituting $\mu=1$ and $\tau_1=\infty$ in Eqs. (10) and (11) and proceeding similarly to $I(0, +\mu)$. The net flux $F(\tau)$ is given by

$$F(\tau) = \int_{4\pi} I(\tau, \mu) \mu d\Omega \approx 2\pi \sum_{j=1}^{2n} w_j \mu_j I(\tau, \mu_j) \quad (B1)$$

Figure 12 shows the enhanced effect of the scattering albedo $\tilde{\omega}$ on the numerical results calculated for a painted layer containing TiO_2 pigment and normally irradiated by a unit incident flux. A clear effect of the scattering phase function can be noticed by comparing the results between the cases of predominant forward ($\lambda=0.45\mu\text{m}$) and predominant backward scattering ($\lambda=2.4\mu\text{m}$).

Fig.12 Effect of $\tilde{\omega}$ on $I(\tau, \pm 1)$ and $F(\tau)$