ISSN: 0379-5462
Indian Pulp and Paper Technical Association

An Innovative & Green approach for Synthesis of optical brightening agents and their applications in Paper Industry





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Abstract

The requirement of high brightness & whiteness in paper and board has increased dramatically during recent years. The brightness of pulp, fillers and coating pigments are not high enough to reach these brightness targets. Therefore there is a need to use an additive called optical brightener. These chemicals are also known as optical whitening agents (OWA), optical bleaching agents (OBA) or fluorescent whitening agents (FWA). Most of the OBAs on the market are derivatives of bis(triazinylamino) stilbene. There are three types of optical brighteners used in the paper industry, all based on the stilbene molecule. The main difference is the number of solubilizing sulphonic groups. Di-sulphonated OBAs have two sulphonic groups; the two other substituents could be hydrophilic groups. This type of OBA has a very good affinity but limited solubility and is mostly used at wet-end of papermaking. Tetra-sulphonated OBAs are versatile products because of their characteristics of medium affinity and good solubility. They can be used in most applications in the paper industry: wet-end, size-press, and coating. The hexa-sulphonated OBAs are specially used in coatings where high brightness is required. The present study represents an innovative & green approach to synthesize different derivatives of OBAs, characterization and their applications at wet end of papermaking & paper coating. The study revealed that green chemistry methods can be utilized to synthesize OBA as an environmental friendly approach. The results of the study also revealed that the performance of laboratory synthesized OBAs were comparable to that of commercially available OBA generally being used at wet end and paper coating in pulp & paper industry.

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

Introduction

History and applications of different Optical Brightening Agent (OBA) has already been discussed elsewhere by the authors (1). More specifically regarding applications of OBA in paper industry, these are used as an additive that enhances the optical properties of paper. 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). In paper industry, most of OBA are derivative of triazinylamino stilbene and contain 2/4/6 sulphonic groups as sodium salt for good solubility and interaction with fibre. The number of sulphonic acid groups ($-SO_3H$) i.e. 2, 4 and 6 is used to classify these products according to their properties as different classes exhibit distinct differences in application (3-5). Literature study revealed that these OBA may contain some formalin based toxic chemicals also while non-toxic OBAs are imported from foreign at higher cost. The purpose of this research work is to synthesize chemically different compounds exhibiting properties of OBA through green chemistry approach without use of any toxic chemical/solvent. The present paper communicates the synthesis of different chemicals which may act as OBA, their characterization, application in wet of papermaking and paper coating.

Materials and Methods:

All the chemicals used for the synthesis of intermediate products and 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. The un-sized papers were used as base paper for coating application.

General procedure for synthesis of OBAs:

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 ^oC 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 reactant-1 (R_1) (20.8 mmol) was added, wherever required. The mixture was heated to 50 ^oC 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 reactant-2 (R_2) were added, wherever required. The temperature was raised from 50 °C to 90 oC 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 details of the different OBAs synthesized in lab are given in table-1.

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% Na_2CO_3 solution before their dilution using distilled water. The results were compared with commercially available OBA containing same number of sulphonic group.

Table-1: Details of synthesized OBAs and commercial OBA used under study

S. No.	Name of OBA	R_1	R_2	Type	E-value	Application
1.	DOS*	-	-	Di	502	Wet end
2.	D2A*	Aniline	-	Di	393	Wet end
3	4-SSP*	p-sulfanilic acid	-	Hexa	358	Coating
4	APM Liquid*	p-sulfanilic acid	m-sulfanilic acid	Hexa	312	Coating
5.	Commercially available	No data available		Di & Hexa	300-500	Wet end & coating

** Synthesized in laboratory*

Refining of Pulp: The bleached mixed hard wood pulp (MHW) was refined in PFI Mill to get 30°SR as per TAPPI Test Method T 248. The freeness of pulp was measured using Schopper Riegler (°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-2. Handsheets of 70 g/m² were made on sheet former as per TAPPI Test Method. Sheets pressing and drying was done according to 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).

Table-2: 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

Preparation of coating slurry: Required weight of GCC slurry was taken in beaker and kept under agitation. Coating clay slurry and calculated amount of water were added to it to get targeted solid concentration. The speed of the agitator was lowered to avoid any foam formation during addition of polymeric emulsion. Lubricant and rheology modifier were added at the vortex after fixed interval of time. Finally optical brightening agent was added to the color. The pH of the color was adjusted to 8.5–9.0. The total solids of coating slip were kept around 65+2%. Coating color formulation marked "control" was prepared without addition of OBA while reference was prepared with 0.25 parts of commercially available OBA. All the coating chemical were added per hundred parts of pigments. The parts of other additives were fixed throughout the experiments in all batches. During the complete study, the attempts were made to adjust the viscosity of coating color to the desired level (1500 ± 200 cP at 100 rpm) while maintaining the solid level of coating color at 65±2.0%, and also to impart the necessary degree of water retention. Results revealed that addition of OBA had no major impact on viscosity of coating colour.

Application of coating color on base paper: The coating color was applied to 21.0 cm × 29.7 cm size base paper sheet (80 g/m² as basis weight collected from a paper mill) using an automatic bar coater (K Control Coater, Model 101). The sheets were preconditioned for 24 h at 27°C and 65% relative humidity. The coat weight was maintained around 14+1 g/m² with bars used for applying the coating color on base paper. The coated sheets were immediately placed in an oven maintained at 105°C for 60s to dry. Coated handsheets were supercalendered at plant scale by applying a constant linear nip pressure of about 76 bars at 50°C. All the sheets were passed through single nip.

RESULTS AND DISCUSSION:

The detailed study about the application of synthesized OBA at wet end application of papermaking with Ground Calcium Carbonate (GCC) and Talc filler has been described earlier and exhibited comparable optical properties as those of commercially available (1). The present paper describes the extension of the earlier work and includes synthesis of different types of OBAs, its application in wet end of papermaking using Precipitated Calcium carbonate (PCC) as filler and in paper coating (1).

Characterization of synthesized OBAs: The laboratory synthesized OBAs were characterized through different analytical techniques viz. Fourier Transform Infra Red (FTIR) Spectroscopy, 1H NMR and 13C NMR spectroscopy. The results of the characterization study revealed that the desired products were synthesized as exhibited though various techniques. The FTIR spectrum of lab synthesized OBA (DOS) is given in figure-1.

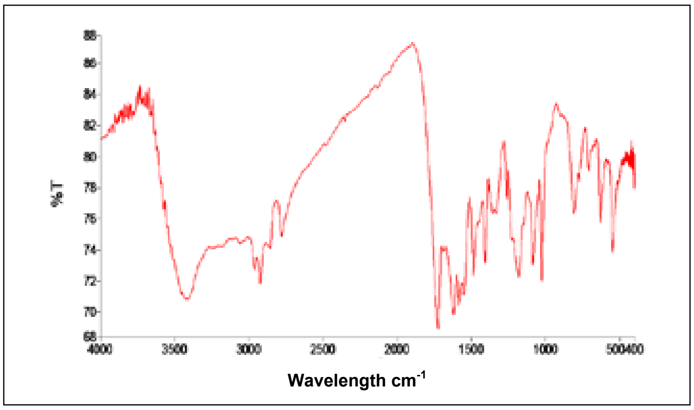

Figure-1: FTIR spectrum of lab synthesized OBA (DOS)

Optical properties of handsheets made with lab synthesized OBA using PCC as filler

In the present study, 2 different di and hexa-sulphonated OBAs, respectively were synthesized. As per literature, both the di-sulphonated OBAs were used at wet end of papermaking while hexa-sulphonated OBAs were used for coating application. 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 PCC as filler to find their impact on optical properties. The comparison of optical properties with lab synthesized and commercially available OBA using GCC filler in wet end application of papermaking as already been reported (1).

The initial brightness of the handsheet using PCC as filler at an ash level of ~21 % was 82.7 %; marked as control where all the wet end chemicals were added except OBA. By adding D2A a laboratory synthesized OBA, the ISO brightness was increased from 82.7% to 87.6% when the dosage was increased to 8 kg/t of pulp. Similarly, CIE whiteness was also increased to 102.7 from 75.9. With the use of DOS (another derivative of OBA synthesized in laboratory with two sulphonic group), the ISO brightness and CIE whiteness was increased to 88.3% and 103.8, respectively (Figure-2 & 3). The other optical properties of handsheets were also improved by adding the laboratory synthesized OBAs. The results revealed that these laboratory synthesized OBAs exhibited the properties of OBA as evident from the optical properties of handsheets. The complete results are given in table-3

Table-3: Comparison of optical properties of handsheets with lab synthesized OBAs using PCC as filler

Parameters	Control	Lab synthesized OBA		(D2A)	Lab synthesized OBA		(DOS)
OBA added, kg/t	Nil	4	6	8	4	6	8
Basis weight, g/m^2	70.2	70.1	71.1	71.0	71.3	70.4	71.0
Ash, %	20.0	19.9	20.2	20.0	20.3	19.7	20.5
ISO Brightness, %	82.7	86.1	86.8	87.6	86.2	87.3	88.3
CIE Whiteness	75.9	95.1	100.0	102.7	95.9	101.3	103.8
Fluorescence	0.70	6.63	6.96	7.90	8.35	9.01	12.7
Yellowness	4.28	-2.42	-2.51	-2.55	-3.01	-3.16	-3.57
L*	94.0	94.8	94.8	94.6	94.8	94.9	94.9
a*	0.25	1.05	1.07	1.10	0.84	0.88	0.98
b*	2.11	-1.66	-1.70	-1.71	-1.88	1.91	2.06
Opacity, % ISO	86.1	87.1	86.2	85.8	86.0	87.3	85.6

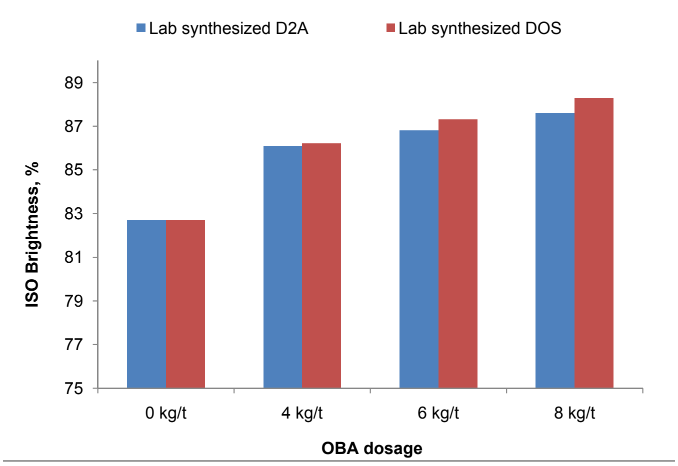

Figure-2: Effect of OBA dosage on ISO Brightness using PCC as filler

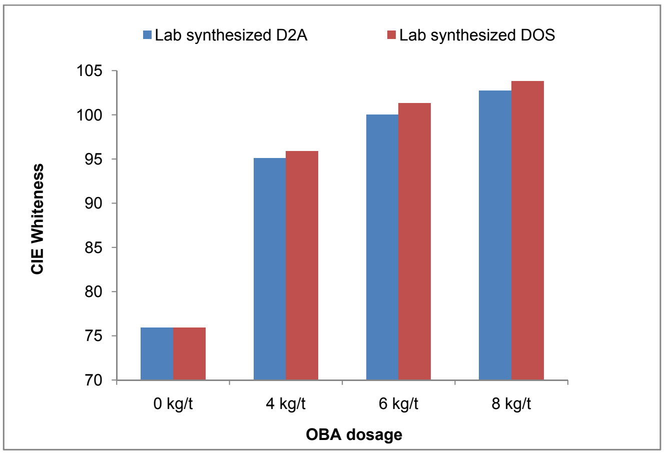

Figure-3: Effect of OBA dosage on CIE whiteness using PCC as filler

Optical properties of coated paper sheets made with lab synthesized OBA using a standard coating formulation

In case of paper coating, 0.25 and 0.50 parts of two different OBAs were added in coating slurry and results of optical properties of coated paper have been compared with 0.25 parts of commercially available OBA used in paper coating.

The two different laboratory synthesized hexa-sulphonated OBAs (4-SSP and APM liquid) were used in the present study for coating application. A standard normal coating formulation was prepared with and without commercial OBA marked as "Ref." and "Control", respectively. The details of the coating colour formulation are given table-4. In control (without OBA), the ISO brightness and CIE whiteness was 83.4% and 88.6, respectively which was increased to 88.1% and 122.7 with the addition of 0.25 parts of commercial hexa-sulphonated OBA being used for coating application in paper industry. However, to study the effect of laboratory synthesized OBA on optical properties of coated paper, 0.25 and 0.50 parts of two different OBAs were added to coating formulation. It was observed that OBA had no major impact on rheological properties of coating slurry. However, it greatly impacted the optical properties of coated paper. With one of laboratory synthesized OBA, the ISO brightness and CIE whiteness was increased to 86.9% and 117.7, respectively at 0.25 parts. The same properties were further increased to 88.1% and 125.2 while increasing the parts of OBA to 0.50 parts. While comparing the second laboratory synthesized OBA, the value of ISO brightness and CIE whiteness was 90.5% and 129.8, respectively with 0.50 parts of OBA (Figure-4 & 5). The results of this revealed that second laboratory synthesized OBA was better to exhibit optical properties to coated paper as evident from table-5. The same is also evident from the E-value of OBAs.

Table-4: Coating colour formulation details

Ingredient	Control	Ref.	Lab synthesized OBA (4-SSP)		Lab synthesized OBA (APM liquid)	
OBA added	Nil	0.25	0.25	0.50	0.25	0.50
GCC	90					
Coating clay	10					
Polymer emulsion	11					
OBA carrier	0.6					
Lubricant	0.75					
Rheology modifier	0.20					

Table-5: Comparison of optical properties of coated paper

Parameters	Control	Ref.	Lab synthesized OBA (APM liquid)		Lab synthesized OBA (4-SSP)	
OBA added	Nil	0.25	0.25	0.50	0.25	0.50
Basis weight, g/m^2	93.6	95.1	93.8	93.9	93.9	95.7
ISO Brightness, %	83.4	88.1	86.9	88.1	88.6	90.5
CIE Whiteness	88.6	122.7	117.7	125.2	122.9	129.8
Fluorescence	3.10	13.4	11.2	12.3	11.3	14.0
Yellowness	-2.25	-15.5	-11.4	-12.8	-11.3	-14.2
L*	93.0	93.4	93.1	93.2	93.6	93.8
a*	0.17	2.45	2.51	2.03	2.66	2.80
b*	-1.21	-8.52	-7.40	-7.65	-7.23	-7.74
Hunter Gloss, %	25-30	24-28	26-30	25-28	25-30	26-30

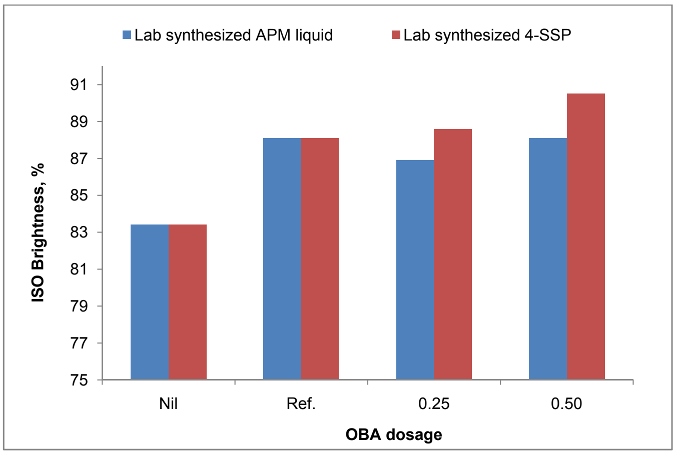

Figure-4: Effect of OBA dosage on ISO brightness of coated paper

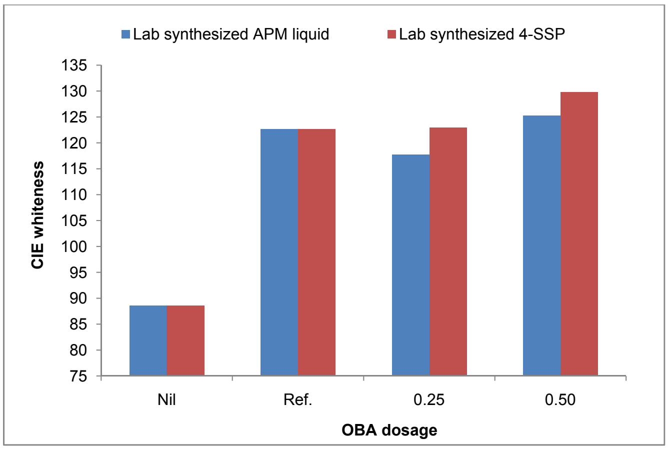

Figure-5: Effect of OBA dosage on CIE whiteness of coated paper

CONCLUSION:

The di and hexa-sulphonated triazinylamino stilbene derivatives of OBA were successfully synthesized through green chemistry approach in the laboratory with good yield. Different analytical techniques also confirm the synthesis of OBA. Moreover, the E-value of the synthesized OBA was comparable with commercially available respective sulphonated OBA used in wet end application of papermaking and paper coating. The laboratory synthesized OBAs exhibited good optical properties when used at wet end of papermaking and also in coating application.

ACKNOWLEDGEMENT:

Authors wish to thank Department of Science and Technology (DST), New Delhi, for providing the financial support to carry out this research work. Authors would also like to thank Director, ACIRD for continual motivation during the project work.

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