Chemistry Of Optical Whitening Agents And Their Activation For Better Performance in Paper Coating

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ABSTRACT

Besides physical properties of paper, its appearance in terms of brightness, whiteness and shade is of primary concern to papermakers as well as to end users. The common methods to increase the brightness and whiteness of paper include bleaching of pulp to higher level, addition of high bright fillers/pigments and optical whitening agent (OWA) to the paper. It is well known that OWA plays a significant role in improving the optical properties of the paper. The result of the study revealed that sulphonic groups present in the OWA also affect the optical properties of coated paper. The optical properties of coated paper are directly proportional to the number of sulphonic groups present in the OWA. For manufacturing coated paper through multilayer coating and to have better effect of OWA it is better to add it in top-coating colour formulation rather than in under-coating formulation. The result also revealed that increased dosage of OWAs improved the optical properties upto greening point but it is not possible to further improve the same. Addition of OWA carrier increases the brightness and whiteness of coated paper beyond the greening point and the efficacy of OWA could be increased several times if used along with carrier/activator.

Key words: Coating colour, rheology modifier, water retention, OWA, booster, brightness, whiteness

Introduction

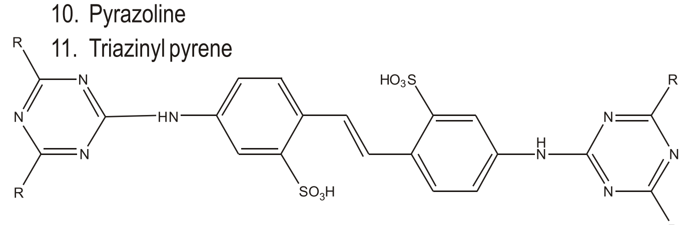
P. Krais in 1929 discovered effect of optical whitening agent (OWA) to improve the optical properties while first industrial application began in 1935, and these agents came into full-scale industrial use in late forties. In 1941, OWAs were produced and introduced commercially in the market. OWAs were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 Today many of the earlier OWAs are no longer used, or have been replaced by superior chemicals having better whitening efficacy with many more benefits in usage (1).

Now a days OWAs have become a part of everyday life; as these have found an increasing use in diverse fields and they are widely used in the pulp & paper, detergent and textile industries. OWAs have a common property to improve the optical properties like brightness, whiteness and shade and are different in action as compared to bleaching agents. OWA is also known by other names viz. Fluorescent Brightening Agent (FBA) or Fluorescent Whitening Agent (FWA). OWAs are dyes that absorb light in the ultraviolet and violet region (usually 340-370 nm) of the electromagnetic spectrum, and re-emit light in the blue region (typically 420-470 nm). After detergent industry, the paper industry consumes large amount of OWAs either at wet end or in coating applications. OWAs in paper industry are used as additives that paper manufacturers put into paper in order to help a paper look whiter. 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.

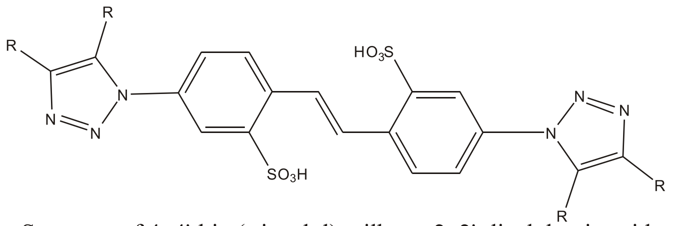
OWAs can be classified, based on structure and properties, into some 11 major chemical families, each containing numerous sub-families, hundreds of compounds, and thousands of different formulations (2). All OWAs are highly-substituted ring (aromatic) structures that contain many double bonds which are activated by UV light. Thousands of OWA formulations have been evaluated by the manufacturers, but relatively few have met the requirements of all the industry.

The most common classes of chemicals which act as OWA (along with their chemical structure) are derivative of the following:

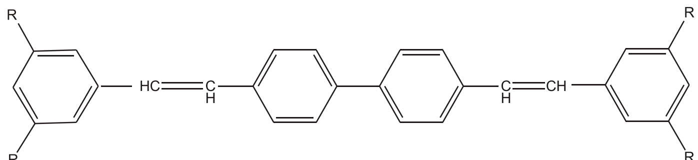
1. Triazinylamino stilbene
2. Triazolyl stilbene
3. Distyryl biphenyl
4. Diphenyltriazinyl stilbene
5. Benzoxazolyl stilbene
6. Stilbenyl naphthotriazole
7. Styryl stilbene
8. Benzimidazole
9. Coumarin
10. Pyrazoline
11. Triazinyl pyrene



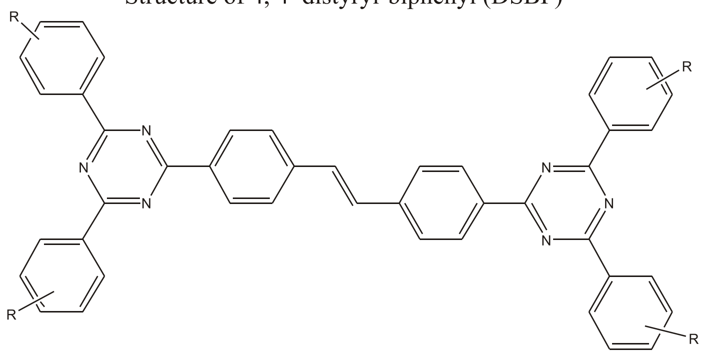
Structure of 4, 4'-bis-(triazinylamino)-stilbene-2, 2'-disulphonic acid



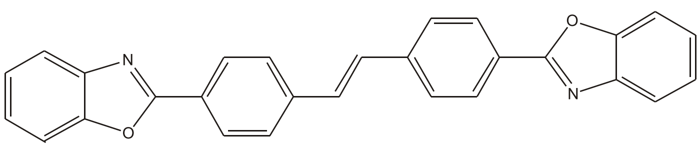
Structure of 4, 4'-bis-(triazolyl)-stilbene-2, 2'-disulphonic acid



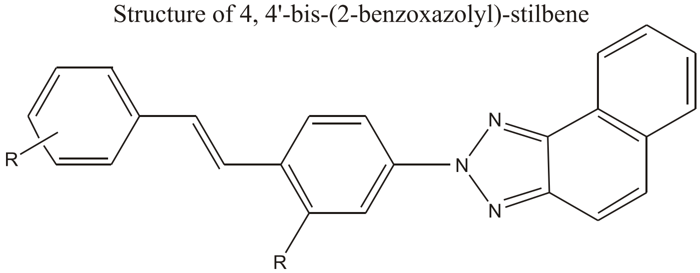
Structure of 4, 4'-distyryl-biphenyl (DSBP)



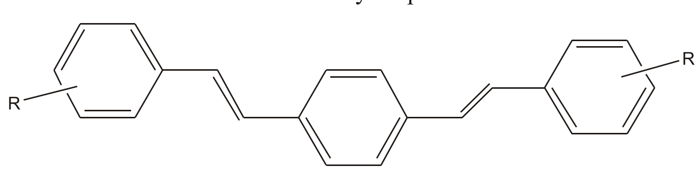
Structure of 4, 4'-bis-(diphenyltriazinyl)-stilbene



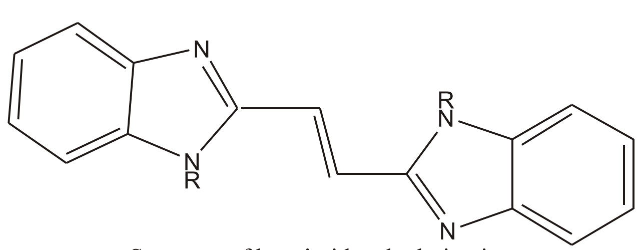
Structure of 4, 4'-bis-(2-benzoxazolyl)-stilbene



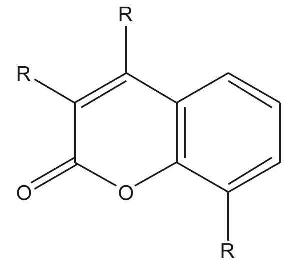
Structure of stilbenyl-naphthotriazole



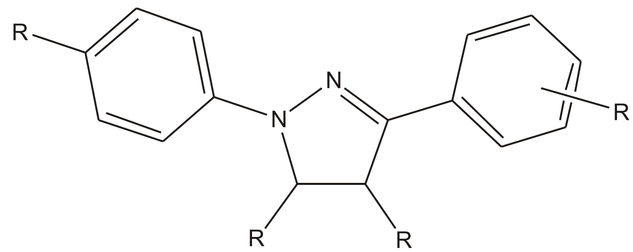
Structure of styryl-stilbene



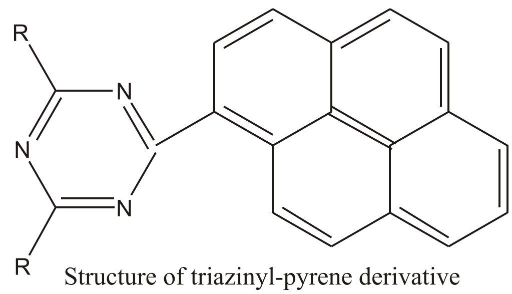
Structure of benzimidazole derivative



Structure of coumarin derivative



Structure of pyrazoline derivative



Structure of triazinyl-pyrene derivative

To achieve better fluorescent activity, an OWA should have the following characteristics:

- Conjugated system of bond as shown in above structure
- Planner structure

The molecule should also contain a group like amino (-NH_2), hydroxyl (-OH), sulphonic (SO_3H), alkoxy (-OR) and alkyl and many more which intensify the fluorescence depending upon their number and position.

The most of OWA used in paper industry are derivative triazinylamino stilbene and contain 2-6 sulphonic groups as sodium salt for good solubility and interaction with fiber. 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 OWAs 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 (3).

Coatings improve certain properties of the paper to make the printed image sharp, clear and more appealing to the eye. This is done by filling the non uniform surface of the paper by applying pigmented coating and calendering the surface to get desired coated paper quality.

Pigment contributes around 85 to 90 % in weight of any coating colour;

pigment characteristics, viz. particle size, size distribution, and morphology, play fundamental role in determining the coating structure (4). Despite the use of pigments of high brightness, OWA is used to reach and boost the optical properties of finished sheet. Overall coating imparts both visual and functional enhancements, providing a smooth surface that increases image fidelity for printed applications (5). Coated paper of high brightness and whiteness can also increase the advertising value of printed materials by making it possible to create innovative effects and design.

The present paper communicates the effect of different sulphonic group present in OWAs and efficient use of OWAs in coating recipe and their activation for improved properties for coating application.

Materials And Methods

Coating base paper with a basis weight of 78 g/m^2, manufactured by using hardwood and softwood pulp combination, was used for coating application. Commercial grade GCC of coarser and finer grade was used in precoat and topcoat coating formulation, respectively. Styrene butadiene (Tg: 17°C) based synthetic binder and polyacrylate based dispersing agent were used in coating formulation. Carboxy methyl cellulose (CMC)/starch and acrylic copolymer were used as a natural and synthetic rheology modifier, respectively. Chemicals containing different sulphonic group as OWA and AZC based compounds were used as insolubilizer. Calcium stearate based compound was used as lubricant.

Preparation of pre-coat coating colour

Required weight of $CaCO_3$ slurry was taken in a dry 1000 ml plastic beaker and kept under agitation. Calculated amount of water was added to it to get targeted solid concentration. The dispersant was added and the slurry was agitated for 5 min. The pH of the slurry was maintained at 8.5-9.0 by adding alkali. The slurry was agitated at high speed for 10 min for complete dissolution. Natural rheology modifier was added very slowly at the vortex to avoid any viscosity shock or lump formation. The polymer emulsion and insolubilizer were added at the vortex with 5 min interval of addition for each. OWA was added (if required as per formulation) before the addition of synthetic thickener. Synthetic thickener was added as the last component. The total weight of coating colour mixture was maintained at 1000 g.

Preparation of top-coat coating colour

Required weight of $CaCO_3$ slurry was taken in a dry 1000 ml plastic beaker and kept under agitation for 5 min. Throughout the experiment the ratio of GCC to clay was kept constant. Clay slurry was added to it slowly and agitated for another 5 min. Calculated amount of water was added to get targeted solid concentration followed by addition of dispersant. Cooked natural rheology modifier was added slowly at the vortex of pigment slurry. The slurry was agitated at high speed for 10 min for complete dissolution of rheology modifier. The polymer emulsion, lubricant and insolubilizer were added at the vortex with 5 min interval of addition for each. OWA was added to the colour as per the formulation. The chemical for boosting the OWA effect was added as per plan of the experiment. The pH of the slurry was maintained at 8.5-9.0. The total weight of coating colour mixture was maintained at 1000 g. All the ingredients were added on parts per hundred parts of the pigment.

Paper coating application

The coating colour was applied to 21.0×29.7 cm^2 base paper sheet using an automatic bar coater (RK-Print Coat Instruments Ltd., U.K., model K 101). The sheets were preconditioned for 24 hour at 23°C and 55% relative humidity. The coat weight was maintained at 15 and 10 g/m^2 with bars of different number for pre-coat and top-coat, respectively. The coated sheets were immediately placed in an oven maintained at 105 °C for 60 seconds to dry. Coated paper was supercalendered in plant scale supercalender by applying a linear nip pressure of 76 bars at 50 °C. All the sheets were passed through two nips.

Analytical techniques

Viscosity of coating slip was measured on Brookfield Viscometer model no. DV-II pro as per Tappi Test Method T 648 om-97. Water retention value was measured on AAGWR water retention meter as per Tappi Test Method T 701 pm-01. Basis weight of coated sheets was measured as per Tappi Test Method T 410 om-98. Thickness of coated sheets was measured on L&W thickness tester as per Tappi Test Method T 411 om-94. Gloss value of the coated sheets was determined on Hunter lab gloss meter as per Tappi Test Method T 480 om-92. Optical properties of coated sheets were determined by using Technibrite brightness tester (Colour Touch) as per Tappi Test Method T 452 om-92.

Results And Discussion

Effect of number of sulphonic group in OWA on viscosity of coating colour

Two dosages of each OWA were selected to see its effect on low shear viscosity of coating colour and optical properties of coated paper. The addition of same dosage level of OWA containing different sulphonic group affects the viscosity of coating colour. Higher is the number of sulphonic group higher was the viscosity of coating colour at same dosage level (Figure 1). The increase in low shear viscosity might be because of large and complex structure of OWA which imparts resistance to the flow. Higher dosage of OWA containing either number of sulphonic group also increased the viscosity of coating colour (Figure 1). Water retention capacity of the coating colour was more or less same with OWA containing different sulphonic groups.

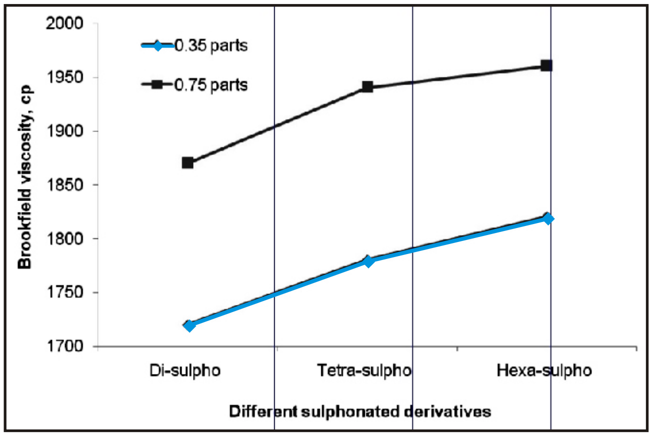


Figure 1: Effect of differently substituted OWA on low shear viscosity

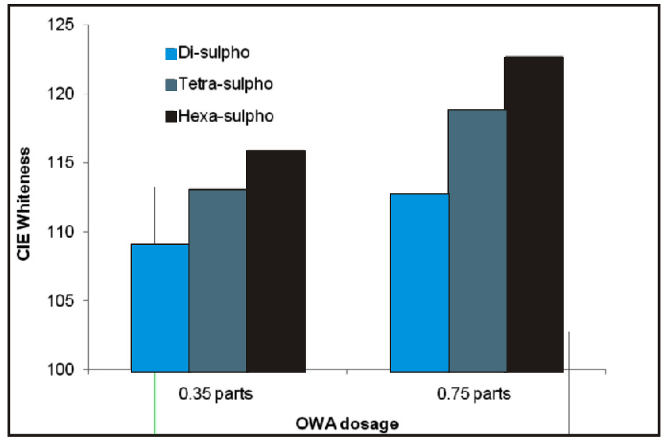


Figure 3: Effect of differently substituted OWA on whiteness of coated paper

Effect of number of sulphonic groups in OWA on coated paper properties

As discussed earlier, the derivative triazinylamino stilbene containing different sulphonic groups are used as OWA in pulp & paper industry. Three different OWAs containing 2, 4 and 6 sulphonic groups of triazinylamino stilbene were selected for this study. These different OWAs were added in top-coat formulation at two dosages (0.35 and 0.75 parts) to see their impact on brightness and whiteness of final coated paper. At 0.35 parts the brightness of coated paper was around 87% with di-sulpho derivative of OWA which was further increased to 87.7 and 88.5% with tetra and hexa-derivative of OWA, respectively. At 0.75 parts the brightness of coated paper was increased to 89 and 90.6% with tetra- and hexa- sulphonated OWA, respectively from an initial level of 87.9% with di-sulphonated OWA (Figure 2). The same trend was observed in the whiteness of paper also; increased from 109.1 to 115.9 when 0.35 parts of hexa-sulphonated OWA was used. The increment in whiteness was by 10 points when the hexa-sulphonated OWA dosage was increased from 0.35 to 0.75 parts. Further on comparing at two different dosage levels with same OWA it was found that the whiteness of coated paper was increased by 3.6, 5.7 and 6.8 points with di-, tetra- and hexa-sulphonated derivatives, respectively (Figure 3).

Effect of addition of OWA in coating formulation on coated paper properties

The dosage of OWA was increased from 0-0.95 parts based on per hundred parts of pigment. Two different set of experiments were planned to see the effect of addition OWA in coating formulation. In first set of experiment the dosage of OWA was increased up to 0.95 parts in pre-coat formulation and no OWA was added in top-coat formulation. In second set of experiment OWA was increased up to 0.95 parts in top-coat formulation while no OWA was added in pre-coat formulation. The dosages of other ingredients were kept constant. The brightness of final coated paper was increased by 4 and 5% as the dosage of OWA increased to 0.95 parts in pre-coat and top-coat formulation, respectively (Figure 4). Similarly the whiteness of paper was increased to 117 and 123 from an initial level of 97 when the OWA parts were increased to 0.95 parts in pre-coat and top-coat formulation, respectively. Brightness and whiteness are much better when the OWA was used in top-coat formulation compared to pre-coat formulation (Figure 5).

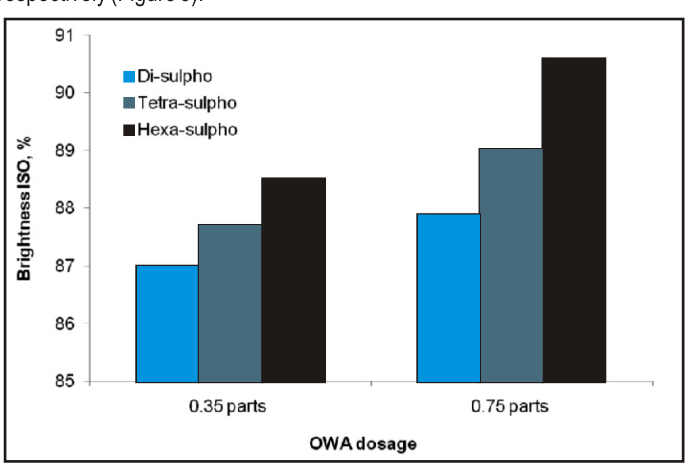


Figure 2: Effect of differently substituted OWA on brightness of coated paper

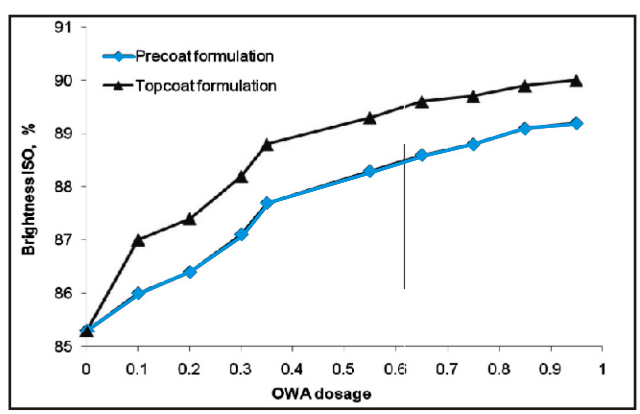


Figure 4: Effect of addition of OWA in coating formulation on brightness of coated paper

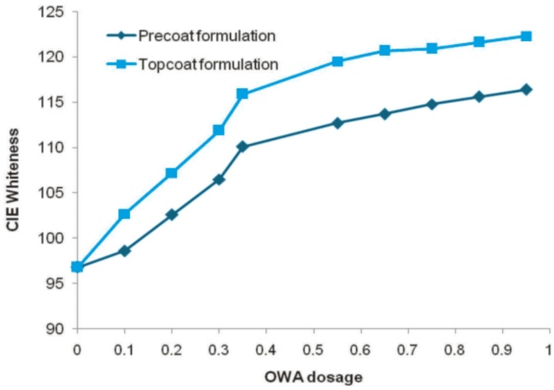


Figure 5: Effect of addition of OWA in coating formulation on whiteness of coated paper

Activation of OWA

After a certain point; greening point, the brightness and whiteness of coated paper cannot be increased even by adding higher dosage of OWA. To meet this higher level of brightness and whiteness of coated paper, some chemical can be used which increases these properties after greening point. These chemicals significantly improved the optical properties of coated paper to great extent. The two dosage levels (0.5 and 1.0 parts) were selected to study the effect of addition of booster in coating formulation. With normal formulation, the brightness increased from initial level of 88.5 to 90.2% when the dosage of OWA was increased from 0.35 to 0.95 parts. The initial brightness level reached to 93.8% after the activation of OWA through the addition of 1.0 part of booster (Figure 6). The booster increased the OWA activity many folds. The similar trend was observed in whiteness of coated paper. Whiteness of coated paper was increased to 135.7 with 1.0 part of OWA activator/booster when 0.95 parts of OWA was used in coating formulation while whiteness was around 123.4 without any booster at same dosage level. Addition of OWA booster improved the optical properties of coated paper significantly which could not be achieved by simply increasing the OWA dosage (Figure 7). The improvement in the optical properties of coated paper with OWA booster might be due to the presence of polyhydroxyl group present in the booster.

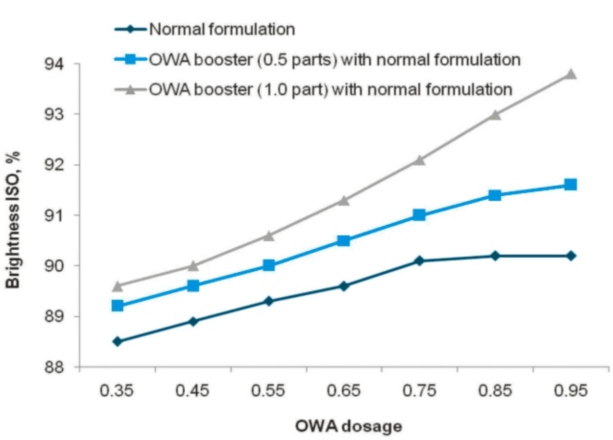


Figure 6: Effect of OWA booster on brightness of coated paper

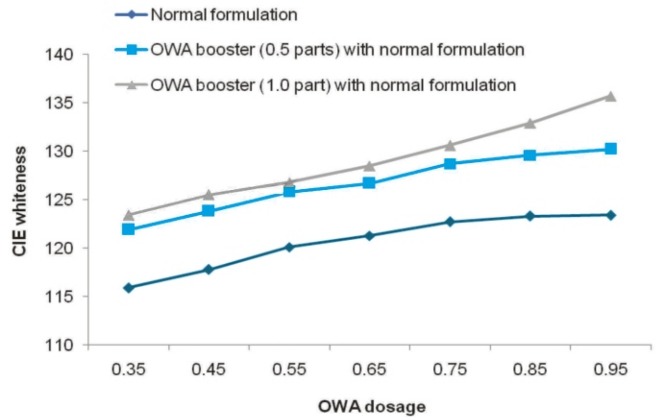


Figure 7: Effect of OWA booster on whiteness of coated paper

Conclusion

The high-sulphonated triazinylamino stilbene derivatives are better for the brightness and whiteness of coated paper as compared to its lower derivatives i.e. dia- and tetra. To get maximum benefit of OWA to improve the optical properties of paper, OWA is to be added in top-coat formulation compared to under-coat formulation. After the greening point, the optical properties of coated paper cannot be further improved by adding extra dosage of OWA, but the same can be improved significantly by addition of certain polyhydroxyl chemicals called boosters which are compatible with OWA. Use of OWA booster in coating recipe provides a better choice to improve the optical properties of coated paper like brightness, whiteness and also shade. The improvement in optical properties of coated paper through activation of OWA can also potentially reduce the formulation cost.

Acknowledgement

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