MICROSTRUCTURE OF WEATHERED PAINT AND ITS RELATION TO GLOSS LOSS: COMPUTER SIMULATION AND MODELLING

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Abstract. The role of pigment particle size, pigment volume concentration and dispersion in gloss loss of paint films on weathered surfaces is unclear. Because reproducibile and cost effective data is difficult to obtain, an approach based on computer simulation and modelling is a promising supplementary tool. We describe the simulation of a painted surface consisting of pigment particles of known size, pigment volume concentration and dispersion, situated in a binder that erodes over time due to exposure to ultraviolet radiation. Pigment particle size, geometry, pigment volume concentration and pigment particle dispersion are parameters of the model. Our purpose is to illustrate how simulation can be used to aid the development of formulation strategies for the design of coatings with desirable gloss characteristics.

1. INTRODUCTION. The task of defining gloss is a dificult one, involving a consideration of issues from a number of scientific areas including, physics, chemistry, the physiology of vision, and psychophysics. In a consumer product context, we obviously want to isolate the observable and quantifiable characteristics of product appearance associated with high customer appeal. In the coatings industry, particularly that part concerned with automobiles, gloss has traditionally been considered to be such a quantity. J. Braun [1] focused on two factors that define gloss; first, the intensity of an image, controlled by the refractive index of the surface and angle of illumination, and secondly the distinctness of image (DOI) which is assumed here to be controlled by surface roughness. Most glossmeters measure intensity but from a human point of view DOI is the salient characteristic. Indeed, it is well known that human beings are capable of sensing DOI with an accuracy that is several orders of magnitude better than the best available measuring devices ([1] and also see the earlier reference [2]). Despite this, as Braun notes the two correlate well enough to identify them for the purposes of paint characterization.

Our purpose here is to investigate the effects of initial coating characteristics on the subsequent gloss loss of a painted surface that erodes during weathering and exposure to Ultraviolet Light. The theory presented in [1] and [3] assume gloss loss occurs while the paint film is drying and aging. However Braun and Cobranchi in [3] concede that the end of the aging process is likely to coincide with the beginning of weathering. And it is quite reasonable to assume, we believe, that some surface gloss is still present and is lost as erosion proceeds. In all cases we suppose the mechanism for gloss loss is surface roughening so the coating characteristics that we will be most concerned with are those that affect the surface structure of the film and the layers of coating that are exposed in the weathering process. An experimental approach to this problem would involve determining the surface structure of the paint film, measuring the degree of gloss, and then systematically varying the surface structure by varying the paint composition to identify the relationship between surface structure, paint composition and gloss loss over time. Experiments of this type are expensive,time consuming and involve a multiplicity of variables. Here simulation and modelling can play a role. By examining an albeit simplified caricature of the weathering process, we hope to identify relationships between a limited number of coating characteristics and gloss (as measured by surface roughness). By quantifying these relationships we hope to organize some of the relevant coating variables that would need to be a part of any experimental effort. Generally, the conclusions of a simulation effort can serve as hypotheses to be tested and the formulation of mathematical models sharpen the experimental design process;

helping to distinguish the important variables from the less important.

This paper will describe the results of a simulated erosion of a coating consisting of spherically shaped titanium dioxide pigment particles embedded in a polymer binder. For simplicity we follow the changes in a two dimensional section of the coating calculating the roughness in terms of the standard deviation of the surface heights. The microcstructure of the simulated coating is characterized by the pigment particle diameters, pigment volume concentration and pigment dispersion. The latter is modeled by adjusting the minimum nearest neighbor distance or when studying flocculation, the mean number of pigment particles per cluster. Gloss (as expressed in terms of roughness) is studied over time as a function of the variables determining the microstrucuture of the unweathered paint film. Our results support the contention that paint films composed of large numbers of small well dispersed pigment particles retain gloss best. This advantage holds (after an initial transient period) throughout the weathering process.

2. DESCRIPTION OF SIMULATION:. The two dimensional simulation begins with a 900 x 400 array of pixels representing a two dimensional cross section of a paint film consisting of polymeric binder and pigment particles that are randomly placed in the binder subject to the constraints of a prespecified pigment volume concentration (PVC). At present the pigment particles are either spherically or disk shaped, the latter used in metallic finishes, and vary in size from a diameter of 0.1 -0.3 μm for titanium dioxide particles, to 100-300 μm for metallic particles. In the program the diameters of titanium dioxide range from 15 to 43 pixels. Particle dispersion is modelled by varying the minimum nearest neighbor distance between randomly placed pigment particles from the smallest to the largest value consistent with the PVC. Thus at high PVC, the range of possible nearest neighbor distances is limited. The second and we believe more realistic approach appears to be new to modelling of organic coatings. Pigment particles are distributed according to a Poisson point process (also known as the Neyman distribution) to simulate the "clustering" or flocculation of pigments in poorly dispersed paints. This model is applicable in 2 dimensional or 3 dimensional simulations. The two parameters of the distribution λ, the mean number of clusters or floccules per unit volume (or area in two-dimensional simulations) and ν the mean number of pigment particles per cluster, can be adjusted to simulate the range of particle dispersions. At the same time, the actual number of pigment particles in any cluster can be randomly assigned; thus, we can simulate local fluctuations in PVC observed in real coatings. Recently Fishman et al [4] proposed the existence of local fluctuations in the PVC that modify the predicted behavior of coatings at CPVC (critical PVC). In realistic situations these should be expected if only because of variability in the application of the coating. A second advantage of the use of the Poisson process is the ability to obtain a theoretical PVC from the distribution parameters λ and ν as will be seen in the Appendix. Thus pigment dispersion and particle size effects can be examined analytically as well as numerically.

To simulate photolytic degradation, a collimated and uniform "beam" of UV light is projected onto the surface of a paint film penetrating the binder matrix with a strength that decreases exponentially with depth. As the beam proceeds downward, it damages the binder matrix directly by absorption by binder or indirectly as light radiation is reflected off pigment particles and then is absorbed. It is assumed that the damage from the reflected light is uniform over the entire surface and includes binder located in areas that are shielded from direct radiation. Initially pigment particles shield the binder below them. This eventually leads to the formation of "pedestals" that support single pigment particles as seen in the SEM micrographs in Kampf et al [6] (see figure 5a for comparison). Eventually, indirect and reflected radiation erodes the pedestals and the now loosened pigment particles are removed from the simulation. In real coatings this process is called chalking. The damage around a pigment particle is calculated in the following way:

1. When a collimated UV beam hits a pigment particle a portion of the power of the beam is recorded. The portion, called the light strength, is determined by a pre-selected damage parameter. The sum of the light strengths is calculated for each sweep of the UV beam across the matrix.
2. At the end of each sweep the number of binder pixels which have at least one edge exposed to the air is calculated. This is the area to which the reflected damage will be applied.
3. The amount of damage applied to each pixel in this area is calculated by taking the sum from step 1 and dividing it by the total number of pixels calculated in step 2.
4. The damage is applied by taking the damage per pixel sum calculated in step 3 and subtracting it from the strength value of each pixel counted in step 2.

Binder pixels whose pixel strength fall below a threshold are then removed by being converted to air pixels.

Chalking can also be caused by anatase or unstabilized rutile titanium dioxide pigments. These pigments damage portions of the binder at the pigment-matrix interface by creating hydroxyl and peroxyl radicals when the pigments are hit by UV photons. Figure 15 shows a closeup of the pigment particles and binder in such a simulation. Such photolytically active pigments can be modelled and the resulting weathered surface and its gloss properties characterized. In this way the strategy of inserting a certain fraction of photolytically active pigment particles to enhance gloss can be explored.

3. Modelling and Analysis of Gloss in Photodegraded Surfaces. Distinctness of image is largely affected by surface roughness so that a reasonable study of gloss can be undertaken by studying the texture of a randomly generated irregular surface. We begin with the physical optics theory as summarized in [7] that, at least in principle, predicts the angular distribution of light flux reflected off a rough surface as a function of the angle and wavelength of the incident light. This theory has limitations however. For example, it cannot account for masking and shadowing effects and it assumes the surface is a perfect conductor. Nevertheless it is the foundation for more sophisticated scattering theories and is adequate as a first approximation. Specular intensity and mean reflectance (or mean scattered field) will be used as quantitative measures of distinctness of image gloss even though the correlation between the two is not perfect. Better characterization of distinctness of image is a complex problem that involves human psychophysics and for this reason is beyond the scope of the model discussed here.

However we are working on the use of computer graphic renderings of surfaces based on good physical models of reflectance and this approach should be useful in dealing with some of these difficulties. A recent discussion of these and other issues surrounding the measurement and modelling of coating appearance can be found in [8].

Weathering is essentially a random process so the resulting roughened surface may be considered to be random. Following Beckmann we will assume the surface profile can be described by $z = \zeta(x)$ where x is the horizontal coordinate, $-L \leq x \leq L$, and z is the vertical height coordinate. ζ is assumed to be a random normally distributed variable that is independent of the second horizontal coordinate y; however this assumption can be dropped with suitable modifications to the formulas. If the mean or expected value of ζ is μ and the standard deviation is σ, then these quantities can be estimated from the surface heights of the simulation as follows: Letting N be the number of surface heights used in the calculation, the mean profile height is given by

(1) $$\mu = \sum_{k=1}^{N} z_k / N$$

where $\{z_k\}$ are the surface heights and the standard deviation is given by

(2) $$\sigma = \mathrm{SQRT}(\frac{1}{\mathrm{N}} \sum_{\mathrm{k}=1}^{\mathrm{N}} (\mathrm{z_k} - \mu)^2)$$

Aside from σ another crucial quantity in determining gloss is the correlation length T. This quantity is determined by the Gaussian random process (x, y, ζ) and can be estimated from the profile heights as follows. First,

$$C(j) = \frac{1}{\sigma^2(N-j)} \sum_{k=1}^{N-j} z_k z_{k+j} \tag{3}$$

where $j = 1, \cdots N-1$ is a variable representing the spatial delay in equation (4), is used to estimate the correlation function $C(\tau)$ for $\tau \geq 0$. T, the value for which $C(\tau) = e^{-1}$, is found by interpolation.

The human eye cannot detect polarization so in our application we may, with Beckmann, neglect it and concentrate on the scalar component of the scattered light. Define $\rho(\theta)$ to be the ratio of the field scattered in the direction θ to the field scattered in the direction θ_{inc}. Angles are measured with respect to the direction normal to the x-y plane. ρ is a random number since the reflecting surface is random; hence the mean scattered field $\boldsymbol{E}(\rho(\theta))$ and $I(\theta)$ the mean power of light scattered in the direction θ are used to quantify reflectance. I, also called the intensity is,

$$I(\theta) = \boldsymbol{E}(|\rho(\theta)|^2) \tag{4}$$

Gloss or specular reflection is measured by $I(\theta)$ and $\boldsymbol{E}(\rho(\theta))$ when $\theta = \theta_{inc}$. The latter expression is,

$$\boldsymbol{E}(\rho(\theta)_{spec}) = exp(\left(-1/2\left(\frac{4\pi\sigma cos(\theta)}{\Psi}\right)^2\right) \tag{5}$$

where Ψ is the wavelength of the incident light. $I(\theta)$, can be expressed in terms of σ and T. Using the assumption $T \gg \Psi$, Beckmann's analysis shows that

$$I(\theta) \approx \begin{cases} \frac{2\pi^{5/2}\sigma^2 \mathrm{T}[1+\cos(2\theta)]^2}{\Psi^2 \mathrm{L}} & \text{if } g \ll 1 \\ \frac{\Psi(\mathrm{T}/\sigma)}{\sqrt{(\pi)}\mathrm{L}\cos(\theta)} & \text{if } g \gg 1 \end{cases} \tag{6}$$

and if $g \approx 1$,

$$\frac{\sqrt{(\pi)}F^2Tg}{2L}\exp(-g) \leq I(\theta) \leq \frac{\sqrt{(\pi)}F^2T}{2L} \tag{7}$$

where $F = sec(\theta_{inc})^2$ and $g = g(\theta, \theta_{inc}) = [2\pi(cos(\theta_{inc}) + cos(\theta))]^2(\sigma/\Psi)^2$.

Experimental evidence for the relationship between roughness and gloss as we have defined it here can be found in the work of Lettieri et al [9] in their study of light scattering from glossy coatings on paper. Using an array of laser light detectors they measured the spectral reflectance (light scattering patterns) for a full range of incident angles and a sample of glossy papers with different degrees of roughness. The data clearly showed that the intensity of gloss increased as the roughness as measured by the standard deviation, decreased (see e.g. Figure 9 in that paper). Surface heights of the paper samples were measured using mechanical stylus profilometry and values of the standard deviation and correlation length were calculated. Using a power law model for the correlation the authors were able to predict the light scattering pattern by using Beckman's formula. The results compared favorably with light scattering measurements.

4. Results of Simulation:. The heights of the peaks in the weathered profile after any cycle time are assumed to be normally distributed. Evidence supporting this is depicted in Figures 1a-c which show the normal probability plots at fixed values of

x. Each graph was computed from 100 heights corresponding to 100 different runs of the weathering process after 1200 time cycles or midway through the weathering cycle. The heights were ordered from small to large.

If the simulation heights are normally distributed, a plot should lie scattered along a straight line. Normal probability plots for x located at various horizontal positions in the profile show that agreement is reasonable. That is, the assumption that the heights are normally distributed appears to be justified.

Using formulas (1) and (2) of the previous section, the mean μ, the standard deviation or roughness σ, and the correlation length T, were computed from a simulated weathered surface after 250 and 1200 cycle time steps, for several pigment sizes s and dispersion values dF. The flocculation parameter dF is the minimum distance of two pigment particles, hence it controls the degree of dispersion. The parameter dF was obtained by placing pigments in the initial coating randomly in close approximation to random close packing. Pigment particles were placed at a distance greater than or equal to a minimum set by the parameter dF. If dF=0, the pigment particles can be at arbitrarily small distances from each other (actually they are allowed to touch) producing a pigment distribution with the maximum degree of flocculation. The larger the value of dF, the greater the minimum and the larger the amount of pigment dispersion. This is consistent with the observations of paint technologists [1]

Our results qualitatively support Steig's [10] observations that the rate of gloss loss of coatings depends on the particle size distribution and dispersion of the pigment particles. In particular, as the surface erodes revealing the underlying structure, flocculation or the presence of large pigment particle clusters can lead to rapid gloss loss while coatings with many small uniformly distributed particles retain their gloss, even in the presence of many dry particles. Our simulation provided a qualititative demonstration of these observations and illustrated the effects of pigment size and flocculation separately. As formulas (5) and (6) show, gloss is essentially controlled by surface roughness σ, so we focus on the dependence of this variable on pigment particle size and degree of flocculation.

Figures (2a-b) through (5a-b) illustrate the relationship between surface roughness, pigment volume concentration and flocculation. For each pair of figures the original microstructure consisted of a coating having the same PVC (pigment volume concentration) but different degrees of flocculation. As can be seen in each case, the rougher weathered surface came from the surface with the higher degree of flocculation (or equivalently lower dF values). The comparisons were made at 1200 cycles for PVC=15, 25 and 35% with dF=0 and 4, and at 250 cycles for PVC= 25%, dF= 0 and 4. After an initial period of about 250 cycle times, we see that roughness of the weathered surface decreases as the the PVC of the unweathered surface increases. Figures 6 through 8(c) confirm this observation for a range of PVC and dF values. Braun [1] confirms the experimental validity of these conclusions. Braun found that an increase in PVC leads to a decrease in gloss until the CPVC is reached.

To investigate the effect of pigment particle size, the photodegradation was simulated of coatings with a distribution of large and small pigments where the pigment size ratio of the two types in diameters was 3 to 1. s was the percentage of small pigment particles in the initial coating. After weathering, surfaces with different values of s were compared and as depicted in Figures 9 and 10, the simulation results imply that coatings containing larger fractions of small particles are smoother. Calculations for these figures were carried out at 1200 cycles. Figure 11 shows roughness plotted as a function of PVC and s, at 1200 cycles. This phenomenon was investigated in somewhat more detail in Figures 12 a-b and 13 a-b. After an initial transition period, they show that through most of the weathering cycle roughness decreases as the percentage of small pigment particles increases. Figure 12a and b, are at PVC= 30% while 13 a,b are at PVC= 15%. Figure 11 illustrates this point for a range of values of PVC and s. It is interesting to note that these simulation results are also consistent with a recent study by Braun and Fields [5] on the gloss performance of unweathered water- based and solvent- based titanium dioxide paints. Comparing coatings with different size distributions of pigment particles they found a direct correlation between the percentage of large pigment particles (coarse tail of particle size distribution) and 60^o gloss. Thus, despite the obvious complexity of the UV degradation process, the simulation suggests that this relationship will continue throughout the weathering process.

4.1. CONCLUSION:. To better understand the link between formulation and gloss retention of painted surfaces subject to UV degradation we presented the results of a computer simulation that capture some of the physical aspects of film and surface appearance changes during the weathering process. Pigment particle size and particle dispersion are parameters that can be controlled in the simulation. Pigments were randomly placed in an approximation of random close packing and to model flocculated and poorly dispersed paints, we also used a Poisson point process (see Appendix). Our results showed that after an initial transient period, surfaces with a high PVC had a higher degree of gloss (as measured by roughness) than those with low PVC. Similarly, after some initial transient, we observed the highest gloss in surfaces with the largest numbers of small pigment particles. These results were valid through a range of PVC values and are consistent with earlier experimental and theoretical work by Steig and later by Braun and others.

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APPENDIX:

In this section we will discuss the results of using a so-called Neyman-Scott point process to determine the placement of pigment particles. We propose this distribution as a model of clustering or flocculation. $\boldsymbol{N}$ random uniformly distributed points (x_i, y_i) $i = 1, \cdots \boldsymbol{N}$ are selected to be the centers of $\boldsymbol{N}$ flocculates of pigment particles. Within the ith cluster,we next select $\boldsymbol{M}$ points uniformly distributed in a circle with center (x_i, y_i) and radius R. The numbers $\boldsymbol{N}$ and $\boldsymbol{M}$ are discrete Poisson random variables with mean values μ and ν respectively. Thus the parameters controlling pigment placement in this scheme are μ, ν, and R. Note that for a fixed volume V, the number μ may be expressed in terms of an intensity parameter λ as $\mu = \lambda V$. Figure 14 (a)-(c) shows the results of calculating σ for a weathered surface with an initial pigment distribution with parameters $\lambda = 3\text{x}10^{-5}$ and $\nu = 1, 4, 10$ at cycle time 250. In each run all pigments had the same diameter.

Simplified estimates of the pigment volume concentration, and degree of flocculation can be obtained in terms of the parameters of the process, thus allowing the introduction of some precision in the discussion of these variables. The following expression called the theoretical PVC or TPVC makes use of the fact that $\mu\nu S$, where S is the volume of a single pigment particle, is an estimate of the total volume of pigment in the coating. If V is the total volume of the coating,

$$TPVC = (\mu\nu S)/V \tag{8}$$

For convenience, we will confine our subsequent discussion to two dimensions, that is, to area measurements. Let Ω be a planar region with area $A(\Omega)$. The expected number of pigment particles in Ω, that is the mean value of the random number $n(\Omega)$, can be written as $\boldsymbol{E}(n(\Omega)) = \nu\lambda A(\Omega) = \nu\mu$ [11]. The degree of flocculation can be expressed in terms of the fluctuation in the number of pigment particles as one samples different regions Ω. Using the fact that the Neyman-Scott distribution is a homogeneous Poisson point process we can express this fluctuation in terms of the variance of $n(\Omega)$ [11]

$$var[n(\Omega)] = 2\pi p^2 G_1 + p\nu G_2 + pA(\Omega) - (pA(\Omega))^2 \tag{9}$$

where $p = \lambda\nu$, G_1 is a geometric constant depending on the area and shape of Ω, and

G_2 is another geometric constant that depends only on R which we assume is fixed. These constants are known for simple geometric shapes Ω. Let us suppose that λ and ν can vary in such a way that their product p is fixed. If p is fixed it follows from (8) that the TPVC is fixed since $\mu = \lambda A(\Omega)$, and

$$TPVC = \lambda \nu S = pS$$

Here S is the area of a single pigment particle. Equation (9) shows that the variability of $n(\Omega)$ can be increased by increasing the average cluster size ν and keeping p fixed. Thus we have a theoretical description of how control of flocculation can be achieved by controlling the cluster size and number of clusters without changing the PVC-precisely the effect of adding surfactants to a coating formulation. Indeed Figures 16 and 17 show two realizations of a Poisson process with $\mu = 10, \nu = 30$ and $\mu = 30, \nu = 10$, respectively. Although realizations were selected so that the PVC differs by no more than 0.1%, the pigments in Figure 17 appear to be better dispersed than those in Figure 16.

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