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# Photocatalytic inks based on $TiO_2$ nanomaterials for water remediation

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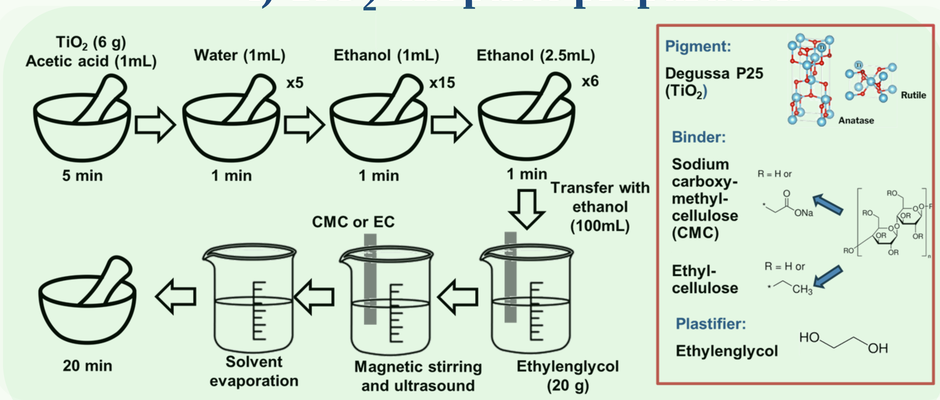
## Introduction

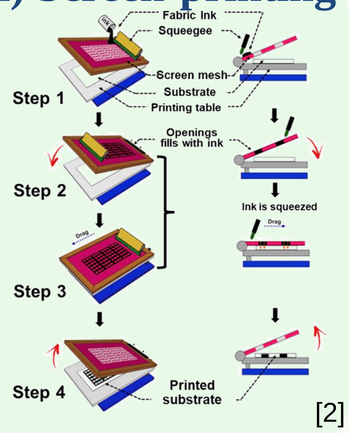
The development of wearable devices deserves great attention. Transferring properties of nanostructures into textiles could have a great impact on society's every day life. For example, heterogeneous photocatalysis has gained attention in recent years as a method to clean wastewater, due to its great potential for the mineralization/breakdown of organic pollutants via advanced oxidation processes (AOP) [1]. Unfortunately, most materials used for research in this field are employed in either powder form or supported over a rigid substrate, both of which are unsuitable for largescale applications. Our work aims to evaluate the photocatalytic efficiency of screen-printable inks based on $TiO_2$ nanomaterial pigments, proposing them as a promising alternative for large-scale wastewater cleaning. Progress has been made on the incorporation of commercial Degussa P25 powders in cellulose-based inks/pastes, as well as the tuning of its viscosity for screen-printing applications. Quantitative studies have been performed to understand the interaction of our $TiO_2$ with different substrates and probe their stability in aqueous media of varying acidity. Qualitative analysis of ink pattern cross-sections was used to study the effect of polymeric binder load on the viscosity and performance of our materials.

## i) $TiO_2$ ink/paste preparation




A screen-printing paste has been designed with a commercially available $TiO_2$ powder (Degussa P25; 80% anatase, 20%rutile) used as the active pigment. These pastes were obtained by mixing the pigments with polymeric binders and a plastifier (ethylenglycol), using a mixture of water and ethanol as solvent. Early tests were performed using sodium-carboxymethyl cellulose (CMC) as a binder. Unfortunately, CMC-based inks exhibited poor adherence to textile substrates when submerged in water. As an alternative, a second set of pastes was prepared switching the binder for ethylcellulose, which is not water-soluble.

## ii) Screen-printing




[2]

Inks/pastes were deposited onto textile substrates using a manually operated screen-printing press. The performed procedure is as it follows:

Step 1. Ink/paste is poured onto a screen mesh, on the edge of a cured pattern.

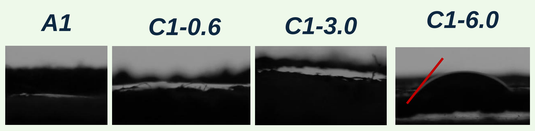
Step 2. Using a squeegee, the openings in the pattern are filled with the ink/paste.

Step 3. The screen mesh is lowered until a deep contact with the substrate is achieved. The squeegee is dragged up and down the pattern in the screen meshed, while pressure is being applied so the ink/paste gets transferred to the substrate.

Step 4. The mesh is separated from the substrate and returned to its original position.

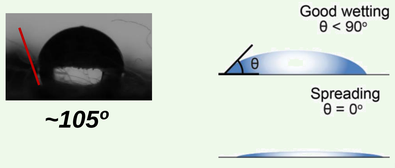
## iii) Contact angle

### a) Water-Ink




*Substrate: Cotton*

### b) Water-Cotton

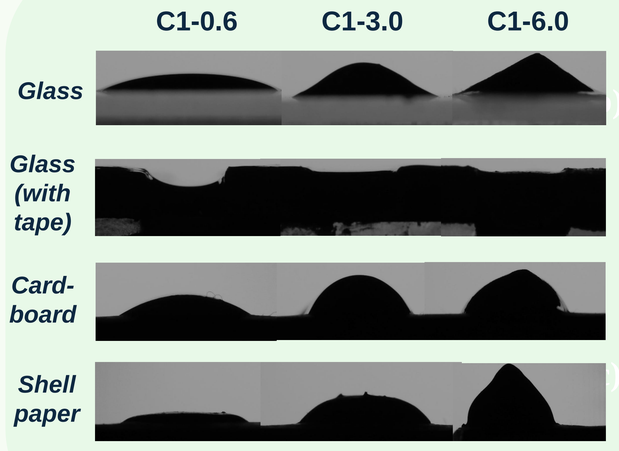



*~105º*

[3]

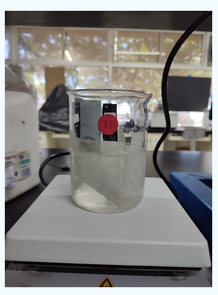
Contact angle measurements were performed on cotton substrates, evaluating its affinity for water droplets before and after printing patterns on their surface with the as-prepared $TiO_2$ pastes. A1 refers to the early formula, where CMC was used as a binder. C1 refer to the later versions, which had their binder switched to ethylcellulose. As it can be seen, the printed patterns exhibited contact angles lower than 90 degrees, some even reaching a near zero value. This can be interpreted as a great wetting capability, meaning water can quickly interact with the component of the inks. Moreover, when compared with the wettability of raw cotton, it can be concluded that our pastes enhance the interaction of water with the substrate, seeing as contact angles for water-cotton were higher than 90º.

## iv) Cross-section analysis



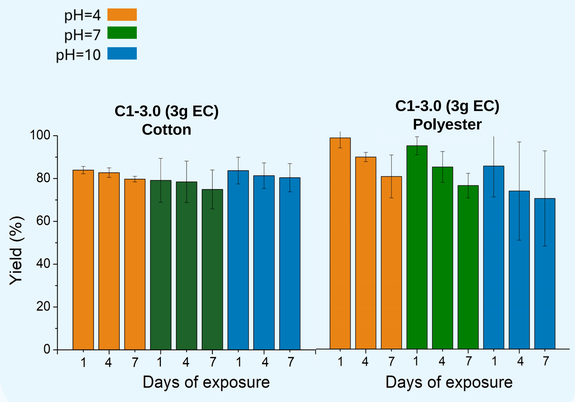

Cross section-analysis was carried out to qualitatively evaluate the rheological behavior of ethylcellulose-based inks. For this goal, droplets of ink/paste were deposited onto different substrates (glass, tape canals on glass, cardboard and shell paper) and allowed to dry at room temperature. The number to the side of ''C1'' represents the amount of ethylcellulose in each paste, ranging from 0.6 g to 6 g of binder per 6 g of $TiO_2$. This effectively altered the observable viscosity of the inks, which can be supported with the results of our experiments. The profiles of the deposited droplets were lower in height as the content of binder was reduced, showing a great amount of spreading for C1-0.6. On the other hand, C1-6.0 droplets maintained their original form, with sharp edges and almost no visible spreading. C1-3.0 stands in a middle point, suffering a decent amount of spreading whilst maintaining most of its original shape. When it came to screen-printing, C1-0.6 and C1-3.0 were properly fixed to cotton fibers, while C1-6.0 properties did not allow its deposition, and no visible patterns were obtained with it.

## v) Stability in water



**Drying: 130ºC**
**Step 1: Heat Plate, 30 s**
**Step 2: Heat Press, 30 s**
**Repeat 5 times**

$$\%yield = \left(1 - \frac{W_0 - W_i}{W_0}\right) x100$$



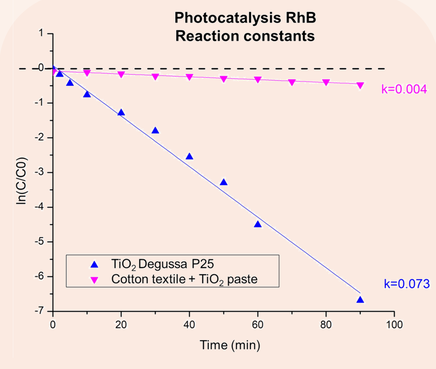

**Stability test:**
**- pH: ~4, ~7, ~10.**
**- Moderate stirring.**
**- Duration: 1-7d**

Once printed onto cotton textiles, $TiO_2$ paste-based patterns were dried and cured using a heat plate and a heat press. The method is as follows: 1. The substrates are dried on the surface of a heat plate at 130ºC for 30 s. 2. While still on the surface of the plate, a heat press (130ºC) is pressed over the substrates, and left unmoved for 30 s. 3. Steps 1 and 2 are repeated 5 times.

Stability tests were performed by submerging these dried textiles in aqueous solutions of different acidity (pH: 4, 7, and 10) with moderate stirring (250 rpm) for 7 days. The weight of the substrates was compared to its original weight after 1, 4 and 7 days.

Out of all the pastes we tested, C1-3.0 had the best performance in every experimental condition retaining close to 80% of its original weight in both cotton and polyester substrates.

## vi) Photocatalytic activity tests




| Catalyst | RhB Degradation |
|---|---|
| P25 | ~100% |
| P25 Paste | 37.5% |

Photoactivity of printed patterns on the decomposition of Rhodamine B (RhB) was evaluated under UV light (352 nm). Tests were performed inside a fixed-bed Rayonet photoreactor with eight 8 W lamps (λ=352 nm). Experiments were carried out by introducing a quartz vase with 250 mL of a RhB solution (10 ppm) and 50 mg of catalyst (P25 powders and cotton textiles with $TiO_2$ paste. Said solution was then subjected to vigorous stirring (2500 rpm), air bubbling (20 cc/min) and light exposure for 90 min. Previous to turning the lamps on, the solution was left mixing for 60 min under dark conditions, in order to account adsorption of the dye onto the surface of the catalyst. P25 powders were able to completely decompose the dye at around 70 min of reaction, while cotton substrates with our paste were only able to decompose about 37.5% of the dissolved RhB after 90 min of light exposure. Nonetheless, these are promising results for the use of versatile and easily recoverable photoactive textiles using screen-printable $TIO_2$ based inks&pastes.

## References

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