

Publications

A few research papers published prior to this work, has been given at the end to give testimony for his aptitude for research work.
INTRODUCTION

CERTAIN organic compounds absorb radiation of short wavelengths in ultraviolet region and re-emit this at longer wavelengths in the visible region. Thus a white surface containing such a compound can reflect more than the total amount of visible light falling on it, giving an intensely brilliant white effect. This effect is only observed when the incident rays contain a significant proportion of ultraviolet light.

The discovery of these type of compounds now known as fluorescent or optical brightening agents (OBA) was made in 1921. The most practical use of this effect is made in enhancing the whiteness of textiles, papers and plastics.

It is necessary to evaluate the effect produced by an OBA in textile processing in order to know the extent of improvement in white that it can make. A direct method of evaluating whiteness is by visual examination of the treated substrate and comparison with some accepted white standard. However, this method is subjective. There are other methods which express whiteness numerically. These methods include from simple measurement of reflectance at a single wavelength to different whiteness formulae computed from the measurements of reflectances at a number of wavelengths in the visible region of the spectrum. Two main types of instruments used normally for reflectance measurement are the tristimulus filter photometer and the spectro-photometer. However, the conventionally used spectrophotometers cannot be directly used for the measurement of enhanced whiteness due to the application of OBA on any substrate. In an earlier study fluorescence intensity has been measured and used to evaluate optical brightening agents.

The work reported in the present paper has been carried out with an objective to see if any of the parameters stated above for characterising the optical brightening agents, viz., extinction coefficient of solution at maximum absorption wavelength in UV, or the Rf value in paper chromatography, is related to the ultimate performance of these substrates.

EXPERIMENTAL

Materials

Optical brightening agents

Commonly used optical brightening agents in the textile industry were procured directly from the manufacturers, which have been coded I to IX throughout the paper.

Substrates

Bleached white poplin cotton cloth and filter paper (Filtroll LA-201) were treated by exhaustion and padding methods.

Chemicals: All reagents used were of analytical and technical grades.
Treatment to cloth

The cloth was pretreated with distilled water to remove any foreign matter.

Exhaustion methods

Five gram cloth samples were treated with different concentrations of OBA at room temperature for 30 minutes keeping the M:L ratio 1:40. 10 ml. of 10% sodium chloride solution was added in each bath. The treatment was carried out for ten minutes further. The fabric was then washed with distilled water, dried and ironed.

Padding method

Fabric samples were padded on a laboratory mangle at different concentrations (0.01 to 0.2%). The pick up was adjusted at 80%. The samples were then dried and ironed.

Treatment to filter paper

Filter papers were soaked with the solution of OBA and dried. Since all the liquor got dried it was assumed that the total OBA content was taken up by the paper. The concentration range of the optical brightening agent used was the same as that used in the exhaustion method for fabric samples.

Measurement of fluorescence intensity

Fluorescence intensity of treated substrates was measured on Beckman DU spectrophotometer using a tungsten lamp. The intensity was measured by irradiating the samples at wavelength of 375 nm and the amount of the reflected light which was enhanced due to fluorescence after cutting off scattered radiation by a UV cut off filter was measured by blue sensitive phototube. An untreated substrate under these conditions gave intensity of zero.

Chromatographic technique

Chromatograms were developed by descending paper technique in "Shandons' chambers.

Measurement of ultraviolet spectra

The ultraviolet absorption spectra of all optical brightening agents at suitable concentrations were obtained on Carl Zeiss VSU-2P spectrophotometer using 1 cm path-length quartz cells and deuterium lamp as the source of radiation.

RESULTS AND DISCUSSION

There are a number of factors which affect the fluorescence when optical brightening agents are taken for treatments on different types of substrates. These are mainly (i) substrate, (ii) saturation, (iii) method of application, (iv) addition of salt, (v) time, and (vi) temperature of treatment.

In the present study attempts have been concentrated primarily on the application methods with respect to textiles. Comparison of substrate effect is done by taking cellulose fabric and paper as two different substrates.

Optical brightening agents used in textile industry for finishing of white cellulosic fabric are applied generally by exhaustion and pending methods. Trends of fluorescence intensity of fabric treated with different OBAs are given in Figures 1, 2, 3 and 4. The data indicate that the maximum fluorescence intensity does not exceed...
about 60 units. Some distinct observations made from the figures are:

(i) There is a limiting concentration of treatment, in either of the application methods, above which the effect of OBA levels off.
(ii) Two methods of application i.e., exhaustion and padding do give identical results.
(iii) Another important observation from the fluorescence concentration curves is that some OBA's are more effective at lower concentrations and the fluorescence intensity also levels off at lower concentrations, whereas for some OBA's the levelling off takes place at higher concentration (I and VIII). These latter type would at times show an apparently strange behaviour in that they will appear at lower concentrations weaker than the former but stronger at equivalent higher concentrations. In ordinary subjective visual observation this anomaly is not likely to be detected but in determination of limiting concentrations for OBA, the correct efficiency will be revealed. It is thus necessary to find out the limiting concentration for a particular OBA, since in practice, higher concentration above this limiting concentration will not give effective increase of fluorescence. Besides that, the total evaluation may not be also correct by assessment on a limited range of concentrations.

Filter paper

In the textile fabric treatments with OBA, it is generally observed that the amount of the material taken for treatment may not entirely be sufficiently effective. This can be studied by the amount of OBA left out in exhaustion bath and calculating from that the amount of adsorbed material. To study this phenomena from a different angle, the substrate was changed and Filter Paper was used as the substrate. It was ascertained that the amount of liquor added was totally taken up by the filter paper. This would ensure that the substrate contained a predetermined desired amount of OBA. Fluorescence intensity of treated papers was then measured.

Figures 5 and 6 show the fluorescence intensity against the weight of the adsorbed OBA by a fixed weight of the paper. The nature of the curves is almost identical to that of the fabric, and the limiting values of fluorescence intensity are also in the same order. Irregular nature of the curves in this substrate is generally because of the fact that the treatment was comparative.

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**Fig. 3. Fluorescence intensity on fabric treated by different OBAs by padding method. (% indicate bath concentration)**

**Fig. 4. Fluorescence intensity on fabric treated by different OBAs by padding method. (% indicate bath concentration)**

**Fig. 5. Fluorescence intensity on filter paper treated by different OBAs**
ly uneven. The above study indicated that the maximum fluorescence values are identical both on fabric and filter paper.

Identification technique for OBA

*Paper chromatography*

The process of chromatography is useful for identification and separation of chemical compounds in a mixture. Rf values in paper chromatography depend on the partition coefficient and the relative amount of the two phases in contact. Like dyestuffs, OBAs move on the filter paper under the influence of an eluent. Two eluents were selected to study the behaviour of OBAs. Ultra violet light was used to see the spots developed. Figures 7 and 8 show the trend of the Rf value for different OBAs.

Some compounds have showed more than one spot indicating the presence of added impurities. However, in each of these compounds only the predominant spot has been taken into consideration. The other spots were extremely faint and hence they have not been considered for calculating Rf values.

Data on fluorescence intensities on fabric and Rf values indicate in general that the higher the fluorescence intensity higher is the Rf value. Although it cannot be claimed to be an absolute, quantitative method of establishing the performance of OBA on fabric, this method of finding out Rf values can be a guiding factor.

Ultra-violet spectra of all the OBAs were measured at different concentrations. It was observed that all the substances have the same nature of the curves with two absorption maxima. They have the same common band of absorption, indicating that all the OBAs taken for study belonged to the same class compounds.

A useful result of ultra-violet absorption spectrum in the derivation of extinction coefficient of the substance is analysed. (Extinction coefficient, defined as the absorbence of unit concentration and thickness, is equal to K, which is specific constant for a particular solvent under identical conditions). These values for all the OBAs selected were calculated for 0.005% solution in one centimeter path-length cell (E at the maximum absorption wavelength of 340 nm. The table given shows the correla
tion between Rf values, extinction coefficients and the end performance of these substances on different substrates. The end performance of OBA has been considered as the fluorescence intensity obtained on the substrate. These values have been obtained by integrating the fluorescence on the substrates at all concentrations, i.e., by calculating the area under each curve. Thus the values, put in the Table give the total effective fluorescence intensity up to a certain concentration on each substrate.

It is observed from the Table that OBA coded V has the highest value of extinction coefficient and also the highest fluorescence intensity on fabric and filter paper. Comparing with this, OBA coded IX and II have these values significantly low. A trend of increasing values of extinction coefficients with increasing values of fluorescence is clearly observed. From the same Table it can be noted that the sample of lower Rf values in both eluent A and B shows low performance on fabric and paper whereas those samples which have shown high fluorescence intensities have high values of Rf.

### SUMMARY AND CONCLUSIONS

1. Ultra-violet spectra of all OBAs selected for the study show that the compounds belong to a single structural group, but their extinction coefficients at the wavelength of maximum absorption, their Rf values on paper chromatography and their ultimate performance differ significantly.

2. While considering the ultimate performance of these type of substances on any substrate, it is necessary to know their limiting concentration beyond which there is a levelling effect of the fluorescence obtained.

3. Study of these selected OBAs has shown that the values of extinction coefficient at wavelength of maximum absorption, Rf values obtained with certain eluents in paper chromatography and fluorescence intensity on substrates like fabric and filter paper are related.

### REFERENCES

Table 1: Layer changes in density and hardness in 40s cotton yarn packages.

<table>
<thead>
<tr>
<th>Length of yarn (yd)</th>
<th>Cone: 1 Density</th>
<th>Cone: 2 Density</th>
<th>Cone: 3 Density</th>
<th>Cone: 4 Density</th>
<th>Cone: 5 Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Full cone)</td>
<td>D H O H D</td>
<td>D H O H D</td>
<td>D H O H D</td>
<td>D H O H D</td>
<td>D H O H D</td>
</tr>
<tr>
<td>2,000</td>
<td>302 44</td>
<td>277 45</td>
<td>274 37</td>
<td>257 39</td>
<td>307 48</td>
</tr>
<tr>
<td>4,000</td>
<td>310 46</td>
<td>285 48</td>
<td>274 41</td>
<td>261 38</td>
<td>318 51</td>
</tr>
<tr>
<td>6,000</td>
<td>315 48</td>
<td>285 48</td>
<td>274 40</td>
<td>254 42</td>
<td>318 48</td>
</tr>
<tr>
<td>8,000</td>
<td>312 49</td>
<td>306 61</td>
<td>263 51</td>
<td>259 58</td>
<td>334 56</td>
</tr>
<tr>
<td>10,000</td>
<td>308 64</td>
<td>295 54</td>
<td>253 58</td>
<td>256 63</td>
<td>334 52</td>
</tr>
<tr>
<td>12,000</td>
<td>331 80</td>
<td>292 61</td>
<td>250 89</td>
<td>258 63</td>
<td>334 52</td>
</tr>
<tr>
<td>14,000</td>
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<td>285 67</td>
<td>263 83</td>
<td>258 73</td>
<td>334 69</td>
</tr>
<tr>
<td>16,000</td>
<td>321 76</td>
<td>300 71</td>
<td>287 79</td>
<td>273 82</td>
<td>336 73</td>
</tr>
<tr>
<td>18,000</td>
<td>334 85</td>
<td>286 85</td>
<td>316 87</td>
<td>282 97</td>
<td>376 84</td>
</tr>
<tr>
<td>Average of 9</td>
<td>318 59</td>
<td>287 58</td>
<td>285 58</td>
<td>258 58</td>
<td>311 50</td>
</tr>
<tr>
<td>Average D of every 2,000 yd reeled off:</td>
<td>283 — 275 — 255 — 258 — 294 —</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(2) Changes in density and hardness at different yarn layers in a cone

In 40s cotton yarn packages, a few cones were taken for a study of density and hardness at different layers within the cone. From each cone, yarns of fixed length (2,000 yd) were reeled out and both the parameters were measured.

Since the cones were of about 20,000 yd, ten such measurements were possible. In all these, it was observed that the density of full cones is equivalent to the average of yarn densities of different layers of 2,000 yd, though the layer densities of cones after removal of layers of 2,000 yd are very different each time. Hardness values of cones after removal of layers of 2,000 yd are also different each time. These results are shown in Table 1.

Fig 7. Layer changes in density and hardness for 40s cotton yarn packages shown on regression line. Each point joined by dotted line shows values after 2,000 yd on the package.
in some cones, the yarn layers up to a certain level follow the regression pattern, whereas in others there is a sudden increase.

Results shown in Table I indicate that the hardness measurement is significant only with full packages. If the layers of yarn are removed, hardness steadily increases until at the end, the effect of the spool becomes predominant. Even the average value of hardness does not equal the original hardness value of a full cone. In contrast to this, the average density of the 2,000 yd of yarn reeled off each time from the packages is equal to that of the full cone as shown in Table 1. Again the densities of the cones after reeling off yarn is not equal to that of the full cone as expected.

This fact should be borne in mind while making use of either density or hardness values towards a practical goal.

(3) Colour strength of yarn in package dyeing

In order to observe the effect of hardness of the package density of yarn packages on dyeing, two shades in vat dyes were studied. Two fairly extreme cases of hardness, soft and hard pecking were taken. Hardness measurements before and after dyeing were carried out. Dyed cones were then further evaluated as follows:

The variation of colour strength between the two cones and the variation of colour within a cone were studied. The yarns from the cones were taken up on weft pirns, and were numbered 1, 2 . . . n, number 1 being from the top of the cone and 'n' from the bottom yarn of the cone. Each pirn contained about 700 to 1,000 yd of yarn. The colour strength of each pirn was measured on the Color-Eye spectrophotometer. The strengths have been expressed as:

(a). In one case the first pirn from each cone has been taken as the standard (100), with respect to which the relative strengths of

Table II Relative colour strengths in soft and hard cones of yarn (40s cotton yarn)

<table>
<thead>
<tr>
<th>Dye</th>
<th>Before Dyeing</th>
<th>After Dyeing</th>
<th>% Change</th>
<th>CV</th>
<th>% Change</th>
<th>CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vat Blue</td>
<td>45</td>
<td>55</td>
<td>107</td>
<td>3.8</td>
<td>107</td>
<td>3.8</td>
</tr>
<tr>
<td>Vat Orange</td>
<td>70</td>
<td>74</td>
<td>110</td>
<td>4.2</td>
<td>98</td>
<td>4.1</td>
</tr>
<tr>
<td>Green</td>
<td>58</td>
<td>65</td>
<td>108</td>
<td>3.7</td>
<td>108</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Note: (a) Top layer of each cone separately = 100
(b) Top layer of soft cone = 100