Extraction of Characteristics of Solid Pigments from Paint Samples

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Abstract

Modern automotive paints have a complex structure and consist of a variety of pigments including the solid ones. There are many tasks related to the correct color reproduction of the automotive paints. But the most practical one is the color matching: obtaining of paint composition needed to get the specified color. This task can be solved with help of lighting simulation inside paint structure. But we have to know optical properties of the paint pigments to do so. In the paper we propose and verify robustness of several different methods to extract pigment properties from the measured BRDFs. All methods are based on fitting of calculated visual appearance to the measured one. The methods differ in sets of the real paint samples which have to be prepared to extract pigment data. We describe operation of the methods and verify their robustness. It happened that among proposed methods one is much more accurate, while others produced significant errors.

Keywords

Color matching, visual appearance, radiative transfer, paint, solid pigment, measurement, fitting.

1. Introduction

Modern automotive paints have a complex structure and consist of a variety of pigments of various nature, such as interference plates, mirror flakes and ordinary solid pigments. Visual appearance is the main characteristic of paint, and it manifests itself through the human perception of objective optical properties: color, brightness (reflection coefficient), glossiness, texture (spatial heterogeneity), etc. In the general case the visual characteristics of a painted surface are expressed by a bidirectional reflectance distribution function (BRDF). Many works are devoted to the problem of correctly displaying the appearance of paints. For example, the authors of articles [1–3] offer visualization models based on the analysis of photographed images or measurement results of real paint samples.

Another approach is to model the optical properties of multilayer paints with complex microstructures in order to reproduce their appearance. Such modeling is a rather complicated task, and does not always provide the required accuracy. A paint model which consists of plane-parallel homogeneous layers was proposed and developed in [4]. Such a scattering model is based on a statistical approach and accurately describes the interaction of light within the paint, including iridescent and pearlescent effects. This model was subsequently used and developed in [5–7].

One of the most practically needed tasks is the obtaining the paint composition (i.e. set of the necessary pigments and their concentrations) to ensure the specified optical properties, namely the paint color at different angles of illumination and observation. Most often, this task is necessary for body repair work, since the original composition of the paint is almost always unknown. Moreover, even if the composition of the paint is known, the appearance of the painted surface may change over time under the influence of atmospheric agents, reagents used on the roads, etc. As a result, the appearance of the surface may differ from the initial one. Attempts to find an automatic solution for this ambitious task have been undertaken by various teams for more than a decade [8–11]. We also made attempts to solve the problem of determining the paint composition by its appearance [12, 13].

Paint appearance modeling is based on a model of the interaction of light with the medium (paint structure with pigments) and “input” data for this model. So to start simulation we need pigment

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concentrations and optical properties of pigments: scattering, absorption cross sections and phase function. The quality (accuracy and level of details) of input data strongly determine the accuracy of calculations. The concentrations of pigments are more or less known (usually it is known how much was put in paint). But optical characteristics must be measured.

There are two main approaches for this. First, we can measure them as directly as possible. For example, scattering cross section gives amount of light which is scattered by one particle. We prepare a paint sample containing the single pigment in low concentration (to ensure there is single scattering) on a translucent plate. Then illuminate it with a parallel light and measure intensity of scattered light. Its angular distribution is phase function, and its integral is scattering cross section times concentration times paint layer thickness. It is more difficult to measure absorption cross section in such an experiment, but it is also possible.

This procedure is similar to what had been done to measure optical characteristics of smog, snowflakes, fogs, etc. in atmospheric studies. Those experiments were quite successful. But there are additional problems with paints. First, now we measure particles in a refractive medium. The boundary between paint and air distorts light distribution, and makes it impossible to observe scattering directions that cannot leave the medium because of the total internal reflection. Second, reflectance of Fresnel boundary from the paint approaches 1 already for angles more than 45 degrees, i.e. for a wide cone. And all this light is reflected back into the paint, and may not leave it otherwise but being scattered by pigments. Therefore it is impossible to ensure single scattering. Then, usually the front paint surface, even if specially polished, is not ideally flat, and thus Fresnel reflectance from it is diffuse. This diffuse BRDF sums with the BRDF of the paint sample and this may lead to serious distortions [14]. At last, the ultimate goal of the work with paints is color matching. Therefore the error of BRDF calculation must be very low, below eye color fidelity. In atmospheric studies requirements are weaker and easier to satisfy. As a result, the direct measurement of the pigments in the paint layer is not practical while formally possible. Either it is simple but has insufficient accuracy. Or it is too difficult and hardly possible at all.

Another way to get pigment data is fitting. This should work well for solid pigments which phase function is rather simple (often isotropic one) and they are used in paint in high concentration. The fitting method finds those properties of pigment(s) which, when fed into the paint model, produce BRDFs that well match the experiments. So, our method must work as follows: we prepare paint with the pigment at interest and measure this paint. Then we calculate BRDF from a paint model, varying the input parameters, and find those which makes it to better match the measured BRDF. These input data (or parameters recalculated from them) are declared as the pigment properties.

It can be suggested several such methods that use different number of paint samples prepared in different conditions and process their measurements differently. Some alike fitting based methods had been used in the past to obtain scattering properties of turbid plastics [14–17]. Sometimes the results were god but sometimes the calculated BRDFs deviated much from the measured ones. So we may say that the fitting methods have different robustness. The more robust method is less sensitive to the errors of measurements and sample preparation.

In current work we propose and verify robustness of several different methods to extract pigment properties from fitting of the measured BRDFs. We describe their operation and compare their robustness. It happened that among 4 proposed methods one is much more accurate, while others (close to [14–17]) produced large errors in our benchmarks.

2. BRDF of painted surface and what it depends on

In the Light transport equation (LTE) model [18–21], BRDF of the painted surface is calculated from

- refraction and absorption of the binder;
- BRDF of the substrate;
- phase function of medium (weighted sum over all pigments);
- total optical thickness $\tau = \mathrm{k_{ext}H}$ of paint layer; extinction coefficient of the medium $\mathrm{k_{ext}}$ is a weighted sum over all pigments and H is the geometric layer thickness;

- relative absorption $\mathrm{a} = \frac{\mathrm{k_{abs}}}{\mathrm{k_{ext}}}$ of medium; absorption coefficient of the medium $\mathrm{k_{abs}}$ is a weighted sum over all pigments.

Typically refraction of the binder is 1.45 ± 0.05 and absorption is negligible. This small uncertainty does not affect results much and can be neglected (i.e. we can adopt 1.45 and zero absorption). Substrate is typically a nearly Lambert surface so we need only its albedo from binder $\mathrm{r_s}$.

In principle, a phase function can be rather arbitrary. But for the so-called solid pigments it is rather simple and can be well approximated with a Henyey-Greenstein [22] or Rayleigh laws, i.e. effectively it is uniquely determined by the single parameter like Henyey's g (assuming that a value outside $[-1,1]$ means Rayleigh). Our experiments show that isotropic phase function ($g = 0$) gives usually the best results.

Therefore, BRDF is a function of

- phase function p of medium (determined by Henyey's g for all pigments);
- relative absorption $a = \frac{k_{abs}}{k_{ext}}$ of medium;
- total optical thickness $\tau = k_{ext}H$ of paint layer;
- substrate reflectance r_s.

$$BRDF = f(v, u; p, a, \tau, r_s), \tag{1}$$

where v, u are the illumination and observation direction. The same function f works for all wavelength, just for the different values of p, a, τ, r_s which usually depend on wavelength.

For $\tau \to \infty$ (i.e. either very thick layer or very high concentration of pigments) the paint completely hides the substrate and even its own deep sublayers, so

$$BRDF = f(v, u; p, a, r_s), \tag{2}$$

Practically, the limiting τ is about 20 in absence of absorption and decreases to even 2 for usual absorption of colored pigments.

Dependence on the albedo of substrate r_s is analytic. If the substrate surface is Lambert the BRDF obeys

$$f(\boldsymbol{v}, \boldsymbol{u}; r_s) = f(\boldsymbol{v}, \boldsymbol{u}; 0) + \frac{r_s \bar{T}^{(\downarrow)}(\boldsymbol{v}) \bar{T}^{(\uparrow)}(\boldsymbol{u})}{1 - r_s \bar{R}^{(\uparrow)}} \tag{3}$$

where

$$\bar{T}^{(\downarrow)}(\boldsymbol{v}) = \int T^{(\downarrow)}(\boldsymbol{v}, \boldsymbol{u}) u_z d^2\boldsymbol{u}$$

where $T^{(\downarrow)}(\boldsymbol{v}, \boldsymbol{u})$ is BTDF of paint layer while illuminated from air at direction $\boldsymbol{v}$ and observed in the binder at direction $\boldsymbol{u}$. Then,

$$\bar{T}^{(\uparrow)}(\boldsymbol{u}) = \int T^{(\uparrow)}(\boldsymbol{v}, \boldsymbol{u}) v_z d^2\boldsymbol{v}$$

where $T^{(\uparrow)}(\boldsymbol{v}, \boldsymbol{u})$ is BTDF of paint layer while illuminated from binder at direction $\boldsymbol{v}$ and observed in air at direction $\boldsymbol{u}$. At last,

$$\bar{R}^{(\uparrow)} = \int R^{(\uparrow)}(\boldsymbol{v}, \boldsymbol{u}) v_z u_z d^2\boldsymbol{v} d^2\boldsymbol{u}$$

where $R^{(\uparrow)}(\boldsymbol{v}, \boldsymbol{u})$ is BRDF of paint layer while illuminated from binder at direction $\boldsymbol{v}$ and observed in the binder at direction $\boldsymbol{u}$. This is a slight generalization of equation in Section 3.6 of [18] or eq. (11) of [19], see also eq. (201) of [20], which accounts for the asymmetry of the paint layer because of the Fresnel transforming boundary at its top.

One does not need to calculate BRDF for each specific value of r_s but it suffices to know it for three different values of r_s (e.g. black, grey and white) and then any r_s can be "nonlinearly interpolated" from the above law.

It is possible to calculate BRDF for given parameters each time anew using e.g. adding/doubling method [21]. But this is expensive because billions of cases are calculated during fitting. So we can first tabulate dependence of BRDF on τ, a for black and white substrates. BRDF for an arbitrary r_s is then calculated as described in Appendix A1. Notice that this process operates BRDF for one wave length. Later, when interpolating from this data, we apply τ, a and r_s for given wavelength and thus obtain

BRDF for any wavelength. This much accelerates calculations. The interpolation data is then used for all fitting cases for all pigments and substrates.

Phase function of medium is

$$p(\boldsymbol{v}, \boldsymbol{u}) = \frac{\sum_i \sigma_{sc}^{(i)} p^{(i)}(\boldsymbol{v}, \boldsymbol{u})}{\sum_i \sigma_{sc}^{(i)}}$$

where the superscript i enumerates pigments, σ_{sc} is its scattering cross-section and $\boldsymbol{v}, \boldsymbol{u}$ are directions of the incident and scattered rays. Notice for solid pigments phase function actually depends only on the angle between them, i.e. on $(\boldsymbol{v} \cdot \boldsymbol{u})$. In case all pigments have the same parameter g, the resulting phase function is also pure Henyey for that g.

The extinction and absorption coefficients

$$k_{ext} = \sum_i D^{(i)} \sigma_{ext}^{(i)}$$

$$k_{abs} = \sum_i D^{(i)} \sigma_{abs}^{(i)}$$

where the superscript i enumerates pigments, $\sigma_{ext}, \sigma_{abs}$ is its extinction and absorption cross-sections and D is its concentration (i.e. the number of particles per unit volume) in dry paint.

To obtain characteristics of pigments it is natural to prepare and measure samples of paints made of that single pigment (maybe several such samples for different concentrations and substrates). In this case, the optical thickness and relative absorption of paint are

$$\tau = HD\sigma_{ext}, \quad a = \frac{\sigma_{abs}}{\sigma_{ext}}, \tag{4}$$

where D is the dry concentration of the pigment (the number of its particles per unit volume of dry paint) and H is the layer thickness.

According to eq. (2), BRDF of a thick layer is independent of extinction of medium but only on its relative absorption a. In case paint is made from a single pigment $a = \frac{\sigma_{abs}}{\sigma_{ext}}$ so we do not need extinction *per se*. But in case of a mixture of several pigments,

$$a = \frac{\sum_i a^{(i)} D^{(i)} \sigma_{ext}^{(i)}}{\sum_i D^{(i)} \sigma_{ext}^{(i)}}$$

where $a^{(i)} \equiv \frac{\sigma_{abs}^{(i)}}{\sigma_{ext}^{(i)}}$ is the relative absorption of the i-th pigment. Therefore, unless extinction cross-sections of different pigments coincide, the value of a (and thus BRDF of thick layer) does depend on these extinctions.

It should be noted that for calculation it sufficient to know not absolute extinctions, but those relative to some pigment, e.g. 0th

$$a = \frac{\sum_i a^{(i)} D^{(i)} \frac{\sigma_{ext}^{(0)}}{\sigma_{ext}^{(i)}}}{\sum_i D^{(i)} \frac{\sigma_{ext}^{(0)}}{\sigma_{ext}^{(i)}}}$$

3. Methods to extract the pigment’s properties

It is natural (though it is not the single way) to obtain characteristics of pigments by measuring paint samples containing only this single pigment. BRDF of optically thick sample is independent of optical thickness and thus of extinction according to eq. (4). Therefore, to get these data we need a sample with finite (and better small) optical thickness.

In all methods below the fitting procedure is done independently for each wavelength.

3.1. Method 1. Absorption from optically thick sample, extinction from translucent one

Absorption. In case the sample is thick, its BRDF is uniquely determined by the relative absorption a, see eq. (2). Geometric thickness and concentration make no effect, which is good because excludes uncertainty in these parameters. The relative absorption can be then obtained by finding its value which makes the calculated BRDF (eq. (2)) maximally close to the measured one. If one wants to improve accuracy, phase function (parameter g) can be also included in fitting; again independently for each wavelength.

Extinction. Let us apply the paint on a glass (or other translucent) plate and illuminate that plate by a parallel light at normal incidence. The initial beam is both scattered and absorbed inside the layer, so the energy in the parallel beam decreases. Obviously, the fraction of energy remained in the parallel beam (i.e. the specular transmission) is

$$T = t_F^2 e^{-\tau}, \tag{5}$$

where t_F is Fresnel transmittance of the air/glass boundary and τ is the optical thickness of the paint layer. In case of single pigment τ obeys (4) which together with (5) yields

$$\begin{gathered} \tau = -\,log\frac{T}{t_F^2}, \\ \sigma_{ext} = -\frac{1}{HD}log\frac{T}{t_F^2} \end{gathered} \tag{6}$$

for each wavelength.

The fitting requires precise thickness of paint layer and concentration of pigment in dry paint to be known. How to get the latter is explained in Appendix A2. Concentrations.

3.2. Methods 2 and 3. Fitting from BRDF

For not thick sample, BRDF (eq. (1)) depends on all parameters (in practice, a and τ) and therefore it is possible to find their values which provide the best agreement between measured and calculated BRDFs. Here it is possible either to fit all parameters simultaneously, or in two steps, when we first obtain a from elsewhere and then fit only τ. In these methods parameter g of phase function must be postulated. If one needs to fit phase function, one must do the fitting procedure (as defined for the current method) for different g and find the value which minimizes the total fitting error (sum of deviations of measured BRDFs from the calculated ones for all BRDFs).

3.2.1. Method 2. Optically thick and thin samples

We prepare two samples, one is optically thick with completely hidden substrate and another one of low optical thickness (the substrate is visible). Any substrate can be used but typically a black one is better.

Absorption. Absorption is obtained from the thick sample exactly like in the Method 1.

Extinction. We vary τ to find the value such minimizes the deviation of the measured BRDF of the "thin" sample from BRDF (eq. (1)) calculated for this τ and absorption a found above.

3.2.2. Method 3. Both a and τ from one sample

We vary both, a and τ, to find their values that minimize the deviation of the measured BRDF of the input sample from BRDF (eq. (1)). Dependence on τ is stronger for thin samples. Therefore, it is advantageous to use optically thin samples. It is better to use a black substrate. Indeed, if absorption of pigment is low or 0, the paint is white too. Painting a white substrate with a thin layer of white paint makes nearly no effect, so fitting is inaccurate (any values of τ give nearly the same calculated BRDF, so the minimum in discrepancy has very low contrast).

3.3. Method 4. Samples with black and white substrates

As said above, it is difficult to fit τ from only the sample on a white substrate. But for a black substrate, one faces another problem. Roughly, there is a whole set of points τ, a where BRDF is nearly the same: one can compensate a stronger absorption with a thicker layer.

Let's suppose the input BRDF (to be fitted) exactly corresponds to the model eq. (1), e.g. it is just generated by calculation (for test). Then the relief of the deviation as a function of τ, a is a very long and narrow ravine. Discrepancy in the centerline of the ravine is then small and changes along it only slightly. Now suppose the input BRDF deviates from the model (i.e. it cannot be reproduced exactly by the function eq. (1) for any parameters), e.g. just due to the errors of measurement. Then the discrepancy along the centerline of the ravine can have minimum in a different point or do not have a minimum at all.

For paint on a white substrate the situation is the same: there is a thin long ravine with nearly the same BRDF. But its centerline is different from the centerline for the black substrates. And the sum of BRDF discrepancies for the black and white substrates is minimal near the intersection of these centerlines since they are not parallel.

Therefore, in method 4 we prepare two samples of the same concentration and geometric thickness on black and on white substrate. And then we find τ, a which makes the sum of deviations of BRDFs minimal. As explained above, this sum is sensitive to both τ, a and thus the best fit point can be found with a good accuracy.

3.4. Reflectance of substrate from the binder r_s

Calculated BRDF in methods 2, 3, 4 also depends on reflectance of substrate r_s which can be obtained from measurement of the substrate. We can measure the substrate (usually this is a sort of other paint) only from air. Meanwhile, our model operates r_s as an albedo of substrate seen from the binder. The simplest model of the real substrate (plate without paint) is: a Lambert surface coated with a clear binder. In this model BRDF from air has the form eq. (9). We can then find the value of r_s which minimizes the deviation of this calculated BRDF from BRDF measured from air.

Experiments showed that the difference between the found r_s and albedo from air is not very large for white or black substrate, no more than about 10% (relative error). For grey substrate, however, it can be really large.

4. Investigation of robustness of the methods

4.1. Test description

If the model of scattering and measurement has limited accuracy, the extracted properties of pigments differ from the actual values. To estimate the errors we take some arbitrary characteristics of pigment a_0, τ_0 and calculate BRDF for them. After that we distort the input data by scaling each its value x independently

$$x \mapsto (1 + \varepsilon\xi)x \tag{7}$$

This imitates the errors of measurement. Here ξ is Gaussian deviate with zero mean and unit variance and ε is the relative inaccuracy of measurement. If the particular method requires reflectance of substrate, the values close to those from real measurements are chosen: $r_s = 0.01$ for black substrate and $r_s = 0.95$ for white substrate. These values were not subject to random variation.

The distorted input data were processed by the described methods. The procedure "distortion => fitting" was repeated 1000 times obtaining each time new (random) a and τ. We then calculate their average and sample variance. Obviously $\langle a \rangle - a_0$ (or $\langle \tau \rangle - \tau_0$) is the systematic error while the RMS is the stochastic error.

For the method 3 the scheme is exactly as described.

For the method 1 we generate BRDF of the optically thick paint sample with the chosen absorption a_0. Then subject each BRDF value to the random distortion (7) and fit a from this distorted BRDF.

There is no simple analytic law for its variation with respect to the change of the input data (BRDF of the thick sample), so they were calculated numerically.

Also specular transmittance to be measured in the method 1 is given by (5) for the chosen τ_0. According to the general scheme we subject this transmittance to random distortion (7) and calculate τ from the resulting value by (6). This gives

$$\tau = \tau_0 - \log(1 + \varepsilon\xi) \approx \tau_0 - \varepsilon\xi + \varepsilon^2\xi^2/2$$

Therefore the result τ is a random deviate with mean $\langle\tau\rangle = \tau_0 + \varepsilon^2/2$ and RMS ε.

For the method 2 we generate two BRDFs for the chosen a_0: one for the chosen optical thickness τ_0 and another for very large optical thickness. Then subject each value of BRDFs to the random distortion (7). We first fit a from the perturbed BRDF of the thick sample and then fit τ from the perturbed BRDF of the thin sample, keeping a found from the thick BRDF.

For the method 4 we generate two BRDFs for the chosen a_0, τ_0: one for black and another one for white substrate. Then subject each value of BRDFs to the random distortion (7) and fit both a, τ minimizing the sum of deviations (from the input BRDFs) for the black and white samples.

4.2. Results of the tests

It happened that in all cases the stochastic error was much greater than the systematic shift, so it determines the overall inaccuracy. The tables below list only the stochastic error (as it is the largest) for several pairs (a_0, τ_0) and $\varepsilon = 0.05$ which imitates a 5% error of measurements.

Table 1 represents the randomness of a_0 keeping τ_0 value fixed. Contrary, Table 2 represents the randomness of τ_0 keeping $a_0$value fixed. Minimal error is bolded for each experiment.

Table 1: Stochastic errors for 5% randomness of a_0

Column 1	$a_0 = 0.025$	$a_0 = 0.1$	$a_0 = 0.2$
$\tau_0 = 0.5$ *(fixed)*			
Method 1	**0.001**	**0.003**	**0.003**
Method 2	**0.001**	**0.003**	**0.003**
Method 3	0.055	0.079	0.104
Method 4	0.002	**0.003**	**0.003**
$\tau_0 = 1$ *(fixed)*			
Method 1	**0.001**	0.003	**0.003**
Method 2	**0.001**	0.003	**0.003**
Method 3	0.028	0.047	0.058
Method 4	**0.001**	**0.002**	**0.003**
$\tau_0 = 2$ *(fixed)*			
Method 1	**0.001**	0.003	**0.003**
Method 2	**0.001**	0.003	**0.003**
Method 3	0.015	0.029	0.036
Method 4	**0.001**	**0.002**	**0.003**

Table 2: Stochastic errors for 5% randomness of τ_0

Column 1	$\tau_0 = 0.5$	$\tau_0 = 1$	$\tau_0 = 2$
$a_0 = 0.025$ *(fixed)*			
Method 1	0.050	0.050	**0.050**
Method 2	**0.008**	0.025	0.115
Method 3	1.500	4.060	6.783
Method 4	**0.008**	**0.021**	0.079
$a_0 = 0.1$ *(fixed)*			
Method 1	0.050	0.050	**0.050**
Method 2	0.011	0.044	2.456
Method 3	1.908	5.007	7.409

Continuation of the table 2

Method 4	**0.008**	**0.023**	0.160
$a_0 = 0.2$ *(fixed)*			
Method 1	0.050	0.050	**0.050**
Method 2	0.014	0.075	3.773
Method 3	2.287	5.921	7.339
Method 4	**0.008**	**0.025**	3.291

One can see that in most cases the best is the method 4 which expectedly works quite well for not too large optical thickness, i.e. it is the least sensitive to the errors of measurement. The method 1 is the next. It can work well with high optical density. The methods 2 and 3 are bad as produce inadmissible errors.

5. Conclusion

Color matching is the most practically needed tasks in the area of the paint color visualization and processing. Its goal is to obtain the paint composition (i.e. set of the necessary pigments and their concentrations) to ensure the specified paint color at different angles of illumination and observation. Paint appearance modeling used in the color matching is based on a model of the interaction of light with the paint structure and the paint pigment data. Additional difficulty is that in many cases the paint producer can only use limited set of really existent pigments. So to start simulation we first of all need to know optical properties of pigments. So the problem of acquisition of data of the real paint pigments arises.

We proposed four methods to extract pigment properties from fitting of the measured BRDFs. For these methods a set of real painted samples should be prepared and measured. Both the sample preparation and measurement can be difficult and may introduce additional error into process of pigment data acquisition. This is why so important to know the robustness of methods. We describe the proposed methods and studied their robustness to the measurement error up to 5%. It happened that one method (the method 4 when the samples with black and white substrate are used) among four proposed ones is much more accurate. Others produced large errors in our tests. Therefore it would be reasonable to start with the method 4 if we need to extract the paint pigment data.

6. Appendices

6.1. Appendix A1. The effect of Fresnel boundary

Paint has a front Fresnel air-binder boundary which is absent in classic studies of volumetric scattering [18–20]. To apply their results, we must first derive the relation between the whole BRDF (accounting for the Fresnel boundary) from the pure layer BRDF whose top boundary is "dummy" i.e. does not change radiation incident on it from either side.

This relation is rather simple and follows from the self-consistent integral equation for radiation just beneath the Fresnel boundary. The equation can be derived similarly to Section 3.6 of [18], only now we have the Fresnel boundary instead of the scattering layer and the pure scattering layer instead of the substrate surface. It is equivalent to the procedure of combination of sublayers (now Fresnel boundary and the pure layer) used in the adding method [21].

Let the air-binder surface be illuminated from air by the parallel beam with direction $\boldsymbol{v}_0$ and unit flux. Denote the luminance at the top boundary of the pure pigment layer (inside binder) as $L(\boldsymbol{u})$. It obeys the self-consistent equation

$$L(\boldsymbol{u}) = t_F(\boldsymbol{v})R(\boldsymbol{v},\boldsymbol{u}) + \int r_F(\boldsymbol{u}')L(\boldsymbol{u}')u'_z R(\boldsymbol{u}',\boldsymbol{u})d^2\boldsymbol{u}' \tag{8}$$

where $R(\dots)$ is BRDF without Fresnel boundary (but maybe with substrate), t_F and r_F are transmission and reflection of that boundary for light going from the binder to air, and $\boldsymbol{v}$ is how $\boldsymbol{v}_0$ refracts into the binder.

Luminance observed from air is naturally

$$\mathcal{L}(\boldsymbol{u}_0) = \eta^{-2} t_F(\boldsymbol{u}) L(\boldsymbol{u})$$

where $\boldsymbol{u}_0$ is direction of observation in air and $\boldsymbol{u}$ is its refraction into the binder, η is refraction of the binder. On the other hand, this luminance is the full BRDF (including Fresnel boundary): $\mathcal{L}(\boldsymbol{u}_0) = f(\boldsymbol{v}_0, \boldsymbol{u}_0)$ so we can obtain the latter.

The above integral equation can be solved numerically.

While our equations require reflectance of the substrate from binder, we cannot measure it. In case the substrate is a Lambert surface, its albedo from binder can be extracted from measurement of the substrate coated with a layer of clear binder. Indeed, now we have formally the case of paint layer with zero concentration of pigment and can use the above formulae. If the substrate is Lambert (from binder!), this means BRDF of the layer without Fresnel boundary obeys $R(\boldsymbol{v}, \boldsymbol{u}) = \frac{r_s}{\pi}$. Substituting it in (8) one sees $L(\boldsymbol{u})$ is independent from $\boldsymbol{u}$ and then this constant is easily calculated as

$$L = t_F(\boldsymbol{v}) \frac{\frac{r_s}{\pi}}{1 - \frac{r_s}{\pi} \int r_F(\boldsymbol{u}') u'_z d^2 \boldsymbol{u}'}$$

which yields BRDF from air

$$f(\boldsymbol{v}_0, \boldsymbol{u}_0) = \eta^{-2} t_F(\boldsymbol{u}) t_F(\boldsymbol{v}) \frac{\frac{r_s}{\pi}}{1 - \frac{r_s}{\pi} \int_0^{\pi/2} r_F(\sigma) \cos\sigma \sin\sigma \, d\sigma} \tag{9}$$

The factor η^{-2} is the usual transformation of the beam luminance by refraction. BRDF from air is not exactly Lambert but close to it save for the cutoff factor $t_F(\boldsymbol{u}) t_F(\boldsymbol{v})$ which is essential only at grazing angles.

6.2. Appendix A2. Concentrations

The concentrations *D* are the number of pigment particles per unit volume of dry paint. In our formulae we always need only product $D\sigma_{ext}$.

The mass fraction PWC of a pigment is

$$PWC = \frac{D\mu}{\rho}, \tag{10}$$

where μ is the average mass of one particle and ρ is specific gravity of the mixed paint. There is PWC (and concentration) in dry paint and in wet paint.

$$\begin{aligned} PWC_{wet}^{(i)} &= \frac{M_{paste}^{(i)}}{M_{binder} + \sum_j M_{paste}^{(j)}} \\ PWC_{dry}^{(i)} &= \frac{m_{paste}^{(i)}}{m_{binder} + \sum_j m_{paste}^{(j)}}, \end{aligned} \tag{11}$$

where the superscript enumerates pigments, the lowercase m stands for the dry mass and the uppercase M means the wet mass.

While mixing the physical paint, one usually knows the mass fraction of the pigment paste (not the pure pigment) in wet paint. We must first convert it to the PWC in dry paint. Then we must calculate ρ as a function of that mass fraction. And then we can get *D*. It will be determined up to the (unknown in principle) scale factor μ. Then the obtained extinction value will be μ times smaller than the actual value; this is OK. We can adopt, for example, $\mu = 1$.

We assume the dry paint consists of the dried binder and the dried pigment paste that, in turn, consists of the pure pigment such as titanium oxide and resin. When mixing any substances their masses sum up. The volume, however, may differ from the sum of volumes if substances are solvable. The change is small when mixing similar organic resins, and when a pigment paste is mixed with a binder, their volumes sum up. This holds for both wet and dry paint. Under such assumptions the density of the dry paint is

$$\rho = \frac{m}{V} = \frac{\sum_j m_{paste}^{(j)} + m_{binder}}{\sum_j V_{paste}^{(j)} + V_{binder}} = \frac{\sum_j m_{paste}^{(j)} + m_{binder}}{\sum_j \frac{m_{paste}^{(j)}}{\rho_{paste}^{(j)}} + \frac{m_{binder}}{\rho_{binder}}}$$

Introducing coefficients of drying $q = m/M$ which are rather easy to measure, and using (11) one has

$$\rho = \frac{\sum_j q_{paste}^{(j)} PWC_{wet}^{(j)} + q_{binder}\left(1 - \sum_j PWC_{wet}^{(j)}\right)}{\sum_j \frac{q_{paste}^{(j)}}{\rho_{paste}^{(j)}} PWC_{wet}^{(j)} + \frac{q_{binder}}{\rho_{binder}}\left(1 - \sum_j PWC_{wet}^{(j)}\right)}, \tag{12}$$

where naturally $1 - \sum_j \mathrm{PWC}_{wet}^{(j)}$ is the weight fraction of the binder in the wet paint.

The mass fraction of the pure pigment in the dry paint is meanwhile

$$\mathrm{PWC}^{(i)} = \frac{C_{pp}^{(i)} m_{paste}^{(i)}}{\sum_j m_{paste}^{(j)} + m_{binder}} = \frac{C_{pp}^{(i)} q_{paste}^{(i)} \mathrm{PWC}_{wet}^{(i)}}{\sum_j q_{paste}^{(j)} \mathrm{PWC}_{wet}^{(j)} + q_{binder}(1 - \sum_j \mathrm{PWC}_{wet}^{(j)})}$$

where C_{pp} is the mass fraction of the pure pigment in the dry pigment paste.

Substituting this formula and (12) into (10), one can now derive the concentration of pigment $D^{(i)}$ we need for the optical model

$$D^{(i)} = \frac{C_{pp}^{(i)}}{\mu^{(i)}} \frac{q_{paste}^{(i)} \mathrm{PWC}_{wet}^{(i)}}{\frac{q_{binder}}{\rho_{binder}} + \sum_j \left(\frac{q_{paste}^{(j)}}{\rho_{paste}^{(j)}} - \frac{q_{binder}}{\rho_{binder}}\right) \mathrm{PWC}_{wet}^{(j)}}$$

where the term $\frac{C_{pp}}{\mu}$ for each pigment is usually unknown, but it is a constant scale factor for concentration and independent of the paint composition. So we can assume this factor to be 1, and then extinction of pigment σ_{ext} will be inversed scale by that constant factor. This is admissible because the optical calculations use the combination $D\sigma_{ext}$ only. This combination is independent of the value $\frac{C_{pp}}{\mu}$.

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