CHAPTER-I

INTRODUCTION

CHAPTER - I

INTRODUCTION

INTRODUCTION :

Fluorescent brightening agents are an important class of dyestuffs used extensively in household and laundry detergents and for the treatment of textiles, paper and plastics. Today, it is practically impossible to obtain white textile fabric or paper that has not been treated by some whitener or the other.

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.

DEFINITION OF FLUORESCENT BRIGHTENING AGENTS AS DYES :

Fluorescent brightening (or whitening) agents[1] are colorless fluorescent dyes. They increase the whiteness of the material to which they are applied. In accordance with their definition as "colorless" fluorescent dyes, their coloristic performance is that of fluorescent dyes, without absorbing light in the visible range of the spectrum.

Fluorescent brightening agents are applied as dyes, the fastness properties of the white shades achieved being evaluated on coloristic principles. Special characteristic 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 colorless 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 daylight andemit 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 daylight. 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 color impression. Fluorescent dyeings are therefore notable for particularly high brilliance.

Similar to a 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 spectral range the color 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.[2,3]

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, naphthalene, 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 $-NH_2$, -OH, -COOH and $-SO_3H$ groups cause hypsochromic or bathochromic shifts in fluorescent compounds.[3]

Requirements for Fluorescence :

(a) Electronic Considerations :

Much of the light energy absorbed by a 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 the 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 occurs through collision with other molecules and may result in the radiationless transfer to the colloiding molecules or in the production of heat.[4] The fluorescence process tends to favour in a compound having the following properties.

(1) A longest absorption wavelength with a high extinction coefficient in the ultraviolet or visible region corresponding to a $\pi - \pi^*$ 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 $n \longrightarrow \pi^*$ transition (common in molecules containing nitrogen, oxygen or sulphur atoms) are often phosphorescent but

seldom fluorescent.[5]

(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.[4]

The physical process of fluorescence in a whitener molecule is briefly outlined in Fig.1. By absorbing energy (photons) from UV light the internal energy of the fluorescent molecule for instance is raised from the ground state (S_0) to a higher excited electronic state (S_2) (singlet state). As a result of non-radiating deactivation (vibrational relaxation) it returns very quickly (within about 10^{-13} sec.) to the lowest level of the (S_2) state. With further non-radiating energy loss the molecule enter singlet (S_1) state (after approximately 10^{-11} sec) and remains in this state, this final transition being accompanied by light emission fluorescence.[2,3] Since energy was lost without any radiation in the earlier phase the photons emitted have less energy i.e. the light is of longer wavelength (Stokes law). The fact that the quantum yield of unity is only rarely observed can be attributed to the various processes of non-radiating deactivation of electronically excited states, such as inter combination transition into triplet state which compete as it were with fluorescence quenching.[2] Even, very small amount of foreign matter (i.e. impurities) may totally quench fluorescence by taking away the excited energy from the fluorescent compound. This is one of the reasons why fluorescent compounds must be produced with high degree of purity.

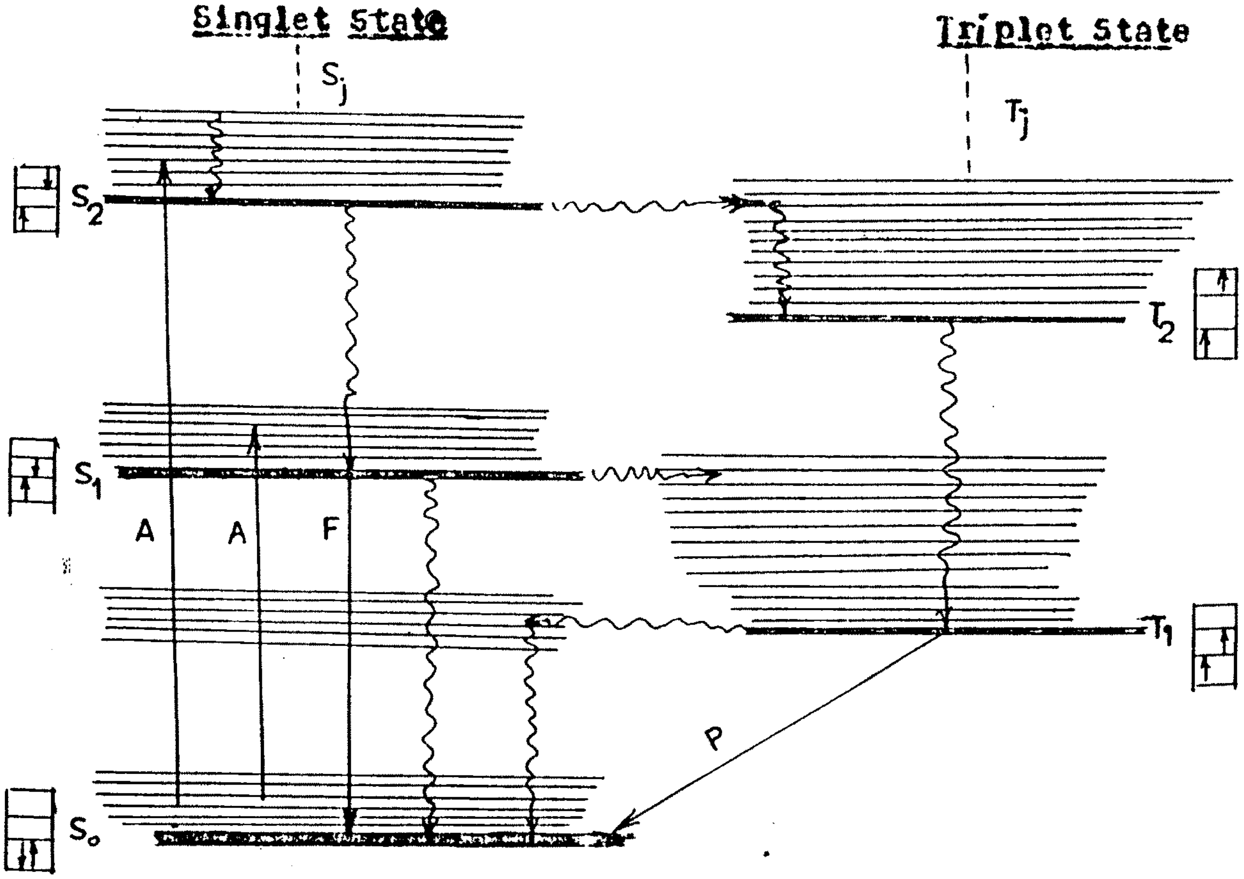


FIG. 1

Radiation transition Non-radiating transition

Vibration state Electronic state

A = Absorption F = Fluorescence P = Phosphorescence

(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 hetero-atoms, the geometrical arrangement 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 fluorescence wavelengths towards the red end of the spectrum and to enhance the mobility of the π-electrons. Increasing the number of mobility of 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 arrangement.

The effect of increasing the number of benzene rings is generally to increase the fluorescence 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 arrangement.[4] For example anthracene has more fluorescence efficiency than that of phenanthracene.

(2) The geometric arrangement of the molecules :

Planarity of the conjugated system appears to be essential for maximum fluorescence. When the planarity of the system is destroyed the free mobility of the π-electrons will be partially inhibated 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[6] i.e. fluorene has a quantum efficiency of about 0.54 in hexane while that of biphenyl 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 very 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 direct 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 tend to diminish the fluorescence.

Some factors influencing the function of Fluorescent Brightening Agents :

1. Substrate :

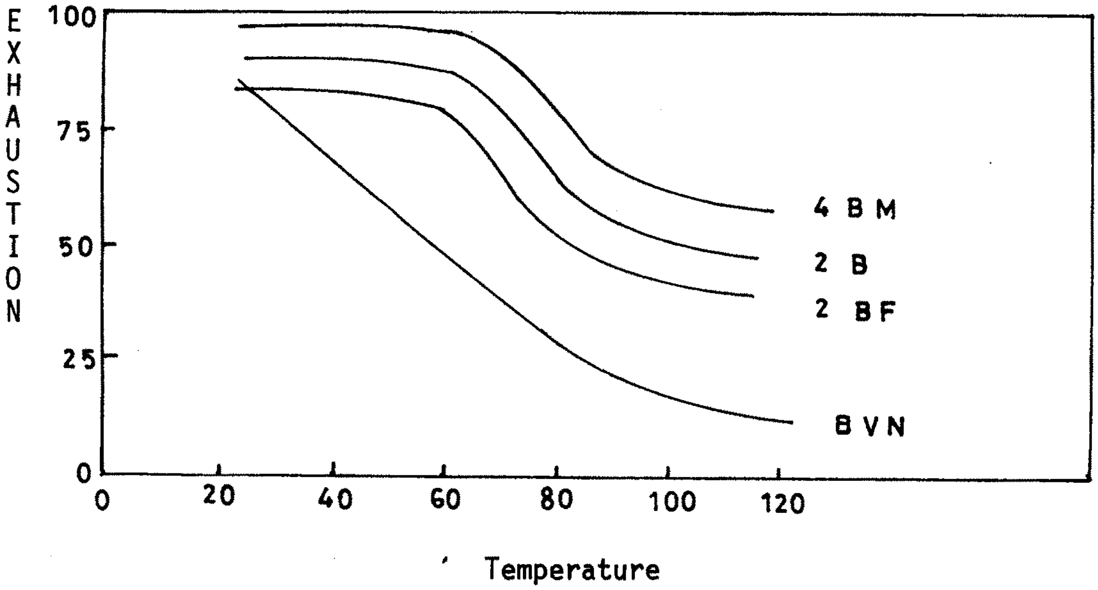
Fluorescent brighteners vary in efficiency when applied to different fibres depending on their affinity (orientation to their fibres) In the absence of sufficient affinity, the application results in yellow to green colour yield.

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 the increased conversion rate of electronic into vibrational energy. This fact shows quite clearly in the graph. For most practical purposes, slight temperature changes are probably unimportant, since the fluorescence intensity seldom falls by more than 1% for a 1° rise in temperature. However, a few compounds (e.g. p-anisidine indole-3-acetic acid) are known[9,10] in which the intensity may vary by about 5% for 1° temperature change. A few instances have been found in which the fluorescence intensity increases as the temperature is raised.[4]



(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, "Dyanamic 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.

When a molecule is electrically excited its dipole moment is changed and it is not in immediate equilibrium with its solvent environment. On the other hand, if a molecule relaxes, it equilibrates with its surroundings in a time shorter than its radiational life time some energy is dissipated and the fluorescence emission is brought well to the red end of the absorption band such shifts will depend both on solvent viscosity and polarity.[7] Thus indole shows a pronounced bathochromic shift in fluorescence wavelength with increasing dielectric constant of the solvent, while the activation wavelength remains constant, 1,2-diphenyl indole, which is incapable of hydrogen bonding shows similar wavelength changes to that in the case of indole. Therefore, these effects must be attributed to the dielectric properties of the solvent.[8,9]

5. pH :

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.[4]

Some compounds, such as sulphapyridine, fluoresce only over a very limited pH range, while compounds such as phenol fluoresce over a much wider pH range. The fluorescence corresponding to unionized phenol remains constant upto pH 9.5. Above the pH 9.5 this fluorescence becomes progressively less and a new weak fluorescence maximum is observed corresponding to the phenol anion. The fluorescence of phenol molecule at pH 10 falls to 50% of its maximal value at pH 1.

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.

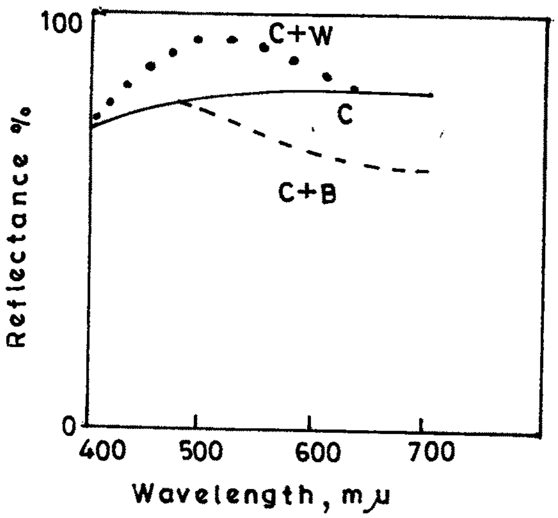
Mechanism :

Organic substances 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 wavelengths; these have found uses comparatively recently in the so called daylight fluorescent printing inks for posters.

To act as brightening or whitening agents compounds must re-emit 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 radiation, 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 artificial light the effect is even less than in daylight, as the ultraviolet content of most artificial lighting is very small indeed.



C : Ordinary bleached cotton

C+W : Treated with fluorescent brightening agent

C+B : Treated with blue colorant
(Ultramarine, C.I.pigment, Blue 29)

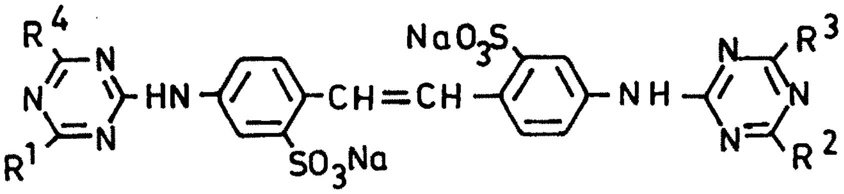
The whitening effect given by fluorescent brightening agents, therefore, is an additive effect : the yellow colour is corrected by the addition of blue light, and the total light reflected from the material is greater than from untreated material. On the other hand, the old blue-bag worked by a subtractive 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.

Fluorescent 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 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-, -NHCO-, -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 sufficiently in the range of 340-400 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

(I)



General Structure

Substituents		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.
$-N(CH_3)-CH_2CH_2SO_3H$,	$-N(CH_2CH_2OH)_2$	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
$-N(CH_3)-CH_2CH_2SO_3H$,	$-NHC_6H_4SO_3H$ (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.)

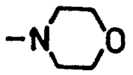
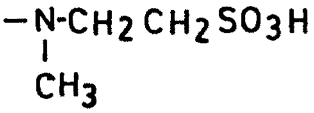
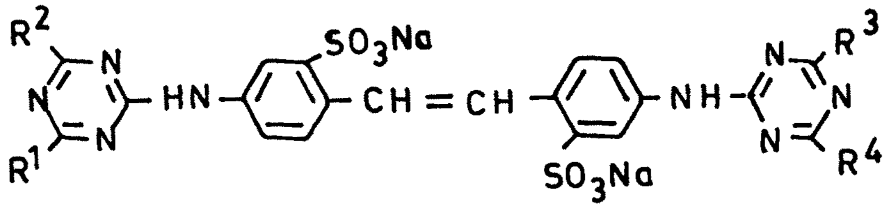
Substituents		Field of application
$R = R^1 = R^2$	$R^1 = R^3 = R^4$	
$-NHC_6H_4SO_3H$ (1, 4)	$-NHC_6H_4SO_3H$ (1,4)	Cotton, Polyamide
$-NHC_6H_5$		Laundry agents
$-NHC_6H_3(SO_3)_2$	Morpholino	Laundry agents
$-NHCH_2CH_2SO_3H$	$-NHC_6H_3(SO_3H)_2$ (1,2,4)	Laundry agents
$-OCH_3$	$-N(CH_2CH_2OH)_2$	Paper
$-OCH_3$	 $-\underset{CH_3}{\underset{\mid}{N}}-CH_2CH_2SO_3H$	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)
$= -NR^5_n$	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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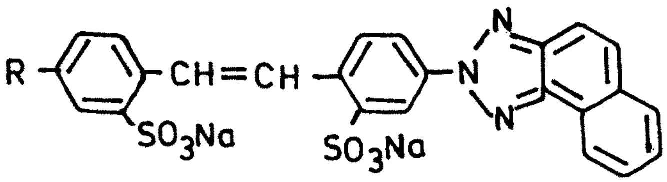
(III)

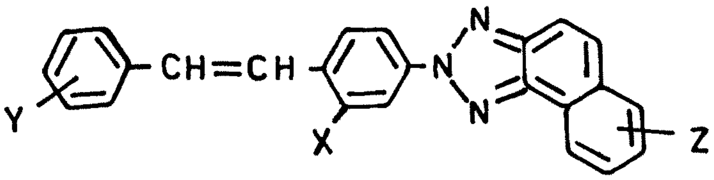


General Structure

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

CHART-1 (contd.)

(IV)



General Structure

Substituents

= SO_3Na, $SO_2NHC_2H_5$,
CN, SO_2CH_3

= H, Cl

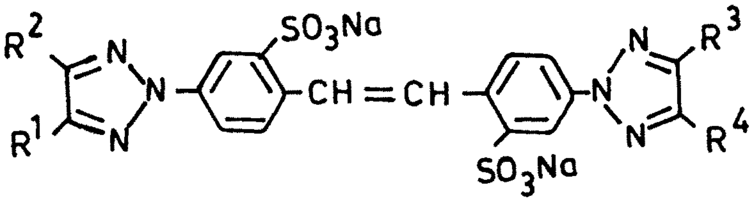
= H, SO_3H

Field of application

Cotton, Polyamide.

* * *

(V)

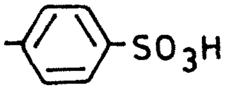


4,4'- Bis (V-Triazol-2-yl) Stilbene-2,2' disulphonic acid derivative.

General Structure

Substituents

= $R^1 = R^2 = R^3 = R^4 =$
H, alkyl, phenyl,



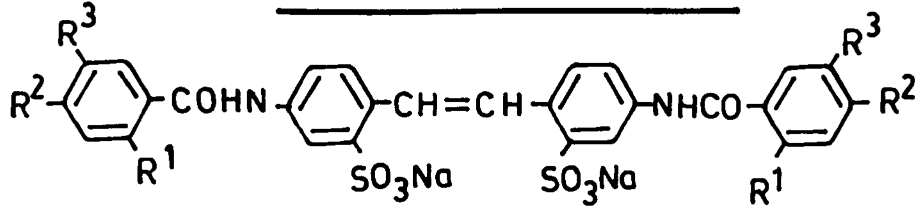
Field of application

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

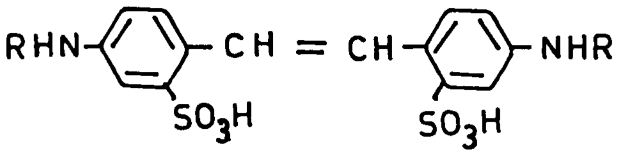
Cotton

Polyamide

Cellulose

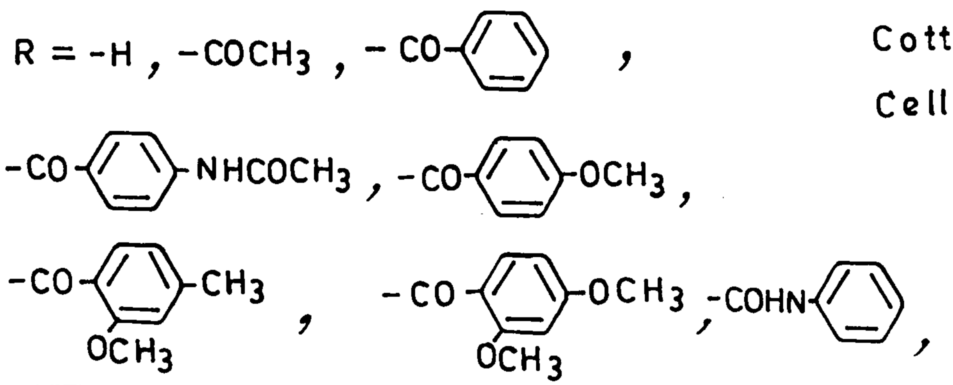
*

(VII)



General Structure

Substituents



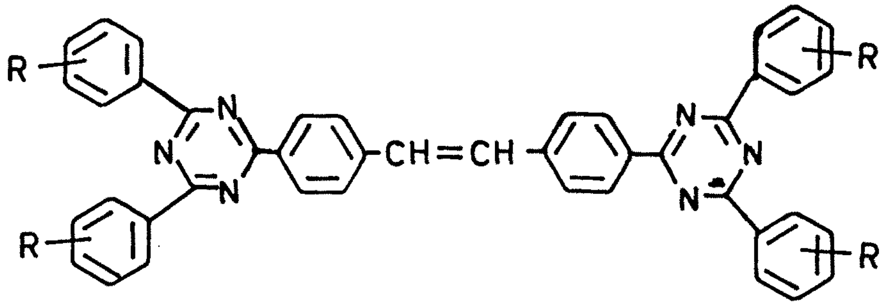
Field of application

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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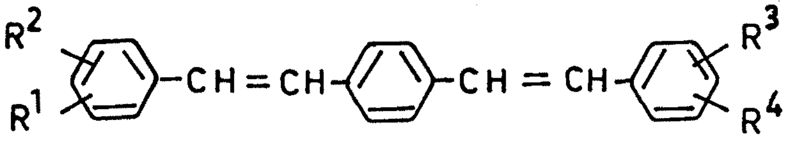
(IX)



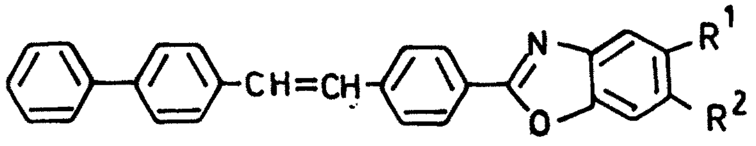
4,4′– distyryl biphenyls

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)
$-OCH_3$, CN, Cl, $-COOCH_3$,	Polyester (T,S)
$-CON$, $(alkyl)_2$.	PVC (K), Polystyrene (K)
	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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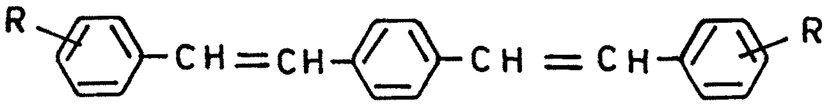
(XI)



4-Styryl stilbene derivatives

General Structure

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

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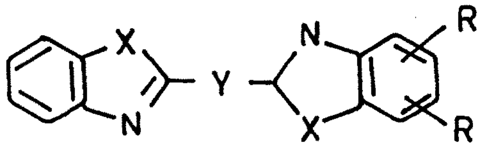
(XII)



Bis (benzazol-2-yl) stilbene

General Structure

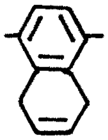
CHART–1 (contd.)

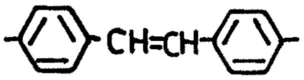
Substituents

When X = O – benzoxazole

X = NH – benzimidazole

X = S = benzthiazole

Y =  , 

 , –CH=CH–

–CH=CH–Ph , R = H , $-C(CH_3)_3$

$-C(CH_3)_2Ph$, $-CH_3$

Field of application

Polyamide (T,W)

Polyester (T,W,S)

PVC (K)

Polystyrene (K)

Polypropylene (K)

Acetate (T,S)

Triacetate (T,S)

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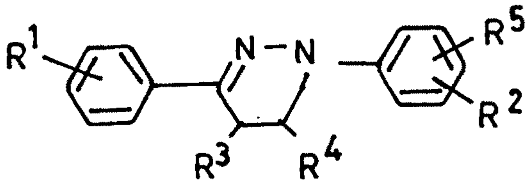
(XIII)



General Structure

Substituents

R^1 = H , Cl , CN ·

R^2 = Cl, $-SO_3H$, $-SO_2NH_2$, $-SO_2NHR$, –COO, alkyl , $-SO_2CH_3$, $-SO_2NH(CH_3)_2$, $N(CH_3)_3$

$R^3 = R^4$ = H , alkyl, aryl .

Field of application

Wool (T) , Silk (T) ,

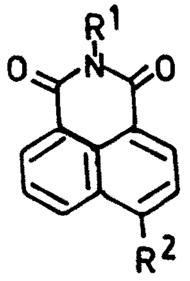
Triacetate (T)

Sec – acetate (T)

Pan (T,W)

CHART-1 (contd.)

(XIV)

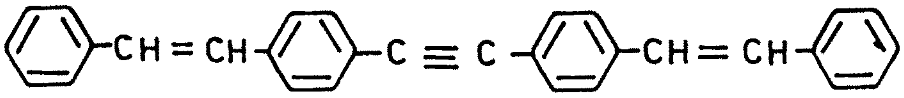


General Structure

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)



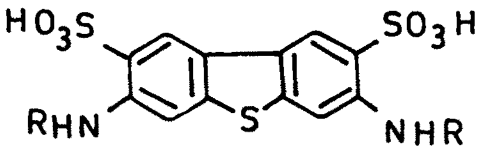
Tolan or Acetylene derivatives.

General Structure

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

*

(XVI)

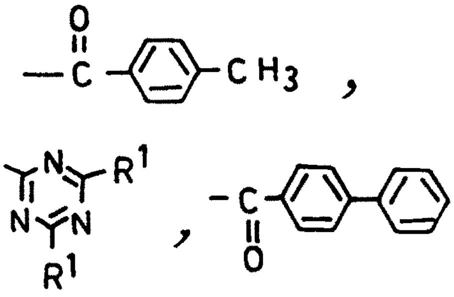


General Structure

CHART-1 (contd.)

Substituents

R =

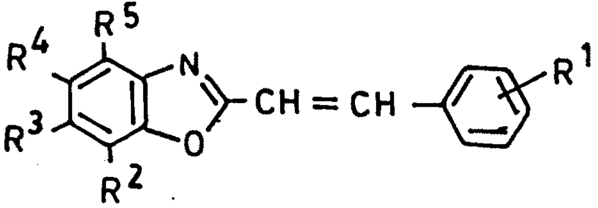


Field of application

Cotton (T)

*

(XVII)



General Structure

Substituents

R^1 = -CN, -COO alkyl, Cl.

R^2 = R^4 = H, alkyl.

R^3 = H, alkyl, aryl.

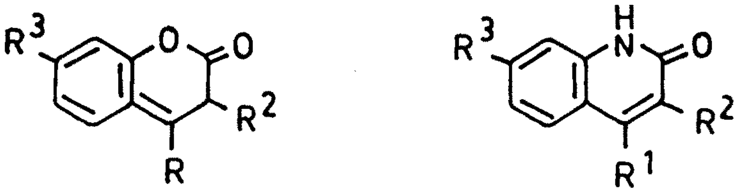
Field of application

Polyamide (T,W)

Polyester (T,W)

*

(XVIII)



Coumarin and Carbostyryl derivatives.

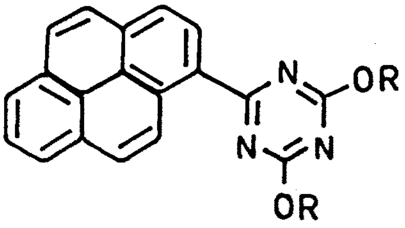
General Structure

CHART–1 (contd.)

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

* * *

(XIX)



General Structure

Substituents	Field of application
R = —alkyl	Polyester (T)
	Sec. acetate (T)
	Triacetate (T)

* * *

The abundent literature on fluorescent brightners render it difficult to give complete account of each class of fluorescent brighteners.[2,3,10-26]

USES OF FLUORESCENT BRIGHTENING AGENTS :

In accordance with their effect as "white dyes" fluorescent brightening agents are applied by well known dyeing method.[27] Substrates to which they are applied include natural fibres, semisynthetic fibres, fully synthetic fibres, plastics, paper, and surface coating[28]

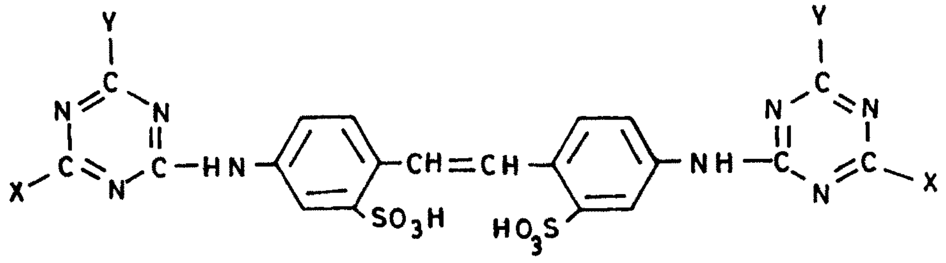
In a similar manner to "colour dyes" fluorescent brightening agents can also be classified according to their dyeing behaviour as direct (substantive), cotton brighteners, acid brighteners, basic and cationic brighteners and dispersed brighteners.[29]

Apart from this, fluorescent brightners are used in various fields. Fluorescence labelled low density lipoprotein for studying cell receptors, fluorophoric glycosides as tool in biochemical and biotechnological research. [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 artificial light and only visible in ultraviolet light radiations occasionally termed as Black light.

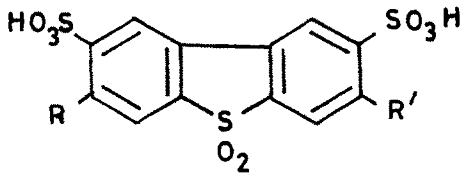
Fluorescent brighteners used in certain classes given in detail as below.

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)

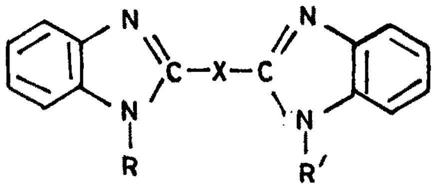


(1)

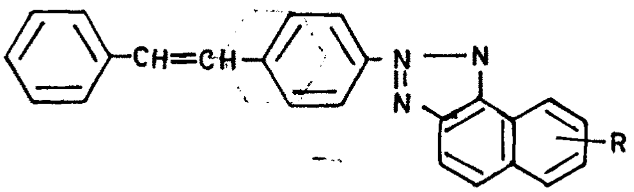


(6)

R,R' = acylamino, triazinyl--amino, naphthotriazole gr.



(15)



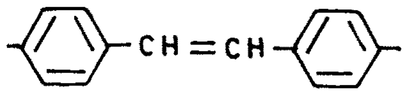
(7)

A = SO_3H, -SOX, -CN

X = -NYY', alkyl, aryl, -O-aryl

R' = -H, $-SO_3H$.

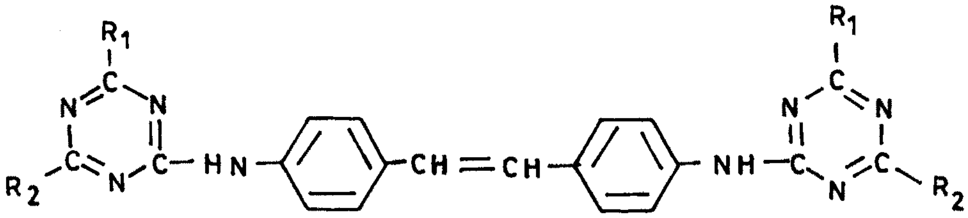
X = -CH = CH-



R,R' = H, alkyl, hydroxyalkyl, etc.

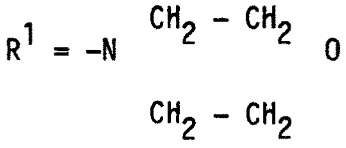
(A) <u>Detergent brighteners</u> :

Today scarcely a detergent exists which does not contain some cellulosic brightner. 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 bistriazinylaminostilbene type whiteners. Brighteners of the type XVIII and XIX however, are suitable for use in the presence of chlorine-active agents.

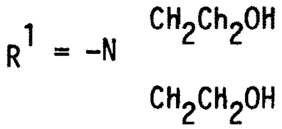


For IX - $R^1 = -NHC_6H_5$

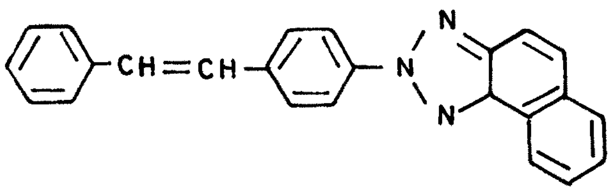
$R^2 = -NHC_6H_5$

X - 

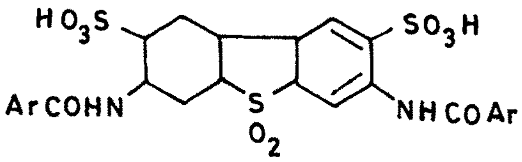
$R^1 = -N\begin{array}{l} CH_2 - CH_2 \\ \\ CH_2 - CH_2 \end{array} O$ $R^2 = -NHC_6H_5$

XI - 

$R^1 = -N\begin{array}{l} CH_2Ch_2OH \\ \\ CH_2CH_2OH \end{array}$ $R^2 = - NHC_6H_5$



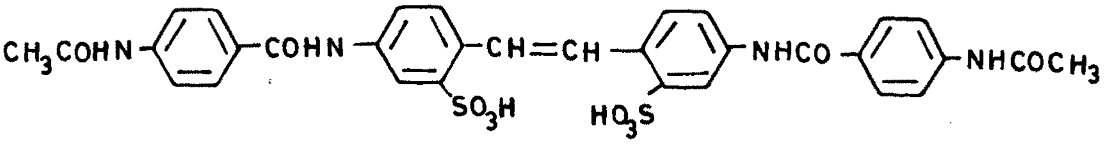
XVIII



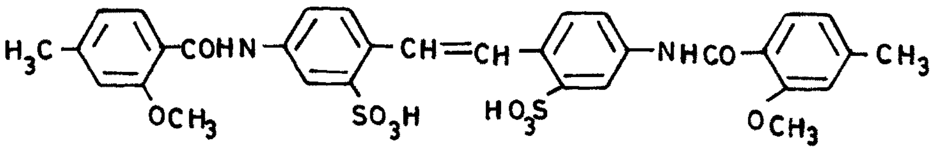
XIX

Although benzidenesulphonic acid derivative (XIX) possesses outstanding stability to chlorine containing bleaches, it tends to build up a considerable greenish line on cellulose 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

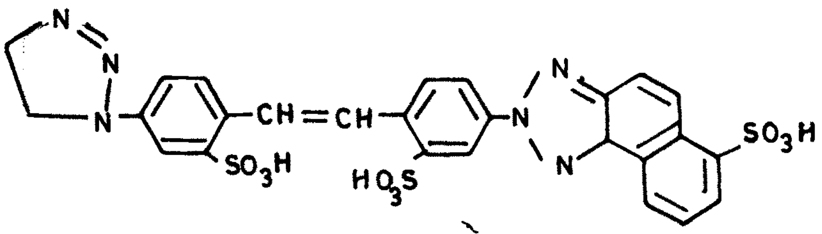


XXI

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 or detergents. Too high a substantivity may lead to uneven application, particularly in package machine treatment of yarns or in winch 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 bistriazinylamino derivatives of value to the cotton textile industry are listed in Table– I

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 :

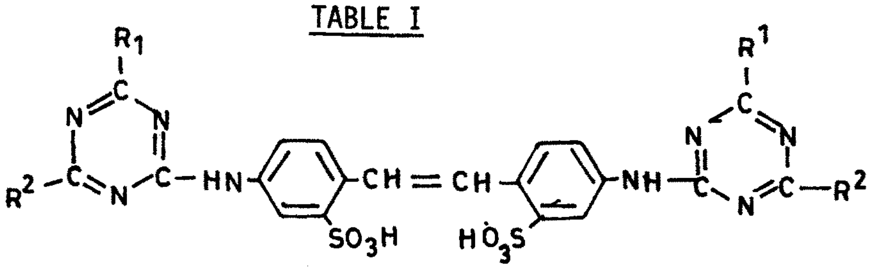
Optical whiteners are used extensively to improve the whiteness of paper. The treatment with brighteners supplements chemical bleaching and avoids excessive fibre degradation. Unbleached pulp cannot be whitened satisfactorily and this is due to the presence of the lignin type which act as UV absorbers.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

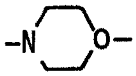
i) Pulp manufacture,
ii) Paper making,
iii) Coating operations.

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 dyein 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 beater, 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 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 :

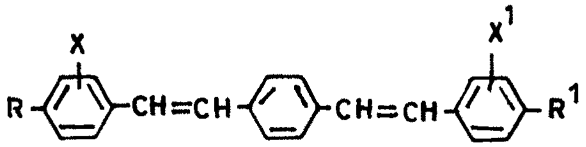
In practice only a limited number of brighteners are available for brightening cellulose fibres, blue to violet fluorescent products from the most varied compound classes can be used for polyamide fibres

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 requirments are same as for brighteners for cellulose.

For Textile Industry :

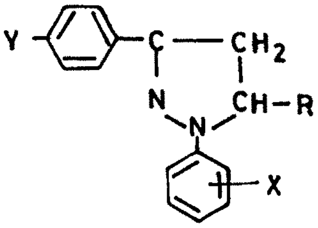
Water soluble anionic brighteners are applied very much like acid wool dyes. Compounds of formula (8), (9) and (1) as well as (5). Cationic products of formula (13) are dyed from a neutral to alkaline bath. Water insoluble forms of compound (7) and (19), (20) and (21) are of technical interest.



(5)

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

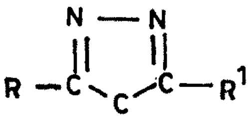
X,X^1 = -H, - SO_3H.



(8)

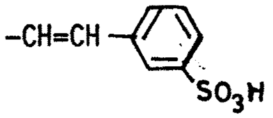
R = H, aryl. Y = -H, -Cl.

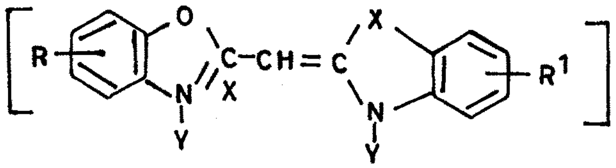
X = $-SO_3H$, - SOYY^1, -COOH, -COO-alkyl, -CONYY^1, etc.



(9)

R,R^1 = aryl,





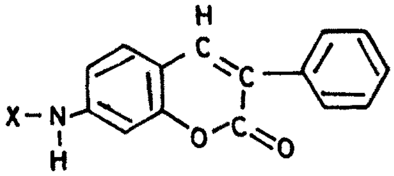
(13)

R = H, alkyl, alkoxy

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

Y = alkyl

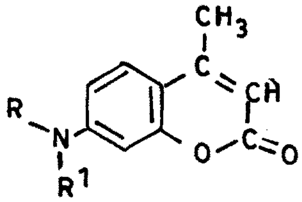
A = colorless anion



(19)

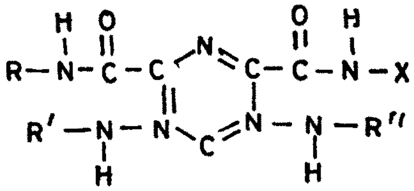
X = RO-CO-, R - NH-CO- R = alkyl,aryl,

V,W = Cl, substd.
amino radicals.



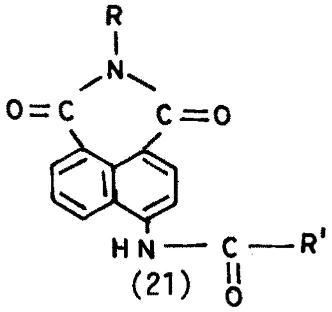
(18)

R,R^1 = -H, alkyl,
hydroxyalkyl, aryl, etc.



(20)

R,R',R" = alkyl
X = alkyl, aryl, etc.



(21)

R = alkyl, aryl,
R' = alkyl, -NH-aryl

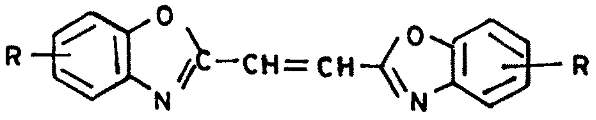
FOR OTHER FABRICS, COSMETICS PREPARATIONS :

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 polyester 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 brightners having structure (14),(7).



R = -H, alkyl, etc.

(14)

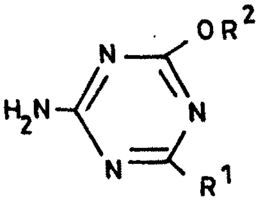
For plastics :

Plastics are brighten in melt. For practical application the brightners 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 :

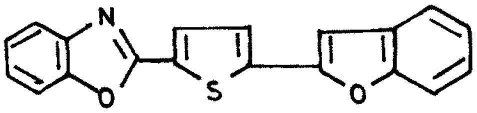
The use of brighteners for cosmetics such as creams, salves, lipstics etc. has been proposed, but no significant commercial usage has as yet developed. Water-insoluble fat-soluble compounds of type may be used for this purpose.

Brighteners for pesticides, drugs :

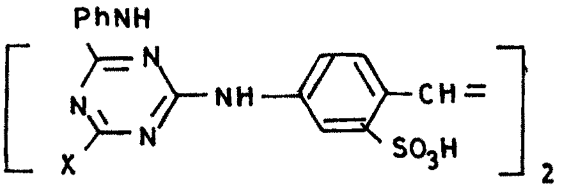


(I)

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



(a)



(b)

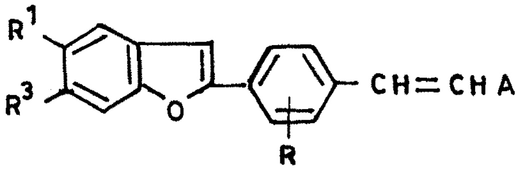
(a) Antibacterial cellulose fibers :

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

(b) Use of optical brightenes 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'-bis [-4-P-Sulpho-anilino-6-dispropanol amino-3-triazine -2-yl amino)-2,2'-stilbene disulfonic acid.

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

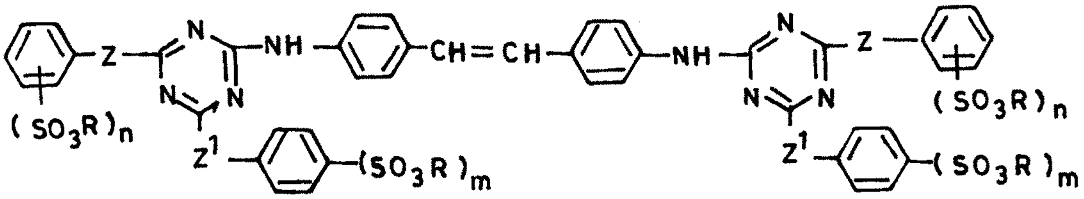


[R = alk or alkoxy of 1-6 or Hal.

R^1 and R^2 = same or different H, alk. oralkoxy of 1-6 carbon

Halogen, dialkyl or alkanoyl amino]

(d) Fluorescent brightners in resin finishing :



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

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

REVIEW OF LITERATURE

Over a century ago, Stokes studied the phenomenon of fluorescence on a scientific basis.[30] In 1921, A.V.Lagorio[31] observed that the content of colours can be enhanced by fluorescent dyestuffs. In 1929, Krais,[32] using Lagorio's principle, showed that yellowed viscose was whitened when dipped in a solution of aesculin, the glycoside of 6:7 dihydroxy coumarin, which is extracted from the bark of horse chestnuts; the treated fabric was comparable with bleached material. However, this compound developed discolouration so rapidly on exposure of the fabric to light that the discovery was never exploited on a wide scale. Some fluorescent properties have been put to commercial use: dehydrothio-p-toluidine and related compounds have been used as colourless marking inks in laundries; Fluorescein has been used for tracing the course of underground rivers; and some 25 years ago derivatives of 4:4'-diamino-2;2'-disulphonic acid were claimed as ultraviolet screening agents for cellophane wrappings,[33] and for producing fluorescent effects on textiles and paper, such as safety marks in banknotes.[34]

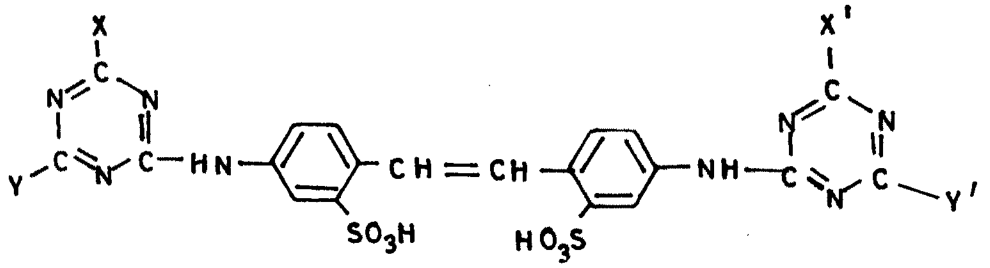
In 1934,[35] I.C.I. patented the use of diacyl derivatives of 4,4'-diamino-stilbene-2,2'-disulphonic acid for producing substantive fluorescent effects on cellulosic textiles and paper.

In 1935, Ultrazell GmbH [36] and Hoffmanns Strake Fabriken[37] patented the use of B-methyl umbelliferone as well as 4-methyl-7-

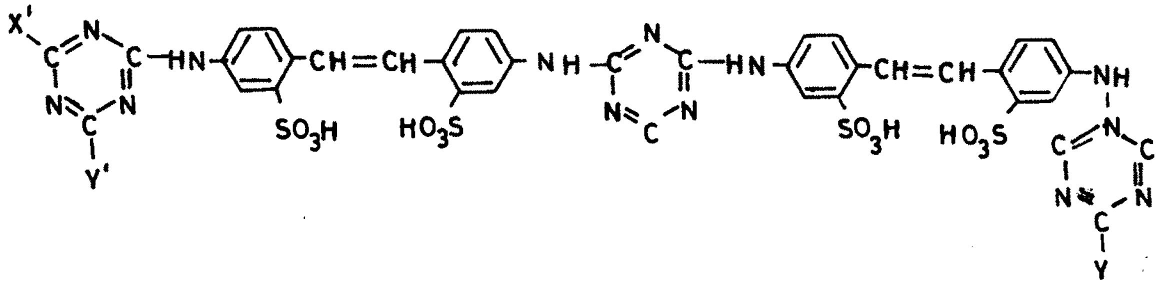
dimethyl amino coumarin under alkaline conditions for the whitening of cellulosic textiles.

In 1939 Meyer patented the use of β-methyl umbelliferone (II) for whitening textiles,[38] and a little later its use for whitening soap itself was also claimed.[39] Shortly afterwards, derivatives of diamino stilbene sulphonic acid, similar to those previously used as protective agents, were patented in Germany by the I.G.[40] and in this country by Lever Brothers[41] for use in soap to give a whitening effect to textiles in washed with them.

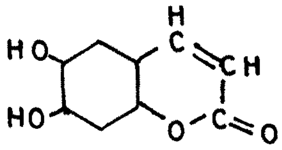
In 1940, Bruno Wendt and coworkers[42] of I.G. Farben found that triazinyl-amino-stilbenes of the following formula could be used from detergents and alkaline baths as substantive optical whitening agents for cellulosic textiles.



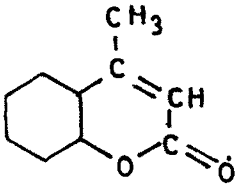
Above structure is the basic common structure of the triazine class. A very high proportion of the fluorescent brightening agents on the market are of this general structure, and many patents have been taken out covering specific groups on the triazine ring conferring specific properties. The most common types are the symmetrical in which X and X^1 are the same, and Y and Y^1 are the same. These are easy to prepare by stepwise replacement of the chlorine atoms of cyanuric chloride. Those in which X and X^1 or Y and Y^1 are different can in general be prepared only in a roundabout manner starting from nitroaminostilbene disulphonic acid, condensing this with cyanuric chloride, replacing stepwise the two chlorine atoms, and then reducing the nitro group and doing the same on the other half of the molecule. Obviously, these unsymmetrical ones are considerably more expensive to prepare, and in general they have very little advantage in properties. In the original Blankophor B, X and X^1 were anilino groups and Y and Y^1 hydroxy. Many more recent products have all four groups as substituted amino groups,[43-61] thus X and X^1 may be anilino, toluidino or anisidino residues, or residues of metanilic acid; Y and Y^1 may be similar or may be aliphatic amines such as methylamino, dimethylamino, hydroxyethylamino, bishydroxyethylamino etc. In other cases X and X^1 are again substituted amino groups, but Y and Y^1 are either phenoxy or thiol groups, or in some cases may be unchanged chlorine.[62-67] Variation in these groups has some effect on the fluorescence, both intensity and colour, the main effect is in altering the other physical properties solubility, substantivity, sensitivity to acids, and so on. In general, all products are unstable to hypochlorite in solution, but some show reasonable stability once they have been applied to the fibre. One of these has three triazine rings, the other one triazine and two acyl groups.[68]



The first commercial use in soaps and detergents of such compounds in this country was in 1942.



Asculetin



β-Methylumbelliferone

The early products on the market were almost entirely for use only on cellulosic materials. Continued research, however, has led to a wide range of products, not only having improved properties of cellulose but having special application to wool, man-made fibres, plastics etc. Well over 100 British patents have been granted, and some 30 or more manufacturers throughout the world are producing a range of between 150 and 200 different products. In 1955 the production in the U.S.A. was 1,375 tons-double the figure 3 years previously.[69] Today the production there is still higher - a sales value of 15 million has been quoted[70]- and the world production must be at least 2,500 tons.

These developments started intensive efforts to develop new whiteners and in the last three decades research has yielded many more fluorescent compounds which are suitable for their whitening effects. The optical whiteners are now used to whiten a wide variety of products including all types of synthetic fibres and fabric.

Fluorescent brighteners were introduced to consumers in the 1940's. By 1956 fluorescent whitening agents were used in the majority of soaps and detergents in bleaches, softeners and in textile

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fabrics. In 1960, the consumption of laundry brighteners in the United States was three million pounds and sales approximated nine million dollars.[71] The sales of fluorescent brighteners increased to twenty-five million dollars by 1964.[72]

The world's annual production of fluorescent brightening agents, including about 200 products of 15 different types, amounts to approximately 27-35 million kilograms, valued at 100-150 million dollars. This represents about 10% of the business in dyestuffs. The total may be broken down as follows :

Detergent mixtures	-	58 %
Paper brightening	-	25 %
Textile finishing	-	12 %
Plastics and spinning compounds	-	5

In 1966 fluorescent brightening agents to the value of 25 million dollars were used in the United States in soaps and detergents.

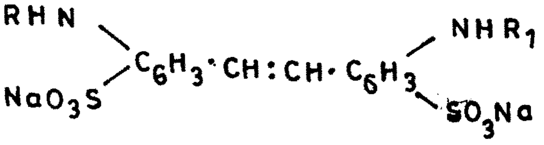
Though the world's annual production of fluorescent brightening agents ranges between 200-250, only small number of such brightening agents have found practical use.

Collectively these compounds belong to the aromatic or heterocyclic series; many of them contain condensed ring systems. These are linked together by direct bonds or small bridges, such as -CO-, NH-CO- -NHCO NH-, -CH=N-, or -CH=CH-. The whiteners possess large conjugated systems, containing π-electrons which can be excited in the range

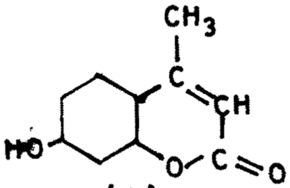
340 nm - 400 nm. Most of the whiteners have absorption maxima around 340 - 380 nm - and emission around 430 - 400 nm. Optical whiteners compensate the yellow cast produced by the absorption of short-wave length light (violet to blue). The brighteners absorb the ultraviolet portion of daylight spectrum invisible to the eye and convert the energy thus taken up into the longer wavelength portion of the spectrum i.e. into blue to blue-violet light.

The first fluorescent compound to be marketed as a whitening agent was the acetate of β-umbelliferone (I). The compounds currently used are, in the main, derivatives of one of the following: stilbene, mainly 4,4'-diamino stilbene 2,2'-disulphonic acid; benzthiazole; benzimidazole; dibenzimidazole; coumarin.

The stilbene derivatives have in general the formula :



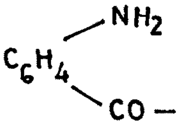
$$\begin{matrix}RHN\\NaO_3S\end{matrix}\!\!>C_6H_3\cdot CH:CH\cdot C_6H_3<\!\!\begin{matrix}NHR_1\\SO_3Na\end{matrix}$$



(I)

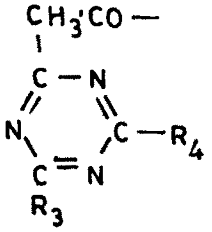
β- Methylumbelliferone

The groups R and R_1 have an important effect upon such properties as light stability and substantivity. The may be of many types, for example :



$$C_6H_4\begin{matrix}NH_2\\CO-\end{matrix}$$

, $C_6H_5\cdot NH\cdot CO-$,



, $C_6H_5CONHC_6H_4$

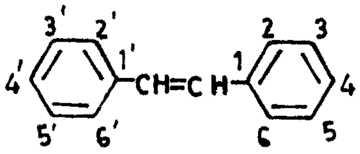
$C_6H_5NH\cdot CO\cdot NH\cdot C_6H_4-$

Stilbene derivatives :

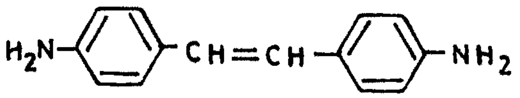
Most water soluble brightener [about 80% of total production] for the more hydrophilic textile materials are stilbene derivatives.

Chemistry of Stilbene :

This hydrocarbon itself possess a U.V. absorption band at 324 nm of the UV auxochromic amino groups in the 4,4'-position of stilbene even 4,4'-diaminostilbene has possibility of excitation at 358 nm.[73-76]



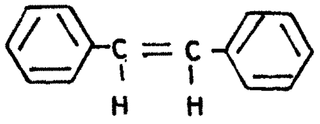
Stilbene



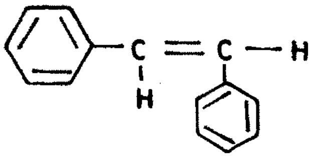
4,4'-diaminostilbene

Diaminostilbene disulphonic acid and cyanuric chloride are two inexpensive industrial intermediates, playing an important role in the field of reactive dyestuffs. Largely independent of amine, alcohol component possess UV absorption band at 350 + 3 nm, the fluorescence maximum is between 442 and 432 nm in the range of blue fluorescent light. Fluorescent intensity are practically equal[79] salient feature of these compounds as fluorescent whitening agents is their performance. On the substrate regard to affinity and substantivity fastness.

cis-Trans isomerism in stilbene :



cis-isomer



Trans-isomer

The stilbene compounds show cis-trans isomerism, isomers can be transformed into each other under the influence of short wave radiation.[79] This isomerism in DAS fluorescent whitening agents has been investigated carefully. Since it is highly important for the brightening effect and for analytical examination.[78] Lewis expressed that the cis-forms of DAS fluorescent brightening agents cannot fluoresce was confirmed by Bochurov[79] and by H.Walz[80] by measurement of absorption bands of dilute solutions (5 PPM) of a DAS fluorescent brighteners on exposure to UV radiation. The extinction of the absorption band at 365 nm which is responsible for the effect of the fluorescent whitening agent, diminishes more and more. While an absorption band at 278 nm is intensified. Trans isomer of DAS fluorescent whitening agent are substantive and fluorescent. Formation of cis-trans isomer is promoted in very dilute solutions.

Chemistry of cyanuric chloride :

Since the specification and chemistry of the cyanuric chloride becoming more and more critical, we have to be fully aware of the influence of all factors such as temperature, pH and spot tests on on the synthesis of our whitening compounds. The two main factors which the plant personnel have to watch carefully are yields and quality.

Cyanuric chloride or 2,4,6-trichloro-S-triazine is the most important of s-triazine derivatives and used at one or another stage for reactive dye. It has high reactivity, versatility and low cost.

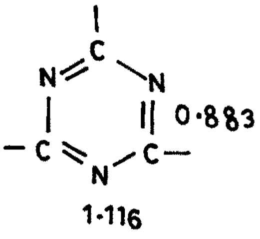
Cyanuric chloride has discovered by Serullas, in 1827[84] and its composition was investigated latter.[82] It is a white solid, M.P., 146°C, b.p. 198°C pungent odour.

Solubility of cyanuric chloride in different solvents :
Acetone 25%, Acrylonitrile 19%, Benzene 19%, CCl_4 7.5%, $ChCl_3$ 20% dioxan 55%, Nitrobenzene 18 gm/100 ml of solvent.

Reactions of cyanuric chloride :

It is highly reactive one, two or three chlorine atoms undergoes replacement with varying degrees with any nucleophilic reagent. First chlorine atom is replaced by amino group at 0-5°C. Second chlorine at 40°C and third chlorine is above 80°C. This general pattern of cyanuric chloride is common to most amines.

The heteroatoms in the ring activate the system for nucleophilic substitution reactions because of their electronegativity. This is clearly shown by charge density distribution.



S-triazine

Replacement of one or more halogen atoms of a polyhalogen heterocyclic compound by other substituents effects the reactivity of the remaining halogen atoms to a greater or lesser extent according to the electrochemical character of the substituent the positional relationship in the ring between halogen atom and the substituent the type of bonding between them.

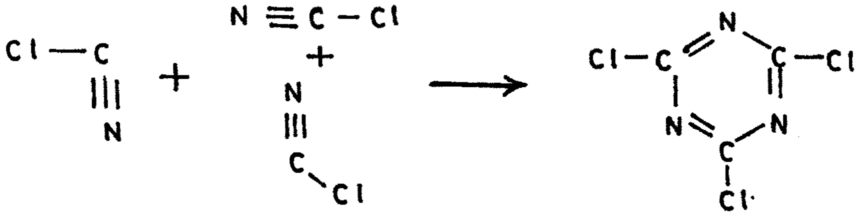
Cyanuric chloride is of interest and importance in dyestuffs research and manufacturers are nucleophilic replacements of the same general type as those undergone by other halogen heterocyclic systems.

A situation is different when the group replacing chlorine atom in cyanuric chloride is alkoxy or aryloxy, because remaining two chlorine are deactivated must more than by amino substituted. In practice, chlorine atoms are more labile under acid than neutral conditions.

Cyanuric chloride is susceptible to alcoholysis and aminolysis as well as hydrolysis at 0°C. The course of substitution reaction is determined not only by the nucleophilicity of the basic reactant but also by the electrophilic character of the triazine. Cyanuric chloride is a monofunctional. The formation of varying amounts of higher molecular weight chlorotriazinyl aminostilbene disulphonic acid must be expected under any conditions in the reactions of cyanuric chloride with bifunctional DASDA.

Preparation of cyanuric chloride :

Cyanuric chloride is prepared by polymerization of cyanogen chloride.


Cyanuric chloride

From an aqueous solution of cyanogen chloride, obtained by chlorination of hydrogen cyanide. Cyanogen chloride is distilled off which is then dried and polymerized in benzene saturated with dry hydrogen chloride at 35-40°C.

SCOPE OF THE PRESENT WORK :

Following the introduction of fluorescent brightening agents to the textile, paper, detergent and allied industries, the development and introduction of new products proceeded rapidly. Research chemists synthesised hundreds of new fluorescent compounds in an effort to market improved and/or lower cost whiteners. The driving force behind these research efforts was the high degree of competition in a new and rapidly expanding market.

Fluorescent brightener usage continued to expand in the U.S. until the early 1970's, when a number of factors resulted in significant reductions in whitener levels and the removal of synthetic fabric whiteners from many detergents. This trend continued through the mid- 1980s. During this period, research in the whitener field also declined dramatically. The remaining manufacturers focussed on addressing toxicological and environmental issues that were raised in the early 1970s.

A new period of innovation in the detergent industry began in the early 1980s and has been accelarating since. In addition to a multitude of new or improved products from the traditional detergent manufacturers; companies with no previous participation in the market are introducing new and innovative brands. These new and often complex formulations, both physically and chemically, have spurred renewed R and D efforts in the whitener field. In addition to improved versions of existing FWA; some new products will required totally new compounds to deliver optimum whitening performance.

In the light of the above discussion and previous survey, synthesis of new stilbene based fluorescent brightening agents has been undertaken. It is desired to test the brightening effect of these new agents on cotton fabric and to evaluate their antimicrobial activity.