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

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OUTLINE OF THE PRESENTATION

- Introduction
- Purpose of the study
- Materials and methods
- Results and discussion
- Conclusions

INTRODUCTION

- P. Krais in 1929 discovered effect of optical brightening agent (OBA) to improve the optical properties while first industrial application began in 1935, and these agents came into full-scale industrial use in late forties.

- OBAs can be classified, based on structure and properties, into some 11 major chemical families, each containing numerous sub-families, hundreds of compounds, and thousands of different formulations.

- All OBAs are highly-substituted ring (aromatic) structures that contain many double bonds which are activated by UV light.

- Thousands of OBA formulations have been evaluated by the manufacturers, but relatively few have met the requirements of all the industry.

INTRODUCTION

- The global OBA production for paper, textiles and detergents is dominated by just a few di/tetra and hexa-sulfonated triazole-stilbenes.

- More than 2000 patents for OBAs exist; there are several hundred commercial products, and approximately one hundred producers and distributors. 50% of OBAs are consumed by the detergent industry, 33% by the paper industry, and 17% by the textile industry. Literature study revealed that these OBAs contain some toxic chemicals and have been banned while non-toxic OBAs are imported at higher cost.

- The purpose of this project is to synthesize chemically different compounds, free from toxic chemicals, that act as OBA through green approach at lower cost.

- Attempts were also made to use these laboratory synthesized OBAs in wet end application of papermaking.

ROLE OF OPTICAL BRIGHTENING AGENTS

Improvement in optical properties of base/uncoated paper

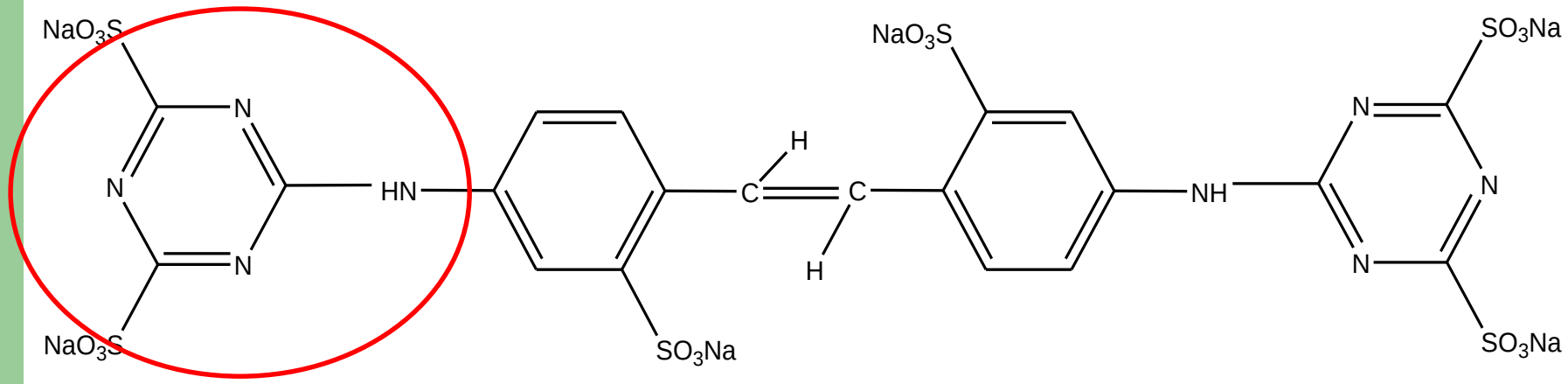
- Bleaching of pulp to higher level
- Addition of high bright filler
- Direct addition of OBA at wet-end or at size press

ROLE OF OPTICAL BRIGHTENING AGENTS

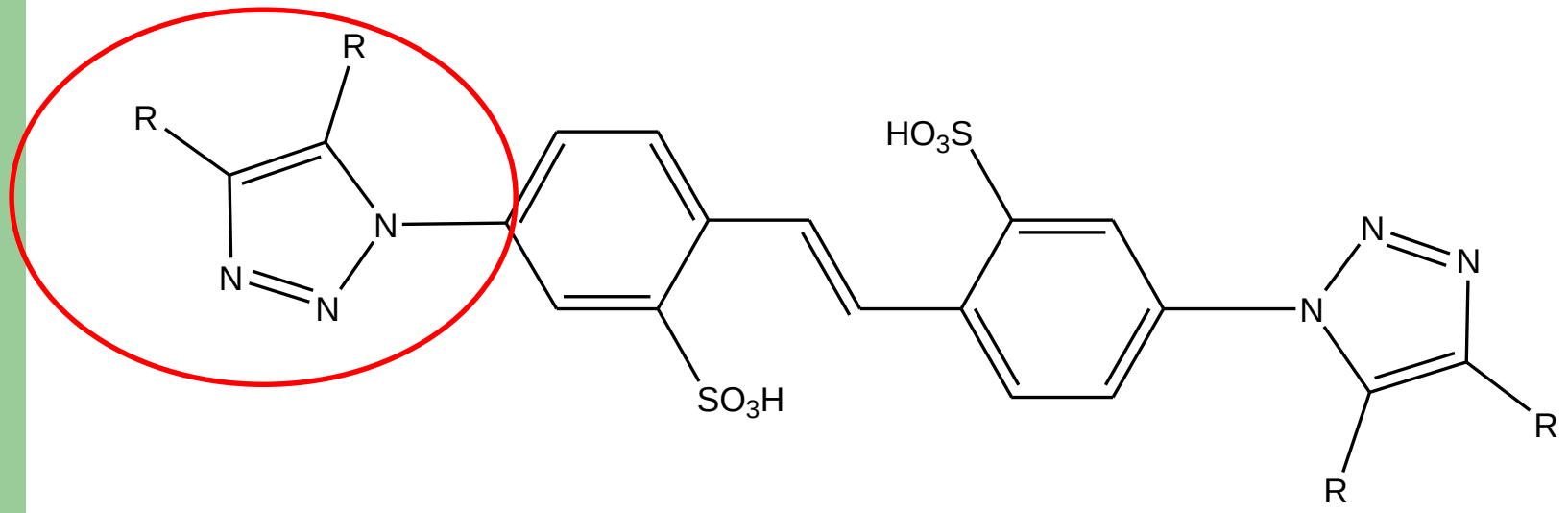
Common optical brightening agents

- Triazinylamino stilbene
- Triazolyl stilbene
- Distyryl biphenyl
- Diphenyltriazinyl stilbene
- Benzoxazolyl stilbene
- Stilbenyl naphthotriazole
- Styryl stilbene
- Benzimidazole
- Coumarin
- Pyrazoline

ROLE OF OPTICAL BRIGHTENING AGENTS



Structure of bis-(Triazinylamino) stilbene containing 6- sulphonic group



Structure of 4, 4'-bis-(triazolyl)-stilbene-2, 2'-disulphonic acid derivative

ROLE OF OPTICAL BRIGHTENING AGENTS

Common optical brightening agents

- Triazinylamino stilbene Containing either 2,4 or 6- sulphonic group
- Triazolyl stilbene
- Distyryl biphenyl
- Diphenyltriazinyl stilbene
- Benzoxazolyl stilbene
- Stilbenyl naphthotriazole
- Styryl stilbene
- Benzimidazole
- Coumarin
- Pyrazoline

PURPOSE OF THE STUDY

- To synthesize new chemicals as optical brightening agent through green approach
- To study their impact on optical properties of paper

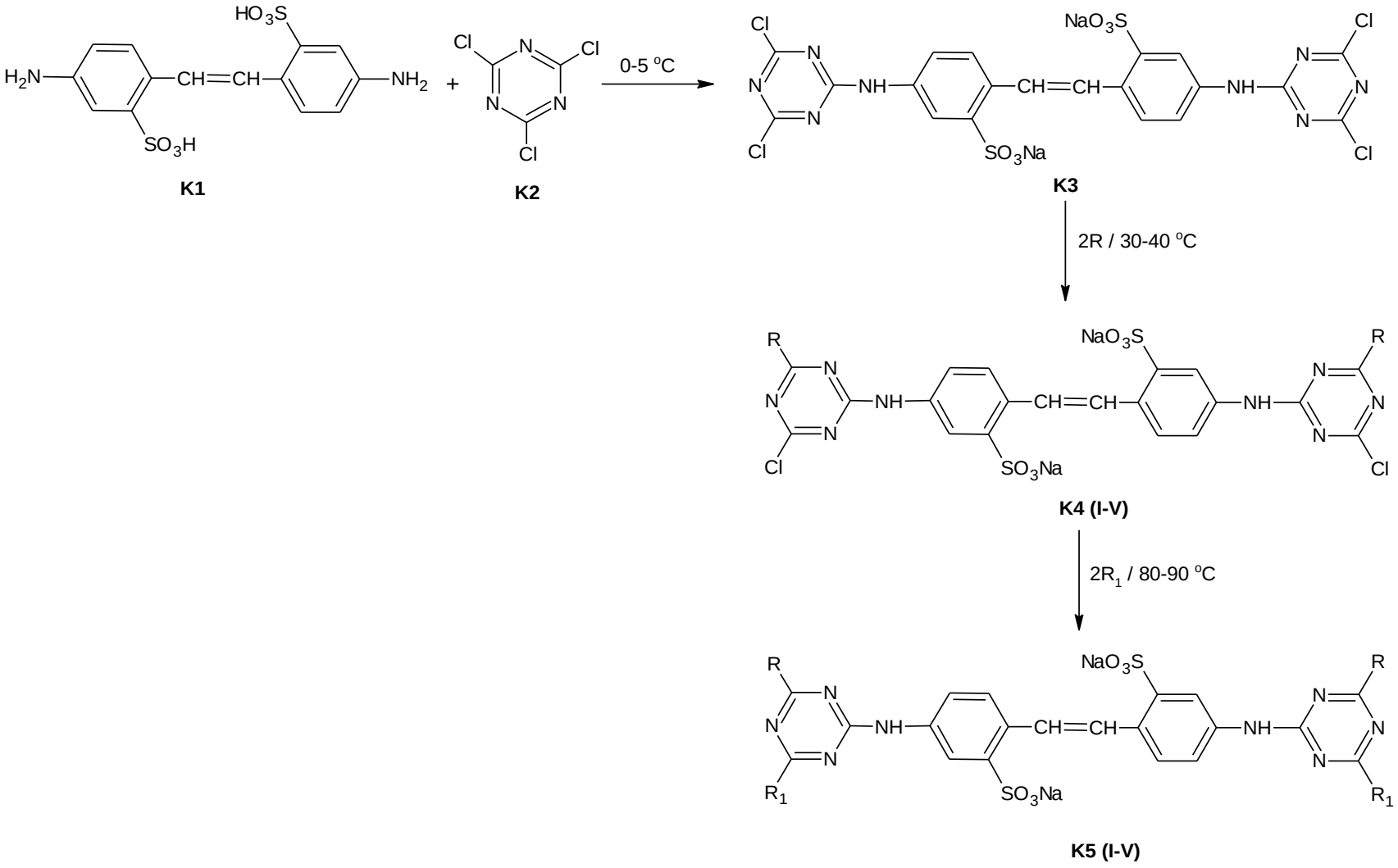
MATERIALS AND METHODS

- ✓ 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).
- ✓ The bleached mixed hard wood pulp (MHW) was taken for the study.

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 and Talc (for 21% ash level)
  - ➢ Cationic Polyacrylamide (CPAM): 200 g/t of pulp

METHOD OF PREPARATION



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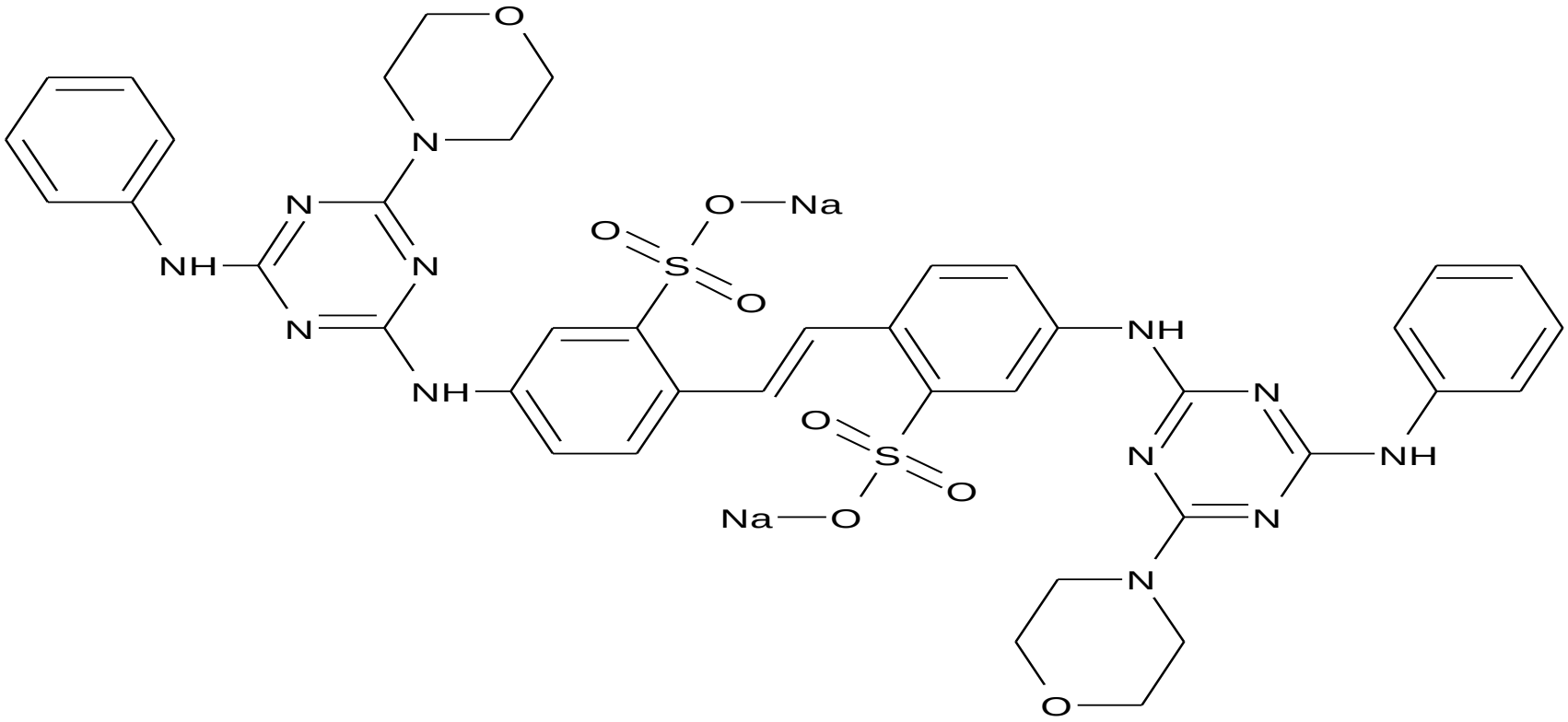
METHOD OF PREPARATION

Disulphonated derivative: Synthesis of 4, 4’-bis [4-morpholino-6-anilino-s-triazin-2-ylamino] 2, 2’-stilbene-disulphonic acid, disodium salt

General method of preparation: A-P-O: 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 ^{o}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 ^{o}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 ^{o}C to 90 ^{o}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 ^{o}C to obtain a yellow solid.

STRUCTURE OF LABORATORY SYNTHESIZED OBA



ANALYTICAL TECHNIQUES

- ✓ All the wet end chemicals were prepared and used as per standard practice.
- ✓ Laboratory 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.
- ✓ Testing of all the properties of handsheets were 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

Characteristics of 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

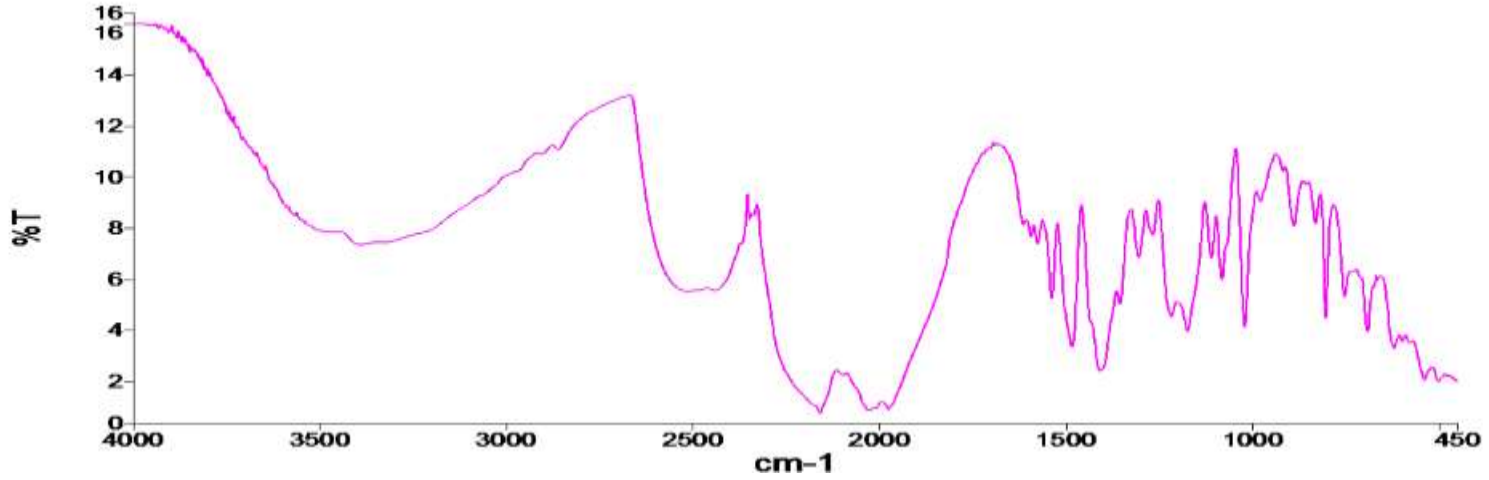
RESULTS AND DISCUSSION

Characteristics of OBAs

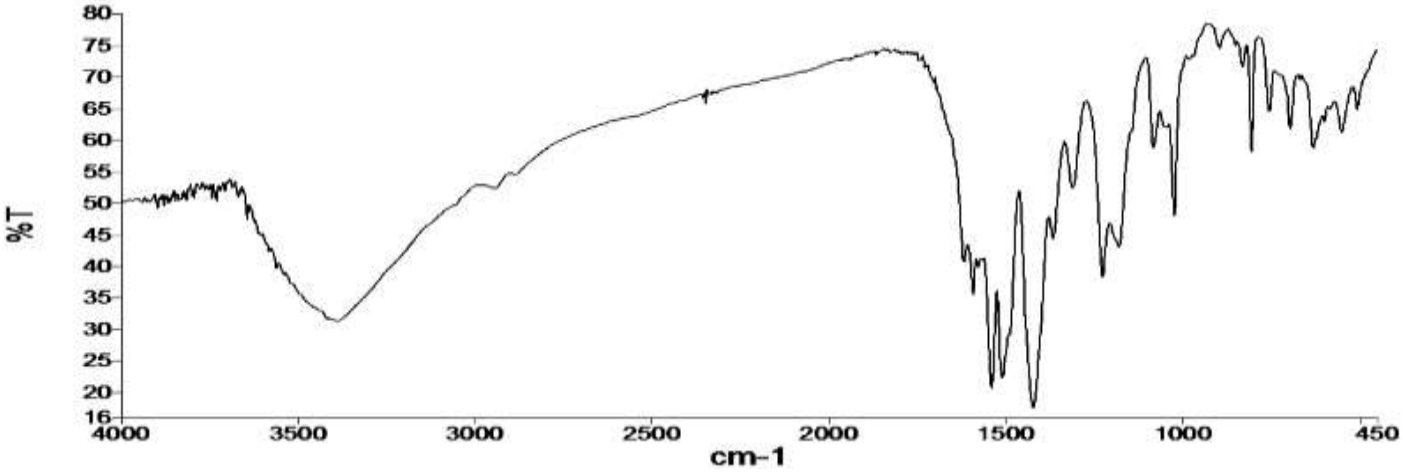
Parameters	Commercially available	Laboratory synthesized
No. of sulphonic group present	02	02
E-value, 1%/1cm	493	505
Presence of stilbene moiety	Yes	Yes
Solubility in hot water	Good	Good

RESULTS AND DISCUSSION

FTIR spectrum of OBAs



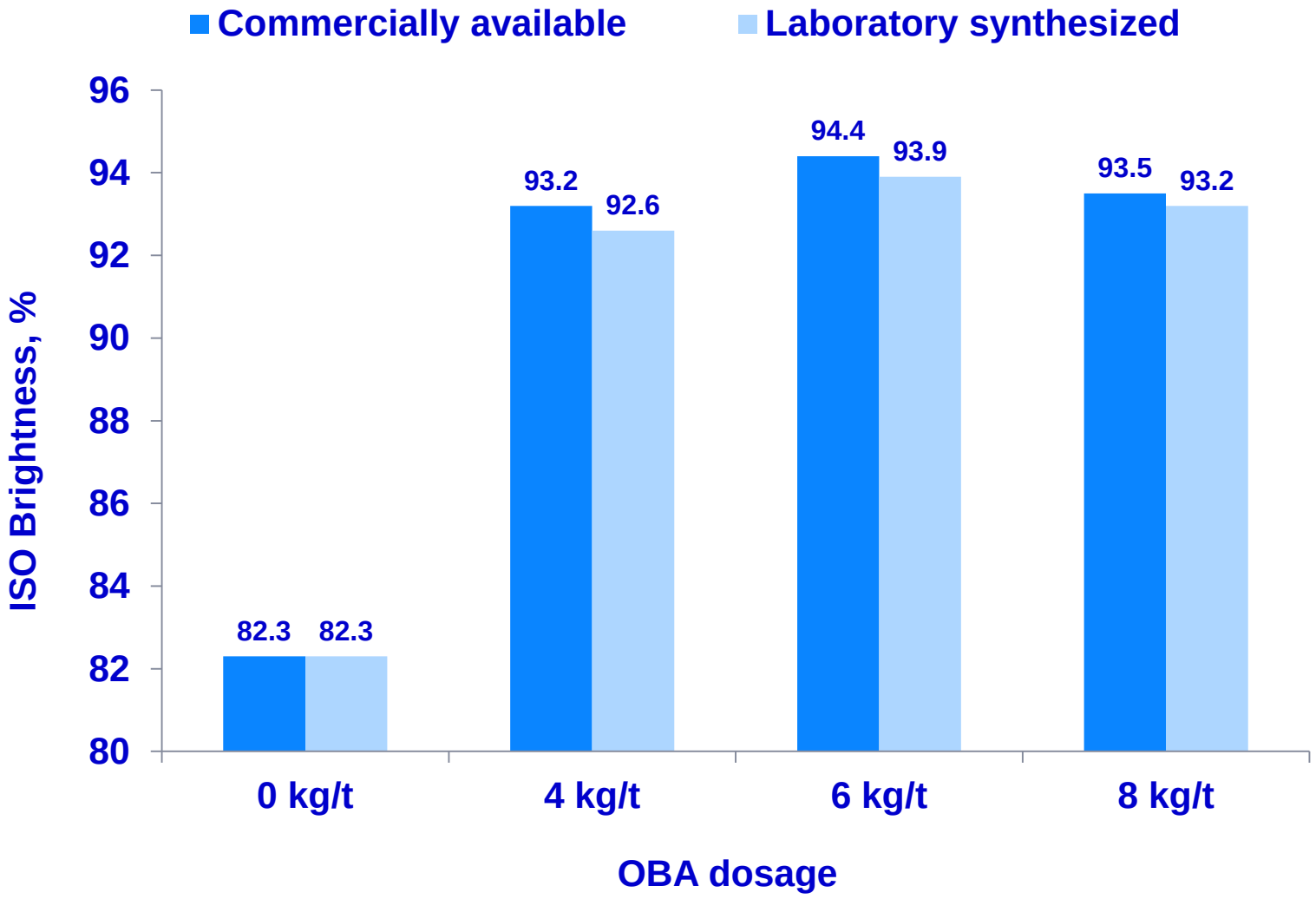
Commercially available OBA



Laboratory synthesized OBA

RESULTS AND DISCUSSION

Effect of OBA dosage on ISO Brightness using GCC filler



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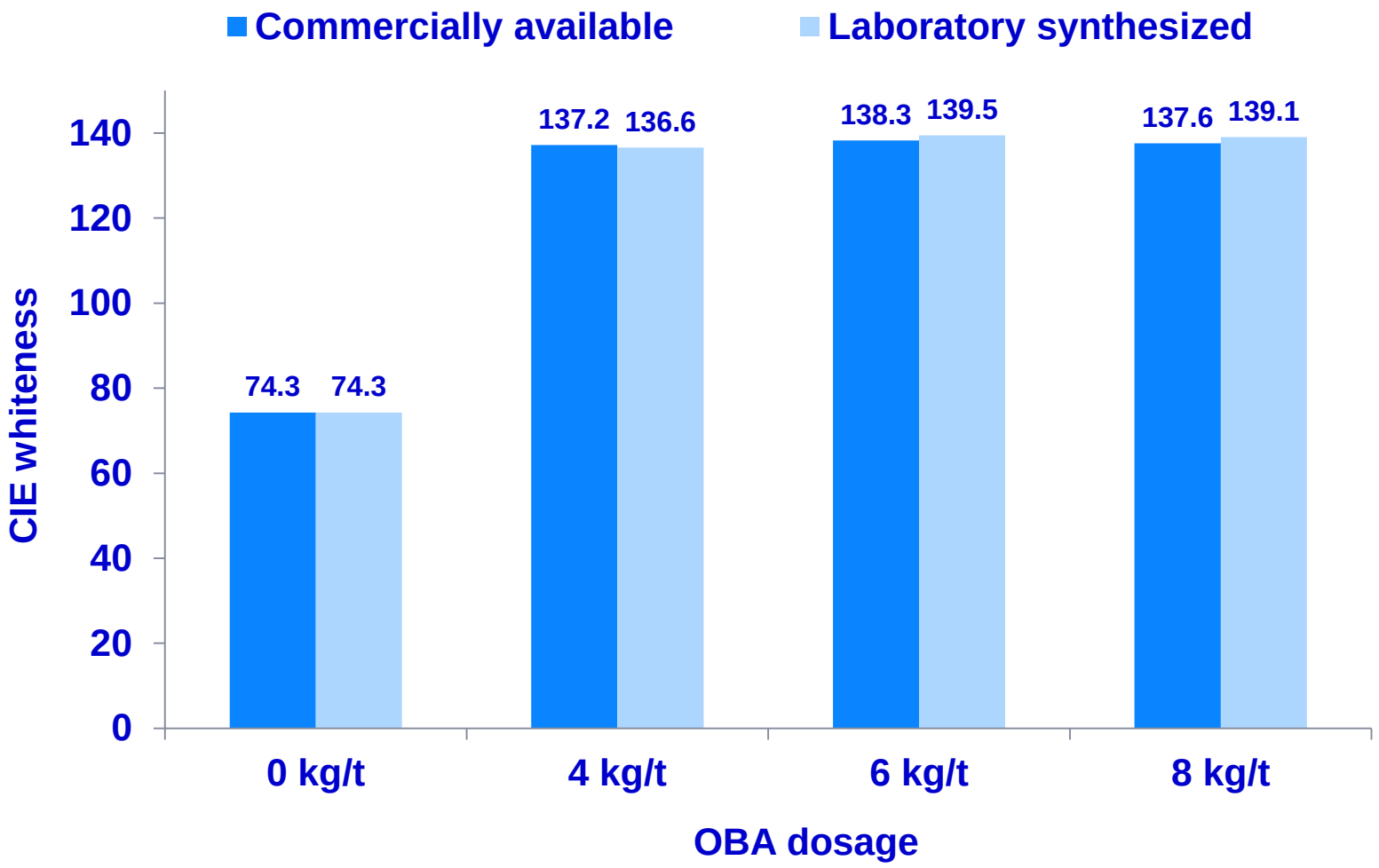
RESULTS AND DISCUSSION

Effect of OBA dosage on CIE whiteness using GCC filler



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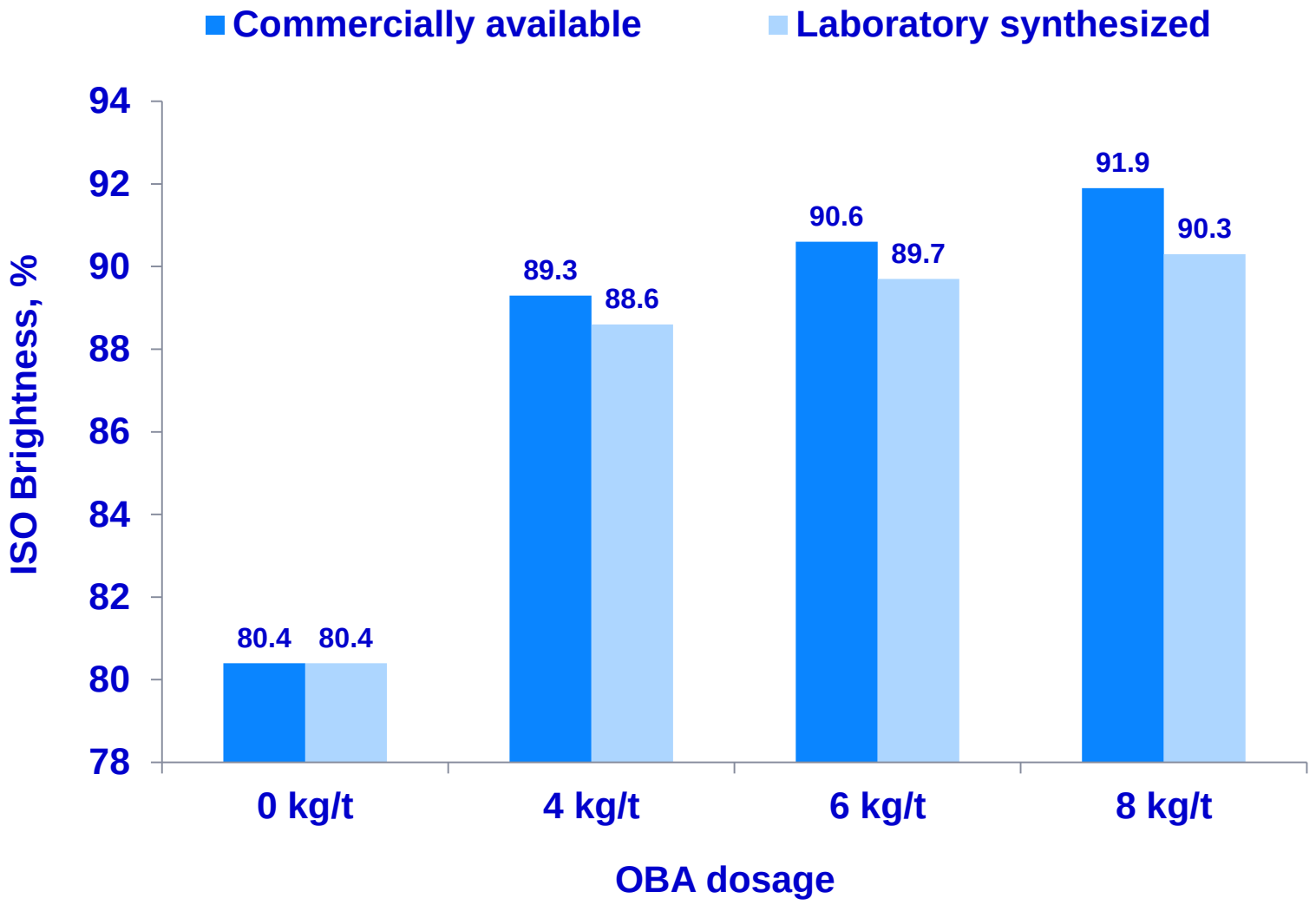
RESULTS AND DISCUSSION

Effect of OBA dosage on optical properties using GCC 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

RESULTS AND DISCUSSION

Effect of OBA dosage on ISO Brightness using Talc filler



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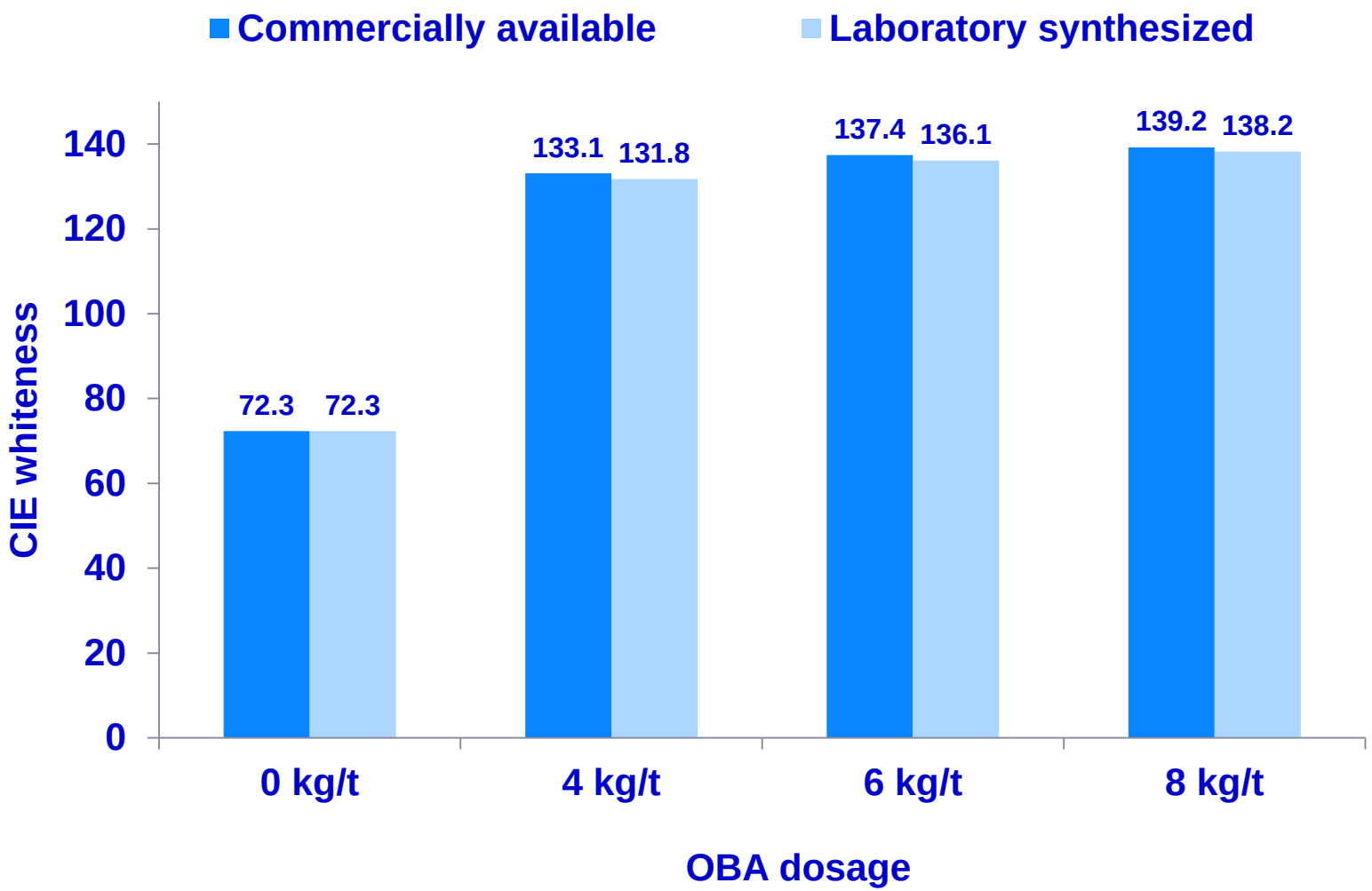
RESULTS AND DISCUSSION

Effect of OBA dosage on CIE Whiteness using Talc filler



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RESULTS AND DISCUSSION

Effect of OBA dosage on optical properties using Talc 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/m²	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

CONCLUSIONS

- ✓ The di-sulphonated triazinylamino stilbene derivative OBA was synthesized successfully with good yield through green approach in the laboratory as evident from FTIR and E-value.

- ✓ Laboratory synthesized OBA exhibited comparable optical properties using GCC filler at 21% ash level.

- ✓ The dosage of each OBA should be optimized based upon the filler and ash level.

- ✓ The optical properties with Talc filler were on lower side as compared to GCC which might be because of low inherent brightness of Talc.

ACKNOWLEDGEMENT

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THANK YOU