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Master's Thesis

Investigation of the Coloring Behavior of Zirconiumdioxide (ZrO2) Dental Ceramics by Ink-jet Printing of Metal-ionic Inks

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Garching bei München, den 01.07.2017

Vorname Nachname

Foreword

Diese Arbeit entstand am....

An dieser Stelle möchte ich...

Ebenso danke ich ....

Garching bei München, Juli 2015

Vorname Nachname

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1 Introduction

Only in Germany more than 1 Million teeth are replaced annually. The replacement procedure is accomplished with an implantation of the tooth replica to provide the aesthetics and the function of the natural tooth. Ancient Egyptians used tooth shaped ivory to regain the function of the missing teeth. Today the technology has evolved to a point where the dental replacement for a single tooth is an assembly of three parts, which are to be seen in Figure 1.1. The implant is the part which is screwed to the lower jaw bone (mandible) and anchors the whole replacement assembly to the chin. The preferred material used for the implant are titanium in the EU and tantalum in the US. The enhanced osseointegration of the porous implant material surface, biocompatibility of the ceramic interface, formed due to the surface oxidation a Young's Modulus, which is similar to the human bone are the main reasons for titanium and tantalum to be the prime materials for this purpose. The abutment takes on the task of a fitting for the crown and is made of the same material as the implant.

Figure 1.1: Single tooth replacement

The crown of the tooth replacement is the part which imitates the visual qualities of the tooth. There are several material, which a crown can be made of or assembled from. The most popular crown material dominating the market is the Yttria-stabilized zirconia (YSZ), which has a cubic fluorite crystal structure and is going to be referred as zirconia in the frame of this thesis. However, zirconia in its pure form is a plain white material with high translucency. In case of single tooth replacement the newle implanted crown would be absurdly white when compared to the neighboring teeth.Even when a full chin dental replacement is conducted, it is abnormal to have a full set of plain white teeth without any shading. This situation makes it a necessity to preprocess the crowns to match the neighboring teeth or another natural shade of choice in case of a fully monolithic replacement. Dentist are using a shade guide seen in the figure 1.2 for a side-by-side comparison to determine the color and the shade of the teeth. One can observe that there are 4 color groups A, B, C and D which are referred as orange-brown, yellow, grey-brown and red respectively (VITA 2014). Each of these colors have shades ranging from 1 to 4. Even though the shades are coded with the numbers from 1 to 4 with increments of 0.5 a total analogue shade acquisition is possible. The number 1 represents the shade with the least and 4 with the most saturated tone for each color.

Figure 1.2: Vitapan Shadeguide

2 State of the Research

Addressing the shading process of the dental zirconia-based ceramics as a combined procedure of drop generation, dispersion of the ink within the porous material and post sintering generation of the color below the surface of the porous material, it can be said that the quantitative coloring process of the dental crowns is an uncharted area for the scientific researches in the present-day.

In 2016 Lee et al. have investigated the absorption behavior of water drops impinging porous stones experimentally and numerically. The investigation includes the phases from spreading to evaporation for a water droplet considering the absorbed amount of the droplet during the depletion and spreading of the humidity within the manner depending on time for three porous materials. Quantitative measurements of the water absorption for the materials are conducted with high-speed imaging and neutron radiography methods during the time range from the impact moment to the end of the spreading phase after absorption. Neutron radiography shows a high resolution quantitative distribution of absorbed water. During the first contact and deposition on the surface the droplets do not exhibit a wetting behavior. As soon as the droplet acquires its maximum diameter on the surface, it gets fixed and the contact angle with the surface remains constant as long as the droplet is not drained by the stone. The absorption behavior doesn't have the same attributes throughout the whole process. At the beginning the material shows a contact resistance blocking the absorption, which is associated with the entrapped air beneath the area encapsulated by the borders of the water droplet. In the second phase the encapsulated air finds a way to diffuse away so the capillary flow takes place flawlessly until the total disappearance of the droplet on the surface is observed. The experimental data shows accordance to the phases of the numerical model for water flow inside the unsaturated porous material. The collision velocity has a huge effect on drop spreading on the surface and impregnation, but not so much on the distribution of the water after the initial absorption. The absorption and distribution rates are highly relevant to the capillary structure of the stones.(Lee *et al.* 2016)

On a different aspect some research has been conducted about the effect of the coloring process on the structural strength of the zirconia. In the research of Shah et al. coloring zirconia with cerium acetate mixtures with a maximum ink weight ratio of 5% provided a distinctive shade and did not cause a mechanical disadvantage. However, the ratios above 5% have decreased the mechanical properties while not increasing the shading level significantly. The paper also includes data for case where the coloring process is conducted using cerium chloride and bismuth chloride. For both cases 1% coloring agent was the limit, if the flexural strength was to be conserved. The low temperature degradation was also observed in the frame of the paper, which did not show any co-dependence with the coloring solution.(Shah *et al.* 2008)

The crystallographic state of zirconia depends on the temperature under atmospheric pressure. Until reaching a temperature of 1170° Celcius the crystallographic structure shows a monoclinic symmetry. After that temperature the structure can be defined as tetragonal until 2370° C , which afterwards becomes cubic up to the melting point. The volume of the material increases about 4.5% during the transformation from tetragonal to monoclinic phases, which is enough to cause a crack induced failure. This evitable transformation begins at about 950° C while cooling down and the only way to stabilize the tetragonal structure is creating CaO, MgO, Y_2O_3 or CeO_2 oxides inside the structure to keep the tetragonal formation at room temperature, which eliminates the crack induction and therefore the structural failure of the material parallel to an enhanced toughness. (Denry and Kelly 2008)

Pecho et al. have conducted experiments to analyse the optical behaviour of dental zirconia and dentin in comparison utilizing Kubelka-Munk theory. The results show that the current zirconia materials alone could not satisfy the luminous transmittance of the natural dentin so an additive application of masking is required to reach an approximate to the natural tooth.(Pecho *et al.* 2015)

The infiltration time of the porous medium was formulated by Markicevic et al. in 2009 as:

$$t_{in} = \kappa \cdot \frac{\mu \cdot {r_0}^{1.85}}{\sigma \cos(\theta) \Phi^{0.38}} \tag{2.1}$$

t_{in} defines the infiltration time and depends on the parameters κ , which is the permeability constant of the medium and μ the kinematic viscosity of the fluid. The initial drop radius is symbolized by r_0. θ stands for the initial contact angle after the impact of the droplet on the surface. The σ in the denominator is the surface tension of the liquid. The higher the surface tension is the harder it is for the liquid to wet the surface of the material because of the increased contact angle and hardened impregnation capability. The last dependency of the infiltration time is the ϕ constant for the material, identifying the porosity level of the material. (Markicevic *et al.* 2009)

Stratov et al. have provided experimental results regarding the spreading phases of silicon oil droplets utilizing capillary forces over different permeable layers and observing the diameters of the droplets and wetted areas over time. They have divided the depletion into two phases, of which the first one is defined by the time to reach the maximum diameter for the drop base and the second one is identified by the reduction of the drop base while the depletion takes place. The findings of the experiments show that the different oils on the different porous material with similar porosity and mean pore dimensions. showed similar spreading characteristics on a different time scale and the contact angle remained constant throughout the second stage.(Starov *et al.* 2002b)

The dispersion behavior of liquid drops inside porous media which are previously saturated with the identical liquid are examined in the work of Starov et al. The study was conducted considering both theoretical and experimental perspectives. The study was conducted both theoretical and experimental perspectives. The spreading of a liquid on a dry solid medium is governed by a power law and it is shown that the same power law applies to the case with saturated medium. The liquid flow within the porous medium is modeled using the Brinkman's equations. The effective lubrication and the liquid exchange between the drop and the porous medium are found to have equal significance through which the drop dispersion equation is generated. (Starov *et al.* 2002a)

$$L = L_0(1 + 10(\frac{4}{\pi})^3 \frac{V^3\gamma}{L_0^{10}\mu}\omega t)^{0.1} \tag{2.2}$$

The formula 2.2 shows the parameters which define the diameter of the covered spot by a deployed drop on the saturated surface of the porous material. L_0 V are the measured initial diameter and volume of the drop. ω is defined as the effective lubrication coefficient and has to be acquired experimentally for each porous medium and impregnating liquid pair. The t as the last parameter of the equation stands for the time as usual.

The properties of the porous medium, such as its porosity, the size and the orientation of the pores and the chemical properties of the surface affect the impregnation and the dispersion behavior of the drops. The Washburn equation is employed by multiple authors to generate a model. These models are grounded on the existence of cylindrical capillaries lying parallel to each other. The Washburn equation describes the behavior of the drops by stating that the wetting is induced bu capillary pressure while the viscous dissipation of the flow causes resistance to the dissipation.

The amount of time it takes for a drop to diffuse completely in the porous substrate, until there remains no more liquid on the surface is defined as the drop penetration time, also called as the wicking time.

2.1 Drop Deployment

2.1.1 Piezoelectric

2.1.2 Electromagnetic

2.2 Ceramic coloring

3 State of the Technology

Even in the most contemporary dental laboratory of today’s world, the coloring process is accomplished manually by a experienced dental technologist, who is following the guidelines prepared by the dental ink companies, which explain how a dental crown has to be colored sequentially using different colors on different areas of a single crown summarized in about 20 basic steps. The application of the ink on the dental crown with brush strokes takes about 5 minutes for each tooth depending on the manual measurements of the ink application process conducted by a dental technologist from Zirkonzahn for educational purposes. On the left side you can see a cutout of a lab card. Dentists mark different areas of the crown with different colors from the guide for the technicians. And on the right side are the tasks of a dental technician, which are mainly. Milling, Manually coloring using a brush, furnacing to burn the color to the zirconia and lastly polishing for a natural look. And the coloring part is the process, on which this thesis is focused.

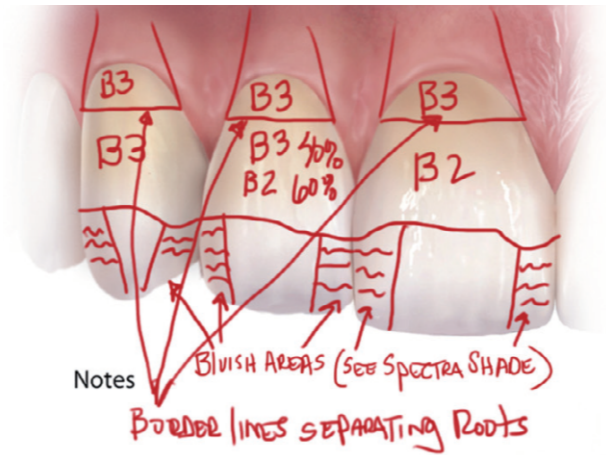


Figure 3.1: Cutout of a lab card (Shapling 2014)

Figure 3.2: Making of dental implants (Zirkonzahn GmbH 2018)

Figure 3.3: False colored crowns after manual brushing (Zirkonzahn GmbH 2018)

4 Review of the State of the Art and Technology

5 Assignment

In frame of this thesis a process is to be developed for generation of the dental color shades using an inkjet printer. The mechanic aspects of responsible for the movement are not included to the project. A stepper motor driven system responsible for the coordinated movement of the axes controlled by a SmoothieBoard v2-mini is provided by the project partner Bredent GmbH. The specifications of the printing system, like a single drop volume or the max printing distance and angle are to be determined. Afterwards an adequate droplet generator is to be selected. The diameter of the nozzle is as important as the driver technology generating the droplets, which has a direct effect on the optical resolution of the printed pattern. With piezoelectric droplet generators, smaller and faster drops are possible but electromagnetic ones are cheaper. The quantitative coloring behavior depending on the absorption characteristics of the dental ceramic is an unknown to the state of the research and the technology. The shades of the dental colors are to be brought about using the main colors with the highest saturation level and and a brightener, which is a water based diluter with an identical composition to the inks, except lacking the metal-ionic coloring agent. The proportions of the ink and the diluter is not the only parameter affecting the shade of the generated color, but also the application sequence can have a significant effect on the optical perception. Since the translucency of the dental zirconia effects the level of color reflection, the depth of the colored section can have an undeniable effect on the natural look of the dental crown. At last the generated shades are to be verified with the existing color standards. The receipt for each single shade generation has to be prepared. The deployed droplets are not fly and settle on the contact point drying on the surface, but are expected to be absorbed and spread inside the porous material. This nature of the interaction between the ink in its fluid form and porous zirconia makes the definition of the system a nonlinear three dimensional fluid dynamics problem. A model is to be generated taking the every compensational aspect of the nonlinear ink behavior, in order to achieve a point accurate color acquisition.

6 Expected Advantages and Functions of the Solution

One of the most important advantages is quantification of the coloring process followed by the printing process. Until this day the crown coloring process is made by dental technologists all around the world. In other words all of the dental replacements are partially handcrafted. In the market hand crafted is another word for made by a craftsman, specifically for the unique owner of the product. Just as any other product on the market, the word handcrafted has a prominent effect on the price tag of the item. The word handcrafted also means the product has some tiny error, a nuance special for each unique sample. If the object of interest is a decor for the home of the consumer, it is one of the most welcome properties, but if the object of interest is an implant, which is to be carried all the time on the comsumer's body as a part of the it, the property everyone is looking for is perfection. A perfect shape, color, consistency and harmony is a standard to evaluate the quality of the work done by the dentist and of course involving the dental technologist. The quantification of the coloring process is the most important advantage of the solution, when it is considered looking from this aspect.Thus, the error can be terminated and the quality deviation can be limited to an acceptable variance.

Another aspect to consider is the ink costs. Each of the ink bottles are labeled with the same price tag by the manufacturer. However not all of the ink bottles contain a material worth the same value actually. The shades of the colors ranging from 1 to 3.5 are only diluted versions of the bottle with the shade 4.0. Buying the most concentrated tone and diluting it is here an economical solution, as it is in every other section of the industry. Also, the whole spectrum of shades can be obtained with only 4 ink bottles and a brightener by halftone printing. The required purchase variety, transportation costs, and the space requirement are all reduced with the usage of only the most saturated shades.

7 Solution Structure

The structural concept is utilization of a 5-axis printing system. 4 base colors with the highest saturation (A,B,C and D4) are to be used with the brightener instead of 16 predefined shades. The amount of the brightener defines the shade of the color. A 3-axis table and the 2-axis nozzle holder are responsible for the coordination during the printing process.

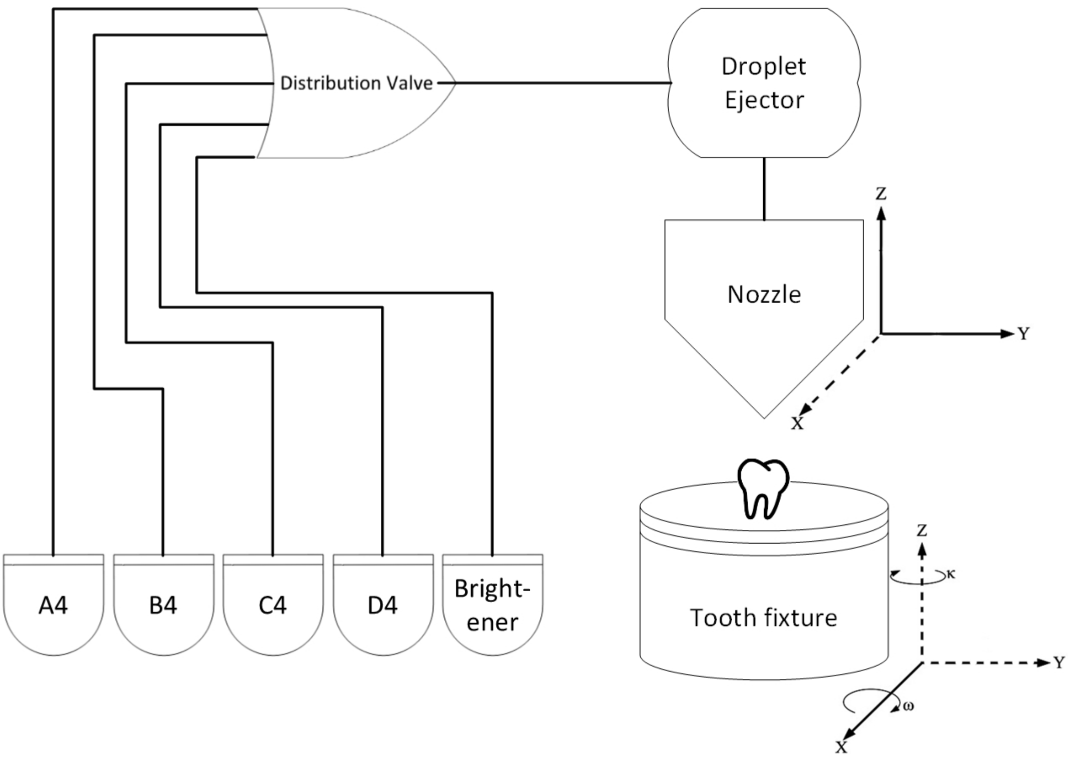


Figure 7.1: Solution Structure

8 Solution Processes

The process concept is realized in three stages. Each stage depends on the previous one and That's the progress so far. First stage is finding the ink and ceramic properties, such as ink viscosity and surface tension, ceramic void fraction and ink absorption time. Second stage is determination of drop properties and deployment metrics, which consist of drop volume, nozzle escape velocity of the drops, the optimal distance between the nozzle and zirconia surface and the angle between the drop projectile and the surface. The aspects to be considered under the third stage color and shade acquisition are trace distance (the distance between two sequential lines on the printed surface), proximity effect, which refers to how the proximity of two colored areas affect the shade of the uncolored area in between and finally the dependency of the shade on the brightener ratio.

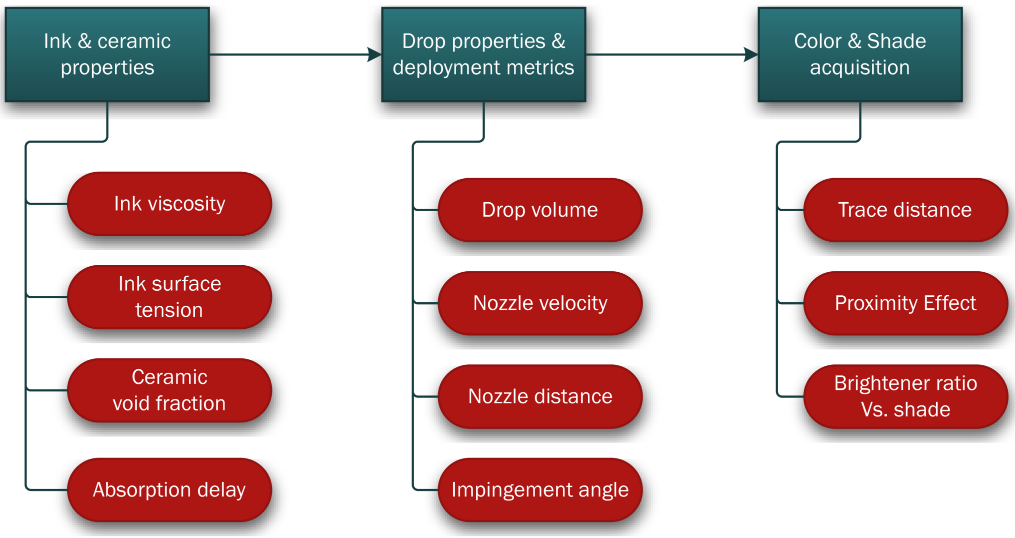


Figure 8.1: Solution Processes

9 Distinctive Features of the Solution

The project is the first automated printing approach in dental coloring and also the first time the shades are generated using the darkest base colors and a brightener.

10 Experiments

Before moving on to the experiments I want to show you the 5 axis printing system prototype provided by Bredent for conduction of the experiments. It utilizes a single nozzle printhead with a piezoelectric valve to generate the droplets. Ink selection, positioning and drop generation commands are given with a G-Code.

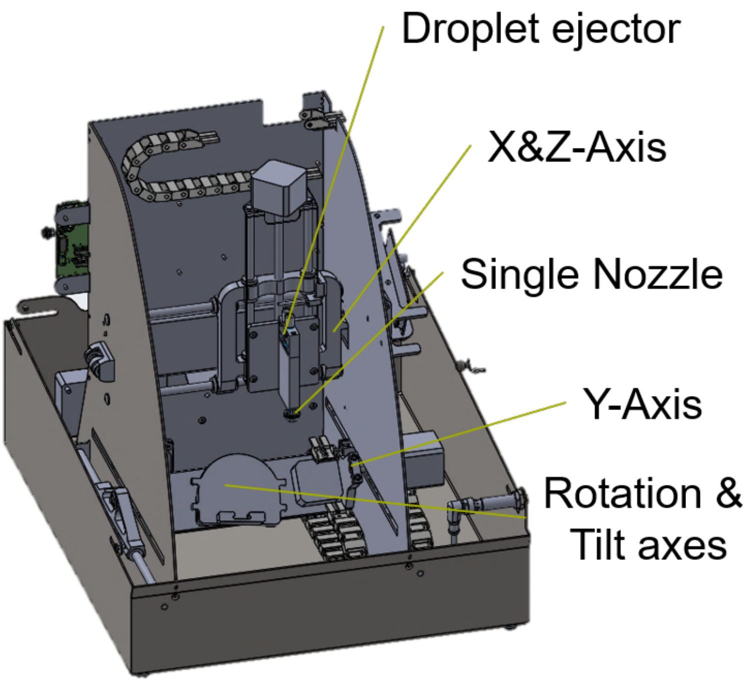
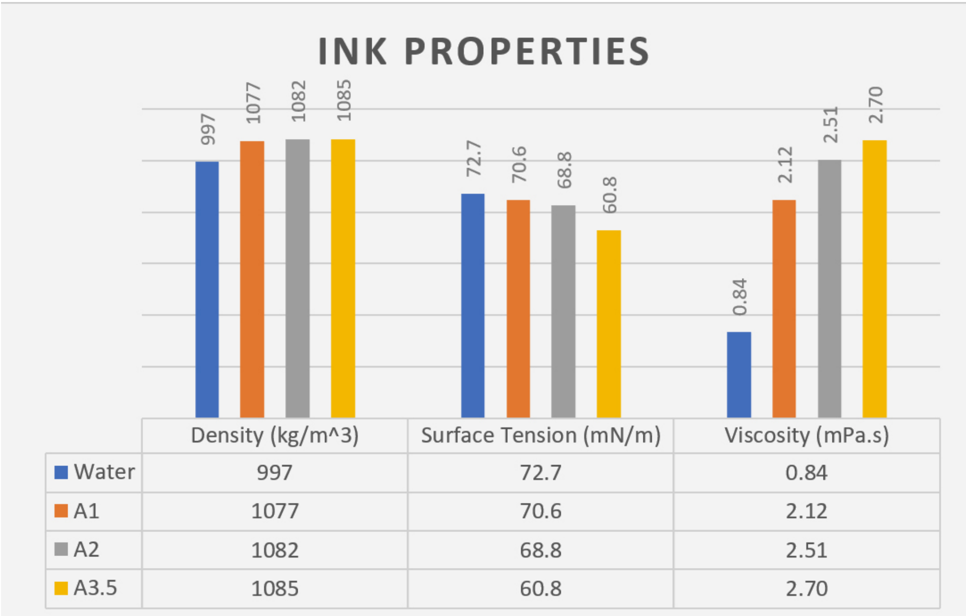


Figure 10.1: 5 axis printer design for dental ink (Matthias Leininger, Bredent GmbH)

10.1 Material Properties

For a dental technician it is totally trivial how viscous the ink is but for an automated printing process the quantization of the properties is highly important. In the first experiment, the properties of the coloring agents A1, A2 and A3.5 are determined and compared to those of water. The inks have a similar density to water, but with increasing coloring agent the surface tension gets lower and the viscosity gets 3 times higher when compared to water.Also, a porosity measurement for the zirconia is conducted, which revealed a 43 percent void fraction. The raw volumetric porosity measurements are 43.09, 43.00 and 43.70. The consistency of the results is also a sign for randomly close packed zirconia powder during the manufacturing procedure. Otherwise the irregular packing would inhibit the fluid drainage and cause macro voids inside the porous material after the dissipation of the impregnating liquid, which would also lead to porosity measurements with a significantly large standard deviation.



	Density (kg/m^3)	Surface Tension (mN/m)	Viscosity (mPa.s)
Water	997	72.7	0.84
A1	1077	70.6	2.12
A2	1082	68.8	2.51
A3.5	1085	60.8	2.70

Figure 10.2: Ink Properties

10.2 Absorption Time

The second experiment is about the absorption time of the droplets, which limits the printing time. We wanted to see whether a heat source can accelerate the absorption or not. The Absorption times are measured at temperatures ranging from 20 to 80 deg cels.The results show that a change of 60 degrees provide a 50% reduction in time.

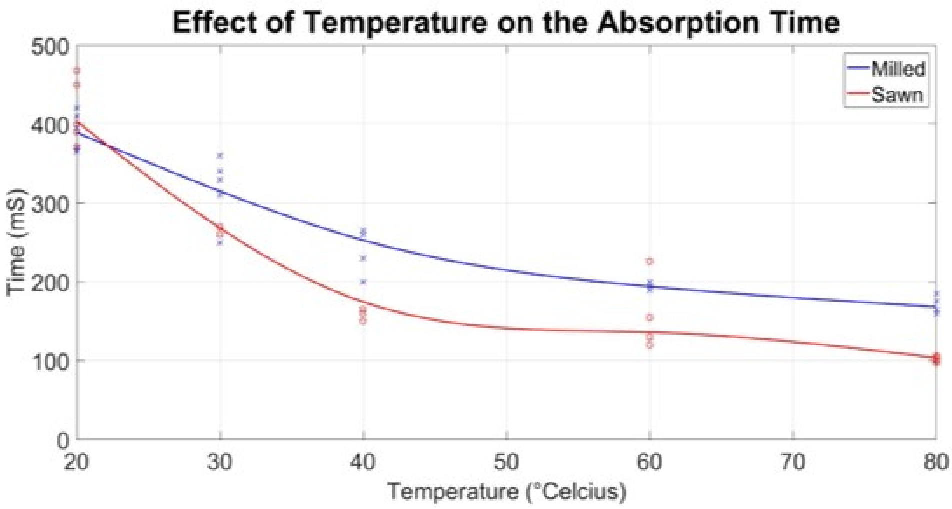


Figure 10.3: Effect of heat on the absorption time

10.3 Drop Size Selection

The purpose of the third experiment is deciding for an adequate drop size. Depending on the drop size the drop generator is to be selected. In this figure you can see a printed zirconia specimen. Each spot on the upper half has a total ink volume of 800 nL and the ones on the bottom half 400 nL. These spots are printed using drops with volumes of 100, 50, 25 and 12.5 nL.The first image shows the spots right after printing. The second one shows the surface after furnacing. A larger drop size results in shorter print duration. However they also tend to expand the spot area more compared to the smaller drops as you can see, which is bad for the resolution.The graphs show the ink intensity along the red lines and the spreading of the ink in lateral direction for each drop volume. 12.5 and 25 nL drops result in a similar spot diameter but the spots tend to get significantly larger with 50 and 100 nL Drops.

10.4 Point Spread Function

The Point Spread Function and Optical Dot Gain Geoffrey L. Rogers Fashion Institute of Technology, New York, NY, USA 1 Introduction Optical dot gain, which is also known as the Yule–Nielsen effect [1–3], has a significant effect on halftone tonality and is caused by the diffusion of photons within the paper upon which the halftone is printed. Any physical model of halftone reflectance must take this effect into consideration in order to accurately predict halftone color. Because of photon diffusion within the paper, a photon may exit the paper from a point different from that which it entered the paper. A

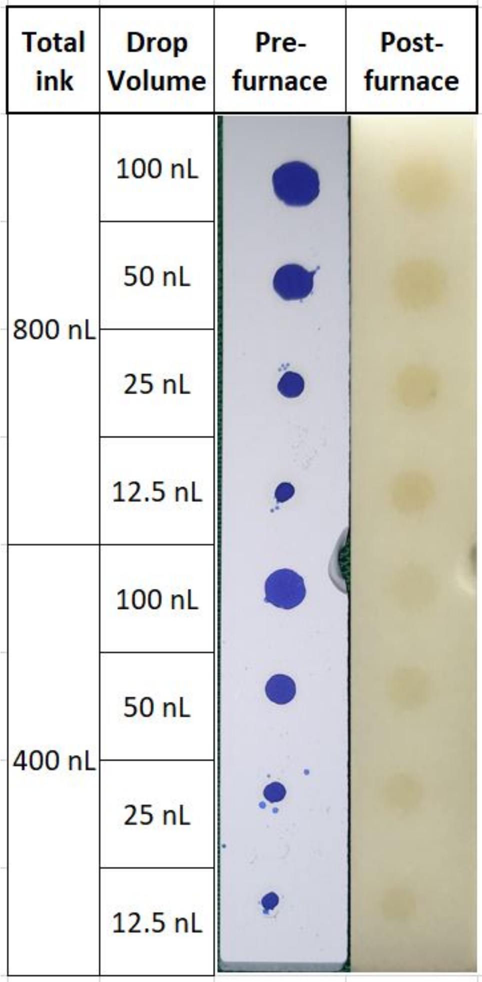


Figure 10.4: Effect of the drop size on the spot area

photon may enter the paper in a region that is void of ink and exit the paper in a region that is covered by ink so that the absorption of light is greater than one would expect based only on dot size. There is an effective dot size that is larger than the actual dot size (Rogers 2015).

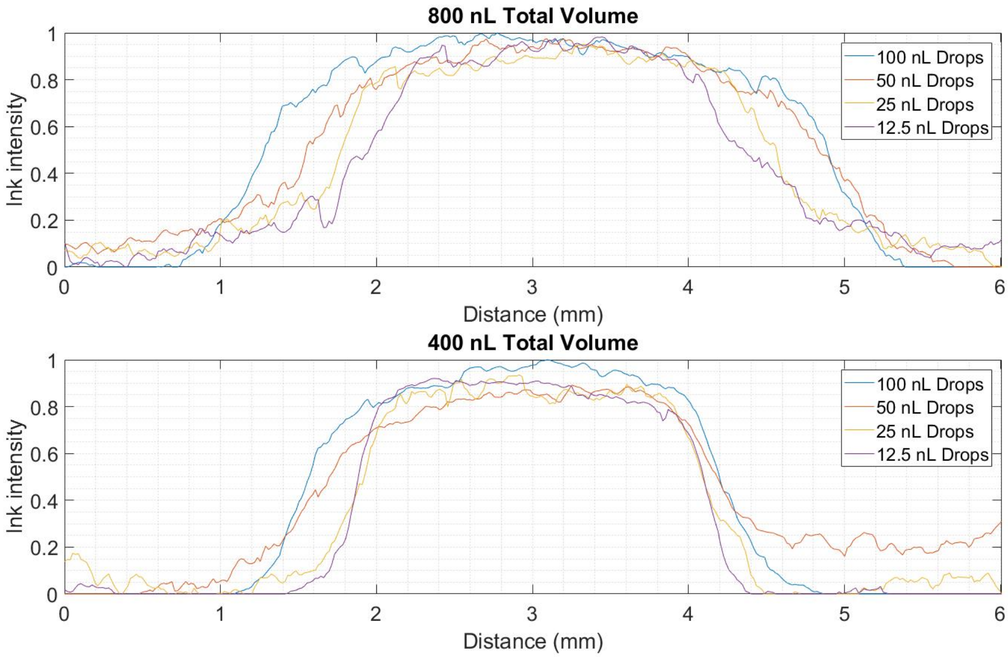


Figure 10.5: Comparison of the spot area results depending on the drop size

11 Summary and Outlook

Vide, quantum, inquam, fallare, Torquate. oratio me istius philosophi non offendit; nam et complectitur verbis, quod vult, et dicit plane, quod intellegam; et tamen ego a philosopho, si afferat eloquentiam, non asperner, si non habeat, non admodum flagitem. re mihi non aeque satisfacit, et quidem locis pluribus. sed quot homines, tot sententiae; falli igitur possumus.

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