DYE MANSION

# DYEING OF SLS PARTS IN RAL
## OPPORTUNITIES AND LIMITATIONS

## COLOR AND COLORVISION

Although color has a physical basis, it is much more than just a material property. Color awakens emotions, warns us of dangers and influences our mood. However, to understand color, one has to understand its origin. Color only comes into being in our heads. From a physical point of view, there is only light with different wavelengths and intensities. If people look at something, the incoming light reacts with the several types of cone cells in the eye. Depending on the stimulation, different signals are sent to our brain. There they are translated into colors. Since every brain ticks differently, color vision is a very subjective process.

And even the same person, sees the identical "physical" color in different ways, if one changes the external circumstances. If you change the lightning, the background, the viewing angle or the size of a raspberry red (RAL 3027) object, the redness will change.

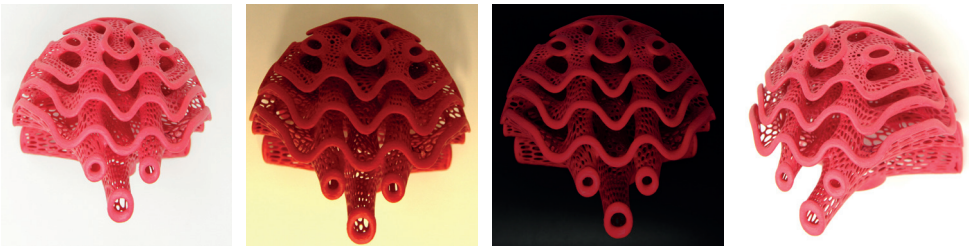


**Figure 1:** Changed color impression of the identical object due to changed lightening, background and viewing angle. From left to right: reference at daylight with with white background; artificial light; black background; different viewing angle.

Although colorvision is very subjective and changes easily, it has a high recognition value. Thus many colors are directly linked to special brands, e.g. Telekom magenta, Milka purple or Nivea blue.

But how can we achieve reliable, reproducible RAL colors with the DyeMansion Print-to-Product workflow?

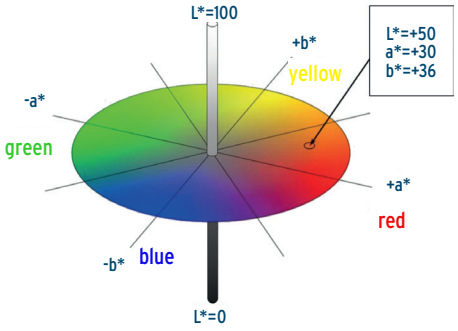



**Figure 2:** 3D illustration of the CIELab color space.

# COLORIMETRY

When it comes to reliable, reproducible colors, you can't get past colorimetry. In colorimetry, the subjective colorvision of human beings is translated to measurable values. In general, color is defined by 3 parameters: hue, brightness and saturation. Within the years various color spaces were invented. Among them, the most popular ones are: rbg, cmyk, CIELab and HSL. Along with these parameterized color spaces, physical color spaces have emerged. The latter are based on a limited number of color patterns. The most prominent physical color spaces are RAL and Pantone. The DyeMansion-RAL palette is based on the combination of directly perceptible colors of the RAL color space with the mathematical-abstract CIELab.

For example the RAL color 3027 (rasperry red) is described by the following L*, a*, b* values of the CIELab color space: L*=43.28, a*=48.99, b*=17.11

To ensure the right color, color measurements are crucial. For the DyeMansion-RAL palette, the spectral method in reflection mode is used to measure the L*, a*, b* values.

With this method, the sample is illuminated and the spectrum (wavelength and intensity) of the reflected light is detected. Since only the components of the light can be reflected that were also used for the illumination, the spectrum of the spotlight is crucial and must also be included. In order to get as close as possible to the subjective color impression, it is recommended to use an illumination source with daylight spectrum. Therefore, DyeMansion uses a D65 illumination. The outcome of the spectrophotometric measurement is a reflection curve, which can be converted to the L*, a*, b* values by integrating the intensities of the individual wavelengths.

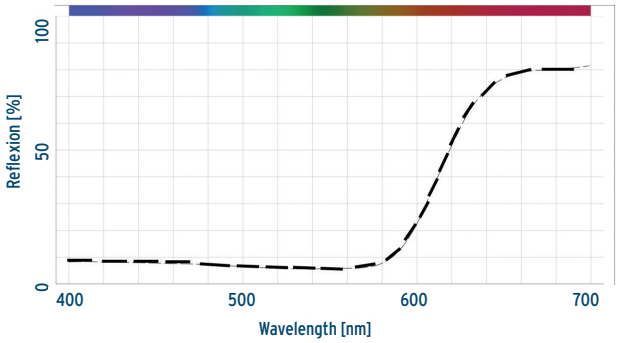



**Figure 3:** Measured reflextion curve of a sample dyed in RAL 3027 showing high relfextion for the red shades.

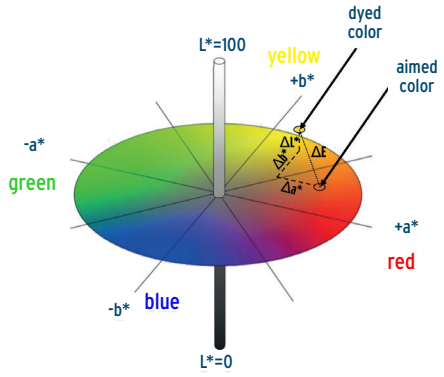



**Figure 4:** 3D illustration of the CIELab color space highlighting, how the deviations in L*, a* and b* sum up to the total dE.

Differences in the L*, a*, b* values indicate color deviations. Using the CIELab color space, theses differences can be easily described by a single value: ΔE. Generally speaking, ΔE<1.5 are not noticeable by the beholder. However, as the sensitivity of the eye is color-dependent, even lager ΔE values might not be visible depending on the color and material (e.g. yellow shades, for which the human eye has a low sensitivity). The exact opposite is true for different shades of grey, where ΔE values of below 0.5 are often noticeable, since all three different types of receptors of the human eye are active and therefore lead to a high sensitivity.

Even a ΔE is not a clear way of communicating color variation. Over time there have been several different formulas for calculating a ΔE value, trying to reflect the subjective visual impression as good as possible. CIE 74, CIE 94 and CMC l:c are just some of the different

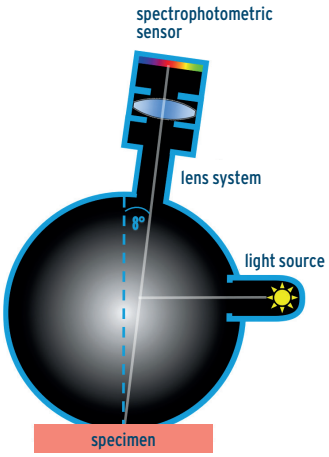



**Figure 5:** Schematic drawing of a spectrophotometer with d/8° sphere geometry.

formulas to calculate a color variation. The industry standard in most cases is CMC 2:1, which is also used by DyeMansion.

However, as the ΔE is only a scalar value without any directional information, it is not straightforward, how to change the dyeing formula to end up with a smaller ΔE. Therefore a complex iterative process is necessary to develop specific colors in the right tone.

In addition to the above, the choice of the spectrophotometer also plays an important role, when communicating color. On the one side each device has tolerances when measuring the exact same sample several times, and on the other side different devices of the same model show variation between each other. In order to keep variances as low as possible, a calibration among different devices might be necessary. There are two main types of spectrophotometers with different measuring geometries. On the one side there is the directional 45°/0° geometry, which is mostly used in quality control, and on the other side the d/8° sphere geometry, which is mostly used for color matching due to the possibility of in- and excluding gloss. The latter enables the user to look into the material without any gloss influence and really see the color, which is not obvious by the visual appearance due to color change under gloss. The tests for this white paper were performed with a d/8° geometry and gloss exluded. In order to have reproducible results it is essential to measure with the same calibrated device every time and use the same settings.

## DYEMANSION RAL-PALETTE

To maintain the colorful RALationship with our customers, DyeMansion has developed the entire RAL classics palette for polyamide 12 (EOS PA2200) parts produced by selective laser sintering (SLS) with the PolyShot Surfacing (PSS) finish. Hence, 170 different colors, covering the majority of industry relevant colors, can be easily obtained using the DM60 coloring system without any waiting times or additional costs for color development.

The DyeMansion coloring system enables colorful parts by dyeing, not by painting or varnishing. This technique allows the dye to penetrate into the SLS part. Consequently, the color is abrasion and scratch resistant. Concurrently, the color impression and also the measured color values are influenced by the quality of the of the part's surface. Therefore, DyeMansion recommends to dye freshly printed parts and treat them with the entire DyeMansion Print-to-Product process.


**Figure 6:** DyeMansion equipment for the three step Print-to-Product workflow, which allows to achieve highly reproducable RAL colors.

## LIMITATIONS

Since the RAL color system is based on industrial requirements and has not been developed specifically for dyeing, there are color shades which cannot be achieved by the DyeMansion coloring system. These RAL colors have metallic, neon, or extreme dark black shades.

While metallic, and very dark black shades can only be achieved with pigments and not dyes, the neon shades would require fluorescent dyes. First tests with fluorescent dyes show, that those color tones work in principal with the DM60 coloring system, but they are not yet released as RAL colors.

So far white shades are achieved with a low concentration of the dyeing solution. If the color is too bright, there is just not enough dyestuff to cover the material color itself and therefore it is not possible to achieve the desired color. Examples for the mentioned cases are summarized in Table 1.

| | | |
|---|---|---|
| **RAL 9001 CREME** | | **BRIGHT WHITE** |
| **RAL 3026 LUMINOUS BRIGHT RED** | | **NEON** |
| **RAL 4011 PEARL VIOLET** | | **METALLIC** |
| **RAL 7048 PEARL MOUSE GREY** | | **METALLIC** |
| **RAL 9005 JET BLACK** | | **DARK BLACK** |

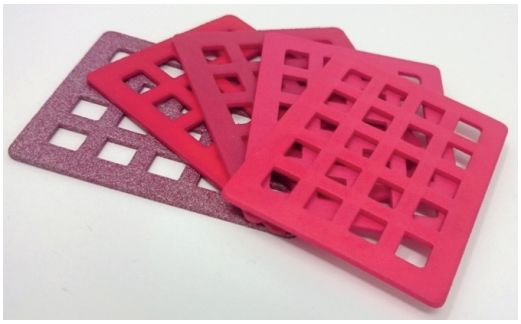
**Table 1:** Overview of RAL shades, which are not covered by the DyeMansion RAL palette yet.

Furthermore there are still colors that are very difficult or impossible to match. Although DyeMansion uses a wide range of dyestuffs which are used to create a dyeing recipe, there are still colors that don't match with any combination of them. Especially some green colors can't be achieved because there are only very few greenish dyestuffs on the market. For most cases a green color is developed with a blue and yellow dye and not a green base dye with some shading components, which makes matching certain green shades difficult.

## INFLUENCING FACTORS

As dyeing always includes the interaction between part material and dye, the final color is highly influenced by the raw material and the dyeing conditions:

- **MATERIAL OF THE RAW PART:** Different polymers offer different affinity to the dyes used in the DyeMansion coloring process. Therefore the RAL color developed for the PA12 (EOS PA2200) SLS parts cannot be reproduced on other materials without additional color adjustment.
- **COLOR OF THE RAW SLS-PART:** Dyeing allows only to change the L* to smaller values. Thus, it is impossible to dye parts in lighter colors than the L* value of the raw part.
- **SURFACE ROUGHNESS:** The dye molecules penetrate from the surface into the part. The more homogeneous the surface, the more homogeneous the dye absorption and thus the dyeing result. As the surface of the up- and down-skin differ, also the dyed part shows little color deviation between up- and down-skin.
- **SURFACE CONTAMINATION:** Fats, dust and blasting material residues slow down or prevent dye absorption and lead to an inhomogeneous dyeing.
- **DYEING PARAMETERS:** Dye concentration, temperature, pressure and time influence the absolute amount of adsorbed dye and thus the final color.



In the following, the influence of some of these parameters is demonstrated. Therefore, dyeing with the RAL 3027 (raspberry red) was performed using different dyeing conditions and materials.

**Figure 7:** Different PA12 materials and finisishes dyed in RAL 3027. From left to right: PSS finished EOS Alumide, VFS finished EOS PA2200, PSS finished EOS PA3200 GF, PSS finished EOS PA2200, untreated EOS PA2200.

## MATERIAL: PA2200, PA2241 FR, PA3200 GF, Alumide

The RAL palette was developed on white PA12 (EOS PA2200) parts. To obtain the same visual appearance on a different material (e.g. PA11), an adjustment of the color is needed. In order to serve as many customers as possible, DyeMansion decided to develop on the most common material EOS PA2200. An adjustment of the color might not be necessary, if customers are using white PA12 from other suppliers than EOS like 3D Systems or Ricoh. This depends on the actual material properties and the chosen RAL color.

| | ORIGINAL RAL 3027 | PA2200 | PA2241 FR | PA3200 GF | ALUMIDE |
|---|---|---|---|---|---|
| L* | 43.28 | 43.30 | 42.71 | 40.36 | 56.62 |
| a* | 48.99 | 49.75 | 42.71 | 40.39 | 17.14 |
| b* | 17.11 | 16.96 | 7.53 | 10.05 | 2.40 |
| ΔE | 0.00 | 0.36 | 6.73 | 5.48 | 15.15 |

**Table 2:** Color deviation form RAL 3027 for different materials.

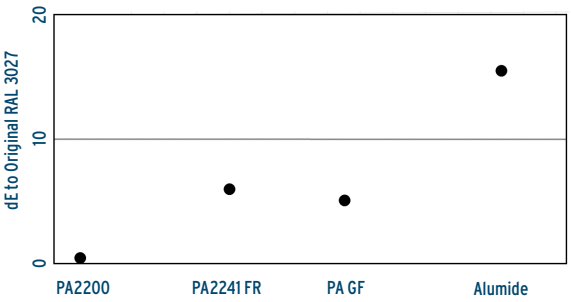



**Figure 8:** Color deviation dE of different PA12 materials dyed in RAL 3027

## TEMPERATURE AND PRESSURE: DM60 vs. pot dyeing

Comparing conventional pot dyeing with the DyeMansion coloring process of the DM60, there are some differences regarding the dyeing process parameters. Using the DM60 enables to perform a dyeing at higher temperatures and under pressure. Both are beneficial for high quality dyeing results. Especially the absorption of dyes deep inside the material is favored in the DM60 process. This allows a long-lasting and abrasion-resistant dyeing.

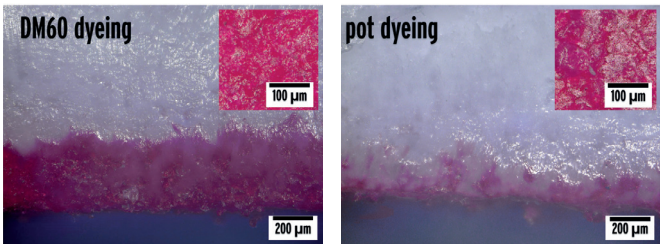



**Figure 9:** Cross-sections of dyed parts. Left: Using the DyeMansion DM60 dyeing process and right: using a simple pot dyeing process. The small inset shows a top view of the respective sample.

| | DM60 @ 115°C | POT DYEING @ 95°C |
|---|---|---|
| L* | 43.30 | 49.71 |
| a* | 49.75 | 54.65 |
| b* | 16.96 | 13.58 |
| ΔE | 0.36 | 4.85 |
| PENETRATION DEPTH | 387±54 µm | 101±27 µm |

**Table 3:** Comarison of dyeing result using DyeMansion dyeing process in the DM60 and pot dyeing.

## SURFACE PROPERTIES: no surface treatment, PolyShot Surfacing (PSS), VaporFuse Surfacing (VFS)

The surface quality and the reduction of its roughness is an essential factor when producing end-use parts with additive manufacturing. To obtain reproducible results with little color variation, a homogenous surface treatment prior to dyeing is indispensible. Therefore, DyeMansion decided to develop the RAL palette on its PSS finish, which offers a glossy look with improved surface properties. When using other surface treatment methods like tumbling or vapor smoothing, an adjustment of the color is necessary to achieve a certain RAL color from the developed palette.

| | NO SURFACE TREATMENT | POLYSHOT SURFACING (PSS) | VAPORFUSE SURFACING (VFS) |
|---|---|---|---|
| **L*** | 42.24 | 43.30 | 42.46 |
| **a*** | 54.56 | 49.75 | 54.66 |
| **b*** | 19.86 | 16.96 | 25.60 |
| **ΔE** | 2.47 | 0.36 | 4.93 |

**Table 4:** Effect of different surface treatments on the final color.

## PART ORIENTATION: up-skin vs. down-skin

Due to different densities, the up- and down-skin surfaces might show slight color variations as shown in the table below. Therefore, a consistent orientation between different parts is essential. The DyeMansion-RAL palette was developed on down-skin surfaces, since the roughness is lower and the look and feel better. When producing parts, the down-skin should be used as the visible surface whenever possible (e.g. housings).

| | UP-SKIN | DOWN-SKIN |
|---|---|---|
| **L*** | 43.30 | 43.30 |
| **a*** | 50.85 | 49.75 |
| **b*** | 17.61 | 16.96 |
| **ΔE** | 0.73 | 0.36 |

**Table 5:** Overview about color deviations that result from different part orientations.

## AGED PA2200: new, white PA2200 vs. old, yellowish PA2200

Most polymers age over time and their mechanical properties degrade. This is also the case with polyamide 12, where the parts turn yellow after already some months. This yellowing not only leads to a shift in the color, but also inhibits the penetration of the dye, resulting in a lighter and more yellowish color. Therefore, a freshly produced white part is key for achieving the desired color.

| | NEW, WHITE PA2200 | OLD, YELLOWISH PA2200 |
|---|---|---|
| **L*** | 43.30 | 46.00 |
| **a*** | 49.75 | 48.24 |
| **b*** | 16.96 | 12.28 |
| **ΔE** | 0.36 | 3.25 |

**Table 6:** Influence of part degradation (yellowing due to irradiance) on the finally achieved color.

Although the entire RAL palette is only developed on EOS PA2200 SLS parts with the PSS finish so far, the DyeMansion coloring technology is compatible with all powder-bed based additive manufacturing technologies. By adapting the dye formula, the entire RAL palette can also be transferred to other materials and technologies. Soon, the RAL palette will be also available for HP Multi Jet Fusion parts.

## CONCLUSION

We learned that although color has a physical basis, it is much more than just a material property. As dyeing is a process, which includes infiltration into the part, the color is highly influenced by the nature of the material. To guarantee a high color reproducibility, all production parameters and every single step the part is treated with, must be consistent. With the instant availability of the RAL palette and the capabilities of the DyeMansion Print-to-Product workflow, Additive Manufacturing takes a major step towards serial production and can finally meet the industries requirements regarding finish and color. The whole RAL range is developed on EOS PA2200 and will soon be developed for other common materials and technologies, such as MJF. Until then, you can achieve all those colors on a different material with an individual color development.

**With this in mind, it is now possible to color additive PA12 parts in the entire RAL spectrum by using the DM60 in combination with the DyeMansion RAL-palette without any waiting times or additional costs for color development.**

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