Detergents that Brighten up your Laundry

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Detergents today are no longer products of luxury, but items that are indispensable to continue maintain, cleanliness, health, and hygiene. Detergent consumption varies vastly from country to country and the industry today has considerable economic importance. In this age of changing consumer attitudes and result of continuous media coverage, terms known only to detergent technologists are now familiar words to the person on the street. Who has not heard the often-repeated advertisement on TV? "*Bhala uski sari meri sari se safed kaise*?" & "*Sabun jo de doodh jaise safedi*". People today realise that improvement to the whiteness or brightness of the Detergent results in an improvement in the whiteness delivery of the washed articles, denoting cleanliness and superior detergent efficiency. Presence of speciality chemicals like optical brighteners or fluorescent whitening agents in modern detergents used for washing fabrics does the trick.

We know that all organic fabrics absorb light in the short UV- region, extending slightly into the blue visible region causing a yellowish shade. White textiles; rapidly alter their appearance during usage. The amount of light absorbed in the visible region depends on a variety of reasons. The major causes are the organic and inorganic impurities, which are firmly embedded and difficult to remove, changes that are brought about by mechanical wear and tear of the various constituents of textiles' additives and their subsequent removal during washing. These unremoved impurities of dirt and degradation products extend the conjugated system in the polymer molecule of the fibre, to present a typically yellow shade of washed fabric. Most of these impurities can be eliminated from the fabric by use of bleaching chemicals. One of the methods to remove this yellowish shade in the fabric is by using a bluing agent. (ultramarine blue pigments, indigo, blue dye, etc.) This method of masking the yellow tinge in a fabric is prevalent right from the middle of the 19th century. Bluing reduces the reflectance of fibre in the long wavelength part of the visible spectrum, because of which the fibre takes a neutral white or bluish appearance. In this method, the yellow shade is slightly modified to create a more intense visual sensation of a blue cast. Bluing thus subtracts absorption of yellow light, which, in turn, reduces the brightness making the fabric appear dull and a little greyer.

Present day detergents use fluorescent whitening agents (FWAs), also called optical brighteners, that increases the blue light emitted to compensate the yellow surplus of washed fibres. FWAs are organic compounds that convert a part of the invisible Ultraviolet (UV) radiation in sunlight into longer visible wavelength of blue light. FWAs have the property of absorbing UV light and emitting visible blue light. This phenomenon is called as fluorescence. FWAs thus not only compensates the yellowish shade, but also emit more visible blue light, giving colour more brightness, by acting as a supplementary source of emission. The brightening effect produced by FWAs is significantly higher than the overall effect obtained by using ordinary bluing agents. Due to actual emission of visible light, FWA treated fabrics show a total reflectance much more than the fabrics without any FWA treatment. Optical brighteners are more effective the cleaner and whiter the substrate is. Although FWA usage can make a cleaner and whiter fabrics look more brighter, it can be safely presumed that FWA is not a substitute or an alternative to washing and cleaning process as a whole. The extent of whitening that can be achieved by an FWA is also limited. This is because FWA's themselves exhibit a certain amount of reflectance in the visible region of the light spectrum, in addition to their property of emission. A build up of FWA on textile fibres becomes apparent as the absorption gradually shifts into the visible region of the spectrum, leading to emission at higher wavelength. When very high amounts of FWA's are used, these very factors combine with the colour of the fabric and result in slight visible change of shade. Thus the objective of an FWA in detergents is to maintain the original brightness of fabrics, which, in turn, promote the longer use of fabrics by maintaining them as new as possible. In the case of printed fabrics, FWAs are able to provide colour contrast by compensating background FWA loss and thus behaves as white care additives. P. Krais in 1929 was the first person to discover optical-brightening effects. He recognised that due to the strong blue fluorescence, the whiteness of viscose rayon and semi-bleached flax yarn increased when it was treated with a solution of esculin (a b-D glucoside of 6,7- dihydroxycoumarin), which was obtained by extraction of Horse chestnut bark (1,2). The first industrial application began in 1935, and optical brighteners came into full-scale industrial use in 1940. In 1941, optical brighteners were produced and introduced commercially in the market. FWAs were first introduced in laundry detergents in the fifties. Rapid development was seen in all industrialised nations from 1945 to 1975, leading to thousands of commercially available products with distinct chemical structures and compositions. Today many of the earlier FWAs are no longer used, or have been replaced by superior variants having many more benefits in usage.

THEORETICAL PRINCIPLES INVOLVED IN LIGHT ABSORPTION & FLUORESCENCE IN FWAs

In order to understand the theory of fluorescence, one has to understand the meaning of the 'ground- and singlet-state. These terms arise from considerations of atomic spectroscopy and simply define the number of unpaired electrons in the absence of a magnetic field. If there are 'n' numbers of unpaired electrons, it means that (n+1) fold equal energy states will be associated with the electron spin, regardless of the molecular orbital occupied. Thus, if no unpaired electrons are present (n=0), there is only (0+1) or 1 spin state. Such a state is called a 'singlet state'. Similarly, systems having 1, 2, 3, 4,........ unpaired electrons refer to doublet, triplet, quartet, etc., states respectively.

Most of the molecules in their ground state do not have unpaired electrons ('singlet state'). When such a molecule absorbs UV or visible radiation of the proper frequency, one or more of the paired electrons (generally a p - electron) is raised to an excited singlet state. In this excited state, the spin of the electron does not undergo any change and the net spin is still zero. Another possibility is that one set of electron spins may have undergone unpairing, resulting in two unpaired electrons which make an excited triplet state. One should remember that there is only a small probability of a direct transition from the ground state to the triplet excited state. Absorption of light by the FWA molecule induce transitions from the ground state to the electronically excited singlet states. The electronic state and the vibrational levels reached by a brightener molecule depend on the wavelength of absorbed light. When the molecules are irradiated with light of appropriate frequency, it is absorbed in about 10^{-15} seconds. In the process of absorption, the molecules may move from the ground state to the exited singlet electronic state. Although at normal conditions' molecules may be present in their ground vibrational level, after absorption the excited molecules can end up in any one of the higher vibrational levels. From the excited singlet state, one of the following three phenomena will probably occur, depending on the molecule involved and the conditions.

The first possibility is that the excited singlet state is relatively unstable. In this situation, the excited molecule will return to the ground state by collisional deactivation without emitting any radiation. The second possibility is that the molecules that have been excited to the higher electronic state or vibrational level by absorption of light energy revert to their ground state by emitting or radiating visible light photons by the process, known as fluorescence. Optical brighteners or FWAs fall in this category.

The efficiency of fluorescence is measured by the quantum yield.

Quantum yield f = Number of quanta's emitted / Number of quanta absorbed.

If we compare the absorption and fluorescence spectrum of the same compound, they do not superimpose on each other, as expected, but are mirror images of each other, with the fluorescence spectrum shifted to longer wavelengths. The reason for this is that as the time required to execute a vibration is about 10^{-12} second, which is much shorter than the decay or mean life of 10^{-9} second, most of the excess vibrational energy will be given to the surroundings and then the excited molecules will decay in their ground vibrational levels.

The third possibility is that the molecules with relatively stable excited state may undergo transition to a metastable triplet state and some time thereafter return to the ground state usually by the emission of light energy. This phenomenon is known as 'phosphorescence emission' and the process of crossing from the singlet state (no unpaired electron) to a triplet state (two unpaired electrons) are termed as 'intersystem crossing'. The above mechanism of fluorescence and phosphorescence involving singlet and triplet decay scheme has been confirmed by the magnetic sus-

FWA and tinting dyestuff: Mode of action

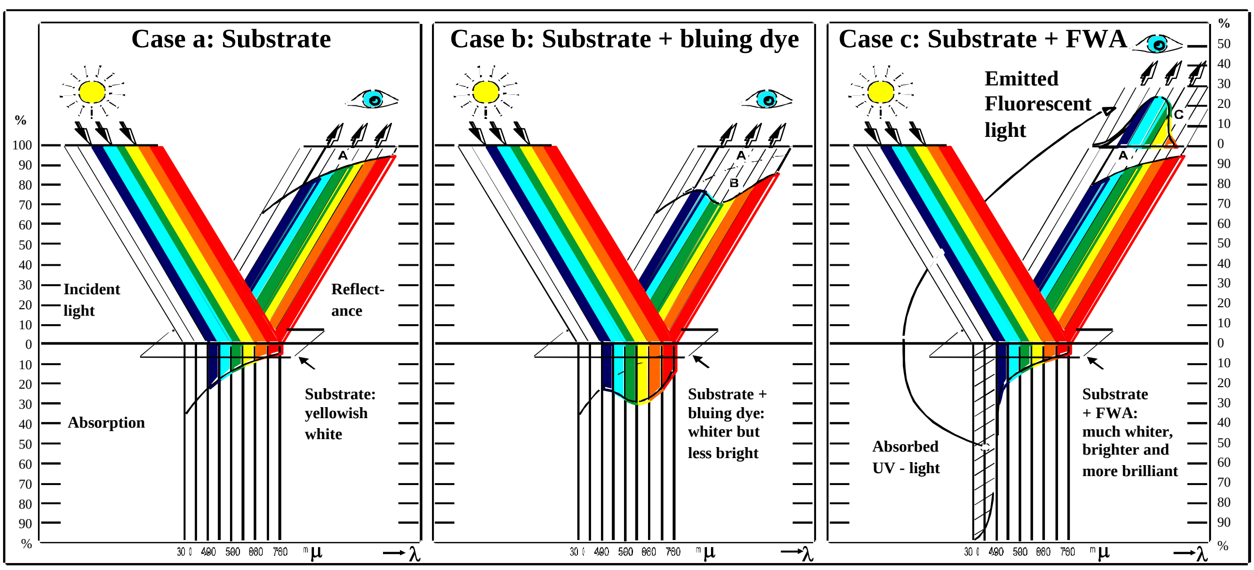


Figure 1: Influence of shading dye and FWA on whiteness

ceptibility NMR and Electron Spin Resonance Spectroscopy measurements. Not all the molecules can show the phenomena of fluorescence. Only such molecules can show the phenomena that are able to absorb UV or visible radiation. Generally, greater the absorbency of the molecule, the more intense the luminescence. The requirements mean that molecules having conjugated double bonds (p-bonds) are particularly suitable as optical brighteners. The chromophores of FWAs must be rigid and their conformations should differ only slightly in the electronic ground state and in the first excited state. Brightener chromophores are combinations of individual blocks with 2p, 4p, 6p, 10p, 12p, 14p, 16p electrons. Individually these blocks absorb at a wavelength too short for a brightener, but by linking them into a system of conjugated double bonds, one is in a position to obtain chromophores that can absorb in longer wavelength suitable for an optical brightener.

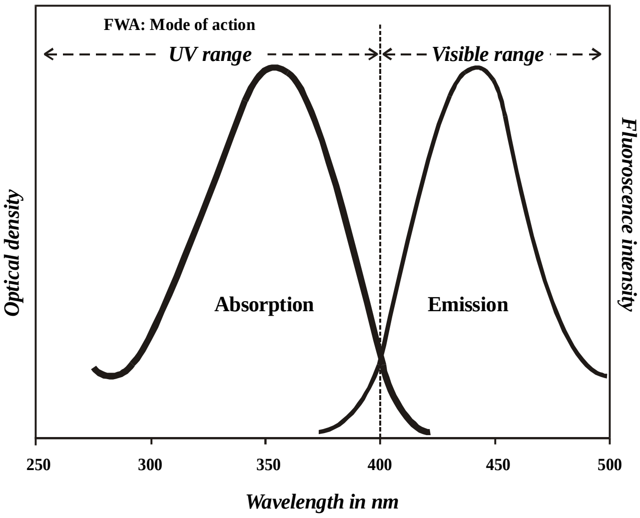


Figure 2

Substituents often exhibit a marked effect on the fluorescence properties of optical brightener molecules. Electron donating groups (substituted amino group, alkyl, & alkoxy) and electron-accepting groups (cyano, alkylsulfonyl, or carbalkoxy groups) can markedly affect fluorescence properties of the brightener molecule, depending on their placement.

BASIC REQUIREMENTS FOR AN EFFECTIVE FWA IN LAUNDRY SOAPS AND DETERGENTS

* FWA should absorb maximum UV light possible and have a minimum inherent colour. The absorption maximum should lie between 350 to 375 nm, and the extinction coefficient should be as high as possible, with the absorption decreasing steeply near 400 nm. Fluorescence should be intense, producing maximum brightness. The fluorescence maximum should be between 415 to 445 nm, and fluorescence should decrease as rapidly as possible on the longer wavelength side of the spectrum.
* Consumer choice or preference of any product is strongly influenced by odour and appearance. Soaps and Detergents with higher whiteness and brightness are preferred. A high level of brilliance in soaps and detergents depends on the raw material used and the optimum level of FWA incorporation in the product. To achieve an acceptable fluorescence requires that FWAs should be even at higher concentrations distributed in soaps or detergent, the washed fibre/textile substrate in the monomolecular form. When the molecules are not monomolecular but aggregated, then it results in poor yellowish cast.
* Whitening effects, as we know, increases with higher concentrations of FWA, but only up to a certain extent, after which it results in visible changes in shade of the substrate. An FWA should therefore be effective at low concentration on weight of the formulation.
* FWAs should have a high degree of wet- and dry-light fastness to ensure whiteness consistency when the laundry is dried out in the open or in the shade.
* FWAs having high solubility will be effective to deliver results both at cold and warm washing temperature. An FWA with good solubility and levelling properties ensures a homogenous distribution to deliver maximum whiteness
* FWAs should have a very good exhaustion on fabrics, which is an important criterion, for shorter wash cycle duration and for low temperature washing. Moreover, the exhaustion should be uniform to prevent localised spots of over-concentrated FWA, leading to complaints, particularly when used for washing garments in pastel shades.
* FWAs should be compatible with different types of detergent raw materials and be stable to bleaches, acids, alkalis, and perspiration. It is very important that the FWA is equally stable in the detergent formulation, as well as in the wash liquor. Stability also applies to the FWAs resistance to chemical change in the course of the washing process and prior to their adsorption on the fibres.
* FWAs should be free-flowing, low dusting, non-toxic easily handled in the traditional manner and in modern, automated handling and metering devices. The low dusting nature is necessary to reduce potential worker exposure to FWA dust and maintain stringent air quality standards in the workplace.
* FWAs should be suitable for addition, with acceptable dispersibility, in a detergent formulation. FWA used in a detergent should be easy to incorporate by different methods of process that are used in a detergent manufacturing unit such as spray drying, post-blending, spray blending, agglomerating or dry mixing.

TYPES OF FLUORESCENT WHITENING AGENTS

The chemical constituents of FWAs are derived from special chromophore structures. Major commercial FWAs currently used in detergents are based on the following five basic structural frameworks:

1) Triazinylaminostilbenes (cyanuric chloride diamino stilbene)
2) Distyrylbiphenyls.
3) Bis (1,2,3-triazol-2-yl) stilbenes.
4) 1,3-Diphenyl-2-pyrazolines.
5) Coumarins

The p-electron system of the chromophore absorbs UV light and re-emits most of the absorbed light energy as blue fluorescent light. The chemical structure of the FWA determines its stability and its effectiveness in a detergent formulation. Triazinylaminostilbenes (cyanuric chloride diamino stilbene) and distyrylbiphenyls are the most important types for the detergent industry. The remaining FWAs are incorporated in detergents in minimal amounts and therefore do not have much relevance in today's changing consumer requirements. The two major types of FWAs presently in use worldwide by the soap and detergent industry are briefly described.

Triazinylaminostilbenes (cyanuric chloride diamino stilbene)

(Tinopal® DMS-X, Tinopal® 5BM, Tinopal® UNPA, etc.)

1,3,5-Triazinyl derivatives of 4,4'-diaminostilbene-2-2'-disulfonic acid have been available since 1941 and are an important class of optical brighteners in terms of quantity sold. Some 75 derivatives are available commercially in the market. Only some of these compounds have good whitening effect, efficiency, and adequate light fastness. Unfortunately they have only partial fastness to bleaches and are unstable in chlorite solution.

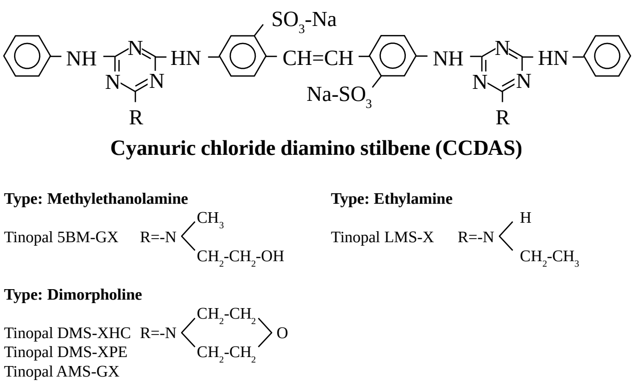
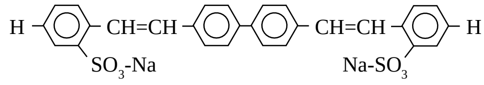


Figure 3: Conventional stilbene FWAs

Distyrylbiphenyls

(Tinopal® CBS-X)

4,4'-Distyrylbiphenyls was discovered in 1967 and anionic distyrylbiphenyls have very high efficiencies and are chlorine stable brighteners. These super brighteners are nowadays very widely used for laundry soaps and detergents around the world, and are progressively substituting other types of optical brighteners.



Distyrylbiphenyl (DSBP)

Figure 4: Tinopal CBS-X

Both the above classes of FWAs undergo photo isomerisation on irradiation of incident sunlight. They form E/Z isomers, 'trans/cis' isomers. These photo-isomers do not fluoresce. In case of a distyrylbiphenyls FWAs the extent of photo-isomerisation is very small, remaining almost unaffected whereas, cyanuric chloride diamino stilbene FWAs give reduced fluorescence. This explains the significantly superior light fastness of distyrylbiphenyls FWAs compared to cyanuric chloride diamino stilbene. Similarly, both distyrylbiphenyls FWAs & cyanuric chloride diamino stilbene based FWAs undergoes oxidative degradation when exposed to sunlight. However, their reactivities significantly differ. Cyanuric chloride diamino stilbene based FWAs, have a number of bond cleavages which on further N-oxidations give rise to numerous degradation products in comparison to distyrylbiphenyls FWAs. Some of the degradation products of cyanuric chloride diamino stilbene based FWAs are precursors of dyestuffs. These degradation products can undergo further oxidation to form deeply coloured anilino derivatives. Traces of dyestuff formed in the course of degradation of cyanuric chloride diamino stilbene based FWAs lower the base whiteness of the fabrics significantly. In case of a distyrylbiphenyls FWAs, all degradation products are colourless and so have a significantly superior light fastness in comparison to a cyanuric chloride diamino stilbene based FWA.

TOXICOLOGY & ENVIRONMENTAL ASPECTS OF FLUORESCENT WHITENING AGENTS

Although fluorescent whitening agents are adsorbed by fabrics during the laundering process, a part of it is also introduced into the waste water in course of repeated washing. Sewage sludge is sometimes used as fertiliser, soil conditioners, or landfills. FWAs are adsorbed by sludge and so the extent to which they may be leached into the ground water that may be sometimes used as a source for drinking water becomes all the more important. FWAs should not contaminate ground water sources, but undergo complete biodegradation. FWAs used in soaps and detergents should be non-toxic and give no indications of adverse effects like irritation, skin sensitisation or subacute toxicity, allergy, carcinogenic, mutagenic or tetratogenic effects. FWAs used should be non-toxic to aquatic organisms, agricultural plants, and animals. They should be biodegradable and be environmentally acceptable.