Effect of Cayenne and Paprika Pigments on the Color and Spreadability of Paint

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Abstract

Determining if cayenne and paprika are suitable for creating red paint can benefit the environment, the creativity of artists, and the accessibility of painting. Samples with five different mass fractions of pigment for both spices were evaluated. Spreadability—as defined as work of shear of the paint under compression—was measured using a conical rig on a texture analyzer, analogous to work exerted by a brush. Red color is represented as a ratio of the "R"-factor of the average RGB value from swatches of each sample. Properties for spice-based paints were compared to commercially available paint to inform how these paints can be adopted into regular practices. Paprika was found to be more red than cayenne at lower pigment concentrations. For both paints, 12% pigment concentration was most similar to commercially available paint in terms of work of shear and 12 to 30% in terms of redness.

Keywords: Paint, cayenne, paprika, spreadability, rheology, RGB

1. Introduction

Spices have been used as pigments throughout history, such as saffron-based dyes in ancient India [1]. Most red paint pigments, however, are inorganic, derived from iron oxides and cadmium, which can pose health and environmental risks. Iron oxide, a common red pigment, has been demonstrated to slow the aging of polypropylene microplastics in seawater [2]. Cadmium is a proven carcinogen that tends to accumulate in plants and animals with a half-life of 25-30 years [3], and its solubility increases risk of paints with cadmium red pigments to leach into soil [4]. Due to the these environmental and human and animal health impacts, red pigments made from organic materials may be a sustainable alternative. Furthermore, artists are also always looking to experiment with new media that can expand their creative pursuits. Artists may be attracted to the unique textures and scents of spice-based paints that can expand the sensory experience of a piece. Home-made paints made from spices can be an affordable, non-toxic alternative to make painting accessible to artists, amateurs, and children alike. Determining if spices are suitable to creating red paint can benefit the environment, the creativity of artists, and the accessibility of painting.

Characterizing the color and spreadability of paint composed of cayenne and paprika can inform the suitability of these candidates for a new kind of red, plant-based paint. Spreadability is defined by the work of shear of the paint under compression, which gives insight into how paint is affected by a brush applying a shear force. Correlating the color of paint with conventional red paints provides painters with a better understanding of how to adopt these spice-based paints into their regular practices.

The suitability of paprika and cayenne as paint pigments was investigated by measuring work of shear and RGB values of paint samples under varying concentrations of each pigment and comparing the results. Five samples each of five different mass fractions of pigment for both spices were mixed using consistent technique and proportions of water and a Liquitex Matte Acrylic Medium. A texture analyzer measured the compressive force experienced by each sample sandwiched in a conical rig, generating a force curve. The area under this curve, which represents work of shear, was calculated for each sample for each concentration. To determine color, a swatch of painted paper for each sample was photographed in controlled lighting. The RGB values were determined from the photographs using MATLAB. The proportion of the "R"-value within the RGB color space was graphed for each pigment concentration with 95% confidence interval error bars.

2. Paint Rheology and Material Properties of Pigments

Paprika and cayenne are members of the *Capsicum annuum* species, gaining their red coloration from a mix of carotenoid pigments [5]. Literature studying the properties of organic paint pigments such as carotenoids is sparse, but various methodologies have been used to study conventional paints. Recycled titanium dioxide (TiO_2), a common white pigment, has been characterized using viscometers to measure viscosity and spectrophometers to measure color in the *L*,a*,b** color space which characterizes lightness and the colors red, green, blue, and yellow [6]. Coverage of mica-based paints has been studied by measuring the shear stress and elastic, storage, and loss moduli of the paint during a strain sweep. This study also found that percent solids scaled inversely with quality of paint coverage [7]. The rheological properties of prussian blue and titanium white oil paints have also been investigated by characterizing viscosity, yield stress, elastic, storage, and loss moduli over rate and stress sweeps [8].

The RGB (red, green, and blue) color space is chosen because of its ability to isolate red values in a digital image. Common red paint colors are napthol scarlet and cadmium red, composed of inorganic pigments. Napthol scarlet is defined by rgb(255, 36, 0) and cadmium red by rgb(227, 0, 34) [9]. These values can be correlated to the cayenne and paprika RGB values to create a reference for how artists can substitute conventional paints.

2.1 Carotenoid Properties in Paprika and Cayenne:

Cayenne derives its color from carotenoids apsanthin, lutein and β-carotene and paprika from β-carotene, β-cryptoxanthin, zeaxanthin and capsorubin [5]. Solubility of carotenoids may pose concern during mixing, since they are not soluble in water and sometimes soluble in oils. Oil-in-water emulsions of 2% w/w carotenoids have been shown to demonstrate thixotropic behavior, both when they are prepared fresh and stored. Thixotropy allows for time-dependent shear thinning, which is ideal for painting because the paint will be most viscous upon initial application, preventing dripping, and then thin under shear created by the brush which allows for uniform spreading. Emulsions containing lutein, found in cayenne, and β-carotene, found in both spices, exhibited thixotropic behavior. β-carotene decreases in viscosity when stored in an emulsion over time, while lutein decreased in elasticity modulus over time, likely due to the polarity of these substances [10].

2.2 Spreadability Rheology:

Unlike industrial painting, in which coverage is the main priority, the rheology of artistic painting is best understood through studying the shear forces experienced by a brush. While the spreadability rig and texture analyzer used in this study is not a prevalent methodology for studying oil and acrylic paints, rheometers are often used in current literature, which apply rotational rather than linear motion. The spreadability rig measures work of shear based on an applied compressive force, while rheometers measure viscosity based on applied shear stress. Controlled-stress rheometers sandwich the sample between two plates and apply a torque to one plate (Figure 1).

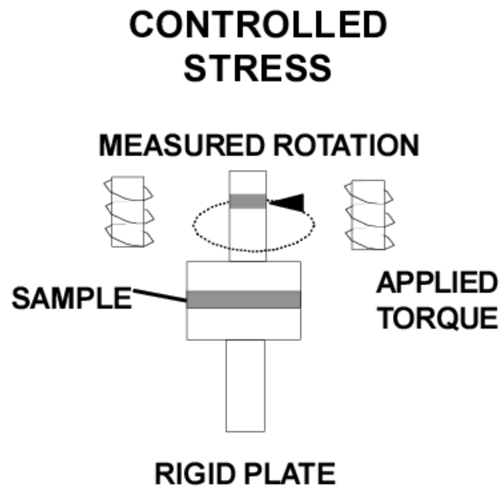

Figure 1: Diagram of controlled-stress rheological measurements, depicting the sample sandwiched between two plates. A torque is applied to the upper plate and the resulting rotation is measured, indicating strain rate in response to shear stress [11].

By subjecting paint to a controlled stress sweep and measuring the strain rate, dynamic viscosity can be derived by the equation:

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{1}$$

where η is the dynamic viscosity [Pa-s], τ is the shear stress [Pa], and $\dot{\gamma}$ is the shear rate [1/s] [12]. Measurements of viscosity versus shear stress using controlled-stress rheometers have been performed on various types of paints.

Oil and acrylic paints are thixotropic, meaning that their viscosity is time-dependent. As shear stress is increasingly applied, the yield stress occurs when the viscosity begins to sharply drop, after which the paint experiences shear thinning (Figure 2). Shear thinning is indicated by an inverse relationship between viscosity and strain rate. This inverse relationship is ideal for brush application because it improves pigment stability, flow properties, brushability, levelling, and prevents sagging of paint, which also improves the ease of building up paint layers before previous layers dry [13]. The ideal viscosity range for shear thinning for ease of brush application is 0.1 to 0.25 Pa-s [11]. Figure 2 demonstrates viscosity responding to increasing shear stress according to this phenomenon.

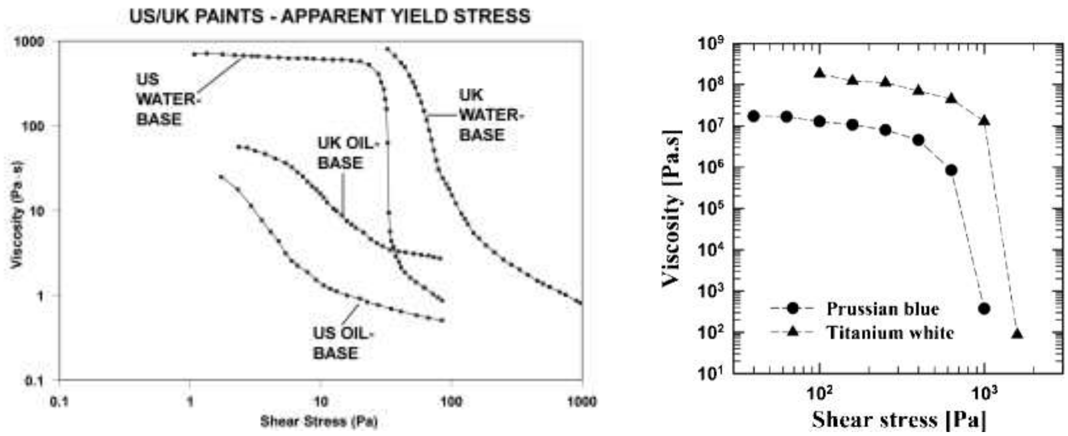

Figure 2: Stress sweeps using a stress-controlled rheometer to measure viscosity for common US and UK paints in general (left) [11] and Prussian blue and titanium white oil paint (right) [8].

The viscosity of paint for roll and spray painting is conventionally measured using viscosity cups. The viscosity of paint can be correlated to the amount of paint necessary to cover a given area for brush or roller painting. It may also determine if the paint is compatible with certain types of sprayers and airbrushes [14]. The optimal viscosity for roll painting for instance is about 100 centistokes, or about 0.1 Pa-s, which is the lower end of viscosity for brush painting [15].

The spreadablity rheology of creams, which is prevalent in pharmaceutical literature, can inform the behavior of paints, since they also display shear thinning behavior by design. The spreadability of creams has been defined as inversely proportional to the minimum shear stress required to initiate flow, or yield stress, of a material. Shear stress can be derived by a vane method, in which a torque is applied to motorized blades immersed in a material until the material begins to flow. The applied torque, M_o, can be related to the shear stress by the equation:

$$\sigma_0 = \frac{2M_o}{\pi d^3}(\frac{h}{d}+\frac{1}{3})^{-1}$$

where σ_0 is yield stress [Pa-s] , M_o is torque required to achieve flow [N-m], *h* is the height of the vane immersed [m], and *d* is the diameter of the vane [m] [16].

Oil paints are suspensions composed of about 60-70% particles of pigment suspended in 25-30% solvent and 1-3% binding medium [8]. Higher concentrations of suspended particles will cause more shear thinning and non-Newtonian behavior of a fluid, which paint is expected to exhibit. Viscosity of a suspension increases with less spherical particle shape and with an increasing size distribution of particles. The effect of particle diameter on the viscosity of a suspension is greater with higher viscosity solvents, which is important to consider when selecting a binding medium for the sample [17]. The viscosity of linseed oil, a common medium used in oil paint, has been studied (Figure 3).

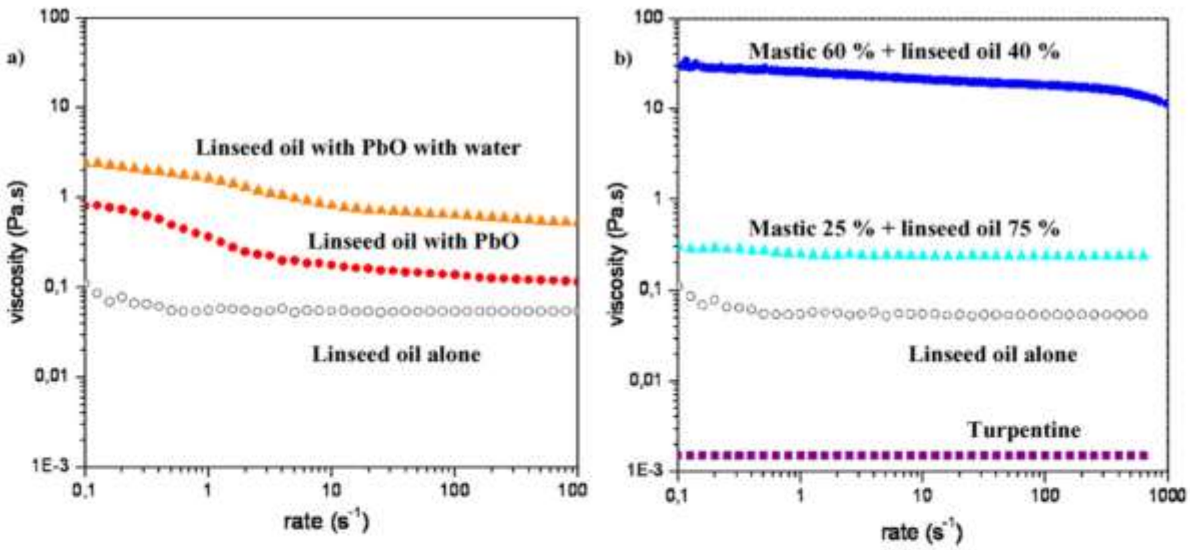

Figure 3: Viscosity versus shear rate for various oil mediums used historically in oil painting. It is demonstrated that boiled linseed oil (with lead oxide), common among Renaissance painters, exhibits thixotropic behavior [13].

3. Experimental Design

3.1 Sample Preparation

Cayenne and paprika-based paint samples were prepared in pigment concentrations of 6%, 12%, 18%, 24%, and 30% mass fractions. The mix consisted of the ground spice pigment, water, and an acrylic binding agent (Liquitex Matte Acrylic Medium). The mass ratio of water to pigment was held constant at 45.45% to allow the pigment to dissolve the same amount and attain consistent moisture during the first step of mixing (Figure 4A). The ratio of pigment and water combined to binder was adjusted to achieve the desired pigment concentration and a total sample mass of 18 g (Table 1).

Table 1: Mass of ingredients in each of the five mass concentrations of samples.

ww%	Pigment (mg)	Water (mg)	Binder (mg)
6%	1080 ± 5	900 ± 5	1980 ± 5
12%	2160 ± 5	1800 ± 5	3960 ± 5
18%	3240 ± 5	2700 ± 5	5940 ± 5
24%	4320 ± 5	3600 ± 5	7920 ± 5
30%	5400 ± 5	4500 ± 5	9900 ± 5

The three ingredients were hand-mixed as depicted in Figure 4 to create samples for both spreadability and color testing. An 8068-series Jewelry Scale was used to measure each component. The desired amount of water was pipetted onto the pigment and mixed with a palette knife until it attained a soil-like consistency as shown in Figure 4A. The binder was added and mixed with a palette knife for about three minutes until the mixture was smooth.

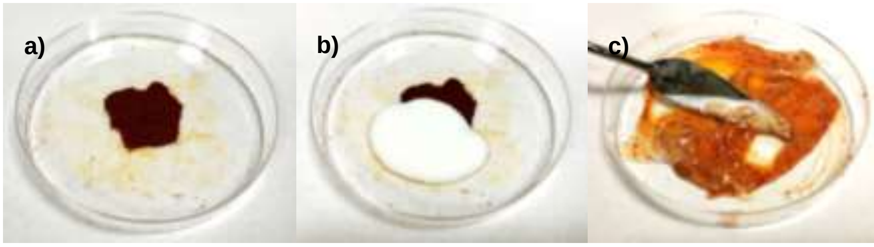

Figure 4: Photographs displaying steps for mixing paint samples. Pigment was first combined with water (a), the binder was added (b), and it was thoroughly mixed with a palette knife (c).

3.2 Experimental Setup and Analysis

Work of shear was determined using a spreadability rig on the Stable Microsystems TA.XT Plus Texture Analyzer. The rig consisted of a tool with conical cavity which was filled by the sample and levelled off as shown in Figure 5. A cone above the tool was lowered into the cavity at a constant speed of 2 mm/s until the tool reached the calibration distance, and then it returned to its original position. Distance was calibrated to zero at the point in which the upper cone experienced 1 N of force (just as the cones touch) to alleviate the effects of force due to deformation of the rig during testing. Since the conical cavity was 18 mm in height, the upper cone began at 20.95 mm above this calibration distance. The force experienced by the upper cone was recorded during the full entry and return cycle. The test was repeated five times for each of the five pigment concentration samples of paprika and cayenne paint, and for the cadmium red paint as a control.

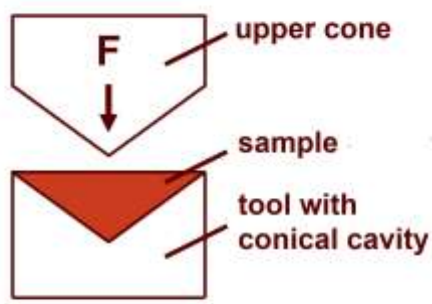

Figure 5: Diagram of spreadability rig used to determine work of shear.

Color was determined by painting three samples of each pigment concentration. The samples were placed in a dark room under a diffused white light to control for environmental interferences. A camera was placed at a fixed distance to photograph the sample.

4. Results and Discussion

Properties of color and spreadability, defined by work of shear, were investigated and compared to conventional cadmium red paint to determine the suitability of cayenne- and paprika-based paint as an alternative.

4.1 Color Characterization and Uniformity

The images of each sample were separated into RGB channels and the average RGB value was calculated. “Redness” was determined as a percentage of R/(R+G+B). Error bars with 95% uncertainty were determined to account for differences between the three samples. A t-test similar to that for work of share was also conducted and the hypothesized mean difference in redness between cayenne and paprika paint was determined. The uniformity of redness was studied by generating a probability density function of the R component of RGB for each pixel in the images. The raw images of paprika and cayenne were processed into RGB channels and averages as shown in Figure 7. Green was more present in paprika and cayenne, contributing to their more orange appearance. It can also be overserved that because the spice-based pigments are ground and not powdered (like cadmium), there is much greater color variation, which will be investigated in the uniformity characterization.

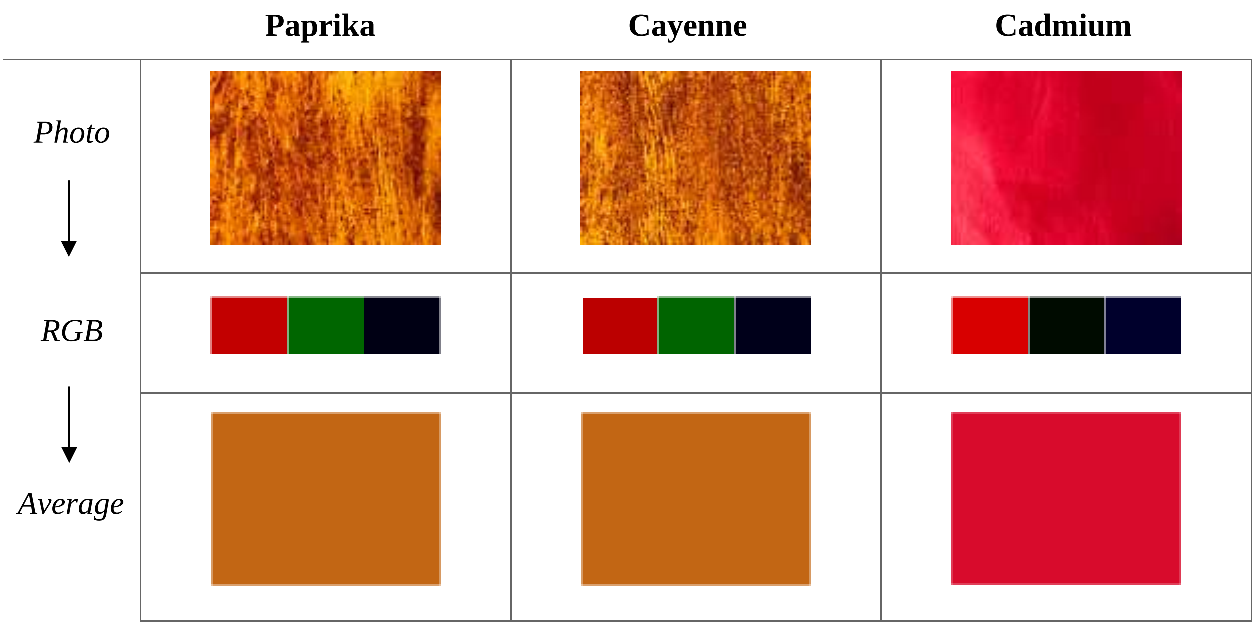

Figure 7: Diagram showing process for splitting images into RGB channels and averaging RGB values, using samples of 18% paprika and cayenne, and cadmium red, as an example.

Figure 8 shows that both spice-based paints are most red and most similar to cadmium red at 18-24% pigment concentration. The redness of paprika is greater than that of cayenne with 95% confidence for 6%, 12%, 18%, and 24% by 3.79%, 0.95%, 0.73%, and 1.11% respectively.

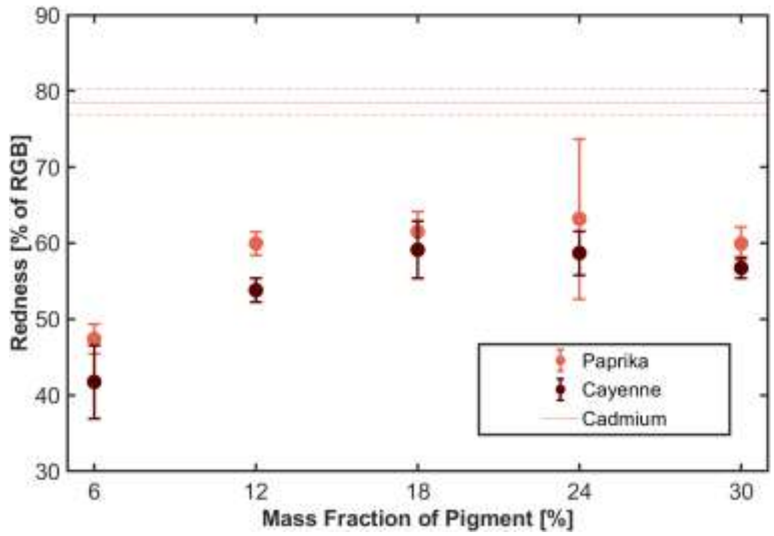

Figure 8: Plot of the red RGB ratio for cayenne and paprika at various pigment concentration levels compared to cadmium red.

The paprika and cayenne samples appeared heterogeneous, which provides for an interesting texture. The uniformity of redness was found for cayenne and paprika as shown in Figure 9.

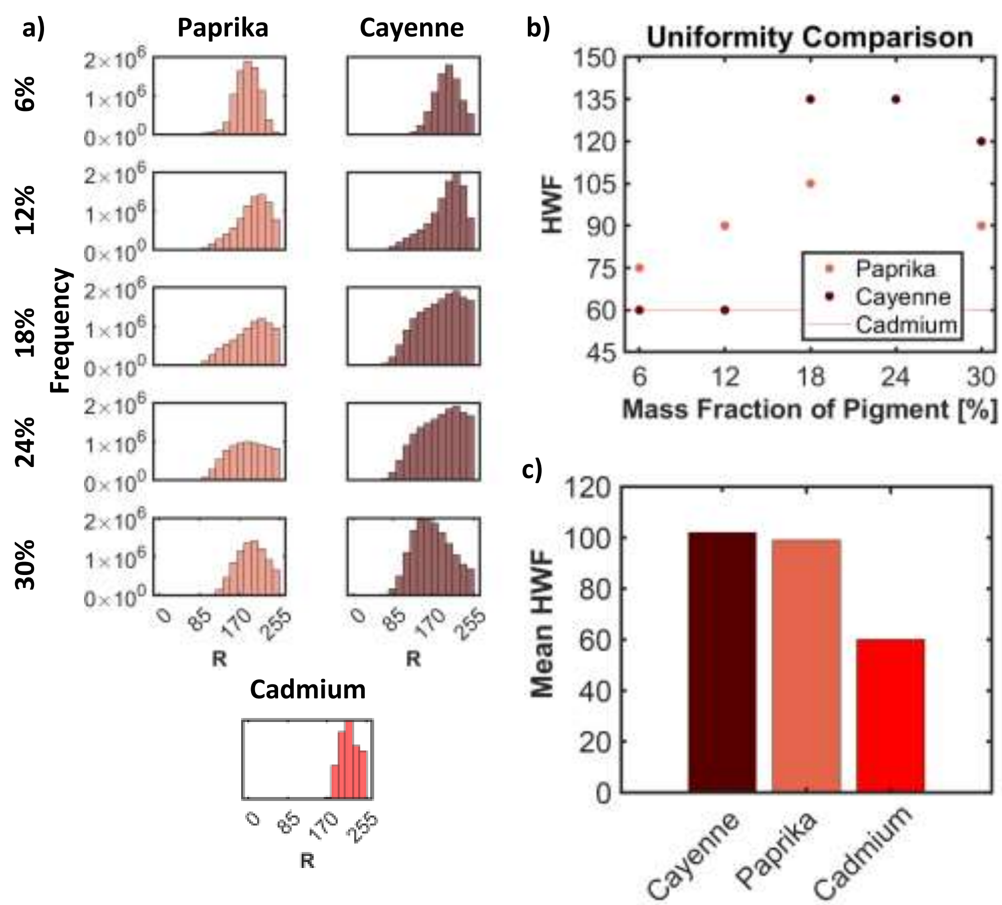

Figure 9: Histogram of the R value of RGB for cayenne, paprika, and cadmium images (a). The width of the distributions at half the peak frequency (HWF) demonstrate how uniform the paint coverage is. HWF for varying concentrations of paprika and cayenne, compared to paprika indicates decreasing uniformity at 18% and 24% (b). The mean HWF demonstrates that cadmium is the most uniform, followed by paprika and closely by cayenne (c).

The R value of each pixel of the combined images for all samples were plotted in histograms with a bin width of 15 over the R value range of zero to 255. The half width frequency (HWF) was calculated, which is the width of the histogram at half the peak frequency, and is inversely related to uniformity. Figure 9A and 9B show that the paint becomes less uniform at higher concentrations of pigment, and paprika may be slightly more uniform than cayenne.

4.2 Work of Shear

A graph of the force over distance was generated for each run similar to Figure 6. The area under the curve was calculated from 2.95 mm (when the upper cone first contacted the sample) to 20.95 mm displacement from the starting position, which correlates to the peak force. The value for area under the curve represents the work of shear, which is analogous to the required work exerted by a brush to spread paint.

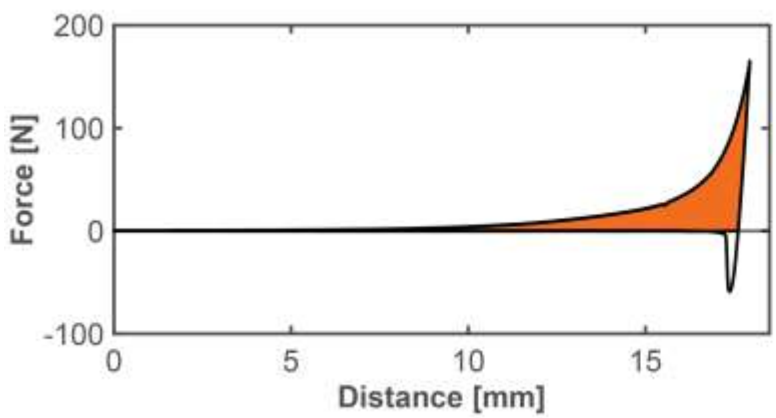

Figure 6: Work of shear is determined by the area under the curve (shown in orange) when the rig just makes contact with the sample until it is at its maximum force.

The force experienced by higher concentrations of paprika and cayenne is greater throughout the spreadability test cycle, as shown in Figure 10.

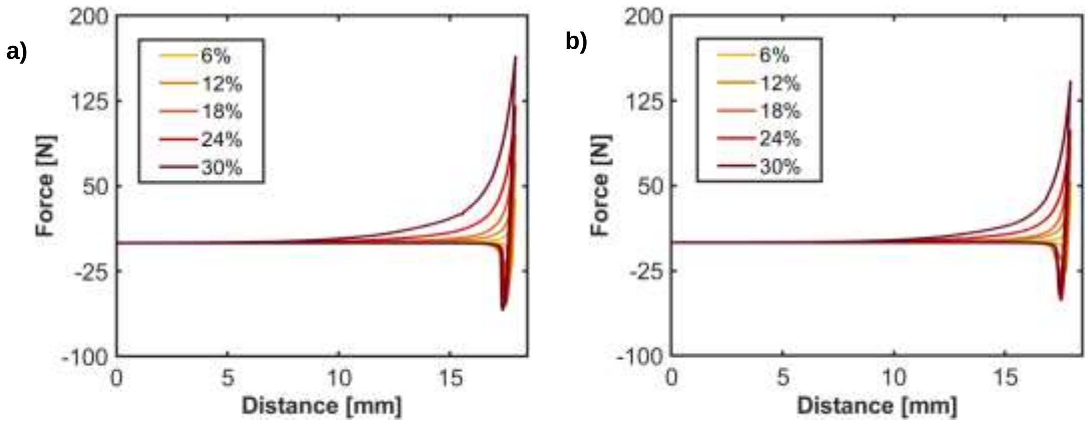

Figure 10: Graph of force exerted on the paint samples by conical rig as it travelled an 18 mm range for paprika (a) and cayenne (b).

The relationship between the work of shear and mass fraction of pigment was studied by fitting an exponential fit with a 95% confidence interval to the 25 data points for work of shear of paprika and cayenne. A two-tail t-test was then conducted to determine if there was a statistically significant different between the work of shear of cayenne and paprika for each of the five pigment concentrations. The hypothesize mean difference was calculated for those with a p-value ≥ 0.05.

Figure 11 shows that spice-based paints are most similar to cadmium red in terms of work of shear at pigment concentrations of 12%. The work of shear of paprika is greater than that of cayenne with 95% confidence for 6%, 18%, and 24% by 1.42 mJ, 13.60 mJ, and 2.49 mJ respectively. However, the exponential fit with 95% confidence intervals indicate that it can not be determined if work of shear of paprika or cayenne are different across pigment concentrations.

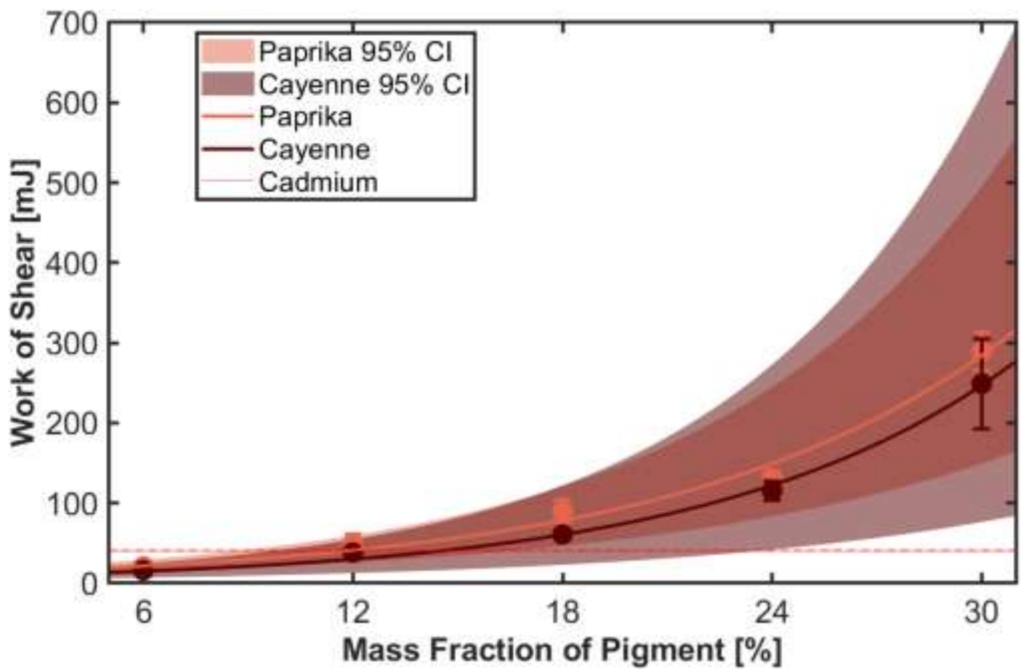

Figure 11: Comparison of work of shear for cayenne and paprika at varying mass fraction of pigments. Error bar represent 95% confidence intervals of precision for each sample. These points are fitted to an exponential fit with 95% uncertainty $y = ae^{bx}$ where $a =$

11.34 ± 3.24 and $b = 0.1074 \pm 0.01017$ for paprika and $a = 7.384 \pm 3.568$ and $b = 0.117 \pm 0.0341$ for cayenne. Confidence intervals are shaded.

Of the paint samples studies, paprika at a concentration is the best replacement for conventional red acrylic paint on the basis of redness, color uniformity, and work of shear. Attaining properties similar to that of conventional paint show promise for these sustainable pigment alternatives to eventually replace inorganic, toxic pigments. It was proven that cayenne and paprika can take on the same work of shear as conventional cadmium red acrylic paint, but fell about 20% short of its redness. Additionally, a painter may use this data to help them create spice-based paint with whatever unique properties they may desire. For instance, an artist may want to experiment with a more heterogeneous rather than uniform appearance, orange color, or thicker consistency than typical red acrylic paint.

5. Conclusions

Paprika is more red than cayenne for pigment concentrations ranging from 6% to 24%. However, it cannot be determined if these spices differ in terms of work of shear. For both spice-based paints, a pigment concentration of 12% is very similar to that of cadmium red. Cayenne and paprika are both approximately 20% less red than cadmium red. Their redness is greatest for pigment concentrations ranging from 12% to 30%. Red paint derived from paprika with a pigment concentration of 12% is most suitable as an alternative to conventional acrylic paint compared to cayenne due to its consistency and redness. Future work investigating spice-based paint when pigment is ground to powder may be completed to allow for more uniformity. A stress-controlled rheological study may also be used to compare shear-thinning effects of spice-based paint to conventional paint.

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