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GREEN APPROACH FOR SYNTHESIS OF OPTICAL BRIGHTENING AGENTS AND THEIR APPLICATION IN WET END OF PAPERMAKING




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Abstract :

Optical properties viz. brightness and whiteness of paper are most important parameters for a good quality paper. To produce paper at high brightness and whiteness levels, there have been many attempts like production of high bright pulp, addition of high bright fillers in the paper, and addition of optical brightening agent (OBA)/optical whitening agent (OWA)/fluorescent whitening agent (FWA) etc. An OBA is a chemical with fluorescent ability to absorb the light from the ultraviolet part of the electromagnetic spectrum and emit in the bluish part of visible spectrum. These chemicals are selectively utilized to increase the brightness and whiteness of paper. The most common classes of chemicals with this property are the stilbene and thus have a significant role in improving the optical properties including shade of paper and are being utilized in pulp & paper industry. The global OBA production is dominated by just a few di/tetra and hexa-sulphonated stilbene. The use of these different types of di/tetra and hexa-sulphonated stilbene depends upon the application. The consumption of OBA has shown a higher growth rate due to a trend of higher brightness and whiteness of paper in the industry. The present study represents the synthesis of different derivatives of OBAs through green approach and their application at wet end of papermaking. The result revealed that green chemistry methods can be utilized to synthesize OBA as an environmental friendly approach. The results also revealed that laboratory synthesized OBA performed well as compared to commercially available OBA, generally used in wet end application of papermaking in paper industry.

Key words : *Synthesis, Stilbene, Papermaking, Brightness, Whiteness*

INTRODUCTION

Optical Brightening Agent (OBA) was discovered by P. Krais in 1929 while first industrial application began in 1935, and these agents came into full-scale industrial use in late forties. In 1941, OBAs were produced and introduced commercially in the market. OBAs were first used for their application in laundry detergents in the fifties. Today many of the earlier OBAs are no longer used or have been replaced by superior chemicals having better whitening efficacy with many more benefits in usage (1, 2).

OBAs in paper industry are used as additives that paper manufacturers put into paper in order to help a paper look whiter (3, 4). These additives are often used to enhance the appearance of colour of paper and fabric, causing a whitening effect, making materials look less yellow by increasing the overall amount of blue light reflected. The mechanism of action of OBA and their classification has already been described earlier (2).

The most of OBAs used in paper industry are derivative triazinylamino stilbene and contain 2/4/6 sulphonic groups as sodium salt for good solubility and interaction with fibre. The number (2, 4 and 6) of sulphonic acid groups ($-SO_3H$) is used to classify these products according to their properties as different classes exhibit distinct differences in application. Di-sulphonic OBAs are mainly used in the wet end application while tetra-sulphonic at the size press and coating. Hexa-sulphonic OWAs are applied in coating application for better optical properties (5, 6). These OBAs contain some toxic chemicals and have been banned while non-toxic OBAs are imported from foreign at higher cost. The purpose of this research work is to synthesize chemically different compound that is free from toxic chemicals and can act as OBA through green approach. The present paper communicates the synthesis of different chemicals which may act as OBA, their characterization and application in wet of papermaking.

MATERIALS AND METHODS

All the chemicals used for the synthesis of OBA were of high purity, analytical grade procured from Sigma-Aldrich and used as such without further purification. The reactions were monitored by percolated aluminum silica gel thin layer plates procured from Merck (Germany). All melting points were measured with a capillary apparatus. The bleached mixed hardwood furnish was used to find the impact of OBA on optical properties of paper during the study.

Synthesis of 4, 4'-bis [4-morpholino-6-anilino-s-triazin-2-ylamino] 2, 2'-stilbene-disulphonic acid, disodium salt (Lab synthesized-OBA) : A 500 ml round bottom flask equipped with magnetic stirrer, pH meter, thermometer, was charged with 20.8 mmol of 2, 4, 6-trichloro-1, 3, 5-trizine. The pH of solution was then increased to 5.8-6.0 by drop-wise addition of aqueous 10 % w/v sodium carbonate solution; 50 ml disodium salt of 4, 4'-diaminostilbene-2, 2' disulphonic acid solution (10.4 mmol) was gradually added to above chemical while maintaining temperature at 3-5 °C with external cooling. The reaction vessel was kept in an ice bath with continuous stirring for 1 h. To the reaction mixture 50 ml aqueous sodium salt of m-sulphanilic acid (20.8 mmol) was added. The mixture was heated to 50 °C and stirring continued for 2 h while maintaining pH 6.0. The final product was isolated by adding 10 % w/v sodium chloride and was collected through vacuum filtration. The wet cake was transferred into another flask for the next step, where 150 ml of de-ionized water and 20.8 mmol aqueous sodium salt of morpholine were added. The temperature was raised from 50 °C to 90 °C and the mixture was stirred for 3 h at pH 8.0. The reaction mixture was cooled and the product was isolated by salting-out with sodium chloride. Precipitates were filtered, washed with ice cold aqueous solution of sodium chloride and dried for overnight under vacuum at 40 °C to obtain a yellow solid. The FTIR spectroscopy technique was also used to find the different functional groups in the lab synthesized OBA.

Measurement of E-value : It is the measurement of absorbance of 1% solution of unit path length. The absorbance is directly depending on the nature of the solution, concentration and the path length of the solution. The absorbance of UV light in a solution at a characteristic wavelength is used for the quantitative determination of efficacy of OBA in solution. Absorbance of 1% (w/v) solution of OBA was measured at 350±1 nm using 10 mm standard quartz cuvette on a UV-VIS Spectrophotometer using distilled water as blank with absorbance zero. The OBA powder was wetted using 2-3 mL of 5% sodium carbonate solution before their dilution using distilled water. The OBAs were evaluated for its E-value as described and results were compared with commercially available di-sulphonated OBA.

Refining of Pulp : The bleached mixed hard wood pulp (MHW) was refined in PFI Mill to get 30^{0}SR as per TAPPI Test Method T 248. The freeness of pulp was measured using Schopper Riegler (^{0}SR) Tester. Prior to stock preparation, the required amount of OBA was weighed on solid basis and was dissolved in hot water at a temperature of 60-65 °C to dissolve it completely.

Stock Preparation : Different components (chemicals and additives) were added to the pulp slurry in the following order with continuous stirring:

- Mixed hardwood pulp (1% consistency)
- OBA (Commercially available and lab synthesized di-sulphonated as per requirement)
- Dye
- Cationic fixing agent (CFA) : 200 g/t of pulp
- Cationic starch: 5 kg/t of pulp
- Alkyl ketene dimer (AKD): 6 kg/t of pulp on solid basis
- Ground calcium carbonate (GCC) and talc as filler (as required for 21% ash level)
- Cationic polyacrylamide (CPAM): 200 g/t of pulp

All the wet end chemicals for handsheet preparation were prepared, evaluated as described elsewhere and the results are given in table-1 (7). Handsheets of 70 g/m^2 were made on sheet former as per TAPPI Test Method. The handsheets were conditioned at 27±2 °C and 65±5% relative humidity for at least 24 h before testing. The ash content of the handsheet was determined as per IS 1060. The optical properties of paper handsheets were measured with the brightness tester (L&W Elrepho). IR spectrum of synthesized OBA was recorded in KBr on a Perkin–Elmer spectrophotometer.

RESULTS AND DISCUSSION

The present paper describes the synthesis OBA and its potential application in wet end of papermaking. The yellow colour product was formed with a melting point greater than 300 °C. The yield was around 87 % and solubility was less as it was having only 2-sulphonic groups. The characteristics of GCC and talc fillers are presented in table-2.

Synthesis and characterization of laboratory synthesized OBA and its comparison with commercially available OBA used in paper industry

The triazine-stilbene based OBAs are widely used in paper industry to increase the optical properties of paper. Desired di-sulphonate OBA was synthesized by reacting 2, 4, 6 trichloro-1, 3, 5-triazine with disodium salt of 4,

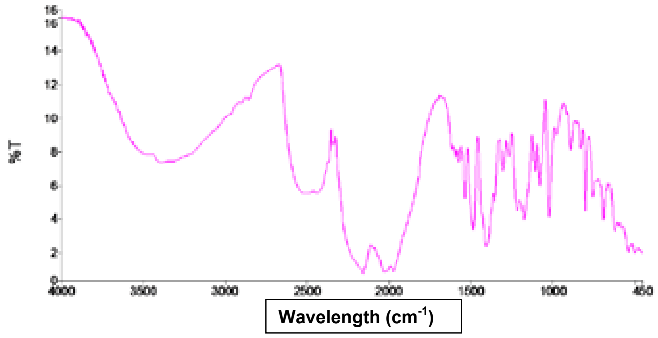

Figure -1 : to Figure 4 should be moved to 'RESULTS & DISCUSSION' Section

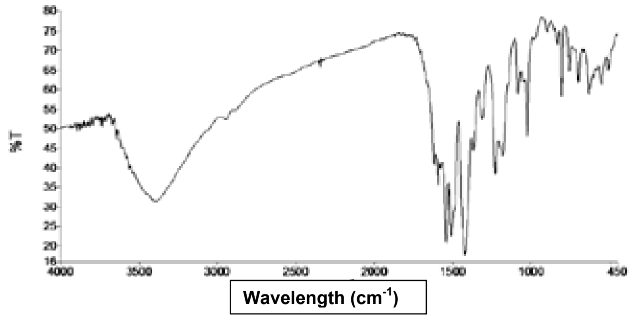

Figure-2: FTIR spectrum of commercially available OBA

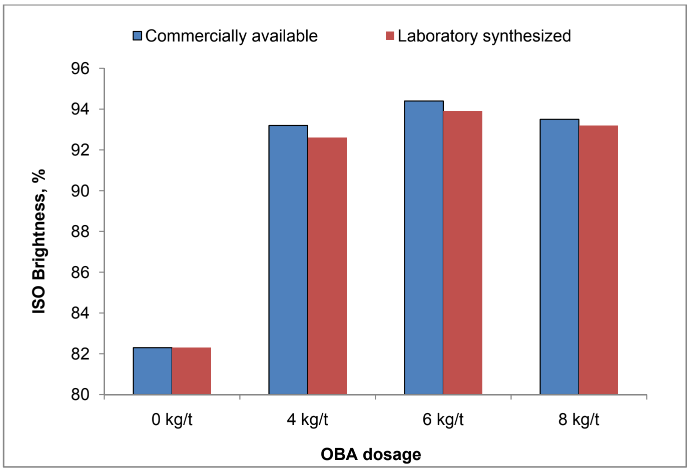

Figure-3: Effect of OBA dosage on ISO Brightness using GCC as filler

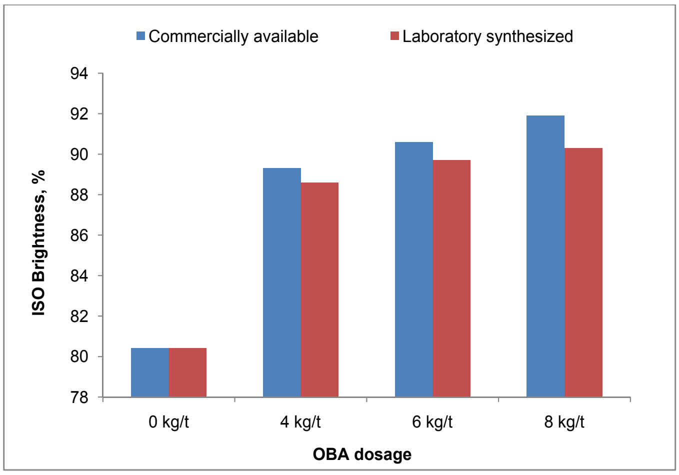

Figure-4: Effect of OBA dosage on ISO Brightness using Talc as filler

4'-diaminostilbene-2, 2' disulphonic acid, a novel organic amine. Maintenance of a low temperature of 3-5 °C was found to be critical for the successful coupling of triazine with aromatic amines. Again for conversion, the careful control of pH and temperature was found to be important for the successful completion of reaction. Finally the nucleophilic substitution with morpholine was achieved at 90 °C to furnish the desired OBA. To find the efficacy of an OBA, the E-value was measured. The results on both laboratory synthesized and commercially available OBAs are given in table-3. The different peaks in the FTIR spectra also confirmed the formation of desired di-sulphonated OBA. The FTIR spectra of both the OBAs are also given in figure 1-2.

Comparison of optical properties of handsheets made with lab synthesized and commercially available OBA

Using GCC as filler : Both the OBAs having 2-sulphonic groups were selected and used under the study to find the comparison of optical properties of handsheets made in laboratory. For this study, different dosage i.e. 4, 6 and 8 kg/t of pulp of both the OBAs were added to the pulp stock using GCC as filler to find their impact on optical properties. The results are presented in table-4.

The initial brightness of the handsheet using GCC as filler at an ash level of ~21 % was 82.3 %; marked as control where all the wet end chemicals were added except OBA. By adding 4 kg/t of commercial and laboratory synthesized OBA, the ISO brightness was increased from 82.3 % to 93.2 and 92.6 %, respectively (Figure-3). CIE whiteness was also slightly on lower side at this dosage level. While increasing the dosage to 6 kg/t, the ISO brightness was 94.4 and 93.9 % using commercial and laboratory synthesized OBA, respectively. But, the CIE whiteness of sheet with laboratory synthesized OBA was more as compared to commercial OBA (Figure-3). 6 kg/t dosage of both the OBA may be selected as optimized dosage for this pulp using GCC as filler at this level because of greening point at this dosage level. Other optical properties of the handsheets were found comparable at same dosage level using commercial and laboratory synthesized OBA.

Using Talc as filler : As described above, both the OBAs were added to the pulp stock using talc as filler at same dosage level to find their impact on optical properties. The results are presented in table-5.

Because of low brightness of talc, the initial brightness of the handsheet at same ash level was 80.4 % with all the wet end chemicals except OBA. By adding 4 kg/t of commercial and laboratory synthesized OBA, the ISO brightness was increased from 82.3 % to 89.3 and 88.6 %, respectively (Figure-4). The CIE whiteness was

Table-1: Characterization of unbeaten, beaten pulp and other wet end chemicals

Parameters	**pH**	**CSF**	**Zeta potential, mV**	**Charge demand**	
				μeq/L	**μeq/g**
Unbeaten	7.91	600	-21.7	12.2	-
Beaten	8.10	462	-22.1	16.8	-
Beaten + Chemicals (without filler)	8.31	470	-16.2	11.7	-
CFA	6.22	-	-	-	3170
CPAM	4.55	-	-	-	1527
AKD	3.94	-	-	-	266

Table-2: Characterization of GCC and Talc fillers

Parameters	**GCC**	**Talc**
pH	8.69	9.81
Zeta potential, mV	-97.4	+105
Charge demand, μeq/g	4.7 (cationic)	1.72 (anionic)
ISO Brightness, %	93.3	89.6

Table-3: Characterization of OBA

Parameters	**Commercially available**	**Laboratory synthesized**
No. of sulphonic group present	02	02
E-value, 1%/1cm	493	505
Presence of stilbene moiety	Yes	Yes
Solubility in hot water	Good	Good

found increased from 72.3 to 133.1 and 131.8 using commercially available and laboratory synthesized OBAs at same dosage level. While increasing the dosage up to 8 kg/t, the ISO brightness was increased to 91.9 and 90.3 % using commercial and laboratory synthesized OBA, respectively (Figure-4). CIE whiteness and other optical properties of the handsheets were found comparable at same dosage level using commercial and laboratory synthesized OBA . The results also revealed that the dosage of OBAs can be further increased to enhance the optical properties of the handsheets as no greening point was observed with both the OBAs upto 8 kg/t.

CONCLUSION

The di-sulphonated triaziny-lamino stilbene derivative OBA was synthesized successfully with good yield through green approach in the laboratory. The different characteristics peaks in FTIR also confirm the synthesis of OBA. Moreover, the E-value of the synthesized OBA was found better than commercially available di-sulphonated OBA used in wet end application of papermaking. The laboratory synthesized OBA also exhibited comparable optical properties while using GCC as well as talc filler.

Table-4: Comparison of optical properties of handsheets made with two different OBAs using GCC as filler

Parameters	Control	Commercial OBA (Di-sulphonated)			Lab synthesized OBA (Di-sulphonated)		
OBA added, kg/t	Nil	4	6	8	4	6	8
Basis weight, g/m^2	70.5	70.3	70.2	70.3	70.2	70.0	70.4
Ash, %	21.6	21.2	21.1	21.0	21.1	21.3	21.1
ISO Brightness, %	82.3	93.2	94.4	93.5	92.6	93.9	93.2
CIE Whiteness	74.3	137.2	138.3	137.6	136.6	139.5	139.1
Fluorescence	1.01	22.7	22.3	23.8	20.9	22.8	23.6
Yellowness	5.08	-20.36	-20.32	-19.95	-19.32	-20.47	-20.48
L*	94.3	95.1	95.3	95.5	95.2	95.6	95.7
a*	0.22	3.11	3.12	2.93	3.30	3.37	3.06
b*	2.55	-10.46	-10.95	-10.92	-10.81	-11.33	-11.23
Opacity, % ISO	88.7	87.1	87.2	88.2	88.5	87.6	88.3

Table-5: Comparison of optical properties of handsheets made with two different OBAs using Talc as filler

Parameters	Control	Commercial OBA (Di-sulphonated)			Lab synthesized OBA (Di-sulphonated)		
OBA added, kg/t	Nil	4	6	8	4	6	8
Basis weight, g/m^2	70.3	70.3	70.2	70.3	70.3	70.4	70.1
Ash, %	21.1	21.0	20.9	21.1	21.0	21.1	21.4
ISO Brightness, %	80.4	89.3	90.6	91.9	88.6	89.7	90.3
CIE Whiteness	72.3	133.1	137.4	139.2	131.8	136.1	138.2
Fluorescence	1.81	21.1	24.2	25.0	20.7	23.8	24.3
Yellowness	4.91	-19.22	-20.56	-20.65	-18.55	-19.89	-20.14
L*	93.3	94.0	94.1	94.0	94.0	94.2	94.3
a*	2.01	3.21	3.23	3.28	3.05	3.18	3.21
b*	0.21	-10.26	-10.80	-11.41	-9.87	-10.98	-11.02
Opacity, % ISO	84.7	84.6	84.5	84.6	84.4	84.6	84.3

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