CHAPTER – I

INTRODUCTION.

CHAPTER I

INTRODUCTION :

Fluorescent brightening agents are now an established feature of detergent, textile, paper and allied industries. Most chemists and technologists know of their uses and abuses, and the general public have come to expect their white textiles to be whiter and brighter than ever before.

During the last three decades the idea of "White" has undergone a radical change,since the production of white on paper, textiles, and plastics is no longer dependent on bleaching mostly with inorganic bleaching compounds nor on the addition of white pigments, initiated and developed in Germany, optical brightening agents with which white can be produced by fluorescence on these materials were introduced at the end of the 1930s, first by IG-Farben-industrie and later also by dyestuff manufacturers in Switzerland, England, and the United States.

The research work so far done in the field of fluorescence is first reviewed here with a view to understand the basics of fluorescence.

The radiations known as fluorescence and phosphorescence which were observed since seventeenth century are commonly known as luminescence. Luminescence is a light emitted without creation of high temperature. There are different types of luminescence depending upon the source of energy which causes excitation of molecules. A few types of luminescence and their sources are tabulated here[1].

	Source of energy	Type of luminescence
1	Ultra-violet light	Photoluminescence
2	Nuclear radiations as γ rays and alpha, beta particles.	Scintillation.
3	Mechanical shock	Tribo or piazo luminescence
4	Heat	Thermoluminescence
5	Chemical reaction	Chemiluminescence
6	Electric fields	Electro or electro chemiluminescence
7	Sound-waves	Sonoluminescence
8	Controlled electrons	Cathodoluminescence

Ingoranic luminescence is due to the excitation of individual atoms or ions. This happens because inorganic solids are atomic solids held together by covalent or ionic bonds. But in the organic solids luminescence is due to excitation of molecules, as organic solids are molecular solids held together by van der wall's forces. Due to presence of these forces the luminescence spectra of organic molecules in all phases are similar. Unsaturated hydrocarbons give rise to strong luminescence due to presence of delocalised π electrons, which can be excited easily and to a greater extent π electrons are the result of hybridization. Therefore presence of $>C = C<$ is preferred over c-c for high degree of luminescence as in c=c π electrons are easily available.

Mechanism Involved in Luminescence and Fluorescence :

Luminescence

As mentioned in the introduction, luminescence is caused by elctronic excitation of organic molecules.

The π eletrons of a diamagnetic molecule when absorb light, get excited and are raised from the singlet ground state (s_0) to singlet excited state (s_1,s_2...). They are unaffected by external magnetic field. Each singlet state has a corresponding triplet state (S_1,S_2,S_3 -> T_1,T_2,T_3).These triplets are split into three zeeman levels by external magnetic field. Excitation higher than S_3 results into excitation of σ electrons which obscure the absorption of π electrons at this stage[2].

The absorption occurs between the ground state s_0 and the singlet state S_1,S_2,S_3 etc. After absorption some radiationless internal conversions may take place. They are usually S_3->S_2 and S_2->S_1. These conversions are in the 10^{-11} to 10^{-13} sec range[3]. The S_1-> s_0 are non-radiative inter conversions. They may be via three paths (1) Internal crossing (2) Fluorescence (3) Inter-system crossing to T_1[4]. In addition to this phosphorescence also is observed. Fluorescence is a radiation emitted in a transition between states of the same multiplicity i.e. singlet-> singlet or Triplet-> Triplet etc., while phosphorescence is observed in the intersystem crossing like T_1->So[5]. These radiationless changes and changes with radiations are schematically shown in Fig. 1.

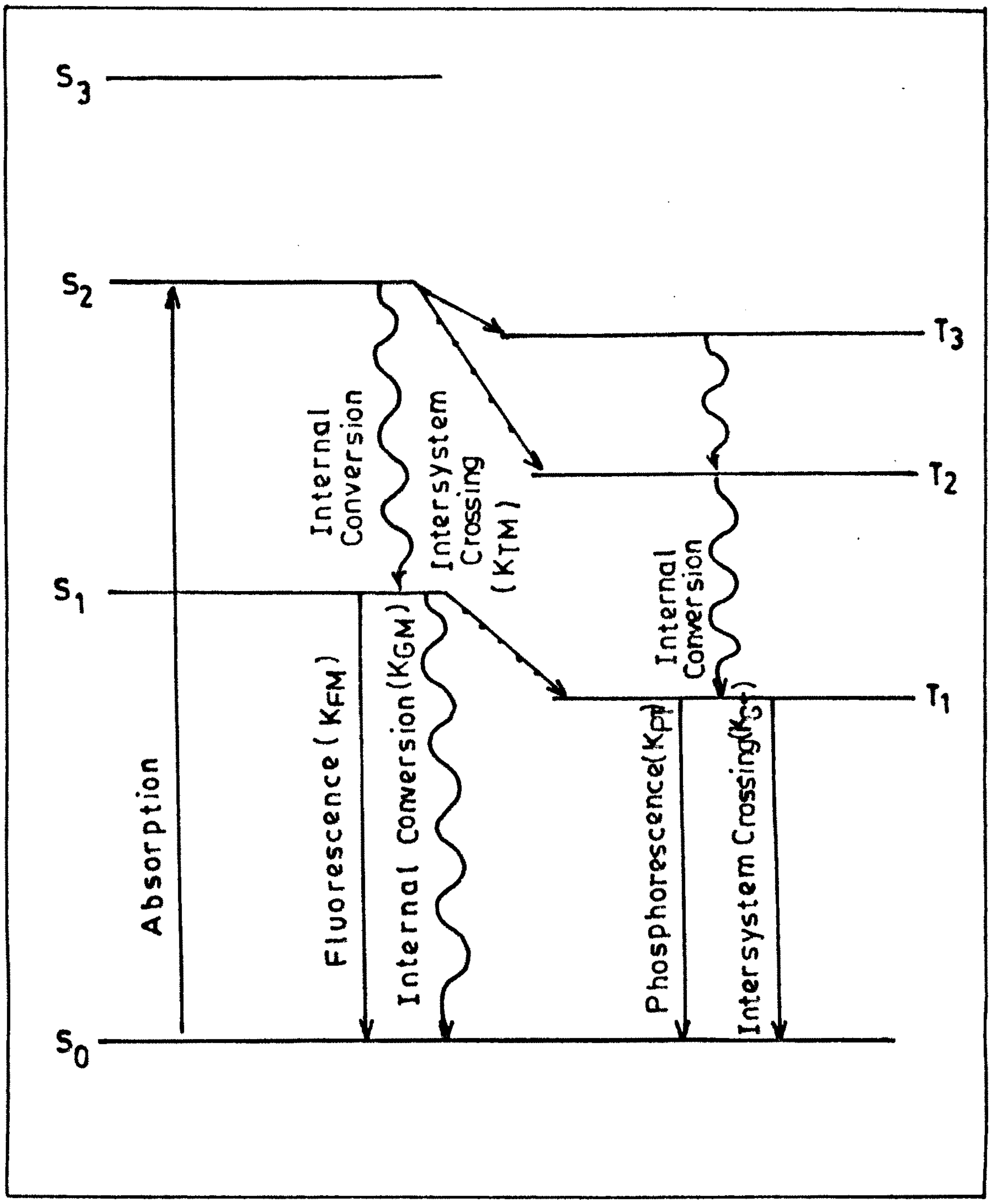


FIG. 1 — π-ELECTRON LUMINESCENCE PROCESSES .

DEFINITION OF FLUORESCENT BRIGHTENING AGENTS AS DYES.

Fluorescent brightening or whitening agents[6] are colourless fluorescent dyes. They increase the whiteness of the material to which they are applied. In accordance with their definition as "colourless" Flourescent dyes, their coloristic performance is that of fluorescent dyes without absorbing light in the visible range of the spectrum.

Flourescent brightening agents are applied as dyes, the fastness properties of the white shades achieved being evaluated on coloristic principles. Special characteristics are required of Fluorescent brightening agents when used in combination with detergent products or in the brightening of spinning compounds. In addition to the coloristic properties as colourless Fluorescent dyes, further requirements are dispersibility and compatibility with the detergent components, as well as resistance to temperature and sublimation.

RELATIONSHIP BETWEEN UV ABSORPTION AND FLUORESCENT BRIGHTENING :

The special position of Fluorescent brightening agents is due to their specific physical properties, they absorb invisible ultraviolet radiation from day light and emit visible, predominantly blue, fluorescent light. Because of their ability to absorb ultraviolet radiation, fluorescent brightening agents are UV absorbers, while they are fluorescent dyestuffs as a result of their ability to emit fluorescent light.

The ideal UV absorber absorbs the entire long wave UV component from day light. It emits no radiant energy.

The fluorescent dye absorbs visible light as a normal dye. Contrary to normal dyes, it transforms the absorbed energy into light of longer wavelength. This combines with the reflected light to produce a total colour impression. Fluorescence dyeings are therefore notable for particularly high brilliance.

Similar to UV absorber, the Fluorescent brightening agent absorbs in the longest wave UV range. In contrast to the UV absorber, the absorbed energy is transformed into Fluorescent light, which is emitted at longer wavelengths in the visible part of the spectrum. Since there is no absorption in the visible range the colour impression is produced by pure Fluorescent light.

In the case of Fluorescent brightening agents, the absorption maximum in the UV ranges between 340 and 400 nm.

Because of the general laws derived from the relationship between UV absorption and the effect of Fluorescent brightening agents. Optical brightening agents are members of those groups of compounds and systems which are naturally Fluorescent.

In the unsaturated compounds it is predominently the easily excited π electrons which are responsible for light absorption in the visible and ultraviolet range. Generally, π electron systems represent double bond conjugated systems such as $-C=C-C=C-C=C-$ or $-N=C-C=C-N=C-$ and such a system is one of the essential features of optical brighteners[7,8].

Kuffmann named luminophores as those basic structures which are common to Fluorescent compounds. Luminophores are promoted by Fluorogens to Fluorophores (i.e. Fluorescent compounds). Typical luminophores are aromatic systems (benzene, phenanthrene, napthalene, anthracene etc) and heterocyclic systems (Coumarin, S-triazine, benzoxazole etc.), typical fluorogens are linking groups of atoms and certain substituents such as -CH=CH-CO, -CH=N-, P-phenylene, -CH=CH-COOH, and -CN. In a similar manner to dyestuffs -NH2, -OH, -COOH and -SO$_3$H groups cause hypsochromic or bathochromic shifts in Fluorescent compounds[8].

Requirements For Fluorescence :

(a) Electronic Considerations :

Much of the light energy absorbed by molecule may be lost by process other than Fluorescence. Indeed it is rare for an organic compound particularly in solution, to emit all its absorbed energy as Fluorescence (i.e. to have a quantum efficiency of unity. The lost energy will be degraded by the competing reactions of internal and external conversions. Energy loss by internal conversions arises either because of intersystem crossing from the excited singlet to triplet state. (When it will be utilized as phosphorescence or lost as heat) or through predissociation (i.e. disruption of chemical bonds of the compounds). Energy loss by external conversion through collision with other molecules and may result in the radiationless transfer to the colloiding molecules or in the production of heat[9]. The Fluorescence process tends to favour in a compound having the following properties.

(1) A longest absorption warelength with a high extinction coefficient in the ultraviolet or visible region corresponding to $\pi - \pi^*$ excitation. Molecules which absorb high energy frequencies (i.e. short wavelengths) are prone to predissociation rather than Fluorescence. On the other hand species in which the longest absorption wavelength corresponds to an $\pi - \pi^*$ transition (common in molecules containing nitrogen, oxygen or sulphur atoms) are often phosphorescent but seldom Fluorescent[10].

(2) The excited singlet state should be relatively stable to the deactivating process described above i.e. it should have a half life of about 10^{-8}sec. If the half life is more than 10^{-8} sec intersystem crossing will be favoured, while a shorter half life implies rapid deactivation of the molecules by other process.

(3) The excited singlet and triplet states should be well separated as in the case of aromatic hydrocarbons. When the two states are very close together, intersystem crossing from the excited singlet to the triplet state can occur. Energy decay from the triplet state may produce phosphorescence but is unlikely to give Fluorescence except in rare cases[9].

(b) Structural Considerations :

The Structural requirements for Fluorescence of an organic compound are dependent on three main factors namely, the nature of the carbon skeleton including the type of bonding with or without heteroatoms, the geometrical arrangment of the molecule and the types and positions of substituents.

(1) The Carbon Skeleton :

Most of the fluorescent compounds contain a conjugated system of double bonds, the presence of which appears to be the essential to Fluorescence. However, all the compounds with a fluorescent, as other requirement must also be satisfied. Increasing the extent of conjugation has two main effects, namely, to shift the absorption and thereby the Flourescence wavelengths towards the red end of the spectrum and to enhance the mobility of the π electrons often results in an increase in Fluorescence intensity. For example, trans stilbene structures although has only one more double bond in conjugation than in biphenyl structure, it is considerably more fluorescent. The molecules which contain conjugated double bonds in a cyclic structure are likely to Fluoresce more strongly than those containing the same in an open chain arrangment.

The effect of increasing the number of benzene rings is generally to increase the Flourescence efficiency. Thus anthracene has a higher fluorescence efficiency than that of naphthalene. Linearly combined rings in a compound tend to be more fluorescent than the non linear ring arrangment[9]. For example anthracene has more fluorescence efficiency than that of phenanthrene.

(2) The geometric arrangment of the molecule :

Planarity of the conjugated system appears to be essential for maximum fluorescence ,when the planarity of the system is destroyed by the free mobility of the π electrons will be partially inhibited resulting in loss of fluorescence.

Molecular rigidity is also necessary for maximum fluorescence. In a non rigid molecule the absorbed energy can be readily dissipated as heat and hence it is likely to be non-fluorescent. This need for molecular rigidity probably explains the much greater Fluorescence of cyclic systems when compared with chain systems.

Comparison of the fluorescence efficiencies of biphenyl and fluorene provides a good illustration of need of planarity. These compounds possess the same degree of conjugation, but the benzene rings in fluorene are held rigidly in a planar configuration, whereas biphenyl are not. This reflects in their fluorescence efficiencies[11] i.e. Fluorene has a quantum efficiency of about 0.54 in hexane while that of bipnenyl is only 0.23.

(3) The types of positions of substituents :

Although the presence of a substituent in a saturated ring may not result in a fluorescent molecule, substitutions in a conjugated system may have profound effect on its fluorescence properties. To exert this effect it is generally necessary for the substituent to be either directly attached to the conjugated system or in its close steric proximity. However, atoms which have a large magnetic field associated with them (bromine and iodine) will tend to reduce the Fluorescence. The substituents should have effect on the π electron mobility and should not produce steric hindrance in order to improve the fluorescence properties of the original molecule. The substituents like CN, F and Cl are known to enhance the Fluorescence. However, a strong electron withdrawing group like NO_2 tends to diminish the Fluorescence.

Some factors influencing the function of Fluorescent Brightening Agents :

1. Substrate :

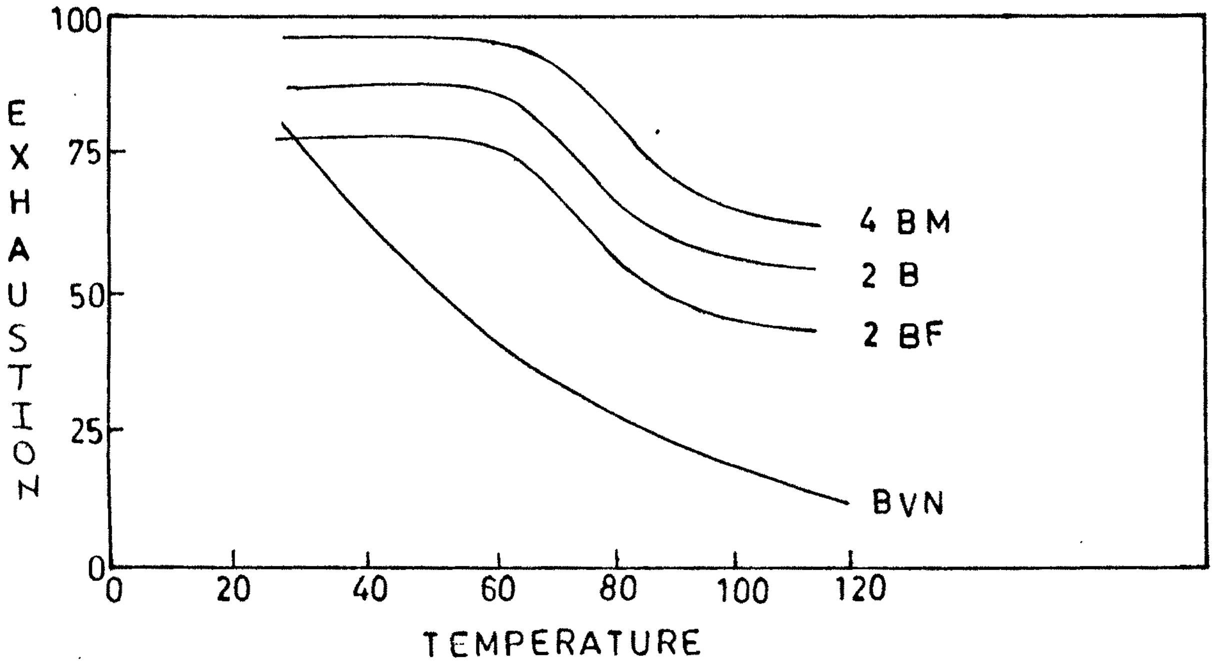
Fluorescent brighteners vary in efficiency when applied to different fibres depending on their affinity (orientation to their fibres). In the absence of sufficient affinity, the application results in yellow to green colour yield.

2. Concentration :

The intensity of Fluorescence is directly proportional to its concentration only in highly dilute solutions. The higher the concentration of the compound, the greater the proportion of emitted Fluorescence reabsorbed. The effect is most likely to occur in compounds in which activation and Fluorescence wavelengths are close enough to overlap considerably. Such inner filter effects may not only reduce the observed Fluorescence intensity, but also result in an apparent shift in the activation wavelength.

3. Temperature :

Fluorescence intensity goes on decreasing with increasing temperature because of increased conversion rate of electronic into vibrational energy. This fact shows quite clearly in the graph. For most practical purposes, slight temperature are probably unimportant, since the fluorescence intensity seldom falls by more than 1% for 1^0 rise in temperature. However, a few compounds (e.g. p-anisidine indole-3-acetic acid) are known[12,13] in which the intensity may vary by about 5% for 1^0 temperature change. A few instance have been found in which the Fluorescence intensity increases as the temperature is raised[9].



4. Solvent :

If a change in solvent produces alteration in both the activation and Fluorescence wavelength "Static quenching" is indicated whereas a solvent change produces a shift in Fluorescence wavelength alone. "Dynamic quenching" is indicated. Halogen bonding, the dielectric constant of the solvent and its viscosity are the basis to explain the solvent-fluorescence relationships. However, in practice, the solvent-fluorescence relationships are largely unpredictable.

5. P^H :

Ionic form of a compound almost always exhibits different Fluorescence characteristics from those of the unionised form. The effect of the PH upon the Fluorescence of a compound is, therefore, of considerable importance and a knowledge of the changes in Fluorescence resulting from altering the PH of the solvent medium can be valuable in a number of ways[9].

6. Time :

The exhaustion rate of Fluorescent brighteners is very rapid and a state of apparent equilibrium is always reached after only few minutes. The danger of unlevel dyeing is also there and great care should be taken to ensure suitable conditions.

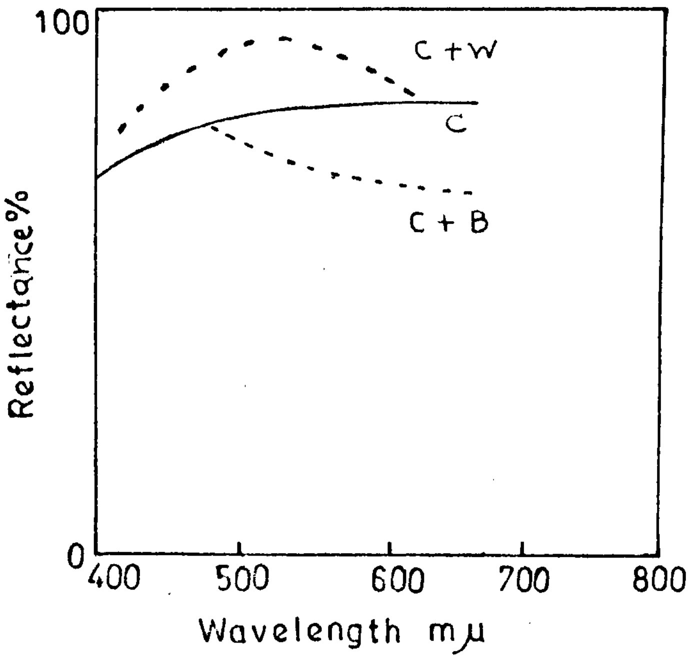
Mechanism :

Organic substance which exhibit Fluorescence normally have a system of conjugated double bonds in the molecule. Such molecules are capable of absorbing light and passing into an excited state of higher energy; these excited molecules then return to the ground state of lower energy with re-emission of light. As some energy is lost in this process, the re-emitted light is of longer wavelength (lower frequency) than the absorbed light.

Most such chemicals are activated only by light in a narrow waveband, usually in the ultraviolet region. Some dyes, however, absorb over a much wider wavelength range and give powerful emissions at fairly high wavelength; these have found uses comparatively recently in the so called day-light Fluorescent printing inks for posters.

To act as brightening or whitening agents compounds must reemit at the blue end of the spectrum, so that the emitted light is essentially complementary to the pale yellow colour normally shown by "white" cellulosic materials. The light absorbed, therefore, must be of still shorter wavelength in practice the near ultraviolet.

As ordinary day light has a limited content of ultraviolet ratiation, the blueing effect obtained is not very great when compared with the effect given by the Fluorescent pigments. Much brighter effects are observed, of course, under ultraviolet radiation. In artifical light the effect is even less than in daylight, as the ultraviolet content of most artifical lighting is very small indeed.



C : Ordinary bleached cotton

C+W : Treated with Flourescent brightening agent

C+B : Treated with blue colorant

(Ultramarine C.I. Pigment Blue 29)

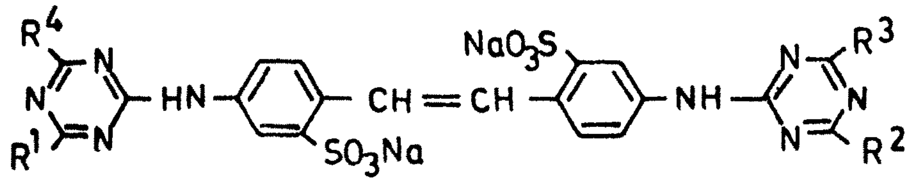
The whitening effect given by Fluorescent brightening agents, therefore, is an additive effect : the yellow colour is corrected by the addition of blue light, and the total light reflected from the material is greater than from untreated material. On the other hand, the old blue-bag worked by a substractive process, the blue pigment absorbing yellow light equivalent to the blue light absorbed by the yellow colour of the untreated material; although the treated material looked whiter, in fact the total reflected light was lower (Fig. 3). Such agents were correctly designated "blueing" agents, whereas the fluorescent compounds are both blueing and brightening agents.

Flourescent effects are from their nature largely surface effects, and in addition the Fluorescence can be quenched at high concentrations by the inability of the molecules to pass to the excited state. In consequence the quantity of fluorescent brightening agent required to give a satisfactory effect is quite small, normally about 0.01-0.10% by weight on the weight of material. In fact, at high concentrations the material. In fact, at high concentrations the fluorescent effect can be offset by the intrinsic colour of the brightener.

All the Fluorescent brightening agents are known upto the present contain aromatic components or pseudo-aromatic (unsaturated) heterocyclic components linked together by direct bonds or small bridges, such as -CO-, -[illegible]O-, -NHCONH-, -CH=N- or -CH=CH-. According to the physical conception, their molecules possess more or less extensive resonance or π electron systems which can be excited s[illegible]iently in the range of [illegible] nm. They can be classified in the definite Fluorescence systems corresponding to the empirical or physical conceptions. These are, in particular, the systems derived from stilbene, coumarin, 1,3-diphenyl pyrazoline, naphthalimide, and from the aryloazoles, all of which allow of numerous variations based on chemical principles.

CHART-1

(1)



General Structure

Substituent		Field of application
$R = R^1 = R^2$	$R^1 = R^3 = R^4$	Cellulose (T)
$-NH_2$	$-NHCH_2CH_2OH$	Polyamide
$-Cl$	$-N(CH_2CH_2OH)_2$	Cellulose, Polyamide
$-\underset{CH_3}{\underset{\vert}{N}}-CH_2CH_2SO_3H$	$-N(CH_2CH_2OH)_2$	Paper, Viscose
$-NH_2$	$-NHC_6H_5$	Cotton, Polyamide
$-NHEt$	$-NHC_6H_5$	Cotton, Polyamide
$-NHCH_2CH_2OH$	$-NHC_6H_5$	Cotton, Polyamide
$-N(CH_2CH_2OH)_2$	$-NHC_6H_5SO_3H$ (1,3)	Viscose, Cotton, Laundry agent
$-\underset{CH_3}{\underset{\vert}{N}}-CH_2CH_2SO_3H$	$-NHC_6H_4SO_3H$ (1,3)	Cotton, Polyamide, Paper
$-N(CH_2CH_2OH)_2$	$-NHC_6H_3(SO_3H)_2$	Cotton, Polyamide, Paper
$-NHC_6H_5$	$-NHC_6H_5$	Cotton, Polyamide.

CHART–1 (contd.)

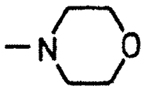
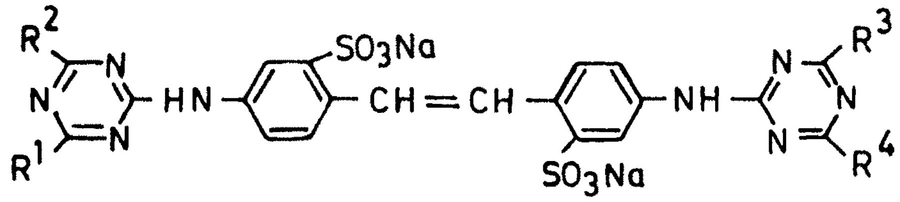
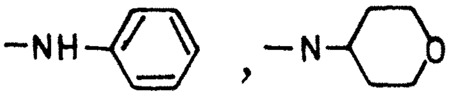
Substituents		Field of application
$R = R^1 = R^2$	$R^1 = R^3 = R^4$	
$-NHC_6H_4SO_3H$ (1,4)	$-NHC_6H_4SO_3H$ (1,4)	Cotton, Polyamide.
$-NHC_6H_5$		Laundry agents.
$-NHC_6H_3(SO_3)_2$	Morpholino	Laundry agents.
$-NHCH_2CH_2SO_3H$	$-NHC_6H_3(SO_3H)_2$ (1,2,4)	Laundry agents.
$-OCH_3$	$-N(CH_2CH_2OH)_2$	Paper
$-OCH_3$	$-N(CH_3)-CH_2CH_2SO_3H$	Paper
$-OH$	$-NHC_6H_5$	Laundry agents, Viscose.
$-OCH_3$	$-NHC_6H_5$	Cotton, Polyamide, Viscose, Laundry-agents.
$-NHC_6H_5$	$-NHC_6H_4SO_3H$	Cotton, Viscose, Polyamide.

CHART-1 (contd.)

(II)



General Structure

Substituents	Field of application
$R = R^1 = R^3 = R^4$	Cotton (T, W)
= 	Polyamide (T,W,S)
= $-NR_n^5$	Cellulose (T,W,P,S)
$R^5 = H, CH_3, -OCH_3,$ $CH_2CH_2OH, CH_2CH_2SO_3H,$ $n = 1$ or 2.	

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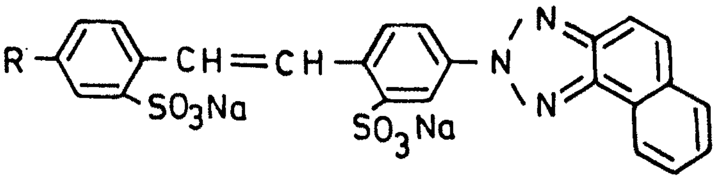
(III)

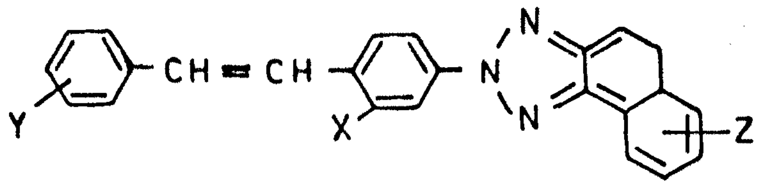


General Structure

Substituents	Field of application
$R = Cl, -NH_2$	Polyester, Plastics.

CHART-1 (contd.)

(IV)



General Structure

Substituents

$X = SO_3Na, SO_2NHC_2H_5,$
CN, SO_2CH_3

$Y = H, Cl$

$Z = H, SO_3H$

Field of application

Cotton, Polyamide.

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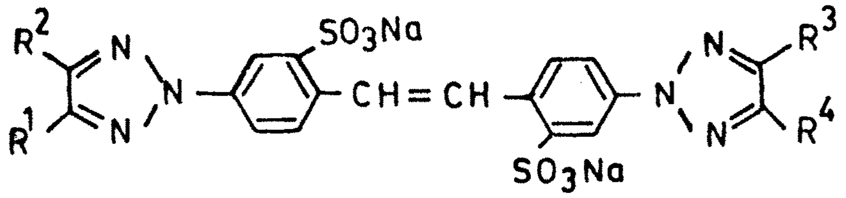
(V)



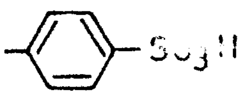
4,4′-Bis (V-Triazol-2-yl) Stilbene-2,2′-disulphonic acid derivative.

General Structure

Substituents

$R = R^1 = R^2 = R^3 = R^4$

= H, alkyl, Phenyl,



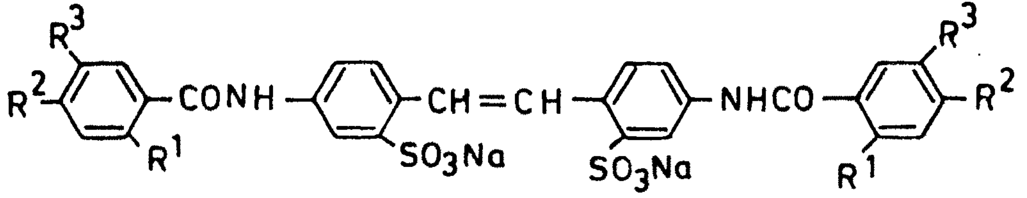
Field of application

Cotton (T, W)

Polyamide (T, W)

CHART-1(contd.)

(VI)



General Structure

Substituents

R^1	R^2	R^3
$-H$	$-CH_3$	$-H$
$-H$	$-OCH_3$	$-H$
$-H$	$-OCH_3$	$-OCH_3$
$-OCH_3$	$-H$	$-OCH_3$
$-OCH_3$	$-OCH_3$	$-H$
$-OCH_3$	$-OCH_3$	$-OCH_3$

Field of application

Cotton,
Polyamide,
Cellulose.

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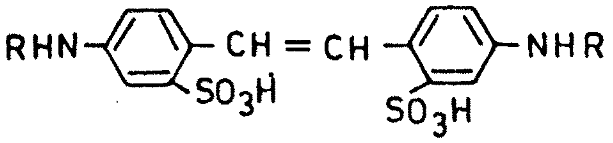
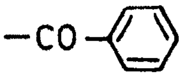
(VII)

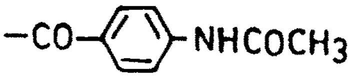


General Structure

Substituents

R = $-H$, $-OCH_3$,





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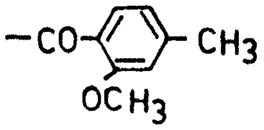

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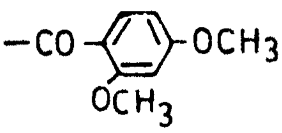

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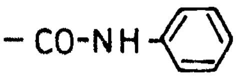

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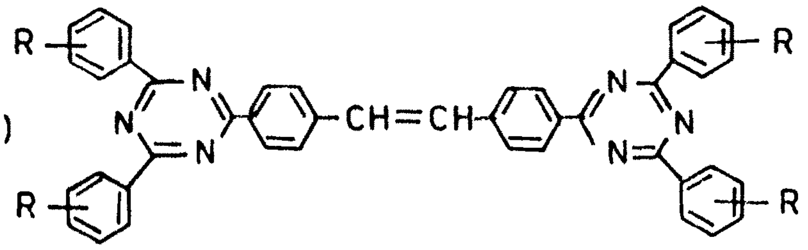
Field of application

Cotton,

Cellulose.

CHART-1 (contd.)

(VIII)



4,4'-Bis-Diphenyl (triazinyl) stilbene derivative .

General Structure

Substituents	Field of application
R= H, $-OCH_3$, -alkyl .	Polyester (S)

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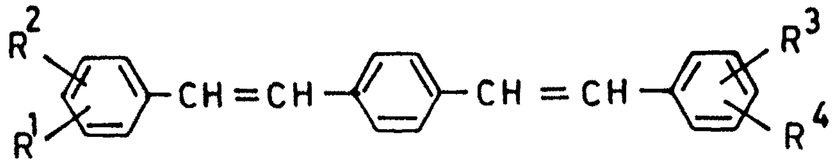
(IX)



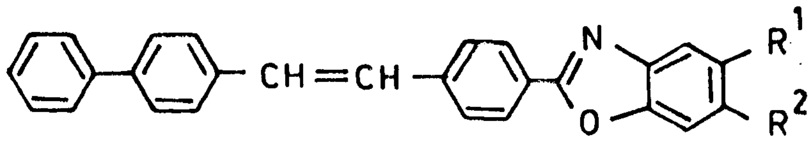
4,4'-distryl biphenyls

General Structure

Substituents	Field of application
$R = R^1 = R^2 = R^3 = R^4 = H$	Cotton (W)
$-SO_3H$, $SO_3N(alkyl)_2$	Polyamide (T, W, S) Polyester (T, S)
$-OCH_3$, CN , Cl , $-COOCH_3$	PVC (K) Polystyrene (K)
-CON , $(alkyl)_2$	Polyurathane (K)

CHART-1(contd.)

(X)



4-Phenyl-4'-benzoxazolyl stilbene derivatives

General Structure

Substituents	Field of application
$R = R^1 = R^2 =$ H, Cl,	Polyester (T)
-alkyl, $-SO_3CH_3$	Polyamide(S)

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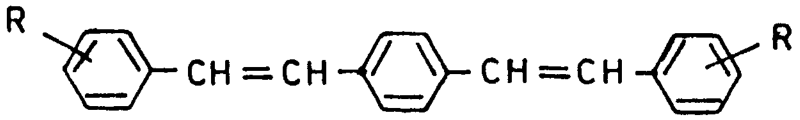
(XI)



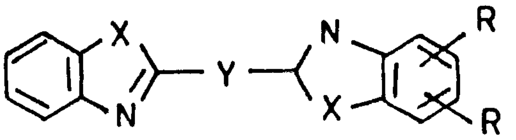
4-Styryl stilbene derivatives

General Structure

Substituents	Field of application
$R = -CN, -CONR_2$	—
$R^1 =$ H, CH_3 etc.	

*

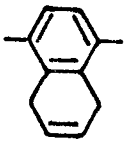
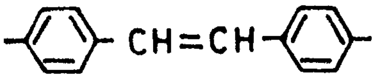
(XII)



Bis(benzazol-2-yl) stilbene

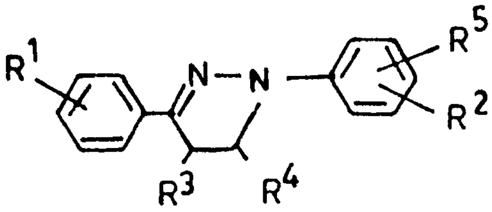
General Structure

CHART-1(contd.)

Substituents	Field of application
When X = 0 – benzoxazole	Polyamide (T,W)
X = NH – benzimidazole	Polyester (T,W,S)
X = S – benzthiozole	PVC (K)
Y =  	Polystyrene (K) Polypropylene(K)
 , –CH=CH–	Acetate (T,S)
–CH=CH–Ph , R=H , $-C(CH_3)_3$	Triacetate(T,S)
$-C(CH_3)_2Ph$, $-CH_3$	

*

(XIII)

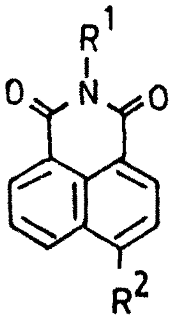


General Structure

Substituents	Field of application
R^1 = H, Cl, CN	Wool(T), Silk(T),
R^2 = Cl, $-SO_3H$, $-SO_2NH_2$,	Triacetate (T)
$-SO_2NHR$, –COO, alkyl,	Sec-acetate (T)
$-SO_2CH_3$, $-SO_2NH(CH_3)_2$	Pan(T,W)
$N(CH_3)_3$	
$R^3 = R^4$ = H, alkyl, aryl.	

CHART-1 (contd.)

(XIV)

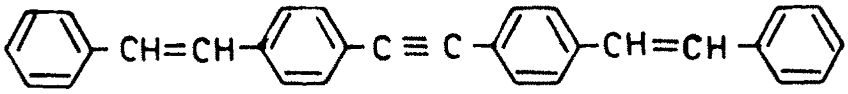


General Structure

Substituents	Field of application
R^1 = alkyl, $-(CH_2)_3$, $\overset{+}{N}(CH_3)_3$.	Polyester(T), Pan (T),
R^2 = o-alkyl, SO_3H,	Sec Acetate (T)
$-NHCOCH_3$	Triacetate (T)

⁂

(XV)



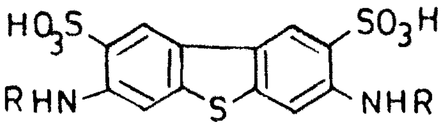
Tolan or Acetylene derivatives

General Structure

Substituents	Field of application
$R^1 = R^2 = SO_3Na$	Cotton (T)
	Polyamide (T)

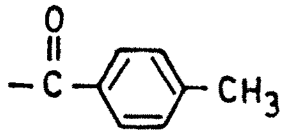
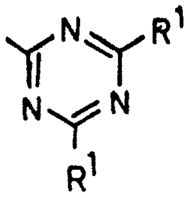
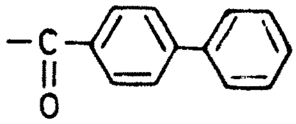
⁂

(XVI)



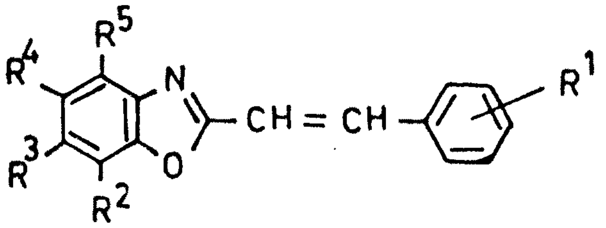
General Structure

CHART-1 (contd.)

Substituents	Field of application
R =   , 	Cotton (T)

*

(XVII)



General Structure

Substituents	Field of application
R^1 = –CN, COO alkyl, Cl	Polyamide (T,W)
$R^2 = R^4$ = H, alkyl	Polyester (T,W)
R^3 = H, alkyl, aryl.	

*

(XVIII)

Coumarin and Carbostyryl derivatives

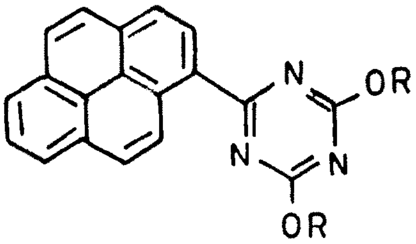
General Structure

CHART-1 (contd.)

Substituents	Field of application
R = H, $-CH_3$, $-CH_2COOH$	Cotton (T)
R^2 = H, $COOCH_3$, aryl hetero aryl.	Wool (T) Polyester (T) Pan (T,S)
R^3 = -N(alkyl), -o-alkyl, $NHCOCH_3$, hetero aryl.	Polyamide (T,S)

*

(XIX)



General Structure

Substituent	Field of application
R = -alkyl	Polyester (T) Sec. acetate Triacetate

The abundant literature on Fluorescent brighteners render it difficult to give complete account of each class of Fluorescent brighteners[7,8,13 -29].

USES OF FLUORESCENT BRIGHTENING AGENTS :

In accordance with their effect as "white dyes" Fluorescent brightening agents are applied by well known dyeing method[30]. Substrates to which they are applied include natural fibres, Semisynthetic Fibres, fully synthetic fibres, plastics, paper, and surface coating[31].

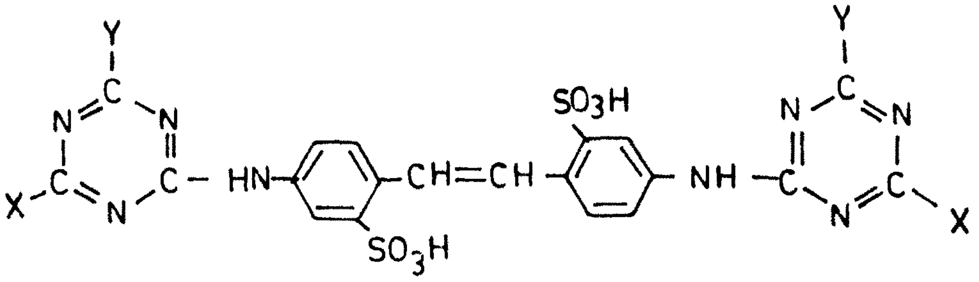
In a similar manner to "colour dyes" fluorescent brightening agents can also be classified according to their dyeing behaviour as direct (Substantive), cotton brighteners, acid brighteners, basic and cationic brighteners and dispersed brighteners[32].

Apart from this, fluorescent brighteners are used in various fields. Flourescence labelled low density lipoprotein for studying cell receptors, fluorophoric glycosides as tool in biochemical and biotechnological reserach. [Detection of differentiation of cellulosic enzymes, oligosaccharides binding to textiles. GS gene fusion system using fluorimetric assays]. Certain fluorescent brighteners used in night clubs for displays which are invisible in daylight or artifical light and only visible in ultraviolet light radiations occasionally termed as Black light.

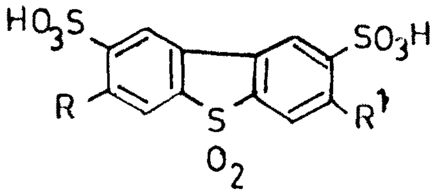
Fluorescent brighteners used in certain classes given in detail as below.

FOR CELLULOSE :

The brightening of cellulose fibers constitutes the most important use of Fluorescent brighteners. Most of these substantive brighteners are from the groups exemplified by compounds (1), (7), (15) and (6)

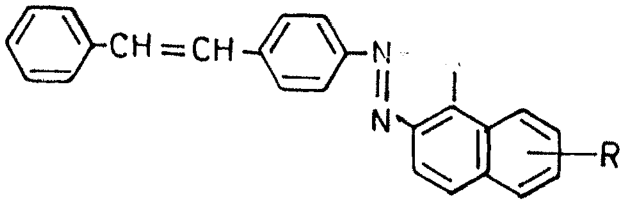


(1)



(6)

R,R^1=acylamino, triazinly-amino, naphthotriazole gr.



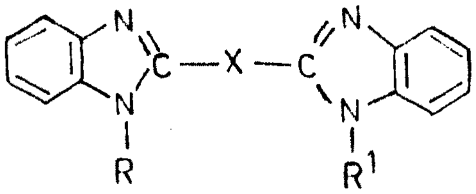
(7)

A=SO_3H, -SOX, -CN

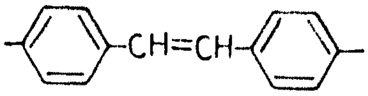
X=-NYY^1, alkyl, aryl, -O-aryl

R= -H, -SO_3H

X= -CH=CH-



(15)

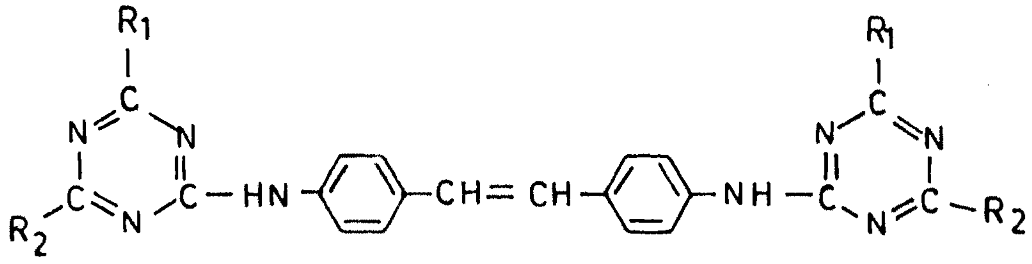


R,R^1=H, alkyl,

hydroxyalkyl, etc.

(A) Detergent brighteners :

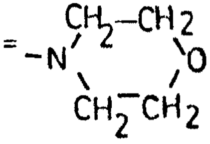
Today scarcely a detergent exists which does not contain some cellulosic brightener. Brighteners chosen must have satisfactory affinity for the fibre in presence of detergents. For example, brightener IX is recommended as a whitener for textiles in anionic systems, but it is less effective in non-anionic systems. On the other hand X and XI are effective in both anionic and non-anionic systems. Another important requirement is that the brightener should have satisfactory build-up in multiple washings without decolourising the textiles. The chemical bleaching additives when added have a harmful effect in many of the bistriazinyl-aminostilbene type whiteners. Brighteners of the type XVIII and XIX however, are suitable for use in the presence of chlorine-active agents.



For 1X - R^1 = $-NHC_6H_5$

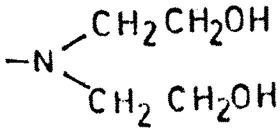
R^2 = $-NHC_6H_5$

X - R^1 =



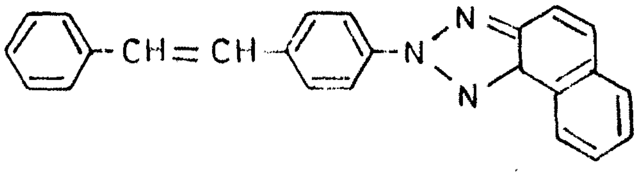
R^2=$-NHC_6H_5$

X1- R^1 =



$-N(CH_2CH_2OH)_2$

R^2=$-NHC_6H_5$



XVIII

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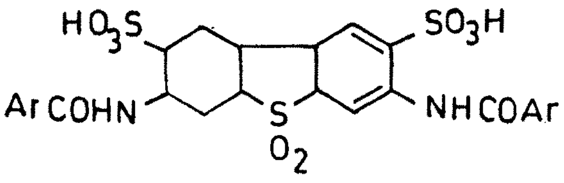
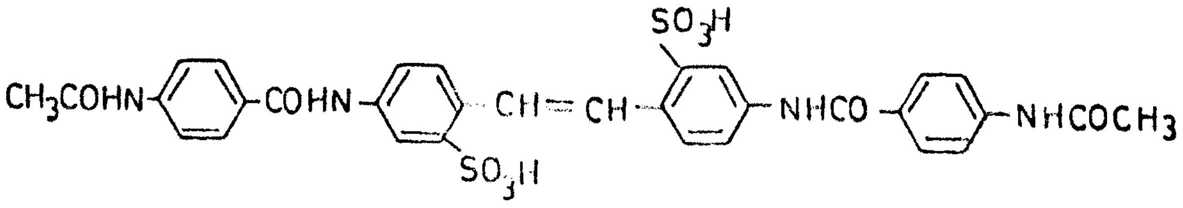


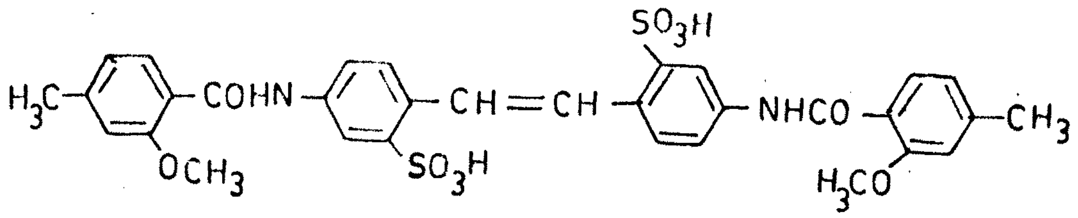
XIX

Although benzidenesulphonic acid derivative (XIX) posesses outstanding stability to chlorine containing bleaches, it tends to build up a considerable greenish line on ceelulose fibres. Today products giving a violet cast are preferred most brilliant shades or white.

XX and XXI are two more examples of whiteners that have found use in detergent mixtures for cotton textiles.



XX

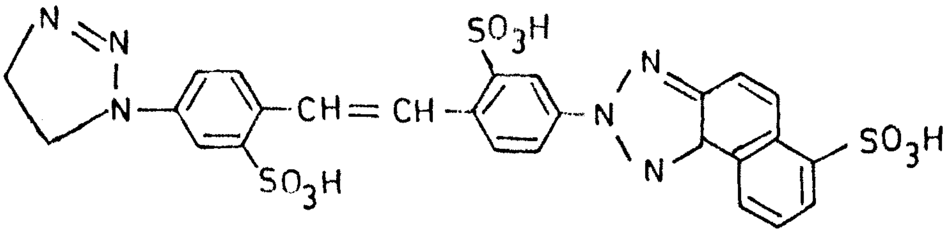


XXI

(B) Brighteners for cellulosic textiles :

Textile finishing requires brighteners of very good solubility and substantivity. Mostly bis (triazinyl - amino) stilbenes are preferred. The degree of substantivity required is of lower order compared to the one required for use in soaps and detergents. Too high a substantivity may lead to uneven application, particularly in package machine treatment of yarns or in which or jig application pieces. The stilbene whiteners behave like direct cotton dyes and their uptake is influenced by a variety of factors, including the temperature and electrolyte content of the bath. liquor-to-foods ratio. etc. Most of these whiteners have light fastness rating of about 4 and is fairly adequate. Some of the bistriazinyl amino derivatives of value to the cotton textile industry are listed in Table-

Very often optical brightening is carried out simultaneously with other textile finishing operations. For example, the brightener may be required to have stability in combined use with chemical bleaching agents. XXII can be applied to cellulosics by the exhaustion process in the presence of active chlorine. X and XIV also possess good chlorine stability. Sometimes brightening agents may be required that are stable to synthetic resins. Because of its high affinity and acid resistance, optical brightening agent VIII is suitable for application along with synthetic resin finish.



XXII

Brighteners for paper :

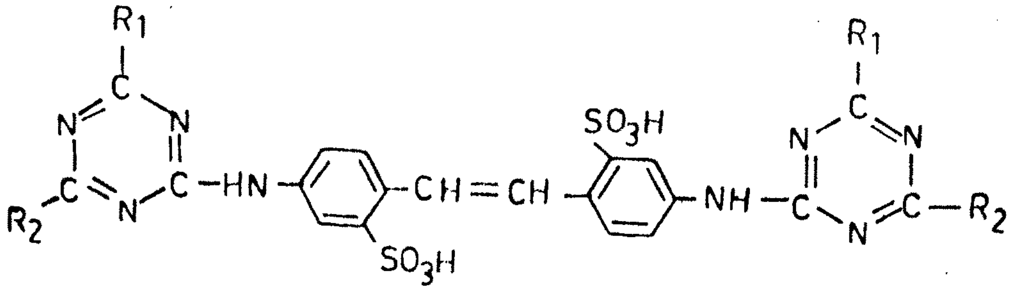
Optical whiteners are used extensively to improve the whiteness of paper. The treatment with brighteners supplements chemical bleaching and avoids excessive fibre degradation. Unbleached pulp cannot be whitened satisfactorily and this is due to the presence of the lignin type which act as UV absorbers. The brighteners may be introudced at any one of the following stages of paper manufacture :

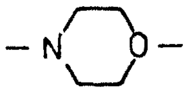
I) Pulp manufacture.
II) Paper making.
III) Coating operations.

Although optical brighteners can be used by any one of the conventional application process, the most widely used and the most satisfactory method is beater addition. General practice is to dissolve the dye in hot water, dilute with cold water, and add to the stock before the alum to the extent of 0.1 to 0.3% of the fibre weight. For application in the beaker, the brighteners should be moderately soluble with good absorptive characteristics. High solubility is required when the brighteners are to be used in conjunction with alum and size or are added in the size process or in the coating machine. The brighteners used for paper should possess good fluorescence even in an acid medium. In addition, good paper brighteners must possess good fluorescence even in an acid medium. In addition, good paper brighteners must possess good alum stability as well as compatibility with paper fillers. With wet strength resins, brighteners unaffected by catalysts are required.

Most of the whiteners developed for paper are limited to the derivatives of 4,4'-diaminostilbene -2,2' disulfonic acid. Some of typical whiteners for paper are represented by V-IX.

TABLE I



R_1 = $-NH_2$. $HN-C_6H_4SO_3n-NHC_6H_5$. 

R_2' = $N\ (CH_2CH_2OH)_2$ $-OCH_3$. $-NHC_6H_5$

FOR POLYAMIDES :

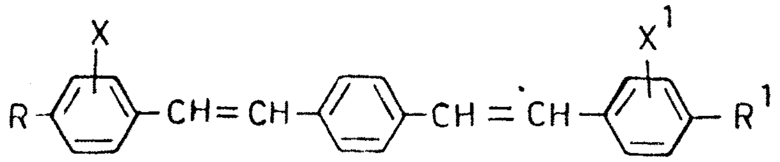
In practice only a limited number of brighteners are avilable for brightening cellulose fibres. blue to violet Fluorescent products from the most varied compound classes can be used for polyamide fibres.

Detergent Brighteners :

Two types of detergents are involved here the light duty and heavy duty detergent. In light duty detergents brighteners are introduced which will exhaust on the fiber from a weakly acid to neutral bath. Compounds having structures (18) and (20) are to be considered here. Heavy duty detergents are used at an alkaline PH and therefore their use is limited to compounds that will exhaust onto polyamide fibers under these conditions, brighten cellulose as well, e.g. structure (7) (Sulphotriazolyl stilbenes), (15) and (1). Other requirements are same as for brighteners for cellulose.

For Textile Industry :

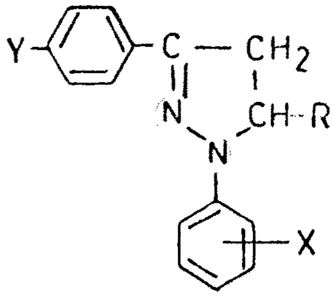
Water soluble anionic brighteners are applied very much like acid wool dyes. Compounds of formula (8), (9) and (1) as well as (5). Cationic products of formula (13) are dyed from a neutral to alkaline bath. Water insoluble forms of compounds (7) and (19), (20) and (21) are of technical interest.



(5)

R, R^1 = Substid amino, carboxyl, acetyl amino etc.

X, X^1 = -H, $-SO_3H$.



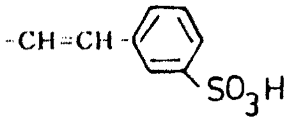
R = H, aryl, Y = -H, -Cl

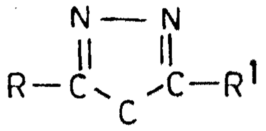
X = $-SO_3H$, $-SOYY^1$, -COOH

-COO-alkyl, $-CONYY^1$, etc.

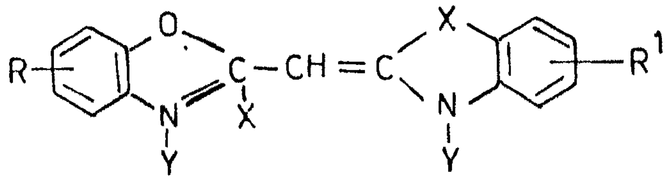
(8)

R, R^1 = aryl,





(9)



(13)

R = H, alkyl, alkoxy

X = -O-, -S-, $(CCH_3)_2$

Y = alkyl

A = colourless anion

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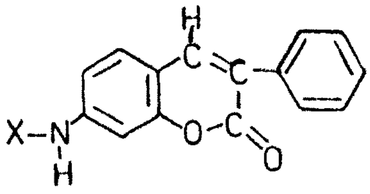


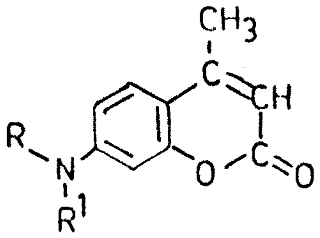
X = RO-CO-, R-NH-CO

R = alkyl, aryl

V,W = Cl, substd.

amino radicals.

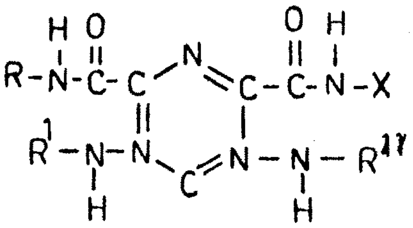
(19)



R = R^{1} = -H,alkyl,

hydroxyalkyl, aryl etc.

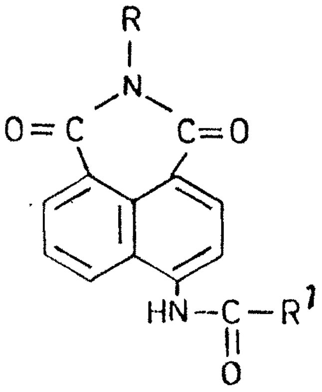
(18)



R,R^{1}, R^{11} = alkyl

X = alkyl,aryl etc.

(20)



R = alkyl, aryl

R^{1} = alkyl, -NH-aryl

(21)

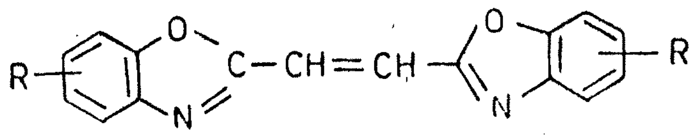
FOR OTHER FABRICS, COSMETICS PREPARATIONS :

Brighteners for polyacrylonitrile :

More or less basic brighteners are suitable for brightening polyacrylonitrile fibers. Basicity of brightener attained through either external amino groups or heterocyclic rings of basic character polyacrylonitrile brighteners must be introduced that is inert to the chemical bleaching agent, active to chlorine.

For polyesters fibres :

All of these are water insoluble products which usually applied with a carrier often the maximum in brightness and fastness is achieved by means of a final heat treatment. Application in the spinning mass has achieved great significance. It is of fundamental importance for the brightener to remain stable at high condensation temperature. Effective polyester brighteners having structure (14), (7).



(14) R = −H, alkyl etc.

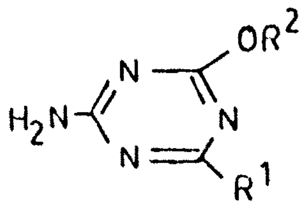
For plastics :

Plastics are brighten in melt. For practical application the brighteners must withstand special conditions. For example, it must have stability to polymerization catalysis (Peroxides); sublimation fastness, and the highest possible light fastness. Good plastics brighteners, which are especially suited to polyvinyl chloride, are having structure (14) (19), water insoluble (7) are employed.

For Cosmetics :

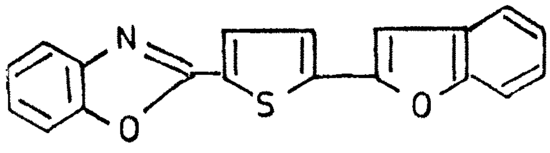
The use of brighteners for cosmetics such as creams, salves, lipstics etc. has been proposed, but no significant commercial usage has as yet developed. Water-insoluble fat-soluble compounds of type may be used for this purpose.

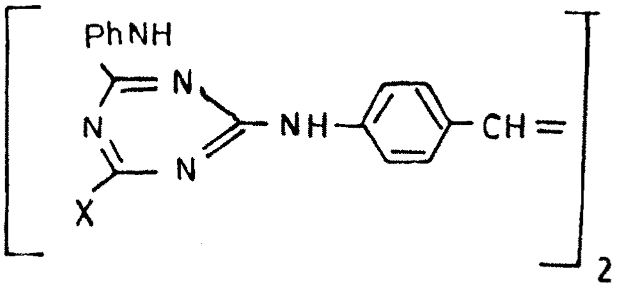
Brighteners for pesticides, drugs :



(I)

The title compound (I) CR^1, R^2= Unsubstituted alkyl, are prepared. The complexes are reacted with stiochiometric amounts of carboxylic acid annydrides, optionally in mixture carboxylic acids.





A
10594

(a) (b)

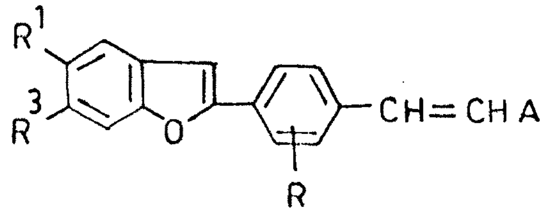
(a) Antibacterial cellulose fibers :

Koho JP 5901, 770 [84, 01, 770]

(b) Use of optical brighteness as fluorochrome, for selective staining of fungal structures in tissues of infected plants.

(c) (i) Fluorescent brighteners with thermosetting, textile resins, sterling drug : USP 3, 766, 083 (1981), Tetra-alkalimetal salt of $4,4^{1}$ bis [-4-P-Sulpho-anilino-6-dispropanol amino-3-triazine-2-yl amino) $-2,2^{1}$- Stilbene disulfonic acid.

(ii) USP - 3, 787, 279 (1971)

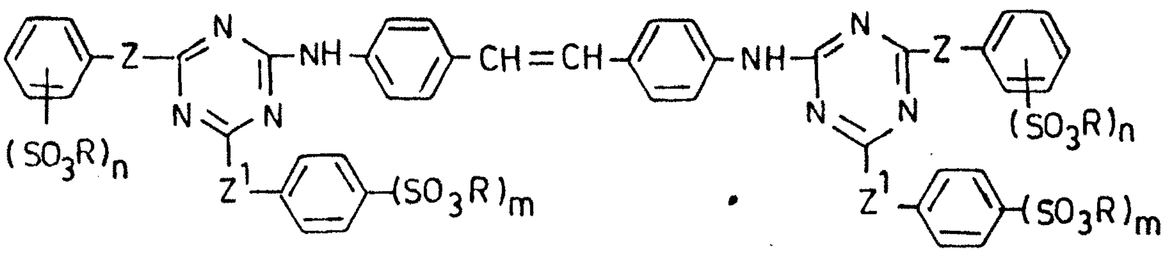


[R = alk or alkoxy of 1-6 or Hal.

R^1 and R^2 = Same or different H, alk.

Oraloxy of 1-6 carbon Halogen, dialkyl or alkanoyl amino]

(d) Fluorescent brighteners in resin finishing



[$Z=Z^1$ = -NH-, -O- R=H, alkalimetal,

alkaline earth metal, m , n = 1, 2]