

## REVIEW OF LITREATURE

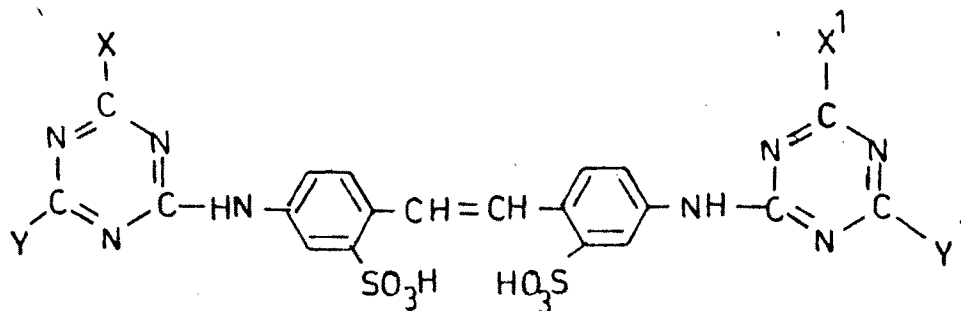
Over a century ago, Stokes studied the phenomenon of fluorescence on a scientific basis<sup>33</sup>. In 1921, A. V. Lagorio<sup>34</sup> observed that the content of colours can be enhanced by fluorescent dyestuffs. In 1929, Kraus<sup>35</sup> using Lagorio's principle, showed that yellowed viscose 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; dehydro-thio-p-toluidine and related compounds have been used as colourless making 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<sup>36</sup>, and for producing fluorescent effects on textiles and paper, such as safety marks in banknotes<sup>37</sup>.

In 1934,<sup>38</sup> 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<sup>39</sup> and Hoffmanns Strake Fabriken<sup>40</sup> patented the use of  $\beta$  methyl umbelliferone as well as 4-methyl-7-dimethyl amino coumarin under alkaline conditions for the whitening of cellulosic textiles.

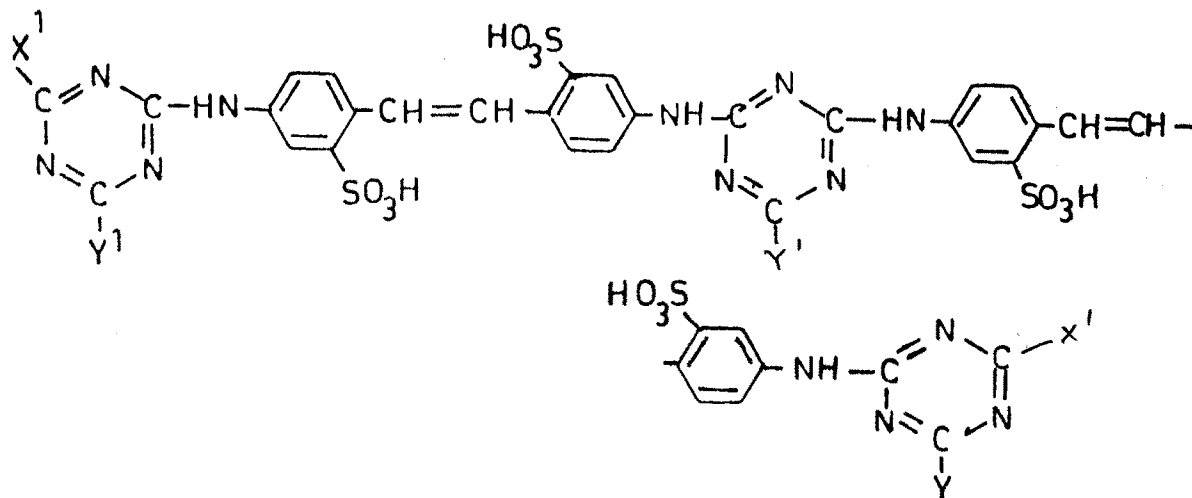
In 1939 Meyer patented the use of  $\beta$  methyl umbelliferone (II) for whitening textiles<sup>41</sup> and a little later its use for whitening soap itself was also claimed<sup>42</sup> shortly afterwards, derivatives of diamino stilbene sulphonic acid, similar to those previously used as protective agents, were patented in Germany by the I.G.<sup>43</sup> and in this country by Lever Brothers<sup>44</sup> for use in soap to give a whitening effect to textiles in washed with them.

In 1940, Bruno wendt and coworkers<sup>45</sup> I.G. farben found that triazinyl-amino-stilbenes of the following formula could be used from detergent and alkaline baths as substantive optical whitening agents for cellulosic textiles.

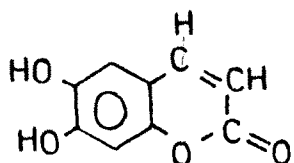


Above structure is the basic common structure of the triazine class. A very high proportion of the fluorescent brightening agents on the market are of this general structure, and many patents have been taken out covering specific groups on the triazine ring conferring specific properties. The most common types are the symmetrical in which X and X<sup>1</sup> are the same, and Y and Y<sup>1</sup> are same. These are easy to prepare by stepwise replacement of the chlorine atoms of cyanuric chloride. Those in which X and X<sup>1</sup> or Y and Y<sup>1</sup> are different can in general be prepared only in a round about manner starting from nitroaminostilbene

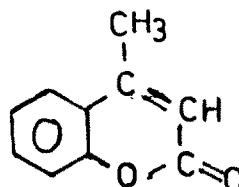
disulphonic acid,condensing this with cyanuric chloride, replacing stepwise the two chlorine atoms, and then reducing the nitro group and doing the same on the other half of the molecule, obviously, these unsymmetrical ones are considerably more expensive to prepare and in general they have little advantage in properties. In the original Blankophor B, X and X<sup>1</sup> were anilino groups and Y and Y<sup>1</sup> hydroxy. Many more recent products have all four groups as substituted amino groups<sup>46-64</sup>, thus X and X<sup>1</sup> may be anilino, toluidino or anisidino residues or residues of metanilic acid ; Y and Y<sup>1</sup> may be similar or may be aliphatic amines such as methyl amino dimethyl amino, hydroxyethyl amino, bis hydroxyethyl amino etc. In other cases X and X<sup>1</sup> are again substituted amino groups but Y and Y<sup>1</sup> are either phenoxy or thiol groups or in some cases may be unchanged chlorine<sup>65-70</sup> 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 acid, and so on. In general, all products are unstable to hypochlorite in solution, but some how 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 X<sup>71</sup>.



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



Asculetin

 $\beta$ -Methyl umbelliferone

The early products on the market were almost entirely for use only on cellulose 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 to 200 different products. In 1955 the production in the U.S.A. was 1,375 tons- double the figure 3 years previously<sup>72</sup> today the production there is still higher a sales value of 15 million has been quoted<sup>73</sup> 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 type 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 fabrics. In 1960, the consumption of laundry brighteners in the United states was three

million pounds and sales approximated nine million dollars.<sup>74</sup>

The sales of fluorescent brighteners increased to twenty five million dollars by 1964<sup>75</sup>.

The world's annual production of fluorescent brightening agents, including about 200 products of 15 different types, amounts to approximately 27.35 million kilogram, 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.

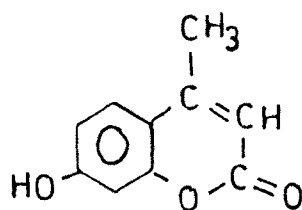
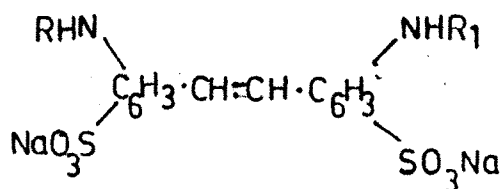
Though the world's annual production of fluorescent brightening agents ranges between 200-250, only small numbers of such brightening agents have found practical use.

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  $\pi$  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-violet light.

The first fluorescent compounds to be marketed as a whitening agent was the acetate of 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.

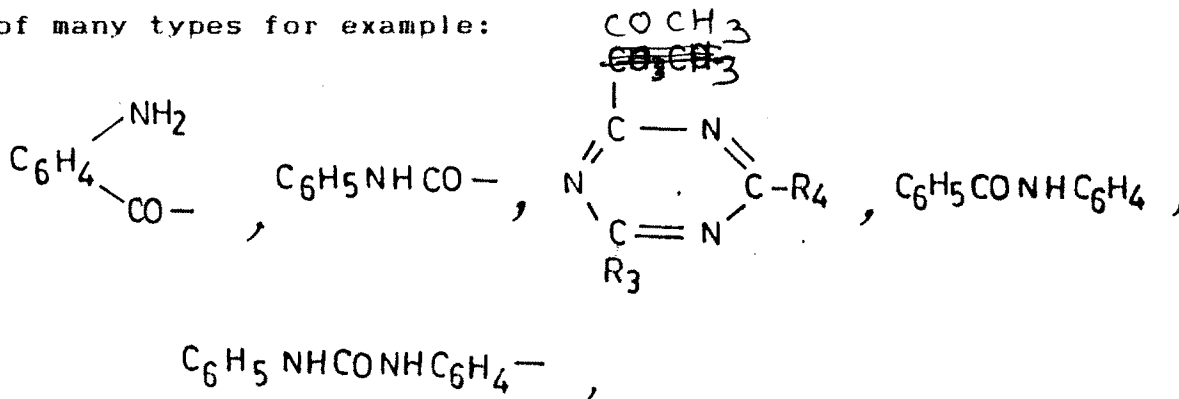
The stilbene derivatives have in general the formula:



(I)

*β*-methylumbelliferone

The groups R and R<sub>1</sub> have an important effect upon such properties as light stability and substantivity. They may be of many types for example:



Stilbene derivatives : -

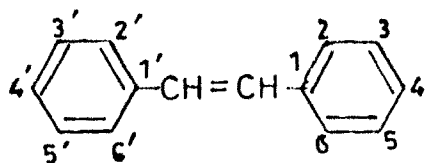
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Most water soluble brightener (about 80% of total production) for the more hydrophilic textile materials are stilbene derivatives.

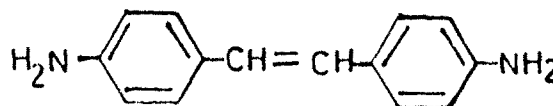
Chemistry of stilbene :

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This hydrocarbon itself possess a U.V. absorption band at 324 nm of the UV auxochromic amino groups in the 4,4<sup>1</sup> position of stilbene even 4,4<sup>1</sup>-diamino stilbene has possibility of excitation at 358 nm.<sup>76-79</sup>



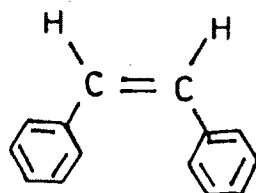
Stilbene



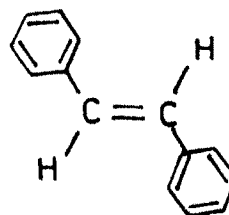
4,4<sup>1</sup> diaminostilbene

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<sup>82</sup> salient feature of these compounds as fluorescent whitening agents is their performance. On the substrate regard to affinity and substantivity fairness.

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<sup>80</sup>.

This isomerism in DAS fluorescent whitening agents has been investigated carefully. Since it is highly important for the brightening effect and for analytical examination<sup>81</sup>

Lewis expressed that the cis-forms of DAS fluorescent brightening agents cannot fluoresce was confirmed by Bochurov<sup>82</sup> and by H. Walz<sup>83</sup> 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 is substantive and fluorescent. Formation of cis-trans isomer is promoted in very dilute solutions.

Chemistry of cyanuric chloride :

Cyanuric chloride or 2,4,6 tri chloro-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 been discovered by Serullas, in 1827<sup>84</sup> and its composition was investigated later<sup>85</sup>. It is a white solid, M.P.  $146^{\circ}\text{C}$ , b.p.  $198^{\circ}\text{C}$ , pungent odour.

Solubility of cyanuric chloride in different solvents:

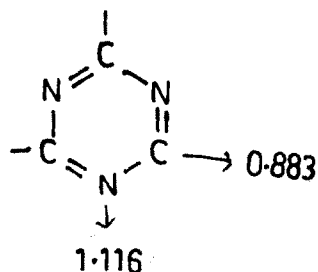
Acetone 25% , Acrylonitrile 19% , Benzene 19% ,  $\text{CCl}_4$  7.5% ,  $\text{CHCl}_3$  20% , dioxane 55% , Nitrobenzene 18 gm /100 ml of solvent.

#### Reactions of Cyanuric Chloride :-

Cyanuric chloride is a very reactive compound, one, two or three of its chlorine atoms undergoing replacement with varying degrees of facility on replacement with almost any nucleophilic reagent. Several such replacement reactions, especially those that occur with amines are capable of being carried out stepwise, so that, according to the conditions, mono, di or tri condensation products may be obtained. This property is of the utmost value and importance in the synthesis of fluorescent brightening agents based upon s triazine.

A cardinal feature of the chemistry of cyanuric chloride is that its properties bear a far closer resemblance to those of the acyl and aroyl chlorides than to those of the polychlorobenzenes and that in many of its reactions it behaves essentially as an acylating agent. Alkoxy s triazines resemble esters rather than ethers.

Halogen atoms attached to s triazine ring are considerably more labile the degree of activity depending upon the positional relationship between the hetero nitrogen atoms and the substituent. The hetero atoms in the ring activate the system for nucleophilic substitution reactions because of their electronegativity. This is clearly shown by charge density distribution.



The stepwise replacement of halogen is clearly exhibited by cyanuric chloride substituents such as amino and substituted amino powerfully deactivate the residual chlorine atoms after the first has been replaced by them and the other groups such as alkoxy or aryloxy cause a lower degree of activation. First chlorine atom is replaced by amino groups at 0-5<sup>0</sup>, second chlorine at 40<sup>0</sup> and the third chlorine is above 80<sup>0</sup>C. This general pattern of cyanuric chloride is common to most of amines.

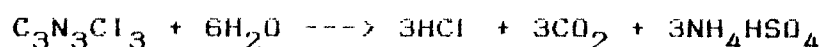
Replacement of one or more of halogen atoms of polyhalogen heterocyclic compound by other substituents affects the reactivity of the remaining halogen atoms to a greater or lesser extent according to the electrochemical character of the substituent, the positional relationship in the ring between the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

A rather different situation exists when the group replacing a chlorine atoms in cyanuric chloride is alkoxy or aryloxy because the remaining two chlorine atoms are then deactivated much more feebly than by an amino substituent.

Most aromatic primary and secondary amines ; whether simple aniline derivatives or complex amino containing compounds, including those containing sulphonic or carboxylic acid groups may be condensed with cyanuric chloride.

According to Fierz-David and Matter, cyanuric chloride is stable in water at 0° for at least 12h but is readily hydrolysed at slightly elevated temperatures<sup>86</sup>. Horrobin<sup>87</sup> has shown that the hydrolysis takes place in steps each involving the replacement of one chlorine atom, with rates depending upon the acidity or alkalinity of the medium.

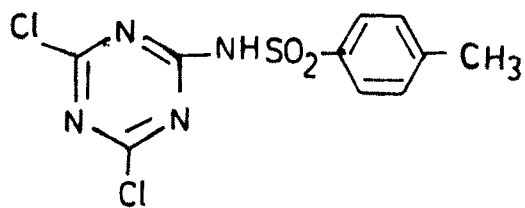
Cyanuric chloride is readily and completely hydrolysed to cyanuric acid by cold aqueous sodium acetate<sup>88</sup>. It is gradually hydrolysed by nitric or sulphuric acid at room temperature<sup>89</sup>, but it is said to remain unchanged when heated with concentrated sulphuric acid at 100° for 5 min, at 150° complete decomposition occurs with rupture of the ring.



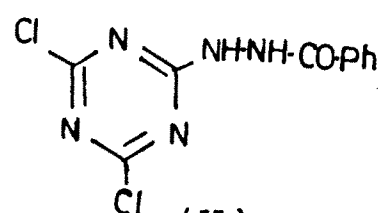
The course of alcoholysis of cyanuric chloride varies according to whether bases are present or not. In the absence of water and bases, cyanuric chloride reacts with alcohols to give cyanuric acid and the alkyl halide with practically none of the alkoxytriazine.

In contrast to the ionised hydroxyl groups<sup>84</sup> alkoxy substituents cause only comparatively feeble deactivation of residual chlorine atoms in chloro-s-triazines, so that when cyanuric chloride is treated with an alcohol in the presence of a base, there is a considerable tendency for mixtures of mono, di and trialkoxy-s-triazines to be formed unless the conditions are carefully selected and regulated.

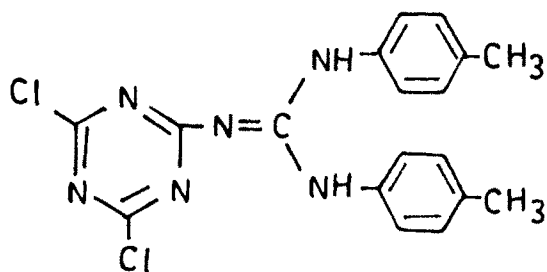
Cyanuric chloride condenses with p-toluene sulphonamide<sup>87</sup> benzohydrazide, di-o-tolyl guanidine and phthalimide<sup>90</sup> respectively to give the dichlorotriazines I, II, III & IV.



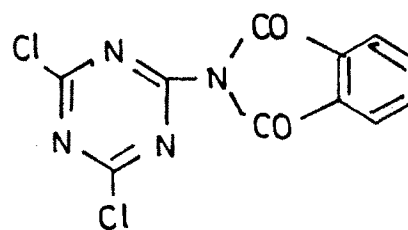
(I)



(II)



(III)



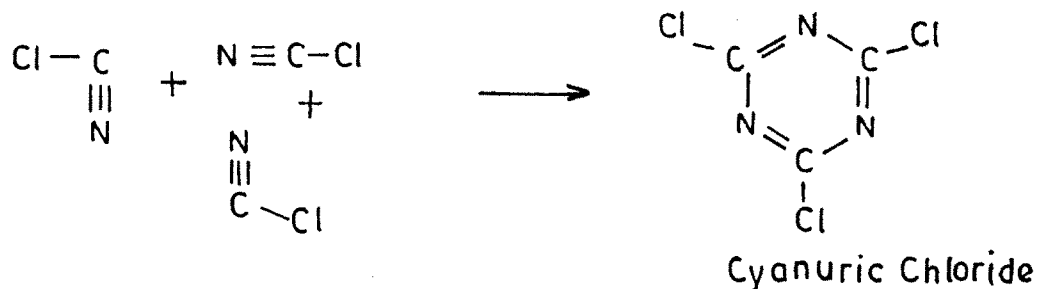
(IV)

Cyanuric chloride undergoes the Friedel-Craft reaction with hydrocarbons or phenols. Cyanuric chloride condenses with active methyl compounds such as diethyl malonate giving the dichloro triazine, but the latter is very easily hydrolysed to the corresponding dihydroxy compounds under moist conditions. With an excess of diethyl sodimalonate the tricondensation product is obtained.

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 DASDSA.

#### 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 PRESENT WORK :  
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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 was the high degree of competition in a new and rapidly expanding market.

A new period of innovation in the detergent industry began in the early 1980s and has been accelerating since. In addition to a multitude of new or improved 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 F W A; 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 cyanuric chloride based fluorescent brightening agents has been undertaken.

It is desired to study the fluorescence spectral intensities of these new agents to test the brightening effect on cotton fabric and to evaluate their antimicrobial activities.