CHAPTER - 3

PART I - FLUORESCENT SPECTRAL STUDIES OF FLUORESCENT BRIGHTENING AGENTS.

PART II - FABRIC TESTING.

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CHAPTER III

III PART-I :-

FLUORESCENCE SPECTRAL STUDIES OF FLUORESCENT BRIGHTENING AGENTS.

INTRODUCTION

Electronic and vibrational absorption sepectroscopy offers sizable information regarding the molecular structure of organic and inorganic molecules with respect to the electronic transitions and the vibrational fine structure.

In many molecules it is possible to excite them with specific radiations when secondary emission of lower. energy is emitted and the emission characteristics provide further help in elucidation of structure. Fluorescence emission spectroscopy is therefore an important tool of the structural chemist. The fluorescent materials in solution phase find many analytical applications as titrimetric indicators, as substrates in enzymology and also as tags for protein molecules, Solid state fluorescence spectroscopy has emerged into a very important ascept of development of photo physics. In technology this branch covers a broad spectrum of applications ranging from optical brightners, luminescent paints, luminescent lamp coatings, phosphors, cold lights to TV screens.

Our aim in the present study is to find out the fluorescence emission intensities of some fluorescent brightening agents.

EQUIPMENT

Shimadzu, Japan make double monochromator recording fluorescence spectrometer model RF 540 was used for recording fluorescence spectra. A short discription of the

instrument and its working is given here.

(1) Light Source :- (a) The light source is 150 W Xenon lamp and its compartment has azoneless housing mechanism (b) The light source monitor the monochromatic light with a dynode feedback control.

(2) Sepectrometer :- (a) The optical system contains a condenser. SiO_2 coated ellipsoidal mirror. (b) The excitation and emission monochromators are off-plane concave diffraction gratings with 900 grooves mm^{-1}. (c) The smaple compartment isqsingle nonthermostatic cell holder for liquid samples and disc holder for solid samples. (d) Filters are provided for solid samples.

(3) Detector :- The instrument has a monitoring photomultiplier (R-212) and a photometric photomultiplier (R-35401).The excitation and emission obtained from the sample is fed to the computer which gives trace of intensity in arbitrary units against wavelength in nm. Print out of the computed data and spectral traces are obtained on thermal paper.

(4) Standardization of the instrument :- The instrument was standardized by comparing the spectra of distilled water and quinine sulphate by using recommended standard procedure.

The instrument is set as per the instruction mannual.

DISCUSSION :---

Fluorescence spectra result from energy transfer processes of electrons[93]. The electrons in ground state so level get excited by absorption of energy and are transferred to higher excited state S_1 or S_2. By losing some energy these electrons revert to So[94]. The electronic energy transfers such as $S_1 \rightarrow S_0$ are known as electronic relaxations[95] Usually the $S_1 \rightarrow S_0$ conversion results in fluorescence [96]

These electronic transfers and ultimately the fluorescence intensity is dependent upon many factors such as structural mobility, substituent effect, hydrogen vibrations, fluorescence quenching, conc. of solution etc. In addition to these, the degree of ionisation of the dye molecule also is known to affect fluorescence

(A) Structural Mobility :-

Increasing the extent of conjugation has two main effects, namely, to shift the absorption and thereby the fluorescence wavelengths towards the red end of spectrum and to enhance the mobility of the π electrons. Increasing the number of mobility of the electron often results in an increase in fluorescence intensity.

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 inhibited resulting in loss of fluorescence

All the F.B.A. synthesised here are planar and have maximum conjugation. Therefore these agents show fluorescence intensities.

(B) Substituents :-

Electron donating groups when present in the molecule are known to enhance the fluorescence intensity with shifting the spectrum to longer wavelengths. The high value of fluorescence intensities in case of the F.B.A. (2) and (3) as compared with (1) are due to the presence of an electron donating methyl group. Presence of alkyl or phenyl substituents and also the conjugated double bonds favour electronic transitions which in turn increases the fluorescence intensity. This happens because these molecules

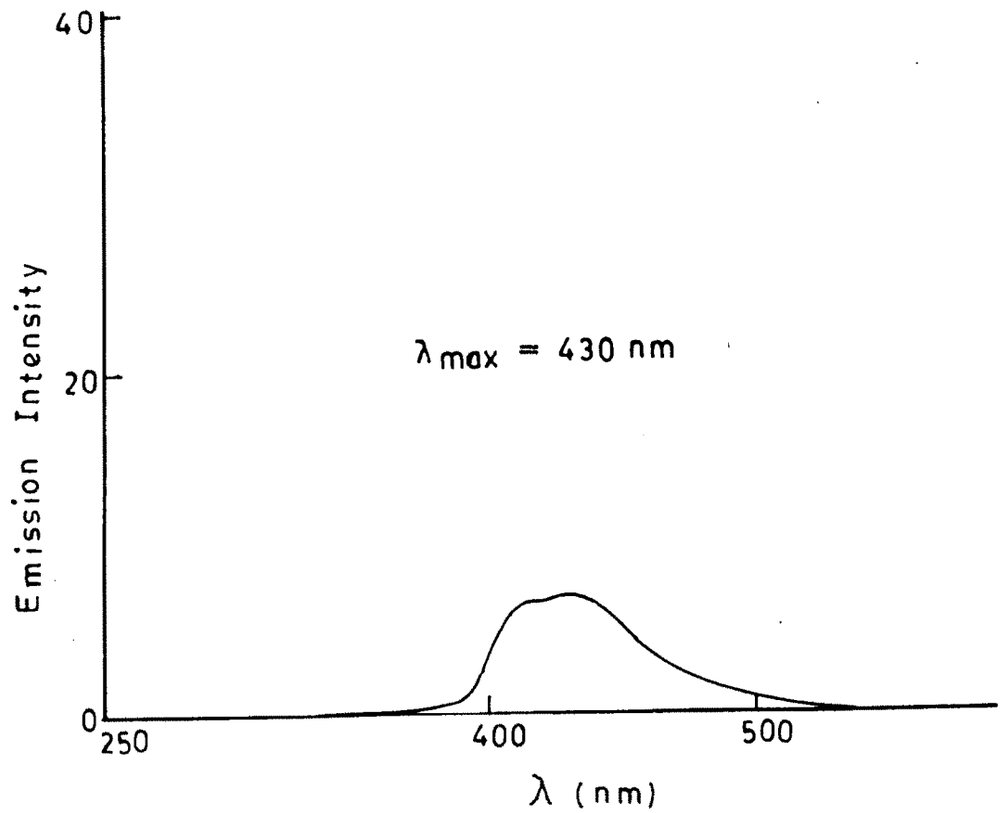
can have high degree of resonance stability and better fluorescence quantum yields. Presence of bulky alkyl group as substituents create steric hindrance, thus reducing the resonance stabilisation of big organic molecule.

Comparison of fluorescence intensities of F.B.A. (2) and (3) , it is observed that intensity is higher in case of (3) since methyl group is at para position thus causing no steric hindrance in its electron donating effect. In the case of (2) methyl is at ortho position thus causing steric hindrance as compared with (3).

F.B.A. (4) also shows better fluorescence intensity because of electronic donating Cl group.

The effect of increasing the number of benzene rings is generally to increase the fluorescence efficiency. Thus napthalene has a higher fluorescence efficiency than that of benzene. Therefore F.B.A. (5) shows the highest fluorescence intencity as compared with remaining fluorescent brightening agents.

FLUORESCENCE SPECTRUM OF F. B. A. NO.1



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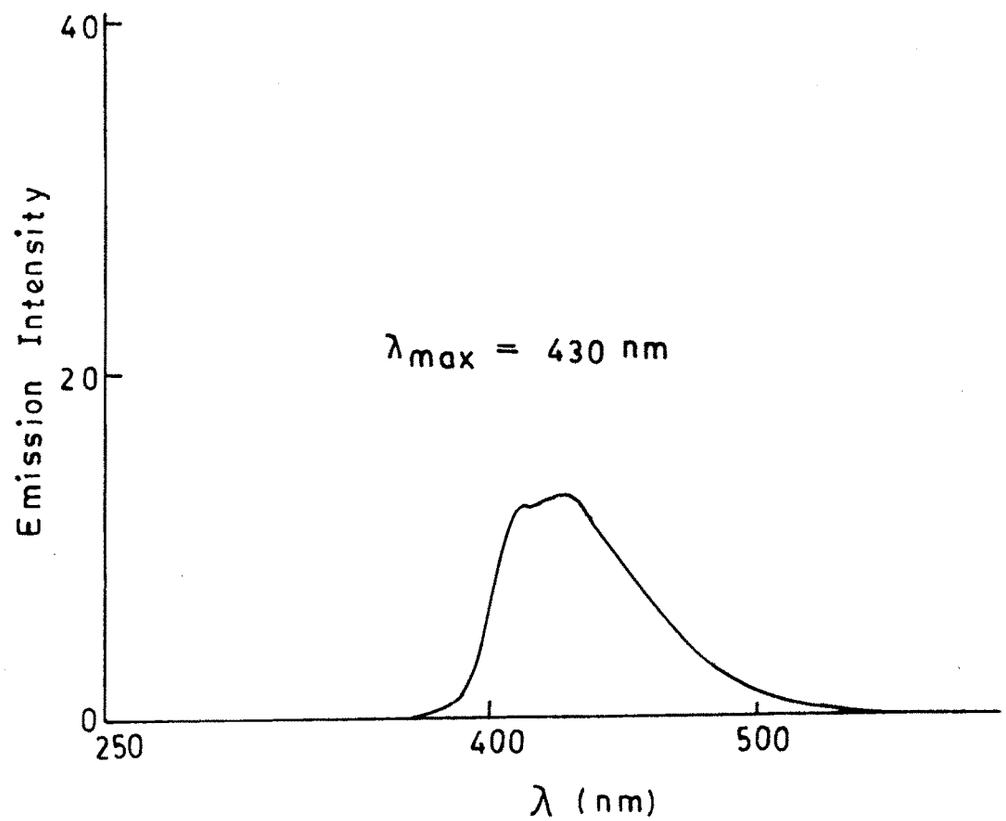
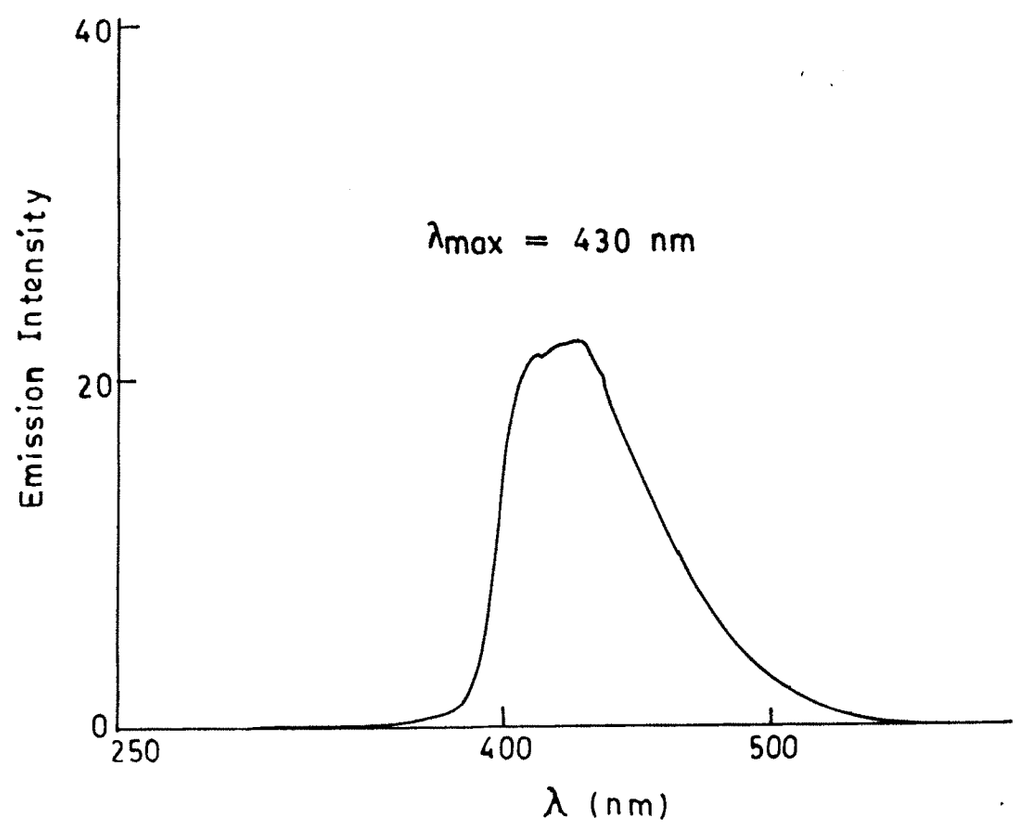


FLUORESCENCE SPECTRUM OF F·B·A· NO. 3



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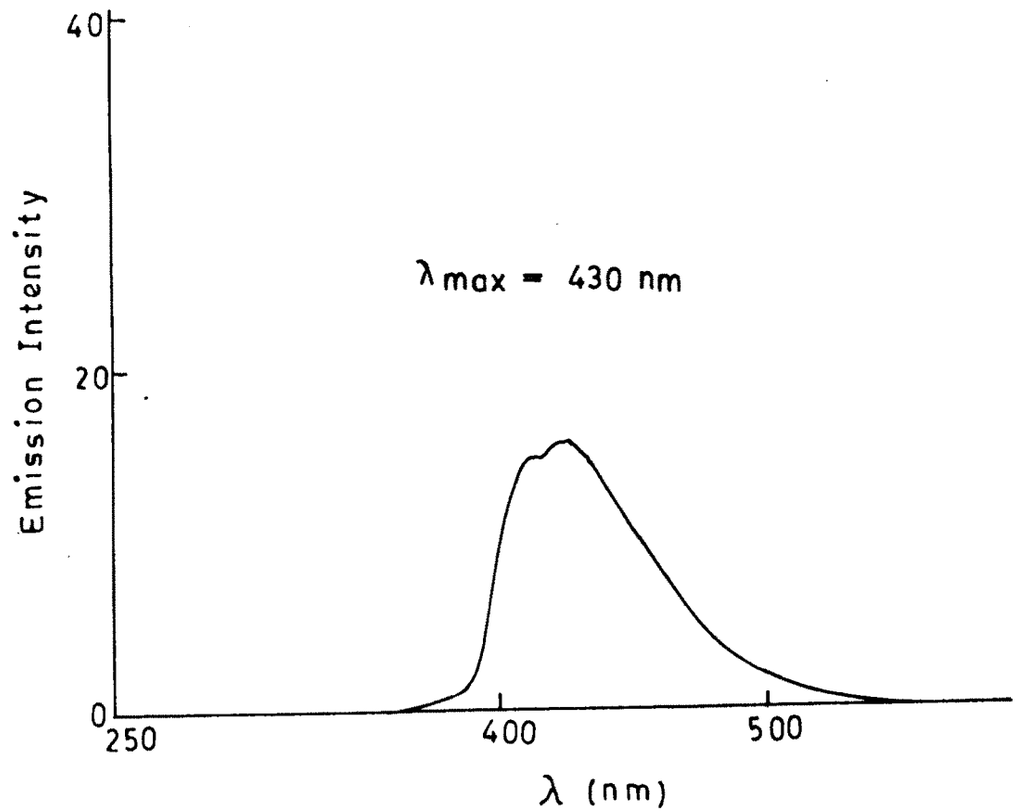
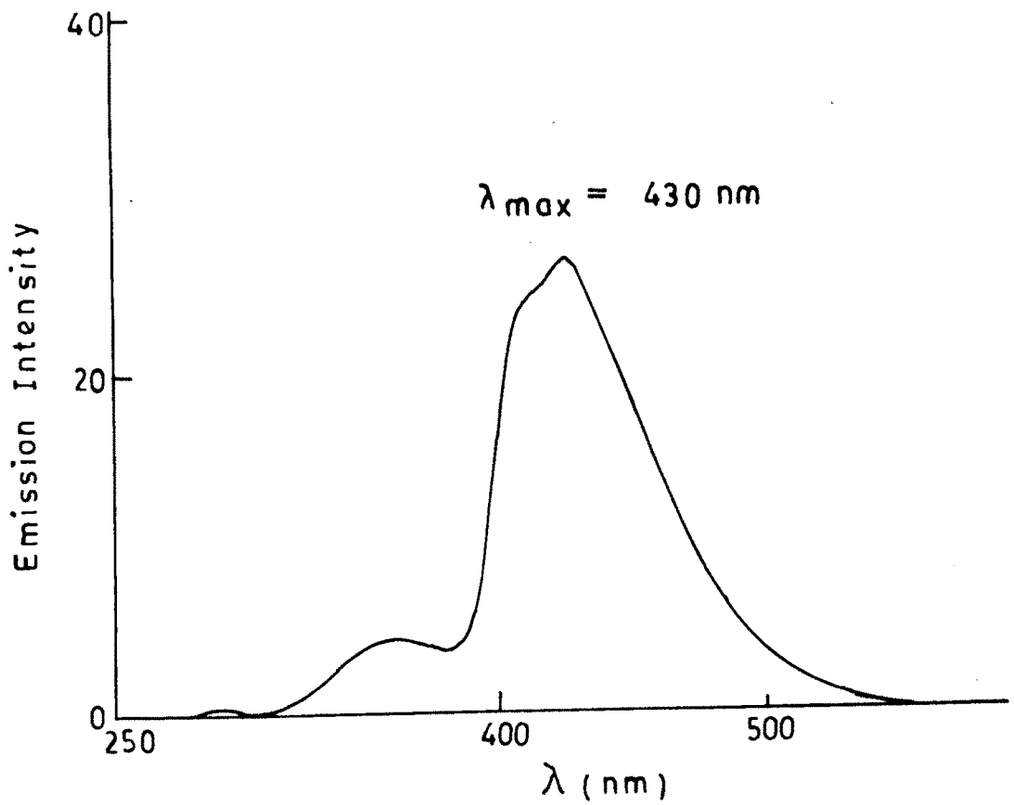


FLUORESCENCE SPECTRUM OF F.B.A. NO. 5



PART II FABRIC TESTING.

The Application of Fluorescence Brightening Agents. :-

The applicaton of colourless fluorescent dyestuffs as optical brightening agents is based on practical coloristic principles.

The effect of fluorescent brightening agent depends to a large extent on its affinity and on the molecular orientation in the substrate to be brightened.

With increasing concentration of fluorescent brightening agents, the fluorescence increases approximately linearly with the logarithm of the amount of brightening agent taken up by the substrate (weber-fechner law) until saturation limit is attained : the white cannot then be further increased. The position of the saturation limit depends (A) On the nature of the fluorescent brightening agent (relative to composition , quantum yield, Fine division or solubility)

(B) On nature of substrate and

(C) in the fluorescent brightening of textiles on the dyeing process (relative to temperature, pH value concentration of the liquor)[97]

Where the optimum concentration typical of the saturation limit is exceeded , the achieved white may be reduced[98], which may possible lead to a total extinction of the fluorescence, self extinction or concentration extinction.

For the application of the usual types of dilute formulations, determination of fluorescent brightener concentration is important. Since the titrimetric methods used in chemistry are not always possible [99]. Optical methods of determining the concentration are often given

preference.

A simple, though inexact method which is often used is the Visual comparis on of the fluorescence strength of the solution of a fluorescent brightening agent under a dark field uv lamp with a known concentration series of the optical brightener to be measured. The evaluation is faciliated and the accuracy improved by spotting the solutions to be compared onto paper and then assessing their fluorescence strength visually under the lamp. Although the fluorescent strength of solutionS of fluorescent brightening agent can also be measured with a spectrophotometer, this method has little practical importance because of the poorer consistency of the measured values.

FOR COTTON FABRIC [100] :-

In order to achieve good results on cotton, pretreatment of the brightening material is necessary, which is, carried out by boiling and chemical bleaching. The highest degree of brightness is achieved by a combination of boiling in an alkaline both at elevated pressure and hypochlorite or peroxide bleaching. For white material boiling under pressure is suitable than boiling at atmospheric pressure.

When cotton is brightened, the fluorescent brightener may be added to the peroxide bleaching bath or to neutral exhaustion bath. Tinopal 4 BM has proved to be one of the best brightening agent for peroxide baths.

In the exhaustion process the brightening agent is added in about 0.2 gm. to 4 gm. per litre of bath water is used.

Fluorescence brightening agent used for brightening of textile materials, even during printing the light fastness properties of fluorescent brightening agents of CC/DAS used for cellulosic materials are medium in daylight and Xenotest. Other fastness properties are good to water and washing at 40 ^{0} C, medium to good for washing at 95 ^{0} C and to heat treatment upto 150 ^{0} C. Medium to heat treatment at above 150 ^{0} C and sanforming.

FABRIC TESTING PRESENT INVESTIGATION :-

The present fluorescent brightening agent of class CC/DAS are used for celluosic fibre are studied as below. Experimental work was done in 'Department of chemistry' Dattajirao Kadam Textile Institute Ichalkaranji.

EXPERIMENTAL :-

Gray, unbleached cotton fabric was taken on the basis of fabric weight (O W F) and bleaching was carried out in following three steps.

PROCESS OF BLEACHING :-

1) DESIZING :- 145 gms Of gray cotton fabric was desized using enzyme (zymage) of concentration (15 gm./lit.), sodium chloride (15 gm./lit.) at 55 to 60 ^{0} C for two hours. Then washed the fabric with hot water (temp. 85 ^{0} C) and rinsed it with water. Removal of peptin takes place.

2) SCOURING :- Desized fabric was boiled with NaoH 3.7 % owf (on the basis of fabric weight) , 1 % sodium silicate, 1.5 % anionic detergent [Lissopal D.]. Boiled the material for two hours keeping material to liquor ratio 1:20 [1 gm : 20 ccs of water].

3) BLEACHING :-

(A) Hypochlorite bleaching :- Treated the fabric with hypochlorite like sodium hypochlorite or with calcium hypochlorite [7.5 gms.] at room temperature for two hours. Washed it thoroughly with cold water.

(B) Peroxide bleaching :- H_2O_2 is used for permanent whiteness. Treated the material with peroxide 3.6% owf [30% H_2O_2] sodium silicate [1.5%], sodium carbonate [1.5%] at 85^0C for two hours washed with hot and cold water and dried. Perfectly white sample we get. It was used for treatment of fluorescent brightening agents.

Bleached fabric material was cut into small pieces. Solutions of fluorescent brighteners of different concentrations were prepared by dissolving weighed sample in distilled water. Solutions of standard fluorescent brighteners were made at the same time. To make comparison between brightness increase of fluorescent brighteners synthe sised and standard. 0.02% to 0.4% concentrations of fluorescent brighteners are used. Liquor ratio was 1:6.

Fabric pieces were dipped in the solutions of fluorescent brighteners for five minutes each. Padding was done for uniform distribution of the brightener on fabric. Fabric was dried to 60^0C. Whiteness or brighteness of fabric was observed by visual methods.

Results and discussion were reported.

Books Referred : Handbook of Textile Testing.

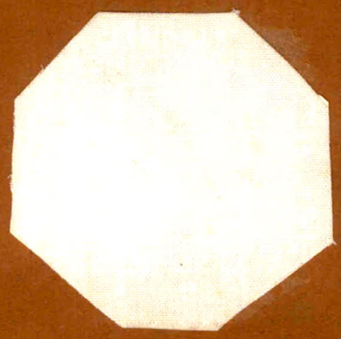
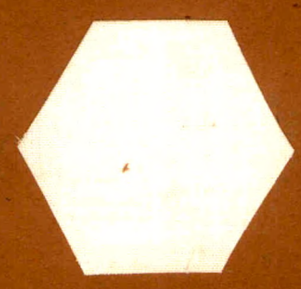
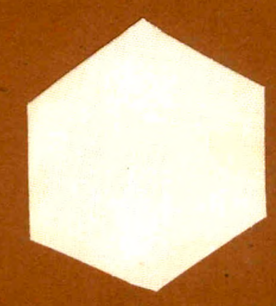
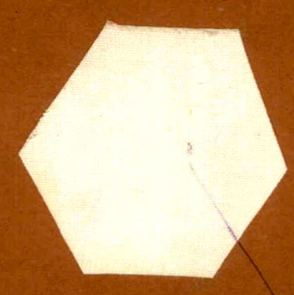
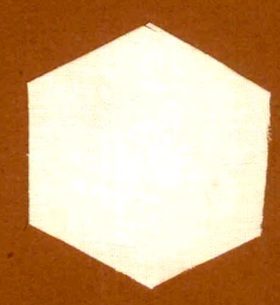
TABLE OF RESULT

F.B.A.	NAME OF COMPOUNDS	CONCENTRATION IN PERCENTAGE						
		0.02%	0.04%	0.06%	0.08%	0.1%	1.5%	2%
1	4,4' BIS [6(P-AM INO BENZENE SULPHONAMIDO) 4 DIETHANOLAMINO 1.3.5 TRIAZIN-2YL] AMINO SITILBENE-2.2' DISUPHONIC ACID.	+	+	+	+	+	+	+
2	4,4' BIS [6(O-TOLUIDINE SULPHONAMIDO)4-DIE--THANOLAMINO-1.3.5 TRIAZIN-2-YL] AMINO STILBENE- 2.2' DISULPHONIC ACID.	++	++	++	++	++	+	-
3	4,4' BIS [6 (P-TOLUIDINE SULPHONAMIDO)-4-DIETHANOLAMINO-1.3.5-TRIAZIN-2-YL] AMINO STILBNE - 2.2' DISPULPHONIC ACID.	++	++	++	++	++	++	-
4	4,4' BIS [6(O-CHLORD ANILINO) 4 DIETHANOL AMINO - 1.3.5 TRIAZIN - 2-YL] AMINO STILBNE - 2.2' DISULPHONIC ACID.	++	++	++	++	++	+	-
5	4,4' BIS [6(1-NAPHTHYL AMINO)-4-DIETHANOL AMINO - 1.3.5 TRIAZIN-2-YL] AMINO STILBENE 2.2' DISULPHONIC ACID.	++	++	++	++	++	+	-
6	STANDARD Photine HVM	+++	+++	+++	+++	++	+	-

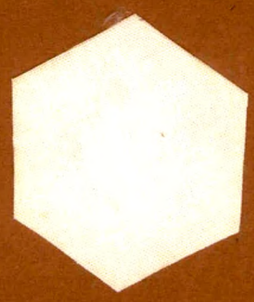
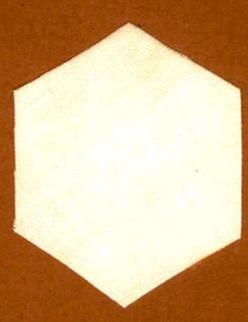
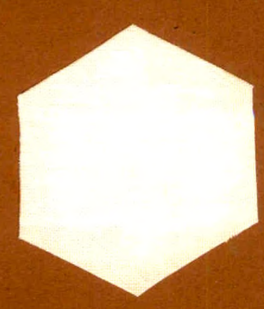
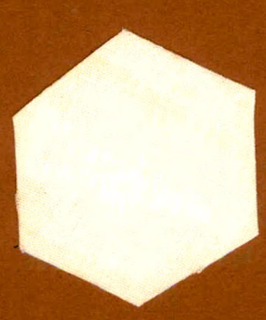
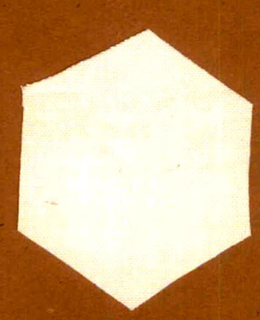
+ + + Very good whitness ++ = Good whitness += Medium whitness - No whitness

By observing above table the brightness or whitness property of the fluorescent brightner decreases by increasing concentration above 1.5% .

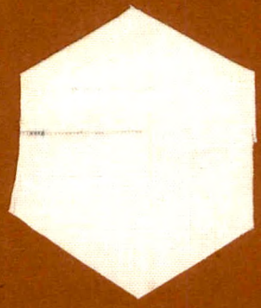
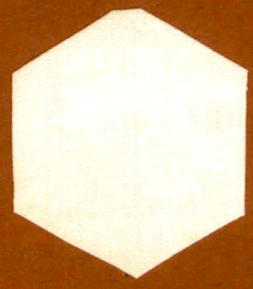
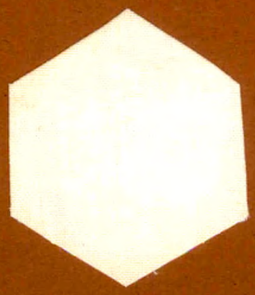
FABRIC TESTED WITH DIFFERENT F.B.A.

STANDARD F.B.A.	F.B.A. NO. 1	F.B.A. NO. 2
 0.02%	 0.02%	 0.02%
 0.06%	 0.06%	 0.06%
 0.1%	 0.1%	 0.1%

FABRIC TESTED WITH DIFFERENT F.B.A.

STANDARD F.B.A.	F.B.A. NO 3	F.B.A. No. 4
 0.02 %	 0.02 %	 0.02 %
 0.06 %	 0.06 %	 0.06 %
 0.18 %	 0.18 %	 0.18 %

FABRIC TESTED WITH DIFFERENT F.B.A.

STANDARD F.B.A.	F.B.A. NO. 5
 0.04%	 0.04%
 0.06%	 0.06%
 0.1%	 0.1%

PART III

ANTIMICROBIAL STUDY OF FLUORESCENT BRIGHTENING AGENT :

INTRODUCTION :-

Many amines show a remarkable antiplasmodial action. When aromatic heterocyclic nucleus[101] is attached to amino group the antiplasmodial action is increased.

Many heterocyclic sulfonamides have been reported which had exhibited an excellent antibacterial activity.

There are some heterocyclic compound like cyanuric chloride and the compound 4,4' diaminostilbene 4,4' disulphonic acid which had exhibited an antibacterial activity when they are as fluorescent brighteners. Thus CC/DAS group is responsible for drug activity.

PRESENT WORK :

The present fluorescent brightening agents in which cyanuric chloride is attached to different substituted amines, report the antimicrobial[102] studies against some representative micro organism, as these derivatives contain heterocyclic nucleus and amino groups.

EXPERIMENTAL :

All the chemicals and solvents used were of Analar or equivalent grade.

Preparation of reagents and stock solutions :

Cyanuric chloride derivatives were prepared as described in (chapter II) .

Fresh solution of all compounds were prepared by dissolving 2 mg in 1 ml distilled water (for low concentratrion) and 5 mg in 1 ml of distilled water (for high concentration). Filter paper discs (6mm dia of whatman filter paper No 1) were then soaked in these solutions. It was observed that 60 filter paper discs could be soaked in 1.0 ml of solution. Each disc thus

corrresponds to the concentration of 33.3 μg and 83.3 , the compound respectively in low and high concentration.

Micro - organism :

The micro organisms used for the present studies were pure culture obtained from "Department of Micro biology, krishna Institute of Medical Sciences, Karad.

The following strains were selected for antimicrobial investigation.

(a) Gram positive bacteria

1) Staphylococcus aureus

(b) Gram negative bacteria

1) Escherichia coli.

Assay Method :-

The 'Disc assay' method used in the present study was same as described by kulkarni P. L. and et al[103]. The details of which are given below.

Nutrient agar was used as a test medium which was prepared by dissolving 'difco' agar, agar powder (2.5 gm), pepton (1.0 gm), sodium chloride (0.5 gm) in hot distilled water (100 ml). The solution PH (7.4) was sterilized by steam at 12 lb pressure and 120^0 for half an hour and then poured in sterilized petridishes.

Test tube culture of the micro organism was shaken with 5.0 ml of plain broth and was inoculated on agar plate by pouring the solution on surface. After about 15 minutes filter paper discs containing the test compounds were placed on the agar surface. Petridishes were then incubated with inverted position at 37^0 for 24 hours and inhibition zones were measured in millimeters. All the experiments were carried out in duplicate and average values of inhibition diameters were noted. All the operations were carried out in complete aspetic condition to prevent

atmostpheric contamination. After completion some photographs were taken.

RESULT AND DISCUSSION :

All the fluorescent brightening agents were tested for their antimicrobial activity against gram positive staphyllococciaureus and gram negative Escherichia coli bacteria but they were found to inactive against these bacteria.

Test book of Microbiology by R. Anantnarayan and Jayram Panikar orient Longman, 2nd Ed.