

# **Fluorescent Brightening agents**

## FBA

- The Fluorescent Brightening agents operate by the phenomena of fluorescence
- In order to understand the mechanism of FBA it is necessary to understand Fluorescence
- **Fluorescence** is the emission of light by a substance that has absorbed light or other electromagnetic radiation. It is a form of luminescence . In most cases, the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation.

## Other names of FBA

- Optical brighteners, optical brightening agents (OBAs), fluorescent brightening agents (FBAs) or fluorescent whitening agents (FWAs) are dyes that absorb light in the UV and violet region (usually 340-370 nm) of the EM spectrum and re-emit light in the blue region (typically 420-470 nm). Fluorescent activity is a short term or rapid emission response, unlike phosphorescence, which is a delayed emission. These additives are often used to enhance the appearance of color of fabric and paper causing a "whitening" effect, making materials look less yellow by increasing the overall amount of blue light reflected.

# Resonance Fluorescence

- However, when the absorbed electromagnetic radiation is intense, it is possible for one electron to absorb two photons; this 2-photon can lead to emission of radiation having a shorter wavelength than the absorbed radiation. The emitted radiation may also be of the same wavelength as the absorbed radiation, termed "resonance fluorescence".
- The most striking examples of fluorescence occur when the absorbed radiation is in the ultraviolet region of the spectrum and thus invisible to the human eye, and the emitted light is in the visible region.

# What are FBA

- Type of dye
  - Dyes absorb color and reflect some colors
  - FBA are type of Fluorescent Dyes
  - Re-emit absorbed light into longer
- Wavelength
  - FBA absorb UV and emits in blue-violet
  - Absorption 340-380 nm , Emission 425-450 nm

## What does FBA do?

- FBA increases the apparent reflectance of the article in the blue-violet region of the Spectrum. Treated material emits more light in the visible region than does an untreated white sample and thus appears 'whiter than white'.

## How does it work

- An efficient FBA must absorb strongly in the ultraviolet region and must also re-emit a major proportion of the absorbed energy as visible light, that is, it must have a high fluorescence efficiency.
- Although fluorescence can occur from the sigma bonds of many organic compounds, strong fluorescence is associated with pi-bonded electrons.
- All FBAs therefore contain a considerable number of
- conjugated double bonds.

- Brighteners are commonly added to laundry detergents to replace whitening agents removed during washing and to make the clothes appear cleaner. Optical brighteners have replaced Bluing which was formerly used to produce the same effect. Some brighteners can cause allergic reactions when in contact with skin, depending on the individual.
- Brighteners are used in many papers, especially high brightness papers, resulting in their strongly fluorescent appearance under UV illumination. Paper brightness is typically measured at 457 nm, well within the fluorescent activity range of brighteners.

- Paper used for banknotes does not contain optical brighteners, so a common method for detecting counterfeit notes is to check for fluorescence.
- Optical brighteners have also found use in cosmetics. One application is to formulas for washing and conditioning grey or blonde hair, where the brightener can not only increase the luminance and sparkle of the hair, but can also correct dull, yellowish discoloration without darkening the hair. Some advanced face and eye powders contain optical brightener microsphere that brighten shadowed or dark areas of the skin, such as "tired eyes".

## Stilbenes as FBA

- The most common classes of chemicals with this property are the stilbenes and older, non-commercial fluorescent chemical such as umbelliferone, which absorb energy in the UV portion of the spectrum and re-emit it in the blue portion of the visible spectrum. A white surface treated with an optical brightener can emit more visible light than that which shines on it, making it appear brighter. The blue light emitted by the brightener compensates for the diminishing blue of the treated material and changes the hue away from yellow or brown and toward white.
- There are approximately 400 brightener types listed in the Color Index, but less than 90 are actually produced commercially and only a handful are commercially important.

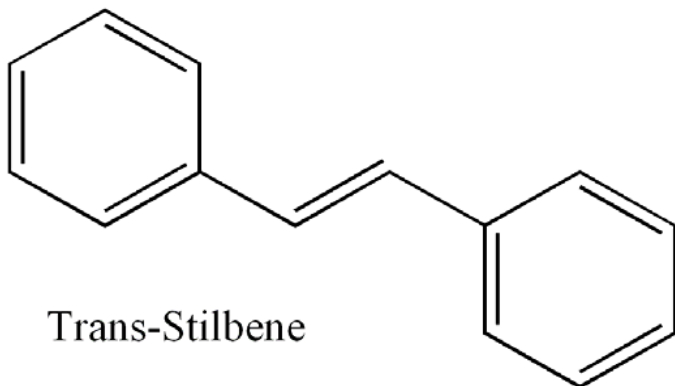
## Types of FBA used

- FBA production for paper, textiles and detergents is dominated by just a few di- and tetra-sulfonated triazole-stilbenes and a di-sulfonated stilbene-biphenyl. These are subject to fading when exposed long term to UV, due to the formation of optically inactive stilbene cis-isomers found at the center of the molecule. Exposed to gases and especially oxygen they will fade too, like most dye colorants. All brighteners have extended conjugation and/or aromaticity, allowing for electron movement. Some non-stilbene brighteners are used in more permanent applications such as whitening synthetic fiber.

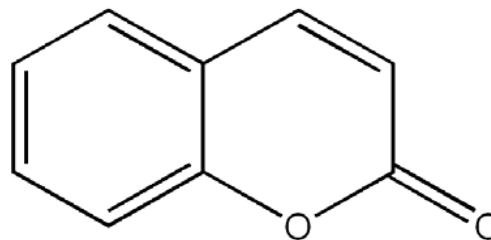
# Types of Brighteners

- Basic class types of brighteners include:
- Triazine- stilbene (di-, tetra- or hexa-sulfonated)
- Coumarins
- Imidazolines
- Diazoles
- Triazoles
- Benzoxazolines
- Biphenyl stilbenes

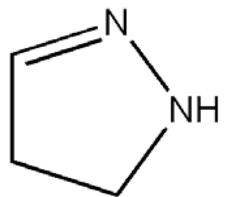
## Different types of FBA



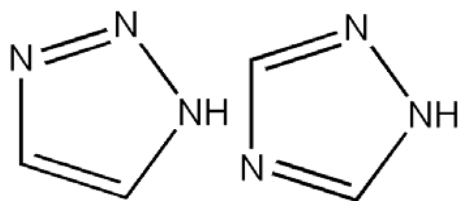
Trans-Stilbene



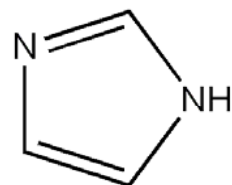
Coumarin



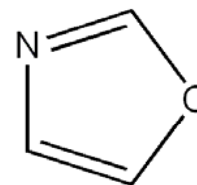
Pyroazoline



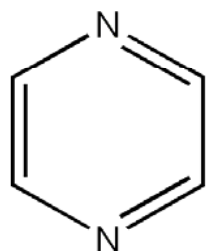
Triazoles



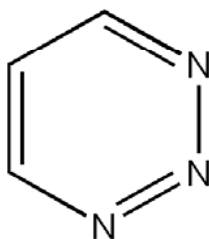
Imidazole



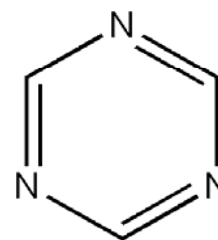
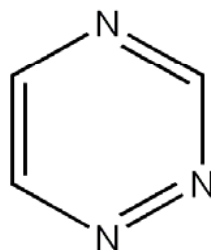
Oxoazole



Pyrazine



Triazines



## Different FBAs

Most FBAs are "derivatives of stilbene. . . biphenyl and five membered heterocyclics, such as triazoles, oxoazoles or imidazoles. . . . six-membered heterocyclics, such as coumarins, naphthalimide, pyrazine, or triazine ." The extensive pi-systems of these often heterocyclic aromatic compounds are associated with the closely spaced electronic energy levels that allow for energy transitions within the visible range (e.g.  $n \rightarrow \pi$  transitions). Table 1 to the right shows some of base structures that FWAs are derived from.

## Booster for FBA

Brighteners can be "boosted" by the addition of certain polyols like high molecular weight PEG or polyvinyl alcohol. These additives increase the visible blue light emissions significantly. Brighteners can also be "quenched". Too much use of brightener will often cause a greening effect as emissions start to show above the blue region in the visible spectrum. Besides the formation of cis isomer in stilbene-containing brighteners (only the trans isomer is optically active), continued exposure to UV-containing light will actually cleave the molecule and start the process of degradation.

## Total use of FBA

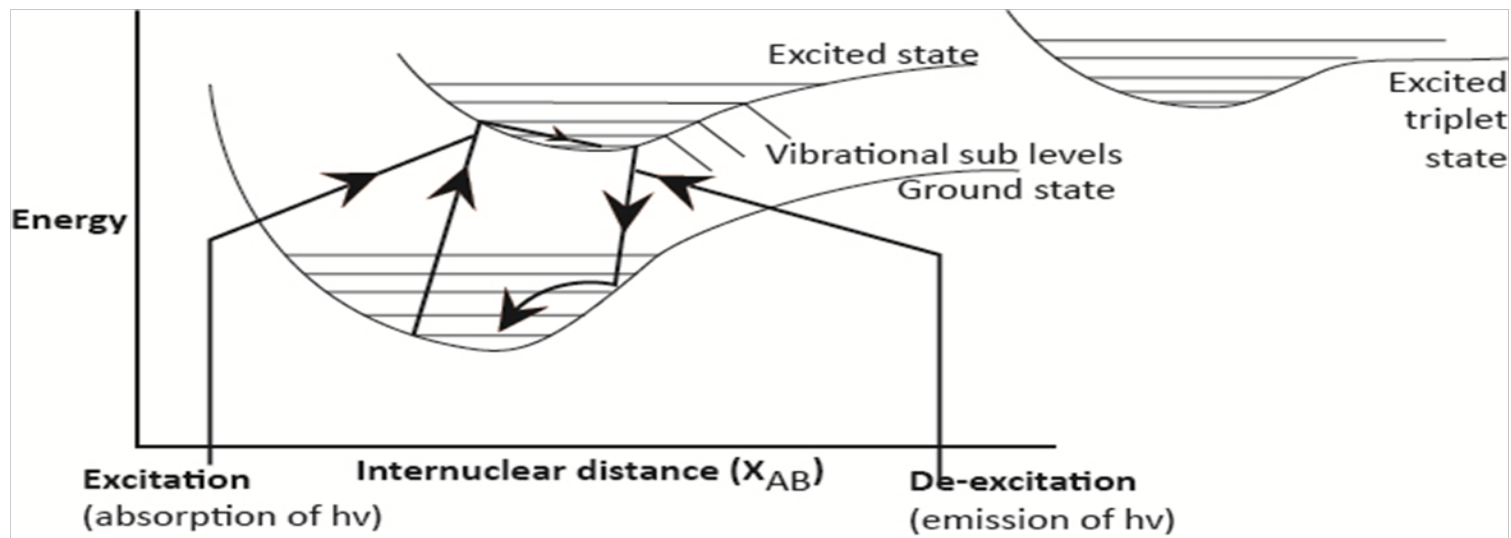
- In 2006, textiles still accounted for 25% of worldwide fluorescent brightener use (1). Synthetics and plastics accounted for an additional 5% of total use .

Fluorescent brighteners are typically incorporated into fabrics and plastics via dying during manufacture to "enhance aesthetics and consumer appeal. " Once incorporated, these brighteners improve coloration and also disguise fading.

A wide range of colored fabrics that can be treated to appear brighter. Optimally, each fabric and shade is treated with the fluorescent brightener that will best enhance the original fabric's hue or base dye, making it more vibrant. For example, some brighteners give off highly fluorescent greenish-yellow shades and would be appropriate for green fabrics.

## Usefulness of FBA

- For a fluorescent brighteners to be considered particularly effective and useful for use in textiles, it must possess the following three characteristics:
  1. **fluorescent emission in the desired range** (i.e. they give off the correct color)
  2. **fastness** to washing, perspiration, and sunlight (i.e. they last long because they bond or adhere well to the base material) and
  3. **nonhazardous properties** (i.e. humans can be safely exposed to them).



FBA exhibits fluorescence as a result of specific electronic and vibrational transitions, shown in

### **1. Absorption of UV light.**

The FBA absorbs UV light as it is excited from the ground electronic state to the excited electronic state (i.e. the two curved Morse energy level surfaces in the diagram to the left). The vibrational states (i.e. the smaller energy levels within each electronic energy level in the diagram to the left) also usually change because the internuclear distance must remain the same during this electronic transition (according to the Frank-Condon principle).

### **2. Radiationless energy transfer.**

The FBA then relaxes to a lower vibrational state within the excited electronic state, often mediated by a collision or vibrational/ rotational motion within the molecule. No electromagnetic radiation is emitted as energy is given off via some kinetic motion.

## Followed by

- ***3. Emission of visible light.***

The FBA then relaxes from the excited electronic state back down to the ground excited state. Because of the radiationless energy transfer, the energy of the light emission is less energetic than the energy of the initial light absorption. The FBA initially had absorbed UV light, but emits visible light

## FBA for cotton

- Fluorescent Brighteners for cotton are Tinopal,
- This is claimed to give excellent results when applied by the exhaustion or padding methods  
And its slightly violet shade imparts a white effect of striking brilliance It exhausts within a pH range of 8-11 or higher Similarly the FBAs for polyamide, polyesters and acrylic fibres