Interaction between additives in paper's *surface sizing*

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ABSTRACT

Paper to acquire its characteristics as a final product needs the application of a solution on it known as *surface sizing*. The surface sizing's compounds comprise a salt, starch, optical brighter agent (OBA) among other compounds that have not been studied in this work. A OBA is responsible for the paper's whiteness (by ble light emission after absorption of UV light) and the interaction between these compounds depends on OBA´s concentration. So, the study was divided into two parts: with diluted solutions to characterize the species present in the surface sizing and to understand the interactions between the components. A spectrofluorimeter and an optical absorption spectrophotometer were required for this study.

In the first part – diluted solutions (low OBA concentrations) – the active compound present in the two optical brighteners was characterized. These experiments led to the conclusion that the active compound is the same in OBA1 and OBA2. However the intensity of OBA1 is about 15% higher. In addition, it was possible to observe a *trans cis* photoisomerization reaction. In contrast, at these concentrations no *quenching* was found. Relative to OBA2, a reasonable amount of suspended solid was detected and it is because of the oversaturation.

In a second phase – concentrated solutions (OBA concentration in the range used in industrial surface sizing) – the same molecular aggregates were formed for both OBA's. Among the aggregates, the j aggregates (whose aggregaton method is due to π- π stacking), known by displacing the emission and absorption to higher wavelengths. When salt is added the relative proportion of j aggregates increased because salt induces the formation of these molecular structures. At the same time, the salts are responsible for *quenching*.

Keywords: surface sizing; OBA/starch/salt; photoisomerization/quenching/j aggregates;

1. INTRODUCTION

Man has always needed to express himself and, over time, has been creating several ways of expressing himself. One of the most important supports for communication, invented by man was paper. Considered by many to be the "most extraordinary product created by Man," the role has come over time to be challenged by the digital world. This has allowed faster access to information. Today, we have already been able to read books through internet-connected devices, consult newspapers, magazines, etc. However, the paper is important, because when we need to write or read something with an official character, what appears to us is a blank sheet, like this one where the dissertation is written. [1].

The paper has a porous surface and consists basically of fibrous materials and has a large number of functions. Since the nineteenth century, the main source for pulp production is the trees and through them the cellulosic paper pulp.

Another possible source of cellulose fibers is cardboard / paper recycling. Papermaking using reclaimed fibers has been a common practice in the Paper Industry in the European countries for more than 60 years. However, it has been in recent decades - thanks to the development, on the one hand, of collection systems and, on the other hand, recycling - that the used paper / paperboard has assumed a more significant position as a raw material complementary to the virgin fibers supplied by the wood. European paper production in 2018 was 92.2 million tonnes and there was a record record of 72% for the recycled paper rate. [2] [3] . *Eucaliptus globulus* (Fig 1) is the forest species that is the origin of the fibrous materials of The Navigator Company. This species was introduced in Portugal around 1830 with the aim of making pulp, but it was only in 1957 that the process of large-scale pulp production began. [4]

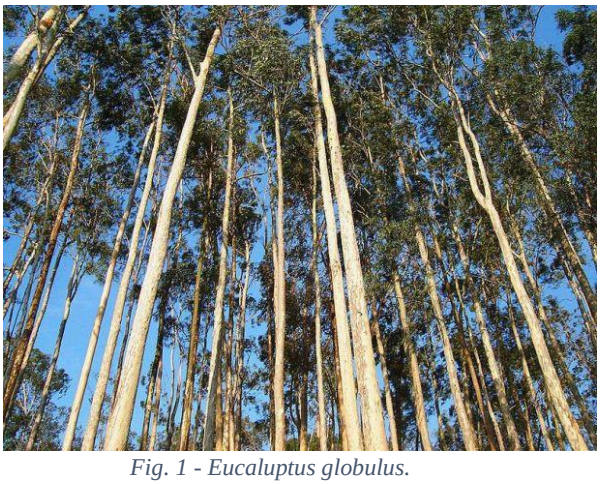


Fig. 1 - Eucaluptus globulus.

Firstly, the wood from the forest undergoes a mechanical process (shredding or pruning) where the trunks are transformed into small pieces with controlled dimensions. These intermediates are known as chips, chips or chips, ranging in size from 5 to 50 mm.

Subsequently the paper pulp is produced, from a baking in the chip digester. This process can be chemical (for The Navigator Company), thermochemical or mechanical. Through the machinery it is possible to transform the paste into surface paper and this process comprises three phases. The wet phase where there is formation of a continuous sheet from the slurry in suspension. Then the pressing, where the extraction of water by compression and finally, the drying, whose objective is evaporation but using the heat.

In most cases, the paper finish is central to its performance and the surface gluing operation that guarantees the color and strength that are characteristic to it.

This collage, also known as suface sizing has as main purposes to increase the print quality, whiteness and brightness. All these properties influence the quality of the paper and therefore the consumption of the same. However the interactions between the constituents of the paper are complex and many are unknown so the formulation of the sizing suface is done on a trial-error basis.

2. GOAL OF THE SEARCH

The work arose due to the need to understanding the difference in efficiencies between two commercial optical brighteners (OBA1 e OBA2) used in the surface sizing that are responsible for the paper's whiteness (by ble light emission after absorption of UV light) using salts.

3. MATERIALS AND METHODS

The Navigator Company sent us two different OBA, OBA2 and OBA1. Also the salts, calcium chloride in 40% aqueous solution (w / w) and the solid state magnesium chloride (pellets), the powdered starch and the enzyme (a-amylase in the aqueous state) used for cooking were provided by the same company.

To prepare the stock solution of magnesium chloride, 40 g of this salt was weighed into a digital scale with an error of ± 0.005 g in a 100 ml flask, thus making a solution of ~ 40% (m / m).

To prepare all diluted solutions, a stock solution of 1/1000 (v / v) dilution was prepared for each OBA. This required a micropipette with an uncertainty of 0.05µl, where 50µl of the OBA bottles were removed, placing that amount of liquid in a 50ml flask.

Optical absorption spectra were obtained using a *Lambda 35 UV / VIS Spectophotometer*. Deuterium (UV) and tungsten (visible) lamps are responsible for the emission of a beam of light. Lamps have a spectrum that covers the range from 190nm to 890nm.

The excitation and emission spectra were obtained in the *Fluorolog spectrofluorimeter*. A xenon lamp is responsible for the beam of light entering the sample, exciting it. The light initially emitted has a spectrum with a band extending from ~ 240nm to ~ 700nm, and maximum at ~ 467nm. The excitation monochromator selects the wavelength of the photons sent to the sample, the intensity of which is controlled by a slit. The software used to analyze the data was the Spectrum.

4. EXPERIMENTAL PART- RESULTS

4.1. Diluted Solutions

Solutions of the OBA with different dilution levels were prepared in order to find the range of concentrations suitable for the detailed study of the three types of spectrum.

The absorption spectra of the two OBA at the dilutions of 1/1000, 1/10000 and 1/100000, where it can be seen that the dilution of 1/10000 is in both cases adequate , having absorbance values sufficiently high but not exceeding.

Thus, it was decided to use half of this value (ie 1/20000) in the rest study of all diluted solutions (any of the OBA) to ensure good linearity and applicability of the Lambert-Beer law. Then the spectrum of botbh species were measured as figure 2 shows.

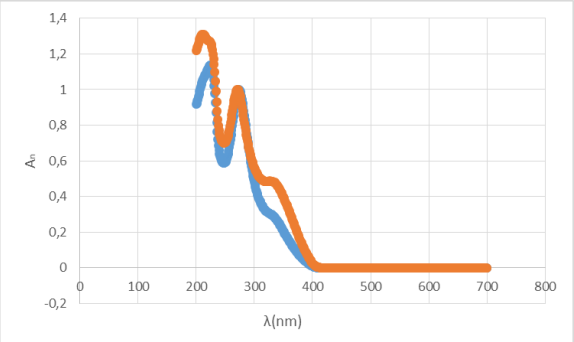


Fig. 2 - Absroption spectra for OBA1 (orange) and OBA2 (blue).

Not considering the zone below 250 nm, due to the possible absorption by the glass cell, it can be seen that both samples have a peak at 270 nm, with an inflection point ("shoulder") at 350 nm, which suggests the

presence in solution of two species that absorb. The difference in relative heights for the two samples indicates a different proportion of these species in the two OBA.

The excitation spectra were collected in the blue at 440nm (Fig. 3) and excitation emission at 270nm (Fig. 4) for the diluted samples (1/20000) for each of the OBA.

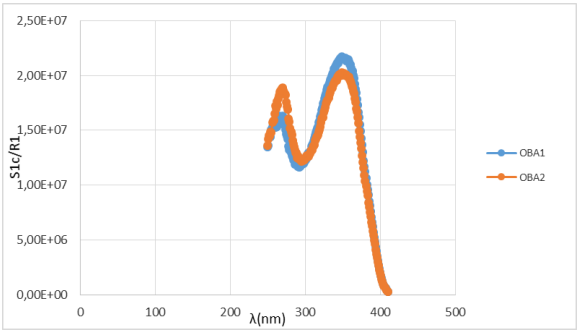


Fig. 3 - Excitation spectra for OBA1 and OBA2.

As can be seen from the excitation spectra, both have maxima at the same wavelengths observed in the absorption spectra, as expected. Note that the intensity at 270nm is higher for OBA2 and at 350nm is higher for OBA1, which reinforces the idea that the photoactive species present in the brighteners have different relative concentrations.

Since the peaks are at the same wavelengths it is possible to assume that the active molecule is the same.

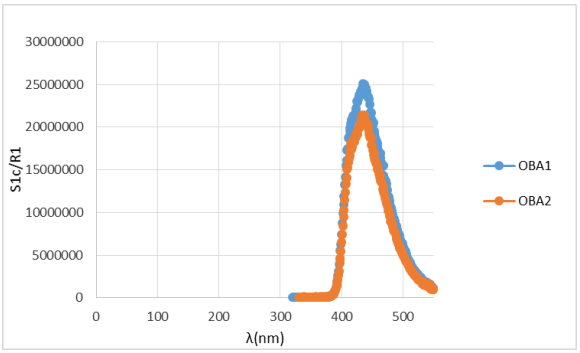


Fig. 4 - Emission espectra for OBA1 and OBA2.

It is important to note that the maximum intensity of the emission spectrum of OBA1 is approximately 15% higher than the intensity of the maximum emission of OBA2, at the same dilution, indicating a priori a better performance for this OBA in the sizing solution. The correspondence between the highest intensity of the peak emission of OBA1 and the highest intensity of its peak at 350 nm in the excitation spectrum indicates that the species that absorbs this wavelength has a higher quantum fluorescence yield.

4.1.1. Photoisomirization

During the above-described study, it was observed that the absorption spectra were not always the same, varying depending on the mode of sample preparation. Figure 5 shows the spectrum of an OBA2 solution prepared from the stock solution as well as a solution prepared directly from the received OBA2 flask (fresh solution) at approximately the same concentration and normalized at their maxima between the 250-700nm.

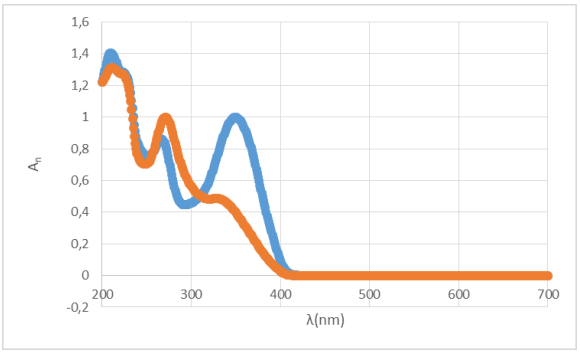


Fig. 5 - Excitation spectra for fress solution (blue) and irradiated solution (orange).

By analogy with the study by Chung et al. on the behavior of another stilbene (4,4'-diaminostilbene-2,2-disulfonic acid) derivative) [5], it was hypothesized to be a phenomenon of photodecomposition or photoisomerization of the fluorophore. In this study, the *trans* isomer was shown to be the most photoactive form of the compound, and that it undergoes a rapid process of cis-trans photoisomerization, with a photo-state being readily achieved when the molecule is exposed to light.

To test the photoisomerization hypothesis for the fluorophore present in the OBA2 solution a diluted sample of this OBA was directly drawn from the recipient vessel and its optical absorption spectrum was measured with different times of exposure to light from the laboratory. The results can be seen in Fig. 6.

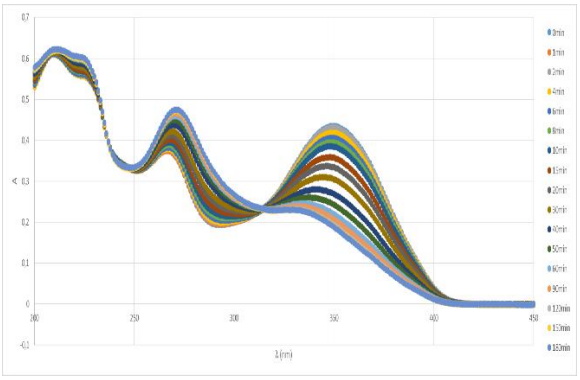


Fig. 6 - Absorption spectra for the same solution with different irradiation times.

Exposure to light causes the peak absorbance to decrease to 350nm and on the other hand the peak increase to 270nm.

It is also important to note that it was not possible to detect photodecomposition in the experimental conditions used in the present study. Once the *cis-trans* equilibrium has been reached, the absorbance of the sample does not decrease with time.

To test the effect of photoisomerization on the fluorescence of the optical brightener studied, emission spectra were also obtained, excited at 300 nm after different exposure times to light (Fig 7).

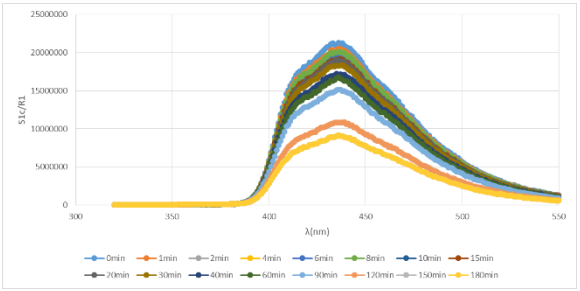


Fig. 7 - Emission spectra for the same solution with different irradiation time..

As seen in this figure, the intensities of the maximum decrease with the time of exposure, so it is concluded that the formation of the cis species impairs the fluorescence. This is because although absorption is increasing at 300nm (excitation wavelength), the maximum emission intensity decreases.

4.1.2. OBA2 & Salt 1 effect for diluted solutions

In this section, it was studied whether calcium chloride has any effect on the photochemical behavior of OBA2.

The solutions presented a colorless appearance and the optical absorption spectra were obtained for crescent concentration (Fig 8).

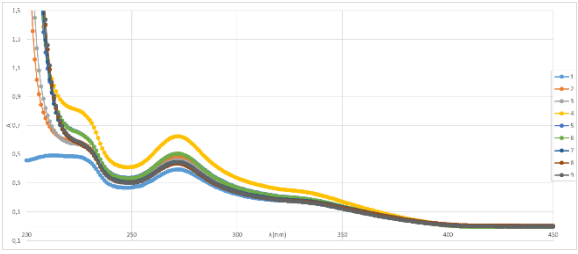


Fig. 8 - Absorption spectra for solutions with salt.

Subsequently, the emission spectra were measured, with excitation at 270nm, in order to look for the existence of quenching (Fig 9).

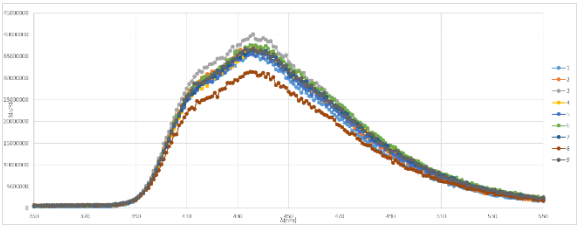


Fig. 9 - Emission spectra for solutions with salt.

It is found that the emission spectra of the different samples are very similar, with no quenching effect evident. In a more detailed way, the representation of Stern-Volmer (Fig 10) was made, representing in the abscissa axis the concentration ([CaCl2]) and in the axis of the ordinates the ratio between the maximum intensity of the emission at each concentration and the maximum intensity of the pure fluorophore (I0 / I-1), where I0 is the maximum spectrum intensity of sample 1.

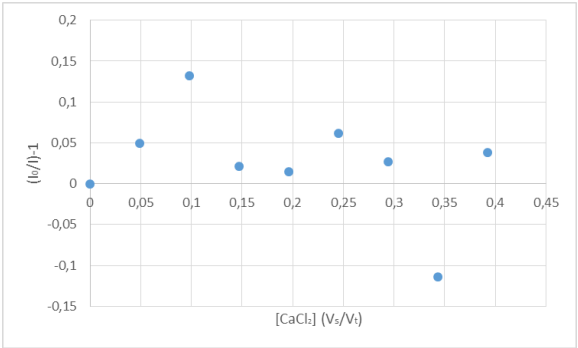


Fig. 10 - Stern-Volmer representation with salt 1.

It is thus concluded that there is no fluorescence oppression by calcium chloride at diluted fluorophore concentrations.

4.1.3. OBA2 & Salt 2 effect for diluted solutions

As was done for calcium chloride, an analysis was also made to ascertain a possible quenching process for magnesium chloride. The Stern-Volmer representation is shown in Fig 11.

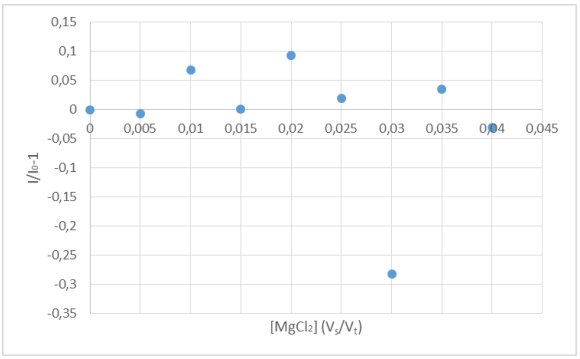


Fig. 11 - Stern-Vomer representarion for solution with salt 2.

Still no prejudicial consequences by adding magnesium chloride.

4.1.4. OBA2 & Starch & salt effect for dilluted solutions

The Stern-Volmer representation for these solutions - which the concentration of salt ($CaCl_2$) was fixed – are shown in Fig 12.

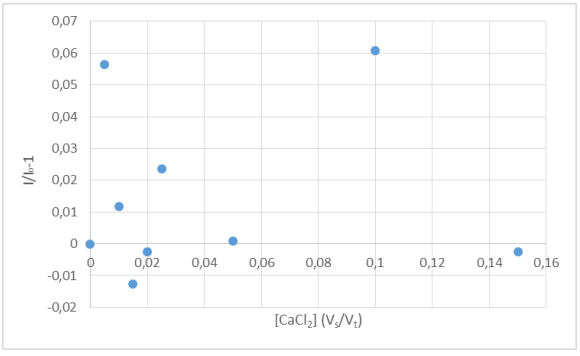


Fig. 12 - Stern-Volmer representation for solutions with salt and starch.

The starch is also a spectator for the process of fluorescence by the OBA's.

4.2. Concentrated Solutions

It was necessary to do these same studies but for OBA concentration in the range of that which is used in paper sizing suface. This concentration, 0.1 (v / v), is the same for all the concentrated solutions studied and this concentration belongs to the range used by the paper industry. In this way, it was necessary to use another tool of the spectrofluorimeter, namely to place the excitation light beam at 22.5 ° instead of 90°. This method is called Front-Face, as previously mentioned.

4.2.1. OBA2 concentrated solutions

The spectra were obtained from a sample having a OBA concentration equal to that used in the surface sizing of the paper. The emission spectrum was obtained by exciting the sample with irradiation at 370 nm (UV). This spectrum was normalized and compared to the spectrum of dilute solutions (Fig 13).

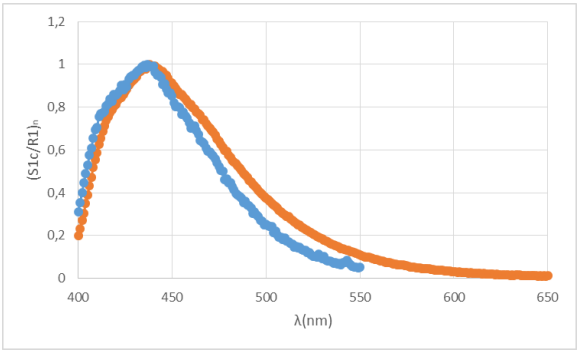


Fig. 13 - Emission spectra for the diluted and concentration solutions.

The maximums of the spectra coincide at 440 nm, which corresponds to the blue color of the electromagnetic spectrum. However, the spectrum of the concentrated solutions has a broader band, indicating that there are different fluorescent species, which will be discussed further below.

Excitation spectra of the same sample were collected at 440 nm, normalized and compared to standardized spectra of dilute solutions – Fig 14.

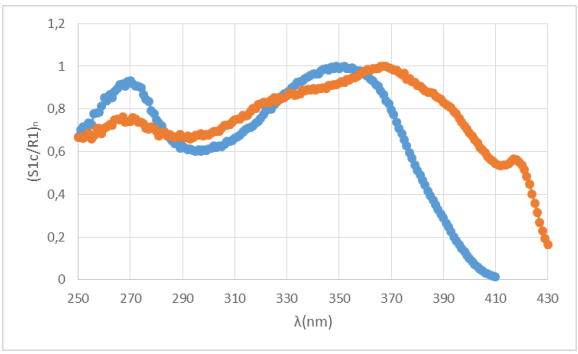


Fig. 14 - Excitation spectra for the diluted and concentration solutions.

For the diluted solutions, the spectrum has two peaks: one at 270nm (corresponding to the cis form) and one at 350nm (trans form).

In the case of the concentrated sample (blue) obtained in FF, the spectrum has three peaks. The former is at 270nm, as in the excitation spectrum of

the diluted solution (orange), and the other two peaks are at 365nm and 420nm. It is also possible to observe an inflection near the characteristic spectrum of the trans form (~ 340nm), suggesting the existence of this species in the concentrated sample. There is also another 380nm inflection, which was not present in the diluted sample.

The spectrum of the concentrated sample presents less defined peaks, with excitation occurring across the range of 250nm to 430nm, thus indicating that a considerable number of species emit blue radiation. As the fluorophore molecule is the same, varying only in its dilution, this spectrum suggests the formation of molecular aggregates of the diaminostilbene hexasulfonic acid derivative.

A molecular aggregate can be considered a cluster of some particles or molecules, which come together without covalent bonds. Its characterization is made taking into account its spatial structure (relative position and organization of particles within the aggregate) and the number of aggregation n (average number of particles in the aggregate). The size of these complex systems can range from a few nanometers (micelles) to several micrometers or more (thin films, membranes). [6]

The tapering and narrow shape of the peak observed at 420 nm in the excitation spectrum is characteristic of a particular type of molecular aggregates, the aggregates j. The aggregates j are known by their ordered way of aggregation, due to the dipole moments of the molecules being parallel, forming an axis of aggregation. These nanostructures were discovered about 80 years ago by researchers Jelley and Scheibe and continue to be the focus of many experts in the field of organic chemistry. Their particular way of aggregation has attracted large investments from the scientific community. Normally, aggregation occurs via a π-π interaction between highly polarized groups with electrostatic interaction between groups with opposing charges. There is evidence in the literature of this type of aggregation for stilbene molecules [7] and it is known that this π-π stacking is unique to *trans* molecules [8]

It was necessary to do a series of tests to prove the formation of this type of aggregates. As mentioned above, the aggregation j induces a red shift in the uptake and consequently the emission. Thus, the area of the excitation spectrum (assumed to be of the aggregates j - in this case ~ 420nm) is expected to become more prevalent as the collection is made for wavelengths further shifted to red. [9]

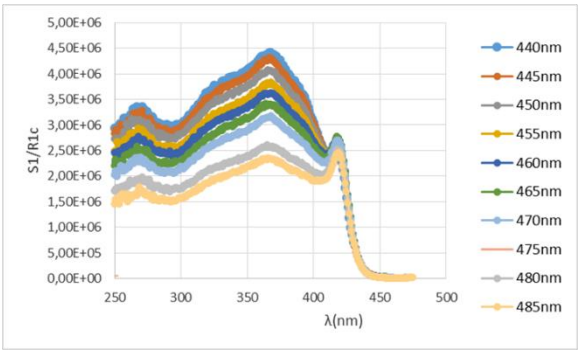


Fig. 15 - Excitation spectra for different wavelange collection.

The intensity of the spectra decreases as the collection is made at longer wavelengths, as expected due to the shape of the emission band (Fig 15). However, the decrease in intensity is almost imperceptible in the area of wavelengths between 410nm and 450nm.

4.2.2. OBA2 & Salt 1 effect for concentrated solutions

In order to test the existence of quenching for the concentrated solutions 9 samples of OBA were made at different concentrations of salt.

By adding salt, the formation of a precipitate is noted at concentrations higher than that of solution 3, as shown in Fig 16.

Fig. 16 - Solutions measured with solid precipated.

As a precipitate formed from solution 4 the measurements were preceded by a stirring and were measured as soon as possible. The emission spectra is presented in Fig 17.

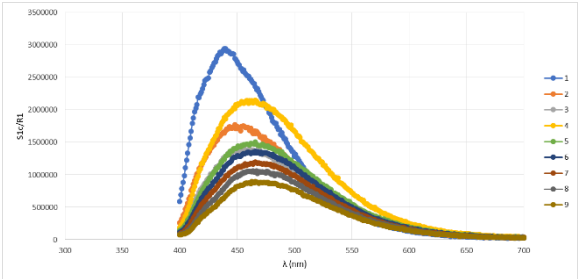


Fig. 17 - Emission spectra for concentrated solutions with salt.

The increasing of salt concentration leads to decreasing of the emission which represents a quenching phenomenon. It is not possible to do the Stern-Volmer graph because of the range of concentrations that were used.

Also the excitation spectrum was normalized (Fig. 18) and, interestingly, the spectra are overlapping from 250 nm to 415 nm (characteristic region of the j-aggregates), from which area they begin to differentiate. The normalization stresses the relative increase in fluorescence intensity at higher salt concentrations when the sample is irradiated at the wavelengths absorbed by the aggregates j. This effect allows us to propose that the salt induces the formation of this type of aggregates.

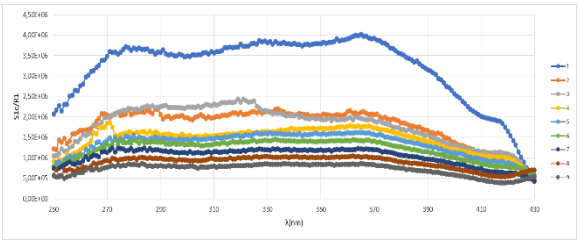


Fig. 18 - Excitation solutions for concentrated solutions with salt.

This effect has already been observed for other types of compounds, and the authors concluded that the formation of aggregates j depends on the salts in solution and the rate of formation of the aggregates is greater as the ionic strength increases. [10]

4.2.3. Surface Sizing Solutions

Finally, the various possible combinations of optical brighteners and salt were compared to the concentration used in the bonding processes. 0.6 (v / v) starch was used in each solution and 0.1 (v / v) and 0.02 (v / v) salt in each sample.

There were then 4 solutions corresponding to the possible combinations of the two OBA with the two salts. The excitation and emission spectra are shown in Figures 19 and 20, respectively.

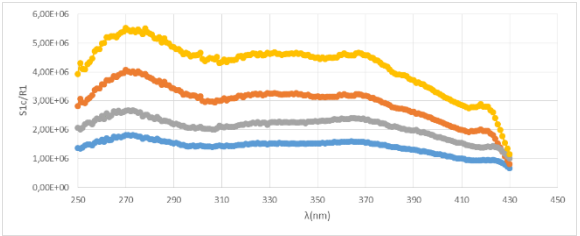


Figura 19 - Excitation spectra for possible combiantion of surface sizing.

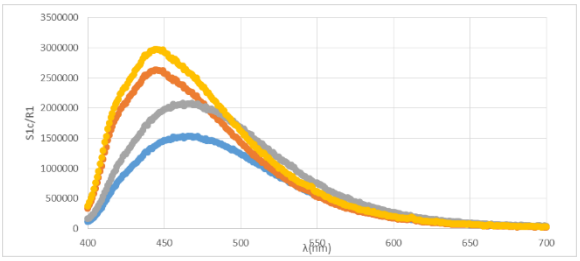
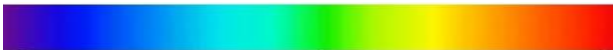


Figura 20 - Emission spectra for different type of surface sizing.

As can be seen, there is clearly an ordering (based on the intensity of the emission peaks) of the performance of the different types of sizing suface. OBA1 is the best brightener and, of the two salts, magnesium chloride has the best results.

It should be noted that the OBA1 solutions maintained their peak at the wavelength of 440 nm, as did the emission spectra of all diluted solutions. On the other hand, the OBA2 solutions are shifted to the red, approximately 25nm, as can be seen more easily in figure 21 - standard emission spectra.



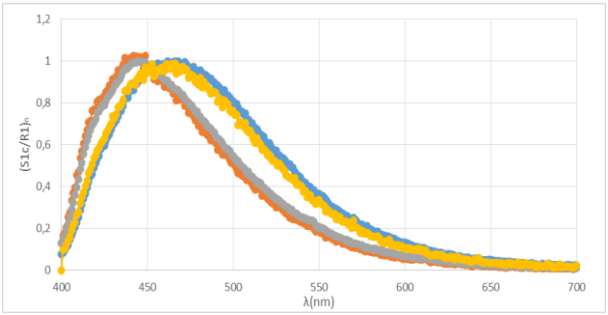


Figura 21- Emission spectra normalized for different type of surface sizing.

As can be seen, the emitted photons have wavelengths between 400nm and 700nm. However for OBA2 solutions it can be seen that more than 50% of the emitted photons have a wavelength greater than 470nm (blue limit).

The excitation spectra were also normalized (Figure 22) and a slight difference in the spectra can be observed which can be explained by the low signal of the excitation spectrum of the two OBA2 samples that may compromise this type of normalization.

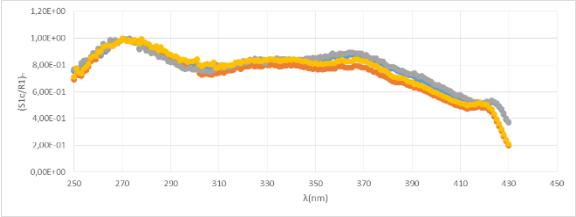


Figura 22 - Excitation normalized spectra for possible combination surface sizing.

It was concluded that the starch do not interact with the fluorescence phenomenon of the OBA.

6. CONCLUSION AND RECOMMENDATIONS

The main objective of this work was to understand the interactions of the different components of the surface bonding of the paper in solution, focusing primarily on the OBA whose purpose is to increase the whiteness of the paper through the fluorescence phenomenon. In this way the samples were studied for diluted concentrations of OBA.

By diluting the two OBAs in the same volumetric concentration, different results were obtained in terms of absolute emission and absorption. In terms of absorption it was possible to conclude that the active species that participated in the fluorescence process was the same. As for the emission spectrum, it was verified that OBA1 had higher values than OBA2, indicating a better performance.

A trans cis photoisomerization process was detected in samples diluted to both OBA, which decreased the emission, the photo-state was reached after 3h of exposure to light and its kinetics is independent of the ionic strength present in solution.

Subsequently, the effect of salts and starch (at the concentrations used in the paper sizing suface range) on dilute OBA solutions was studied. None of these additives decreases the emission, meaning there is no quenching for low concentrations of OBA.

As no results were obtained to explain the decrease in the whiteness of the paper by addition of salt, it was decided to do the same study for concentrated solutions of OBA in the concentration range used in the sizing solution using another method of measurement due to the detector saturation problem (Front-Face). For concentrated solutions, OBA1 continues to emit radiation with more intensity by about 15% than OBA2.

By observing the excitation spectra, it was found that both OBA form molecular aggregates. It was possible to identify one of the types of aggregates, the aggregates j, whose main characteristic is the narrow and tapering form of its peak in the emission spectra.

Concentrated solutions of OBA with the salts were then analyzed. For these concentrations quenching was observed as there is a decrease in the emission as the concentration of salt increases. This effect is more significant for calcium chloride than for magnesium chloride. It was concluded that addition of salt also promotes the formation of the aggregates j that alter the color of the emitted light, greening it. Again the spectra are not altered with the presence of starch. Moreover, it is important to emphasize that these aggregates are formed by π-π interaction of trans molecules, suggesting that their presence in addition to diverting the emission to larger wavelengths also decreases the species in solution with higher fluorescence quantum yield .

Finally, the order of performance in solution of the sizing substrate mixture based on emission intensity was obtained: OBA1 + $MgCl_2$> OBA1 + $CaCl_2$> OBA2 + $MgCl_2$> OBA2 + $CaCl_2$.

For future experimental work I recommend the study of the OBA1 solution at different salt concentrations, both calcium chloride and magnesium chloride, to verify the degree of quenching. In addition, I advise repeating the emission and excitation spectra analysis of the concentrated solutions of OBA but using a different measurement procedure. Instead of stirring the solutions that had precipitated and measuring them then let the decantation process occur by the action of gravity and only later the sample would be measured. Thus it could be verified whether the precipitates influence or not the emission or excitation spectra.

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