OZONATION: A NEW PATTERNING METHOD FOR OPTICAL BLEACHED FABRICS

OZONLAMA: OPTİK BEYAZLATILmiş KUMAŞLAR İÇİN YENİ BİR DESENLendirME YÖNTEMİ

Seher PERİNÇEK

Emel Akin Vocational High School, İzmir, Turkey

Received: 16.12.2015 Accepted: 18.02.2016

ABSTRACT

In this paper, the usability of ozone to remove the optical brightener from cotton fabric is undertaken. For this aim, the direct type optical brightener based on stilbene, with three different concentrations (0.1-0.3-0.5%), was applied to the cotton fabric and then optical bleached samples were ozonated for 15, 30, and 60 minutes. The achieved results clearly indicate that ozonation can be used efficiently to decolorize the optical bleached samples. The efficiency of the process increased with the rise in ozonation time, but it should be paid attention to choose the ideal process time because of the increase in bursting strength loss of fabric. Also, a new patterning method has been developed for optical bleached cotton fabric with this study. It can be said that this new process provides similar results with tie-dyeing, which is not appropriate for optical bleaching, in the light of achieved results.

Keywords: Ozone, optical brightening, color removal, tie-dyeing, batik

ÖZET

Bu çalışmada, pamuklu kumaş üzerinden optik beyazlatıcılarnın uzaklaştırılmasında ozonun kullanılabilirliği incelenmiştir. Bu amaçla, üç farklı konsantrasyonda (%0.1-0.3-0.5) stilben esaslı direkt tip optik beyazlatıcı pamuklu kumaş aktarımı ve sonrasında optik beyazlatılmış numuneler 15, 30 ve 60 dakika süresince ozonlanmıştır. Elde edilen sonuçlar ozonlanmanın optik beyazlatılmış numunelerin renkini gidermede başarılı bir şekilde kullanlabileceği göstermektedir. İşlemin verimliliğini ozonlama süresindeki artış ile birlikte artmaktadır, ancak kumaşların patlama mukavemet kaybı dolayısıyla ideal işlem süresinin seçilmesine dikkat edilmelidir. Aynı zamanda bu çalışma ile optik beyazlatılmış pamuklu kumaşlar için yeni bir desenlendirme yöntemi geliştirilmiştir. Elde edilen sonuçlara bakılarak bu yeni yöntem, optik beyazlatmada kullanılan batık boyama ile benzer sonuçları sağladığı söylenebilir.

Anahtar Kelimeler: Ozon, optik beyazlatma, renk giderimi, batık boyama, batık.

Corresponding Author: Seher Perinçek, e-mail: seher.perincek@ege.edu

1. INTRODUCTION

Optical brighteners are colorless organic compounds that absorb radiation in the non-visible UV part of the electromagnetic spectrum and then reemit most of the absorbed energy as visible light in the blue part of the spectrum (400-500 nm) [1-4]. Optical brighteners normally have a system of conjugated double bounds and should contain electron donating groups such as -OH, -NH₂ etc. [5].

Optical brighteners have found use in many areas such as textiles, detergents, paper, waxes, polishes, cosmetics, hair rinse and plastics to make products whiter and brighter by compensating for the yellowish shade of materials. They are also used in the manufacture of synthetic fiber of all types [1-4, 6-10].

Although, Krais described to whiten cellulosic textiles by aid of optical brightener in 1929, use of optical brightener has been commercialized only in 1940 [4, 8]. It has been found that if gray fabrics, which normally have a dull, yellowish cast, are treated with small quantities of optical compounds, they become whiter and brighter. It is thought that these compounds are excited by ultraviolet rays to emit fluorescence which hinders the undesirable tinge of color in the unbleached fiber [9]. It is requested that optical brighteners used in textile treatments should be optically colorless on the substrate and should not absorb in the visible part of the spectrum [4].

Commercial optical brighteners can be assorted in three major chemical classes, based on the stilbene, coumarin
and pyrazoline structures. Figure 1 shows the chemical constitution of brightener based on stilbene, that are mostly preferred for textile treatments [3, 11].

![Chemical constitution of 4,4′-bis-(γ-triceol-zoyl) stilbene-2,2′ disulphonic acids](image)

**Fig. 1. Chemical constitution of 4,4′-bis-(γ-triceol-zoyl) stilbene-2,2′ disulphonic acids** [5]

On the other hand, there is a classification of optical brighteners as direct, disperse and cationic types which depends on the kinds of fibers used. The direct brightening agents are mostly derivative of 4,4′-bis-diaminostilbene-2,2′ disulphonic acid and are used mainly for the brightening of cotton, paper, viscose, linen and polyamides [5].

It has been known for many years that certain stilbene derivatives exhibit a strong blue fluorescence upon exposure to ultraviolet light and also show a strong affinity for cellulosic materials. Thus, the stilbene derivatives are preferred for treatment of cellulosic textiles to produce whiter and brighter materials [4, 10]. Optical brighteners are applied to textiles as a separate after-treatment process or are incorporated into finishing baths. Also, they can be added to the bleaching bath because of being stable.

When optical brightening agents are applied to cellulosic fibres, they behave like direct cotton dyes. The brightener penetrates the fibre in a monomolecular form, aggregates there, and takes on a greater volume. Henceforth, it can not easily leave the interior of the fiber [5]. Although, this situation can be seen as an advantage for washing fastness properties, it sometimes causes problems during treatment stage in textile mills. For example, when any mistake about recipe is performed, difficulties about removal of optical brightener from the fabric can be observed. In such a case, methods for removal of direct dyes from cellulosic textiles such as hydrogen peroxide or sodiumditionite treatments are preferred to decompose direct type optical brightener.

However, it can not be told that these treatments are fairly efficient. Long treatment sequences have to be performed to remove all of the optical brightener. On the other hand, if the same machine will be used for treatment that not involves optical brightener, inside of machine should be cleaned efficiently after optical bleaching. Because any amount of optical brightener causes staining on the fabric easily because of high substantivity to the cellulosic fibers.

When all these comments are taken into consideration, a new process requirement to remove direct type optical brightener from fabric is arisen distinctly. Therefore, one of the new techniques, ozonation process, is examined extensively in this study. It is well known from the literature that because of being one of the strongest oxidizer, ozone is used as bleaching method of some textile materials and supports the decomposition of many soluble dyestuffs in the waste water [12-22]. There is no study about removal of optical brightener from cotton fabric by ozonation in the literature. So, this study comes into value and seems helpful in terms of textile mills.

One of the other importance of this study is about developing a new patterning method instead of tie dyeing. It is well known that various specialized techniques for decorating textiles were developed in different parts of the world. Batik is probably foremost among these special forms. Batik originated in either China or India, possibly as long as 1200 years ago. It is practiced throughout Indonesia for the decoration of everyday clothing. Batik is a resist dyeing process in which molten wax is applied to the fabric prior to dyeing, thus resisting the action of the dye in those areas. After dyeing, the wax is removed and other areas are waxed-in prior to a second dyeing. One color covering another creates an additional color and thus the process continues. Tie dyeing is another of the specialized techniques developed for decorating woven materials. It is practiced chiefly in central India and on the island of Bali. Plain fabric is tied in knots, tightly bound with thread, and then placed in a dye bath. The areas that have been tied will resist the dye to leave a pattern [23]. High substantivity of optical dyes mostly causes staining and so tie dyeing or batik colorization can not be applied when the matter for discussion is optical dyes. Results of experiments showed that ozonation process of optical bleached fabric can be used to create fashionable products (e.g. upholstery stuffs or waiter dresses) used in the places where in the use of ultraviolet light is preferred.

2. EXPERIMENTAL

30/1 single jersey, scoured and bleached cotton knitted fabric, weighing 310 g/m² and with 85.948 whiteness degree, was used in experiments. Firstly, direct type optical brightener based on stilbene was applied to the cotton fabric in accordance with Table I and Figure 2.

**Table 1. The recipe for optical bleaching**

| Optical brightener (%) | 0.1-0.3-0.5 |
| Salt (g/L) | 5 |
| Temperature (°C) | 90 |
| Time (min.) | 30 |
| Liquor ratio | 1:20 |

![Fiber & Optical brightener](image)

**Fig. 2. Bleaching process**
Laboratory type exhausting machine (Atac) was used during the optical bleaching. Optical bleached cotton fabrics, at pH 6.5-7.5 and 60% WPV (water pick up value) were ozonated for 15, 30 and 60 minutes [12, 15, 17]. The ambient temperature was adjusted to 25±2°C. The capacity of the ozone generator (Ozone & Marine Inc.) was 80 g/h. After ozonation, fabrics were rinsed at 50°C.

In order to determine the change in whiteness degree of cotton fabric arisen after the ozonation, the whiteness degrees of all samples were examined with a Minolta 3600d spectrophotometer according to the Stensby formula. Filter was excluded, which cut off 400 nm, during the evaluation of whiteness degree to observe changes at optical brightener’s effect clearly. The average whiteness values of samples, bleached with 0.1-0.3-0.5% optical brightener, were 118.32, 124.97 and 131.03 respectively.

Meanwhile, the strength losses were measured by James J Heal Bursting strength machine (with 7.5 cm² area and 30.5 mm diaphragm diameter). In the paper WC (Whiteness change, %) and BSL (Bursting strength loss, %) terms were used during construction (equation 1 and 2).

Fehling test was performed to observe the occurred damage on the samples caused by ozonation. This method is generally used for the determination of oxycellulose and hydrocellulose. The sample which will be analyzed is treated with the Fehling solution for 10 min. at boiling temperature and then after a hot and cold rinse, the red and pink colors are controlled if formed [24].

FT-IR analysis of fabrics was carried out with Perkin Elmer Spectrum 100. The results of all assays were compared using a Duncan’s post hoc test.

3. RESULTS AND DISCUSSION

Direct type optical brighteners are generally based on stilbene and applied to the cellulosic fabrics. Also, they are conformable to the use in the bleaching baths because of being very stable [5]. This also helps to explain why removal of optical brighteners from the fabric is so difficult by conventional methods.

In order to investigate the effect of ozonation, concentration of optical brightener and ozonation time on the remove properties of optical brightener from the fabric and thus, on the fabric’s whiteness and yellowness degree, a statistical research was carried out. ANOVA indicated that there was significant impact of ozone and ozonation time on the all dependent variables, while the effect of optical brightener concentration was not reckoned (Table 2).

When the significance values in the ANOVA test results were taken into consideration, it can be said that both of ozononation process and time affect the remove properties of optical brightener from cotton fabric significantly, they differ from each other in terms of importance grade. It was obvious that performing ozonation process offered greater importance than ozonation time. Ozonation time effected whiteness and yellowness degree markedly (Table 2.

Some literatures indicated that ozone molecule act as a dipole, as an electrophilic agent, and as a nucleophilic agent [25]. Molecular ozone reactions are extremely selective and limited to unsaturated aromatic and aliphatic compounds as well as to specific functional groups [25-30]. In Figure 3, some of the organic groups capable of attack by ozone are shown:

Whiteness Change (WC), % = \(\frac{[(W_{\text{After treatment}}) - (W_{\text{Before treatment}})]}{(W_{\text{Before treatment}})} \times 100\)

Bursting Strength Loss (BSL), % = 100 – \(\frac{(B_{\text{After treatment}}/B_{\text{Before treatment}})}{100}\)

![Fig. 3. Organic groups open to attack by ozone [25]](image-url)
During the ozonation process, it is thought that dyes get colorless by the oxidative cleavage of the cromophores. The cleavage of -C=C- double bonds and other functional groups will shift the absorption spectra of the molecule out of the visible region [16]. This sight throws a light on ozonation of optical brightener. It can be said that oxidative cleavage of carbon-carbon double bonds found in optical compound (Fig. 1) is an important ozone reaction and may be of significance during the course of ozone-optical whitening agent reaction.

When the ozonation process was performed, the whiteness change was oscillated between 23% and 32% related to the ozonation time and concentration of optical brightener (Fig. 4). The results of Duncan post hoc test supported this situation too (Table 3). The whiteness degree of optical bleached sample decreased from 125 to 88.5 and yellowness of it increased from -19.5 to 1.13 after ozonation process for 30 minutes. In the Stensby formula, the decrease in whiteness values from higher than 100 to lower than 100 explains that ozonation process supports the removing optical brightener from the fabric efficiently.

Table 3. Duncan post hoc test related with the effect of ozonation time on the whiteness degree of optical bleached cotton fabrics

<table>
<thead>
<tr>
<th>Ozonation time (min.)</th>
<th>Whiteness</th>
<th>Yellowness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>60</td>
<td>86.4908</td>
<td>2.0855</td>
</tr>
<tr>
<td>30</td>
<td>88.3625</td>
<td>88.3625</td>
</tr>
<tr>
<td>15</td>
<td>90.8686</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>125.0665</td>
</tr>
<tr>
<td>Sig.</td>
<td>0.313</td>
<td>0.176</td>
</tr>
</tbody>
</table>

Alpha = 0.05

Although highest $W_C$ was observed with the longest ozonation time, treatment time should not be extended too much. As known from literatures that extended ozonation time causes significant losses at fabric's strength (Fig. 5) [12, 15]. So, ozonation time should be adjusted due to desired $W_C$ and strength loss. Decrease in strength loss is related with the damage occurred by ozonation. So, fabrics were subjected to the Fehling test to observe the aldehyde groups occurred on cotton samples. Aldehyde groups reduce Fehling’s solution to give a precipitate of red cuprous oxide. Therefore, the areas on fibers carrying -CHO groups will be colored pink or red. The increase in damage is explained by the intensity of red coloring that occurs on the fabric [31]. It is clearly seen from the photographs that all ozonated samples were chemically damaged (Fig. 6). But the rate of damage increases with the rise in the ozonation time.

![Fig. 4. The whiteness change of optical bleached cotton fabrics after ozonation process for different treatment times](image)

![Table 3. Duncan post hoc test related with the effect of ozonation time on the whiteness degree of optical bleached cotton fabrics](table)
Fig. 5. BSL of optical bleached fabrics ozonated for different times

Table 4 and Fig. 7 show the FT-IR spectra of optical bleached and ozonated cotton fabrics. The transmittance of the C-C ring breathing band at ~ 1160 cm⁻¹ and the C-O-C glycosidic ether band at ~ 1106 cm⁻¹, both of which arise from the polysaccharide components (that is, largely cellulose), was increased significantly with ozonation (Fig. 7) [32-40]. In other words, the β-glycosidic linkages between the monosaccharides of cellulose decreased after treatments in this order:

Ozonation for 60 min. > Ozonation for 30 min. > Ozonation for 15 min.

When the increased T% of 1028 and 896 cm⁻¹ band were taken into consideration, it can be told that cellulose reacts with ozone and therefore, β-glycosidic linkages between the monosaccharides of cellulose decreased with increased ozonation time (Fig. 7) [34-37]. These results were also supported by the Fehling and bursting strength test results.

Table 4. Infrared transmittance peaks (cm⁻¹) of optical bleached and ozonated samples for different times [32-39]

<table>
<thead>
<tr>
<th>Optical bleached fabric</th>
<th>Sample ozonated for 15 min.</th>
<th>Sample ozonated for 30 min.</th>
<th>Sample ozonated for 60 min.</th>
<th>Possible Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3335.6</td>
<td>3336.53</td>
<td>3334.66</td>
<td>3334.75</td>
<td>OH stretching</td>
</tr>
<tr>
<td>2898.43</td>
<td>2899.99</td>
<td>2899.62</td>
<td>2899.45</td>
<td>CH₂ and CH₃ stretching</td>
</tr>
<tr>
<td>1627.82</td>
<td>1628.16</td>
<td>1627.92</td>
<td>1628.20</td>
<td>Absorbed water</td>
</tr>
<tr>
<td>1560.13</td>
<td>1560.04</td>
<td>1560.06</td>
<td>1560.09</td>
<td>Aromatic C=C stretching</td>
</tr>
<tr>
<td>1426.09</td>
<td>1428.8</td>
<td>1426.15</td>
<td>1426.48</td>
<td>C-H and CH₃ bending</td>
</tr>
<tr>
<td>1362.15</td>
<td>1362.21</td>
<td>1362.38</td>
<td>1361.78</td>
<td></td>
</tr>
<tr>
<td>1334.52</td>
<td>1334.98</td>
<td>1334.43</td>
<td>1334.96</td>
<td></td>
</tr>
<tr>
<td>1314.83</td>
<td>1314.74</td>
<td>1314.81</td>
<td>1314.87</td>
<td></td>
</tr>
<tr>
<td>1160.03</td>
<td>1160.61</td>
<td>1159.86</td>
<td>1159.81</td>
<td>C-C ring breathing,</td>
</tr>
<tr>
<td>1106.08</td>
<td>1107.09</td>
<td>1107.86</td>
<td>1107.43</td>
<td>C-O-C antisymmetric bridge stretching in cellulose and hemicellulose</td>
</tr>
<tr>
<td>1053.14</td>
<td>1053.52</td>
<td>1053.06</td>
<td>1052.74</td>
<td>C-OH secondary alcohol</td>
</tr>
<tr>
<td>1029.25</td>
<td>1029.63</td>
<td>1029.33</td>
<td>1029.63</td>
<td>C-O stretching in cellulose, hemicellulose</td>
</tr>
<tr>
<td>898.19</td>
<td>898.97</td>
<td>898.69</td>
<td>898.55</td>
<td>β-Glycosidic linkage</td>
</tr>
</tbody>
</table>

As mentioned before, it is thought that optical brightener gets colorless by the oxidative cleavage of the cromophores during the ozonation process. This prediction can be demonstrated with the infrared transmittance results. The transmittance of the aromatic -C=C- stretching band at ~ 1560 cm⁻¹ increased after ozonation (Fig. 7). This shows that oxidative cleavage of carbon-carbon double bonds found in optical compound occurred during the ozonation. By this means, the remove of optical brightener from the cotton sample materialized as required.

Besides hopeful results of ozonation mentioned above, a new patterning method has been developed for cotton fabric. It can be said that achieved result of this new method is equal with the results of art dyeing methods. The method has been developed to be predicated on process sequence of tie-dyeing. It is based on dyeing cotton fabric with a direct type optical brightener and tieing it in knots like tie dyeing and then subjecting it to ozonation process. Fig. 8 shows the photographs of fabrics treated by this new method. It is thought that products produced by this method can come into vogue.
4. CONCLUSION

Optical brighteners have long been used in different industrial areas to make products whiter and brighter by compensating their dull and yellowish color. Although, direct type optical brightener, based on stilbene, is mostly preferred agent in textile treatments, it has undesirable...
property. It can be told that one of the nightmares of textile mill is the remove of optical brightener efficiently from the fabric when any mistake is observed during the process. Also, cleaning the inside of machines after optical bleaching has to be performed efficiently to prevent the staining on the fabric during the next processes. Remove of direct type optical brightener from fabric/surface of the dyeing machine by conventional methods is too difficult because of its high stability property. Hazardous chemicals are commonly used to remove it.

This study shows that ozonation process provides better results and is more efficient in terms of removed optical agent. On the other hand, when the applied ozonation time increased, the efficiency of removed optical agent increased, whereas bursting strength of fabric decreased and samples were chemically damaged. So, ozonation time should be adjusted according to the required whiteness and strength. The achieved results are conspicuous for dyeing mills. Textile firms can get over all the difficulties related with the use of optical brightener (such as removal of optical brightener from the fabric or inside of the machine, etc.) by the aid of clean technology, ozone. The use of ozone as a removal process for optical brightener will supply most of advantages (performing ecological and economical process, which consumes less water, energy, time and creates less waste load with the use harmless chemical, ozone) to the textile firms.

Also, a new patterning method has been developed for cotton fabric. This new method provides that optical bleached fabrics can be used in patterning methods to obtain fashionable products like Batik or tie-dyed cloths.

REFERENCES

17. Perincek, S., 2006, “An investigation on the applicability of ultrasound, ultraviolet, ozone and combination of these technologies as a pretreatment process”, MSc Thesis, Textile Engineering Department, Ege University, Izmir, Turkey.